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Author(s)	安村, 駿作
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Rational development of heterogeneous catalysis based
on understanding of active species in zeolite

(ゼオライト内活性種の理解に基づく
合理的触媒開発)

北海道大学 大学院

総合化学院

触媒材料研究部門

安村 駿作

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Chapter 1

General Introduction

1.1. Effect of local structure of active sites in zeolites on catalysis

Aluminosilicate zeolites are well-defined porous frameworks that consist of four-coordinate $[\text{SiO}_4]$ or $[\text{AlO}_4]$ subunits. Various cations can be anchored at the framework anionic $[\text{AlO}_4]^-$ sites (Al sites) in their pores, and the number of sites can be changed by controlling the Si/Al ratio of the zeolites.¹⁻⁸ (Figure 1) The exchanged cations in zeolite can catalyze enormous industrially useful reactions including the transformation of hydrocarbon^{9,10} and purification of diesel exhausts.¹¹⁻¹⁴ Interestingly, the catalytic property of zeolite-based catalysts is significantly changed by not only the type of the exchanged cations, but also the type of zeolite framework, loading amount of the cations, Si/Al ratio, and Al distribution of zeolite.^{7,8,15,16} In many cases, this change of the property originated from changing the local structure of active sites and the surrounding environment. For example, the catalytic property of Ga-exchanged zeolite for alkane dehydrogenation is known to be tunable by controlling the ratio of Ga species at paired Al site (e.g. $[\text{Ga}(\text{H})]^{2+}2\text{Z}^-$; Z denotes Al site) and the one at single Al site (e.g. $[\text{Ga}(\text{H})_2]^+\text{Z}^-$), that is changed by the increase/decrease of Si/Al ratio and Ga loading amount.¹⁷⁻²⁴ Thus, the investigation of the local structure of active sites is very important to provide the rational design concept of zeolite-based catalysts although it is still formidable to gain the atomic-scale understanding of active sites, even by the recent progress in *in situ/operando* spectroscopic techniques and DFT calculation.

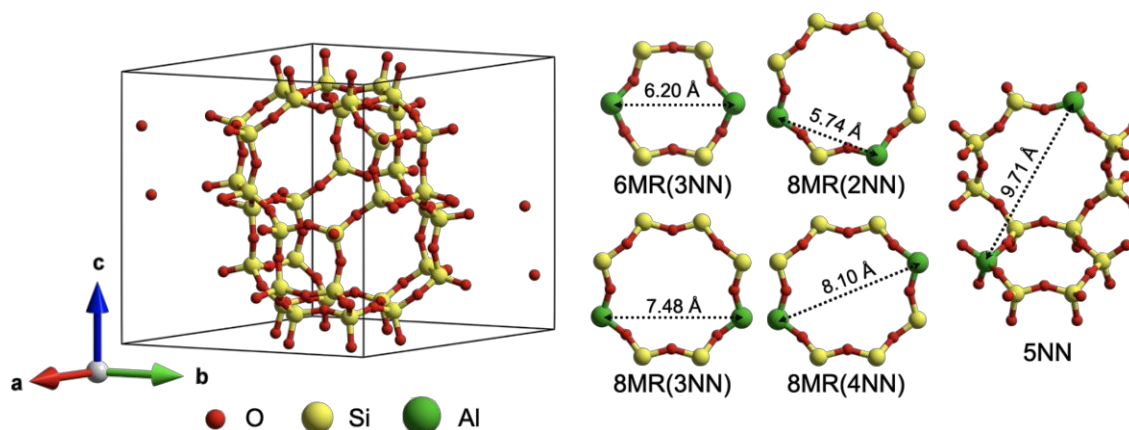


Figure 1 A unit cell of CHA zeolite and the representative paired Al sites.^{15,25}

1.2. Dynamic structural evolution of active metal species

The sizes, shapes, and oxidation states of active sites in heterogeneous catalysts change dynamically depending on the reaction temperature, atmosphere, and adsorbent.^{26–31} Owing to recent progress in *in situ/operando* spectroscopic techniques and density functional theory (DFT) calculations, structural changes in the active species during catalytic cycles have been observed under the working states, leading to a molecular-scale understanding of the reaction mechanism.^{32–44} The molecular-level understanding of heterogeneous catalysis is reported to be less than that of homogeneous catalysis because of the nonuniformity in the structure of the solid surfaces. Well-defined metal complexes or clusters in zeolites are rare examples of structurally uniform heterogeneous catalysts.^{1,2,4,15,45–50}

1.2.1. Multinuclear metal-oxo cluster in zeolite

By the oxidation treatment (typically under O_2 flow at high temperature), multinuclear metal–oxo clusters, which are composed of a few metal and oxygen atoms, are formed in zeolite and show unique catalytic properties different from isolated metal ions and bulk metal oxides (Figure 2).^{36,51–59} To date, various studies have reported metal–oxo clusters (Fe,^{60–63} Ni⁴⁸, Cu^{64,65}, Al⁶⁶, and Ga^{56,67}) immobilized in zeolites. Using *in situ/operando* techniques and DFT calculation, the group of Hensen investigated the multinuclear Ga-oxo cluster formed in zeolite (e.g. $[Ga_2O_2]^{2+}$ and $[Ga_4O_4]^{2+}$) and revealed that their activities of alkane activation were highly dependent on their local structure (i.e. structure–activity relationship).⁵⁶

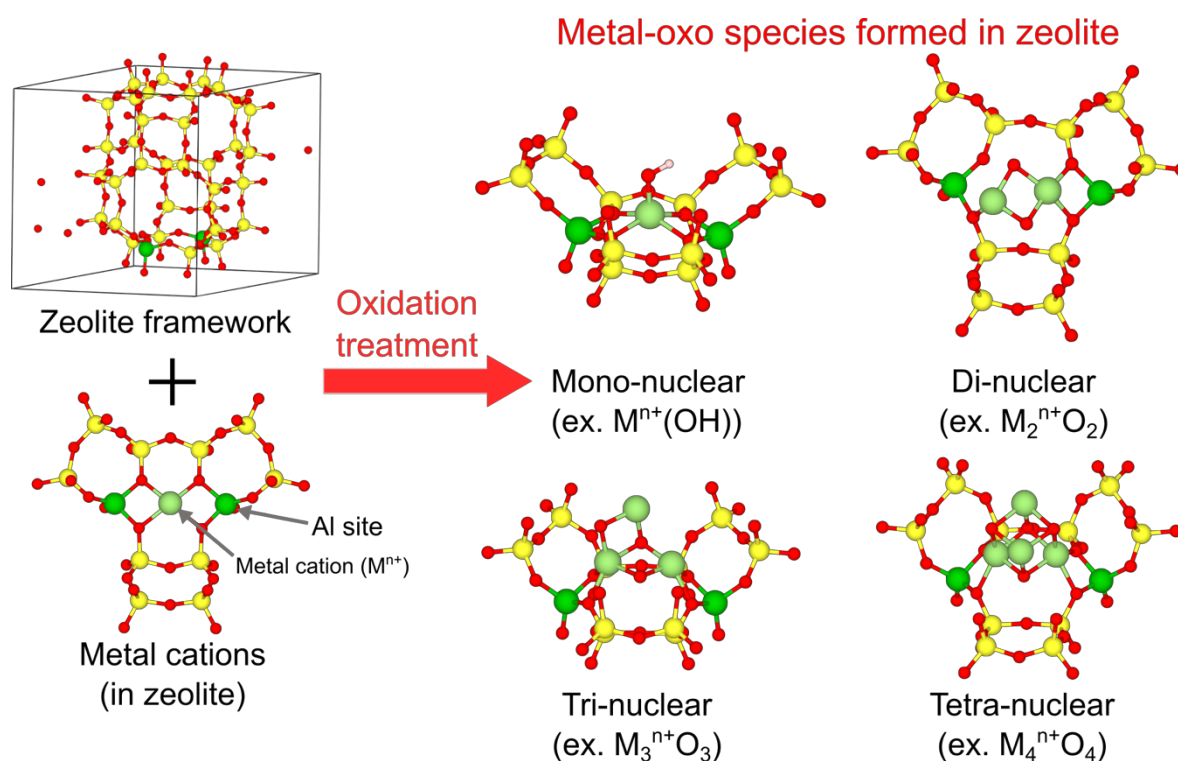


Figure 2 Representative structures of Metal-oxo species formed at Al sites in zeolites.

1.2.2. Metal hydride species in zeolite

In situ formed metal-hydride in zeolite ($[\text{MH}_x]^{n+}n\text{Z}^-$) should also be treated as an excellent example of the structural evolution of active sites under working conditions. Hydrides in/on solid materials have attracted significant attention in many research fields, including energy engineering,^{68–71} electrochemistry,^{72–74} and catalysis.^{75,76} In catalysis, metal-hydrides on solid material are formed *in situ* in the reductive condition (typically under H_2 at high temperature) and involved in heterogeneously catalyzed hydrogenation, dehydrogenation, and hydrogenolysis. Several zeolite-supported metal hydrides containing Ga,^{18,77–80} Zn,^{81–83} Ag,^{84,85} and Rh⁸⁶ have been reported, and these studies demonstrated that zeolites have a potential as effective supports to investigate the formation of isolated surface hydrides and catalytic applications for elucidating the atomic-scale understanding of active metal-hydrides and their structure–activity relationship.

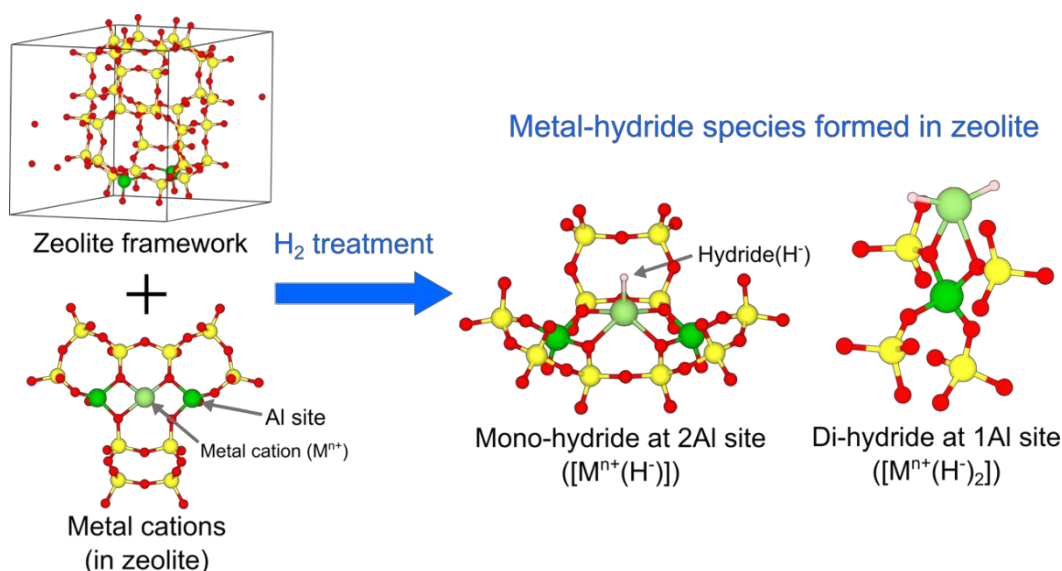


Figure 3 Representative structures of Metal-hydride species formed at single Al site (1Al site) and paired Al site (2Al site) in zeolites.

1.2.3. Dispersion and aggregation of active metal species

In experimental conditions, the nuclearity of active metal is dynamically changed depending on the change of experimental condition. Generally, exposure to high temperatures induces aggregation of metal species to form larger particles via particle coalescence and atomic ripening.^{29,87–100} Particle coalescence involves temperature-induced movement of metal nanoparticles, while atomic ripening occurs via the movement of atomic species on supports or in a vapor phase. As an opposite phenomenon, atomic dispersion of metal species occurs when mobile atomic species are trapped by supports (Figure 4). Several microscopic and spectroscopic studies on atomic dispersion have appeared recently, investigating structural evolution under various reaction conditions and their effects on catalytic and adsorption properties.^{101–107} The atomic dispersion phenomenon can be used to prepare atomically dispersed materials and regenerate the deactivated catalyst due to the aggregation of active metal.^{108–111} In some cases under periodic oxidative/reductive conditions, the dispersed metals aggregate into metal clusters again when the condition switches to the reductive condition. Subsequently, the metals reversibly disperse into atomic ones under the following oxidative condition (so-called “reversible structural evolution”; Figure 4b). Although some papers reported the reversible structural evolution of active metal in zeolite, its effective use for catalysis is still not established.

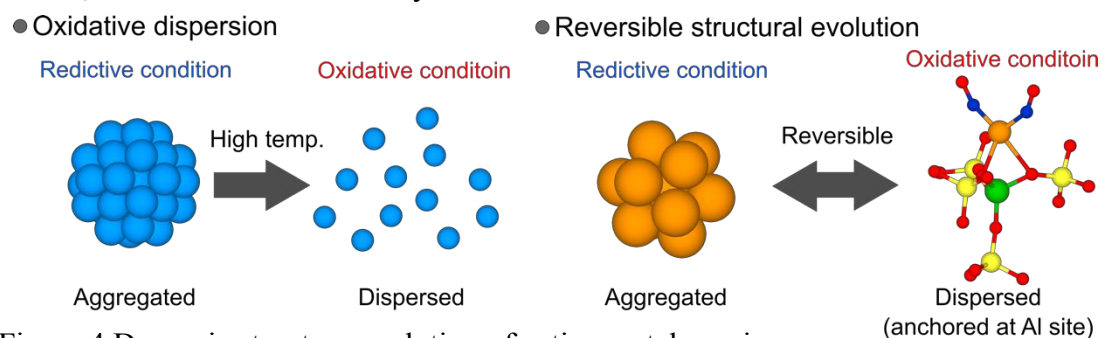


Figure 4 Dynamic structure evolution of active metal species

1.3. Constitution of thesis

This thesis consists of the following 7 chapters. The outline of each chapter is as follows;

In **chapter 2**, the formation of multi-oxo clusters of 13-group elements (In and Ga) and CH₄ activation under mild conditions were investigated.

In, **chapter 3**, the formation of In-hydride species in CHA zeolite and its superior selectivity for non-oxidative dehydrogenation of C₂H₆ were investigated.

In **chapter 4**, the preparation of high-loading Pd-CHA zeolite via oxidative solid ion exchange under NO flow and the structure-function relationship of Pd cation in CHA zeolite were investigated.

In **chapter 5**, the structural evolution of Rh species in CHA zeolite under periodic lean/rich conditions was investigated

In **chapter 6**, the rational design of the CH₄ combustion catalyst using O₃ was investigated.

In **chapter 7**, the summary of each chapter and the outlook for further development.

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Chapter 2

The formation of 13-group metal-oxo clusters in CHA zeolite and its reactivity for CH₄ activation at mild conditions.

2.1. Introduction

Multinuclear metal-oxo clusters, which are composed of a few metal and oxygen atoms, are expected to show unique catalytic differences from isolated metal ions and bulk metal oxides^{1–23}. To date, there have been various studies on polyoxometalates stabilized by inorganic/organic ligands, metal-oxo clusters immobilized on solid supports (bulk metal oxides, zeolite, carbon nanotube, and metal-organic frameworks), and gas-phase clusters vaporized by molecular beam and selected by mass spectroscopy²⁴. Of these, aluminosilicate zeolite-supported metal-oxo clusters are promising from the viewpoint of precise synthesis, as well as catalytic application, because of their characteristics²⁵; for example, the zeolite frameworks are well-defined and usually contain 6- to 12-membered rings consisting of tetrahedral SiO₄ and AlO₄ units linked through oxygen atoms. Paired Al sites are located on the ring, where multiply charged cations can be stabilized by two anionic sites (Si-O-Al). In addition, the high durability and easy handling of zeolites allow their applications in gas and liquid phase reactions. To date, several metal-oxo clusters in zeolites have been developed, making challenging transformations such as the C–H activation of CH₄ and light alkanes possible. Cu-oxo clusters have been most extensively studied for CH₄ activation because they mimic the catalytic activity of copper-containing monooxygenase. For example, the oxidation of CH₄ to MeOH occurs on O₂-activated Cu-exchanged ZSM-5, as reported by Groothaert *et al.*¹⁴, and the dinuclear [Cu(O)Cu]²⁺ cluster was identified as the active site¹⁵. Cu-exchanged mordenite was also active for CH₄ conversion to MeOH, and a similar Cu dimer was proposed by Snyder *et al.*¹⁶. Subsequently, the groups of Lercher and Hensen identified the trinuclear [Cu₃O₃]²⁺ cluster in mordenite by X-ray absorption fine structure (XAFS) analysis combined with density functional theory (DFT) calculations¹⁷. Other metal-oxo clusters, such as [Fe₂(μ₂-OH)₂(OH)₂(H₂O)₂]²⁺ dimer¹⁹ and [Ga₂O₂]²⁺ dimer^{18,26} in zeolites, have been found to be active for the oxidation¹⁹ or dehydrogenation of light

alkanes^{18,26} based on a combination of experimental and theoretical studies.

13-group metal-exchanged zeolites have the potential to activate the C–H bond of CH₄. It has been reported that reductive solid-state ion exchange (RSSIE) between metal oxide and H-form zeolites under an H₂ atmosphere around 700–800 K affords isolated M⁺ cations bound to the lattice oxygen anions^{27,28}. Baba *et al.* reported the reaction of CH₄ with ethylene to propane at 673 K using In-exchanged ZSM-5 (In-ZSM-5), in which the isolated In⁺ cations with lattice oxygen anions were considered to cleave the C–H bond of CH₄ heterolytically to give methyl cation-like species²⁹. They concluded that the CH₄ SCR reaction occurred on the InO⁺ sites in zeolites. Ono *et al.* investigated the use of Ga-exchanged ZSM-5, prepared by using the liquid phase ion-exchange method, as a catalyst for dehydrocyclization reactions of light alkanes/alkenes at 773 K and discussed the mechanism of the process³⁰. In a later investigation, Dooley *et al.* explored reductive solid-state ion-exchange (RSSIE) between Ga₂O₃ and proton-type ZSM-5 to improve catalytic activity by loading more Ga species in the zeolite^{31,32}.

Based on the above studies, we expect that multinuclear In and Ga-oxo clusters would be synthesized using the zeolites with well-defined paired Al sites and that these clusters would exhibit the unique ability for CH₄ activation. In this work, the zeolite-supported In, Ga-oxo clusters for CH₄ activation under mild reaction conditions are described based on experimental and theoretical studies. To achieve this goal, a CHA zeolite was utilized as a support because its framework is more robust under thermal conditions than other zeolites^{33,34}.

2.2. Experimental

2.2.1. Preparation of catalysts

In-exchanged CHA (In(I)-CHA) was prepared through the impregnation and RSSIE as follows. First, 1.0 g of CHA zeolite (Tosoh, NH₄⁺-type, SiO₂/Al₂O₃ = 22.3, NH₄-CHA) was suspended in an aqueous solution containing 0.1 g of In(NO₃)₃•nH₂O (Kanto Chemical Co., Inc.). The water was evaporated from the mixture, and the mixture was dried in an oven and calcined at 773 K in the air for 1 h, to afford In₂O₃ loaded on the CHA zeolite (denoted In₂O₃/CHA). Next, In₂O₃/CHA was treated with H₂ flow (20 mL min^{−1}) at 773 K for 30 min to promote RSSIE^{27,28}. Hereinafter, the obtained In cation-exchanged CHA was denoted as In(I)-CHA. The O₂ activation of In(I)-CHA was

conducted under O₂ flow (20 mL min⁻¹) at 773 K for 30 min. The O₂-activated In-exchanged CHA, InO_x-CHA, was obtained as a white powder.

The preparation of GaO_x-CHA was conducted through impregnation of Ga species, RSSIE with H₂, and O₂ treatment. Specifically, a 1.0 g of CHA zeolite (Tosoh, NH₄⁺-type, SiO₂/Al₂O₃ = 22.3, NH₄-CHA) and a 0.142 g of Ga(NO₃)₃·nH₂O (n = 7-9, Wako) were added to 50 mL of deionized water (Ga/Al = ca. 0.4). The mixture was stirred, and the water was removed in vacuo. The resulting solid was dried in an oven and calcined at 773 K under an air atmosphere for 1 h, giving gallium oxide-modified CHA zeolite (denoted as Ga₂O₃/CHA). For RSSIE, Ga₂O₃/CHA was treated under a H₂ flow (20 mLmin⁻¹) at 973 K for 30 min to form Ga-exchanged CHA zeolite (denoted as Ga-CHA). O₂ treatment of Ga-CHA was carried out under an O₂ flow (20 mLmin⁻¹) at 773 K for 30 min to produce O₂-treated Ga-CHA (GaO_x-CHA) as a white powder.

2.2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on Rigaku Miniflex using Cu K α radiation. N₂ adsorption measurements were conducted by using an AUTOSORB 6AG (Yuasa Ionics Co.). The loading amount of In was determined by energy dispersive X-ray fluorescence (EDX) spectrometry (Shimadzu EDX-700HS). H₂- and O₂-TPRs experiments were carried out using a BELCAT (MicrotracBEL). In₂O₃/CHA (approximately 50 mg) was pretreated at 773 K for 1 h under He. For H₂-TPR, In₂O₃/CHA was cooled to 373 K under He, and then the flow was changed to 5% H₂/Ar at a flow rate of 30 mL min⁻¹. For O₂-TPR, the above H₂-treated In₂O₃/CHA was cooled to 313 K under He, and then the flow was changed to 1% O₂/He at a flow rate of 30 mL min⁻¹. The temperature was increased to 773 K at 20 K min⁻¹, after which the temperature was maintained for 40 min. The H₂ consumption was monitored with a thermal conductivity detector. The O₂ consumption and the amount of gas consumed were investigated by a mass spectrometer (BEL Mass, (MicrotracBEL Inc.)). In K-edge XAFS data were collected in quick mode and recorded in transmission mode at the BL-01B1 and BL-14B2 stations attached to the Si(311) monochromator at SPring-8 (JASRI), Japan (Proposal Nos. 2018B1126 and 2018B1568). For *in situ* XAFS measurement, a flow-type cell connected to a flow reaction system was utilized. The X-ray absorption near-edge

structure (XANES) and extended XAFS (EXAFS) analyses were conducted using the REX ver. 2.5 program (Rigaku). The coordination numbers (CN) and interatomic distances (R) were estimated by curve-fitting analysis using In–O and In–In shell parameters obtained from reference samples of In_2O_3 . Scanning transmission electron microscopy (STEM) images were taken on a JEM-ARM200F microscope equipped with a JED-2300 EDX spectrometer (JEOL) at an acceleration voltage of 200 kV. The Cs-corrector CESCOR (CEOS) was used in STEM mode.

2.2.3. Reaction of CH_4

The IR spectroscopy study of the reaction of CH_4 was conducted with a JASCO FT/IR-4600 spectrometer equipped with a mercury cadmium telluride (MCT) detector using a flow-type IR cell connected to a flow reaction system. The IR disc of catalysts (40 mg, 20 mm) was first dehydrated under N_2 flow at 773 K (90 mL min^{-1}) and then H_2 treatment (20 mL min^{-1}) followed by O_2 treatment (10% balanced with N_2 , 100 mL min^{-1}) was conducted at 773 K. After that, a background spectrum was obtained under N_2 flow at 303 K (90 mL min^{-1}). Then, CH_4 (10%) was introduced to the sample, and the IR spectra were recorded.

2.2.4. DFT calculation

DFT calculations were carried out under the periodic boundary conditions using the Vienna *Ab initio* Simulation Package (VASP)^{35,36}. The generalized gradient approximation by the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional was adopted³⁷, and the dispersion-corrected DFT-D3 method was employed to consider the van der Waals interactions. The Kohn–Sham equations were solved with the projector augmented wave (PAW) method, and only the Γ point was considered for Brillouin zone sampling. A modest Gaussian smearing of 0.05 eV was applied to the band occupations around the Fermi level, and the total energies were extrapolated to $\sigma \rightarrow 0$. The plane-wave cutoff energy was set to 500 eV, and spin–polarization was considered in all calculations. For geometry optimization, the lattice parameters were fixed ($a = b = 13.675 \text{ \AA}$, $c = 14.767 \text{ \AA}$, $\alpha = \beta = 90.0^\circ$, $\gamma = 120^\circ$ and $\text{Si}/\text{Al} = 17$; Figure 1),³⁸ and the forces on atoms were minimized to be less than $0.03 \text{ eV/\AA}$. The climbing image nudged elastic band

(CI-NEB) method was used to locate the transition-state structures for the C–H bond cleavage of methane on the In-oxo species. The spring constant between adjacent images was set to $5.0 \text{ eV/\AA}^2$, and the quasi-Newton algorithm was adopted for relaxing the geometry in the NEB approach.

In K-edge XANES spectra were simulated for the DFT-optimized structures using the FDMNES software^{39,40}. For simulating the In foil, a unit cell consisting of two In atoms ($a = 3.309 \text{ \AA}$, $b = 3.309 \text{ \AA}$, $c = 5.016 \text{ \AA}$, and $\alpha = \beta = \gamma = 90.0^\circ$) was used, while the model of In_2O_3 consisting of 32 In atoms in the supercell ($a = b = c = 10.299 \text{ \AA}$ and $\alpha = \beta = \gamma = 90.0^\circ$) was employed to simulate bulk oxide. The simulated spectra were normalized based on the number of metal atoms in each system.

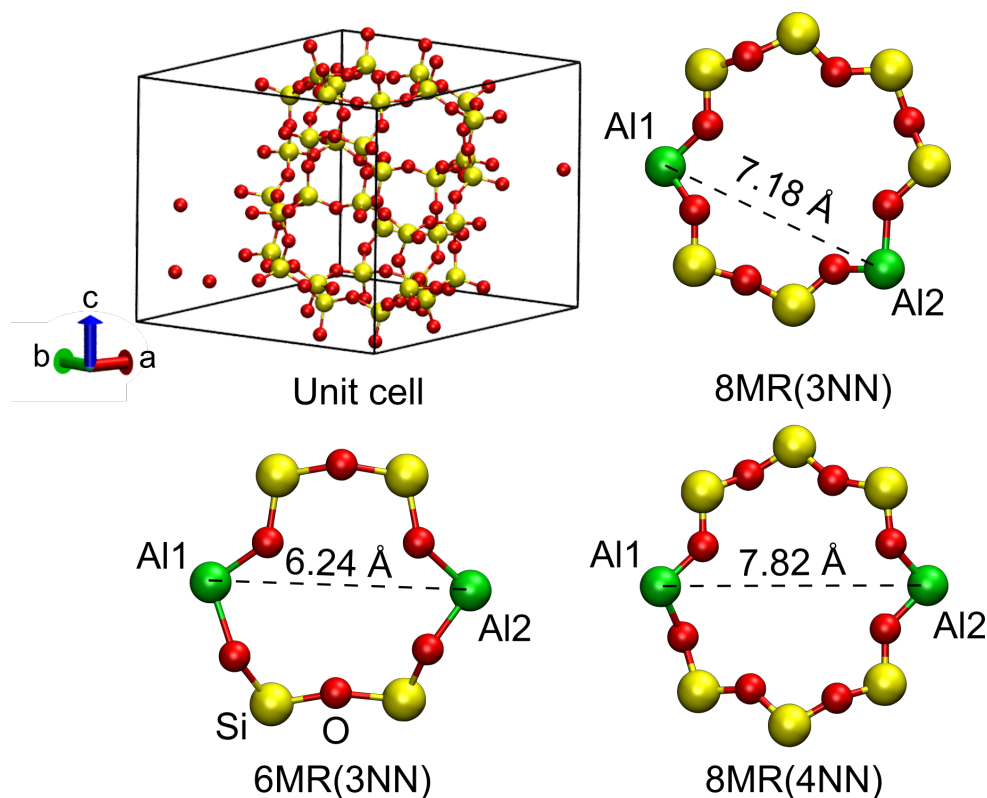


Fig. 1 Unit cell of CHA zeolite and paired Al sites investigated in periodic DFT calculations. Yellow: Si, Red: O, and Green: Al.

2.3. Results and discussion

2.3.1. Morphologies and colors of the In-exchange zeolites

To characterize the morphologies of the zeolites, we carried out XRD measurements and N₂ adsorption measurements of In₂O₃/CHA and InO_x-CHA. The XRD patterns of In₂O₃/CHA and InO_x-CHA were similar to that of H-CHA (prepared by calcination of NH₄-CHA at 773 K) (Figure 1(a)), which indicates that the crystal structure of CHA was maintained⁴¹. The specific surface areas (Table S1), as determined by the Brunauer–Emmett–Teller (BET) method from N₂ adsorption isotherms (Figure 1(b)), of H-CHA, In₂O₃/CHA, and InO_x-CHA were 833, 785, and 710 m² g⁻¹, respectively. The pore volumes of H-CHA, In₂O₃/CHA, and InO_x-CHA were determined as 0.402, 0.378, and 0.344 mL g⁻¹, respectively. These results show that the pore structure of the CHA zeolites did not change during preparation. The smaller specific surface area and pore volume of InO_x-CHA than H-CHA and In₂O₃/CHA are ascribed to the encapsulation of In species into zeolites. EDX analysis of In₂O₃/CHA revealed that the In loading amount was 3.2 wt%, which corresponds to In/Al $\approx$ 0.2. Figure 2 shows photographs of In₂O₃/CHA, In(I)-CHA, and InO_x-CHA. First, after impregnation followed by calcination, In₂O₃/CHA was a pale-yellow color (Figure 2(a)). During H₂ reduction of In₂O₃/CHA, the color changed from pale-yellow to white (Figure 2(b)), indicating the absence of aggregated In(0) metal species in In(I)-CHA. After the O₂ treatment of In(I)-CHA, the white color of the catalyst was maintained but differed from that of In₂O₃/CHA (Figure 2(c)), suggesting the formation of In-oxo species unlike In₂O₃.

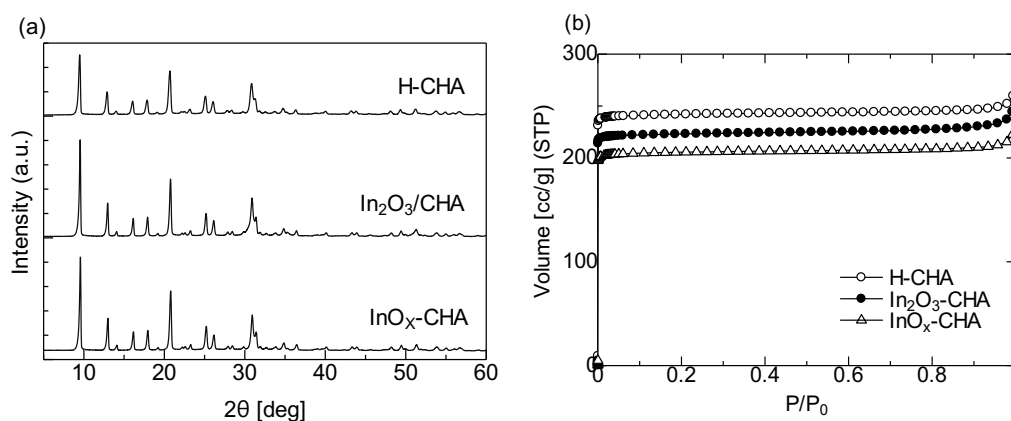


Figure 1. (a) XRD patterns and (b) N₂ adsorption isotherms of H-CHA, In₂O₃/CHA, and InO_x-CHA.

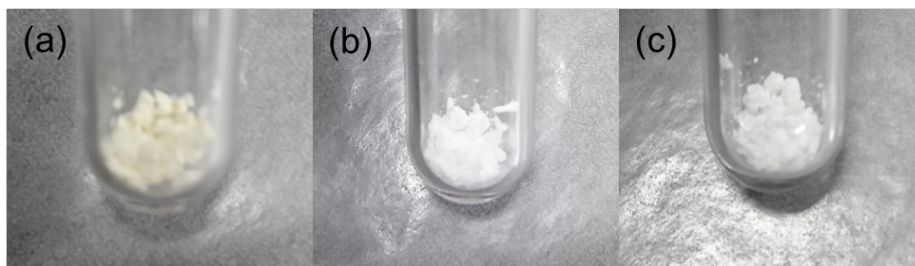


Figure 2. Photographs of (a) $\text{In}_2\text{O}_3/\text{CHA}$, (b) $\text{In}(\text{I})\text{-CHA}$, and (c) $\text{InO}_x\text{-CHA}$.

2.3.2. STEM observation for In-CHA

The formation of highly dispersed In species was supported by STEM observation. The annular bright field and high-angle annular dark-field STEM (ABF- and HAADF-STEM, respectively) images of $\text{In}_2\text{O}_3/\text{CHA}$ show that many aggregated In_2O_3 species (about 10–30 nm) were present on the CHA zeolite (Figure 3). In contrast, the aggregated species was scarcely observed in the STEM images of $\text{InO}_x\text{-CHA}$ (Figures 4(a) and (b)). The distribution of In species was also determined by HAADF-STEM with EDX elemental mapping. The elemental mapping of $\text{InO}_x\text{-CHA}$ clearly shows the high dispersion of In species in the CHA zeolite (Figure 4). Note that aggregated In species formed during STEM observation (Figure 5). This result indicates that highly dispersed In species in the zeolite framework can easily be aggregated by the electron beam, making STEM observation difficult⁴².

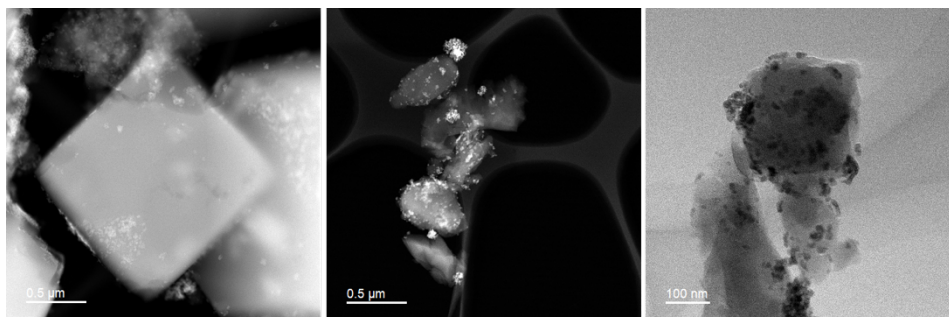


Figure 3. ABF- and HAADF-STEM images of $\text{In}_2\text{O}_3/\text{CHA}$.

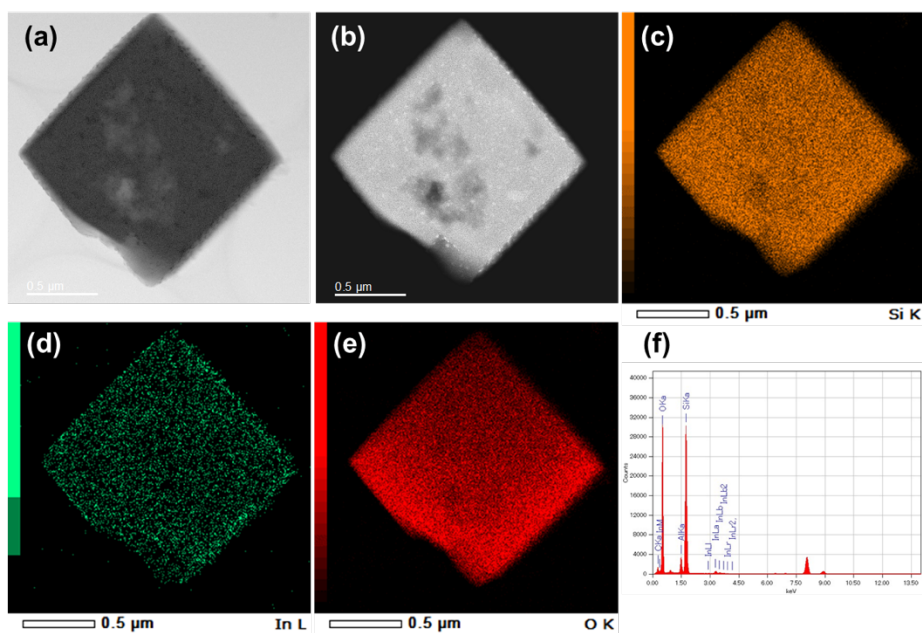


Figure 4. (a) ABF- and (b) HAADF-STEM images of InO_x-CHA. Elemental mapping images of (c) Si, (d) In, and (e) O, and (f) EDX spectrum.

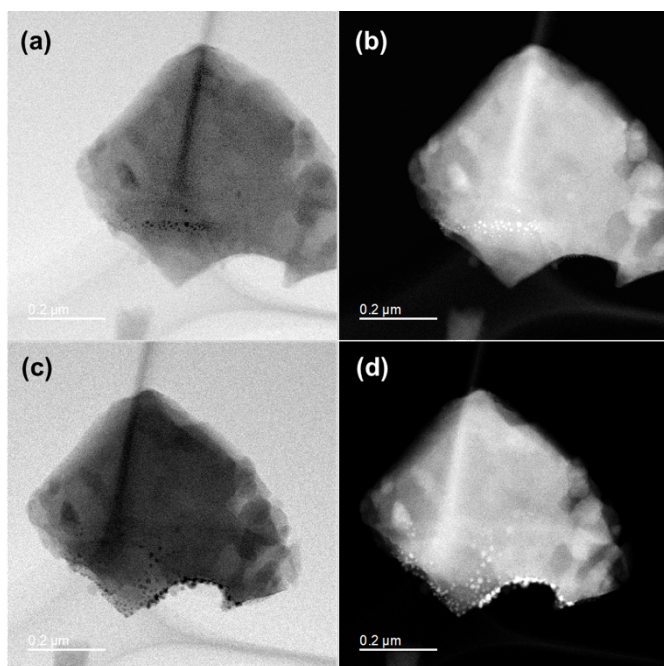


Figure 5. Aggregation of In species during STEM observation. (a) ABF- and (b) HAADF-STEM images of InO_x-CHA. The lower two images ((c) and (d)) were measured 12 min after collecting the upper two images.

2.3.3. H_2 - and O_2 -TPR measurements for In-CHA

The reduction profile of the In species in In_2O_3/CHA was investigated using H_2 -TPR measurements. Figure 6(a) shows the H_2 -TPR profiles. The reduction peak was observed around 573–773 K and the amount of H_2 consumed was determined to be 18 μmol . This value is similar to the amount of In species in In_2O_3/CHA used for H_2 -TPR (In: 15 μmol). Lónyi *et al.* reported that the H_2 -TPR profile for the RSSIE between In_2O_3 and H-mordenite had a reduction peak around 623–773 K and found that the molar ratio of the consumed H_2 and the In species are almost same²⁸. Accordingly, the reduction peak observed after the H_2 treatment of In_2O_3/CHA corresponds to the occurrence of the RSSIE between In(I) ions and protons in CHA zeolite. The oxidation of In(I)-CHA was also carried out by O_2 -TPR. The O_2 -TPR profile (Figure 6(c)) showed a peak corresponding to the oxidation of reduced In species. Furthermore, H_2 -TPR measurement was examined for InO_x -CHA where the position of the reduction peak shifted toward lower temperature (473–723 K) from that in the case of In_2O_3/CHA (Figure 6(a) vs 6(b)). These observations suggest the formation of highly dispersed In-oxo species unlike In_2O_3 , which is consistent with the results of the STEM observations.

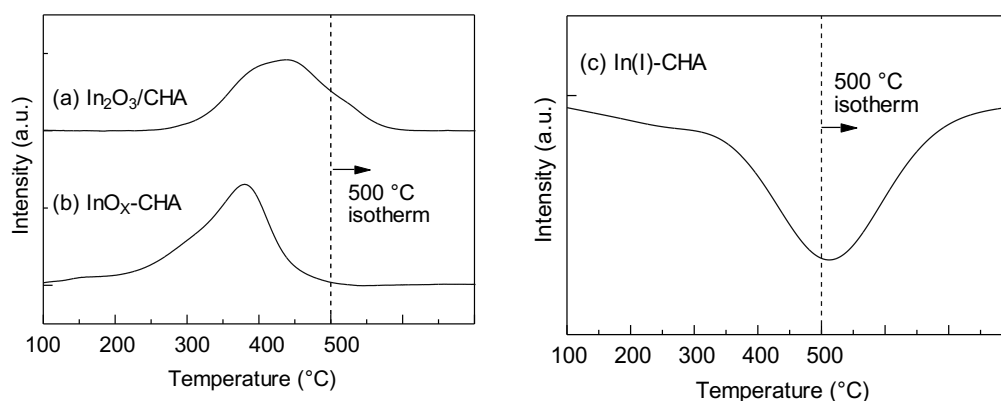


Figure 6. H_2 -TPR profiles of (a) In_2O_3/CHA and (b) InO_x -CHA. (c) O_2 -TPR profile of $In(I)$ -CHA.

2.3.4. XAFS measurement for In-CHA

To obtain insight into the In species in the In-exchanged CHA zeolites, *in situ* XAFS measurements were carried out. The normalized XANES spectra and Fourier transforms (FT) of the k^3 -weighted EXAFS spectra are summarized in Figures 7(a) and 7(c), respectively. First, the edge position of In₂O₃/CHA ($E_0 = 27935.9$ eV) was almost the same as that of In₂O₃ powder ($E_0 = 27935.4$ eV) and different from that of In foil ($E_0 = 27932.6$ eV). The FT of the EXAFS spectrum of In₂O₃/CHA showed three peaks, which were also observed in that of In₂O₃ powder (Figure 7(c)). The first peak can be attributed to the In–O shell, and the second and third peaks are assignable to two types of In–In shells, respectively. These results are evidence for the existence of In₂O₃ species in In₂O₃/CHA.

After H₂ treatment (5% balance with He) of In₂O₃/CHA at 773 K, the absorption edge shifted to lower energy ($E_0 = 27931.7$ eV). Figure 7(b) shows the XANES spectra during H₂ treatment in which three isosbestic points were observed; these are marked with vertical dotted lines. These edge shift and isosbestic points are similar to the observations made for the XANES spectra of Ga-exchanged zeolites during H₂ treatment in a previous paper⁴³, where the type of Ga species (isolated Ga⁺ cation or Ga-hydride species) is controversial. Hock *et al.* claimed that the edge shift can be interpreted as evidence of Ga-hydride species based on a comparison of XANES spectra with organometallic model compounds⁴⁴. In contrast, Lercher *et al.* concluded that Ga⁺ cation was selectively formed based on the H₂-TPR measurement⁴⁵. Considering the RSSIE between In₂O₃ and H-zeolites reported in previous papers^{27,28}, the energy shift in In K-edge XANES spectra can be ascribed to the reduction of In³⁺ species (In₂O₃) to In⁺ cations. However, the simulated XANES spectra suggested the formation of In-hydride (In⁺-H⁻) species^{46–48} rather than In⁺ cations (Figure S1). The speciation of In after RSSIE is currently under study using other spectroscopic and theoretical methods.

After a He purge followed by O₂ treatment (5% balance with He) of In(I)-CHA at 773 K, the absorption edge returned to a similar value to that of In₂O₃ ($E_0 = 27934.7$ eV),

indicating that In^+ ions were oxidized to In^{3+} species (Figure 7(a)). In the FT of the EXAFS spectrum of $\text{InO}_x\text{-CHA}$ (Figure 7(c)), the two peaks assignable to In–O and In–In shells were observed, which is different from the cases of In_2O_3 and $\text{In}_2\text{O}_3/\text{CHA}$. The curve fitting analysis indicated that the CNs are 4.9 and 2.3, respectively (Table 1). From the results obtained from XAFS measurements, multinuclear In-oxo clusters were generated in the CHA zeolites. Thus, in conclusion, the In_2O_3 loaded on H-CHA was reduced by H_2 treatment to afford isolated In^+ ions in the CHA zeolite through RSSIE and, then, the dispersed In^+ ions reacted with O_2 , resulting in the formation of In-oxo clusters.

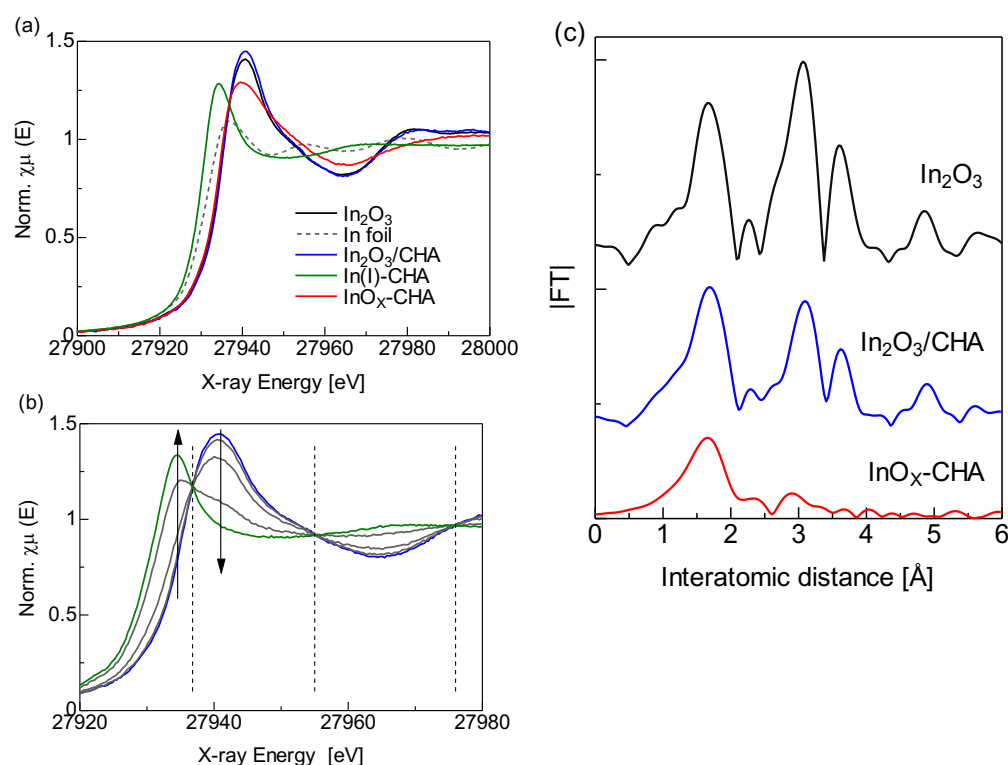


Figure 7. (a) Normalized In K-edge XANES spectra of In_2O_3 , In foil, $\text{In}_2\text{O}_3/\text{CHA}$, In-CHA (after H_2 treatment of $\text{In}_2\text{O}_3/\text{CHA}$), $\text{InO}_x\text{-CHA}$ (after O_2 treatment of $\text{In}_2\text{O}_3/\text{CHA}$). (b) *In situ* In K-edge XANES spectra during H_2 treatment of $\text{In}_2\text{O}_3/\text{CHA}$. Dotted lines show isosbestic points. (c) FT of k^3 -weighted EXAFS oscillations measured at room temperature for In_2O_3 , $\text{In}_2\text{O}_3/\text{CHA}$, and $\text{InO}_x\text{-CHA}$.

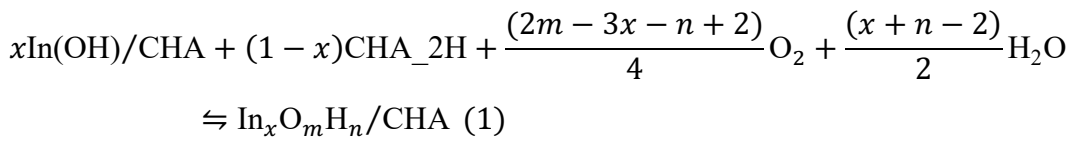
Table 1. Curve-Fitting Analysis of In K-Edge EXAFS of InO_x-CHA

Sample	Shell	CN ^a	R (Å) ^b	ΔE (eV) ^c	Δ (Å) ^d	R (%) ^e
InO _x -CHA	In–O	4.95 ± 1.04	2.12 ± 0.02	-0.122	0.086	3.19
	In–In	2.38 ± 1.58	3.25 ± 0.03	-2.648	0.098	
In ₂ O ₃ (reference)	In–O	6 ^f	2.19 ^f	-	-	-
	In–In	6 ^f	3.34 ^f	-	-	-

a Coordination numbers. b Bond distance. c Increase of the threshold energy. d Debye–Waller factor. e Residual factor. f Obtained from crystallographic data.

2.3.5. *Ab initio* thermodynamic analysis for In species in CHA zeolite

We employed an *ab initio* thermodynamic approach⁴⁹ to predict the structures of the In-oxo clusters in InO_x-CHA. This approach has been utilized for predicting the structures of the key multinuclear metal-oxo clusters of Cu, Fe, and Al cations in zeolites^{17,50–54}. Three types of paired Al sites were examined as coordination sites of the In-oxo clusters. The first type possesses two Al sites that are separated by three Si centers in an eight-membered ring (8MR) and has a connectivity distance of three, denoted as the forth-nearest-neighbor site, 8MR(4NN). The other two are represented as 8MR(3NN) and 6MR(3NN) (Figure 1)⁵³. We consider the following equilibrium reaction:



The corresponding reaction energy is represented as

$$\Delta E = E_{\text{In}_x\text{O}_m\text{H}_n/\text{CHA}} - xE_{\text{In(OH)/CHA}} - (1-x)E_{\text{CHA}_{-2\text{H}}} - \frac{(2m-3x-n+2)}{4}E_{\text{O}_2} - \frac{(x+n-2)}{2}E_{\text{H}_2\text{O}} \quad (2)$$

where $E_{\text{In}_x\text{O}_m\text{H}_n/\text{CHA}}$ is the total energy of the CHA zeolite model containing In-oxo species. $E_{\text{In(OH)/CHA}}$ is the energy of the In-CHA model containing $[\text{In(OH)}]^{2+}$ ions to compensate for the negative charge of two Al atoms in the zeolite framework. $E_{\text{CHA}_{-2\text{H}}}$, E_{O_2} , and $E_{\text{H}_2\text{O}}$ represent the computed energies of the CHA zeolite possessing two H

atoms for charge compensation, gaseous water, and oxygen molecules, respectively. The accompanying change in the free energy, $\Delta\Gamma$, is defined as

$$\Delta\Gamma(T, p) = \frac{1}{A} \left[\Delta E - \frac{(2m - 3x - n + 2)}{2} \Delta\mu_{\text{O}} - \frac{(x + n - 2)}{2} \Delta\mu_{\text{H}_2\text{O}} \right] \quad (3)$$

where A represents the area of the unit cell. The chemical potential, $\Delta\mu$, are described as

$$\Delta\mu_{\text{O}}(T, p) = \frac{1}{2} \left[\Delta\mu_{\text{O}_2}(T, p^0) + RT \ln \left(\frac{p_{\text{O}_2}}{p^0} \right) \right] \quad (4)$$

$$\Delta\mu_{\text{H}_2\text{O}}(T, p) = \Delta\mu_{\text{H}_2\text{O}}(T, p^0) + RT \ln \left(\frac{p_{\text{H}_2\text{O}}}{p^0} \right) \quad (5)$$

Our computational data set includes one monomer, two dimers, one trimer, and three tetramers. Details of models are provided in the ESI[†]. To reflect the reaction conditions of the O₂ treatment of In(I)-CHA, we have shown the computational free energies for the formation of In-oxo ions (Figures 8(a)–(c)) and the phase diagram representing the lowest-energy species (Figures 8(d)–(f)) at 800 K as a function of O₂ and H₂O chemical potentials ($\Delta\mu_{\text{O}_2}$ and $\Delta\mu_{\text{H}_2\text{O}}$, respectively). $\Delta\mu_{\text{O}_2}$ and $\Delta\mu_{\text{H}_2\text{O}}$ are translated into partial pressure scales (P_{O_2} and $P_{\text{H}_2\text{O}}$, respectively) at 800 K in the phase diagram.

In the phase diagram for the 8MR(4NN) site (Figure 8(d)), the equilibrium In-oxo structure is sensitive to the value of $\log(P_{\text{H}_2\text{O}})$, and the $[\text{In}_2\text{O}_2]^{2+}$ ion (yellow) is the lowest-energy In-oxo ion at the lowest H₂O partial pressure. As $\log(P_{\text{H}_2\text{O}})$ increases, the $[\text{In}_2\text{O}_2]^{2+}$ ion changes to a tetrameric structure, such as $[\text{In}_4\text{O}_4]^{2+}$ (gray) and $[\text{In}_4\text{O}_4(\text{OH})_2]^{2+}$ ions (green), and $[\text{In}_2(\text{OH})_4]^{2+}$ ion (blue) is the lowest-energy In-oxo ion at high H₂O partial pressures. At a $\log(P_{\text{O}_2})$ of around -1 or 0 and a low H₂O partial pressure, corresponding to 10% or 100% O₂ flow in dry conditions, the free energy for the formation of the $[\text{In}(\text{OH})]^{2+}$ ion is only slightly higher than that of $[\text{In}_2\text{O}_2]^{2+}$ ion, whereas those of other In-oxo ions are much higher, as shown in Figure 8(a). These results indicate that the $[\text{In}_2\text{O}_2]^{2+}$ ion is a candidate In-oxo cluster on 8MR(4NN) sites under the O₂ condition. Concerning the 8MR(3NN) site, although $[\text{In}(\text{OH})]^{2+}$ ion (red) is the lowest-energy In-oxo ion at low H₂O pressures (Figure 8(e)), the free energy for the formation of the $[\text{In}_2\text{O}_2]^{2+}$ ion is close to that of the $[\text{In}(\text{OH})]^{2+}$ ion and much lower than those of the other In-oxo ions (Figure 8(b)), indicating that the $[\text{In}_2\text{O}_2]^{2+}$ ion is a plausible In-oxo structure for the 8MR(3NN) site. In contrast, for the 6MR(3NN) site, the $[\text{In}(\text{OH})]^{2+}$ ion is the most

stable structure under all O_2 and H_2O partial pressures (Figures 8(c) and 8(f)). From the phase diagrams, we suggest that multinuclear In-oxo clusters are formed at paired Al sites on 8MR, and the $[In_2O_2]^{2+}$ ion is the most plausible structure among the considered multinuclear clusters. Hereinafter, we consider $[In_2O_2]^{2+}$ on 8MR(4NN) and 8MR(3NN) and $[In(OH)]^{2+}$ on 6MR(3NN) as model dimeric and monomeric In-oxo ions for further discussion.

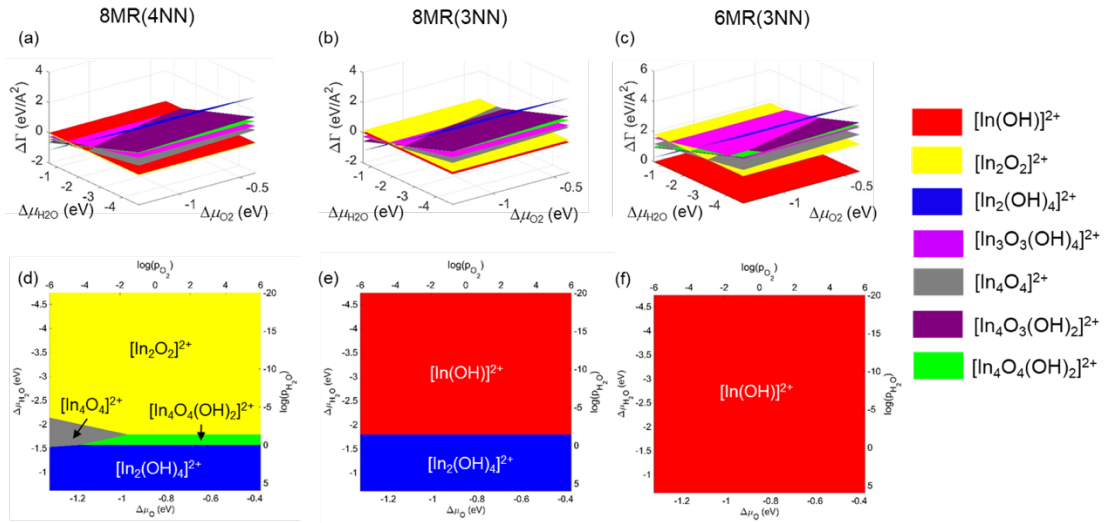


Figure 8. Free energy ($\Delta\Gamma$) for the formation of the In-oxo ions in CHA (top) and phase diagram showing the lowest-energy In-oxo ions (bottom) as a function of O_2 and H_2O chemical potentials ($\Delta\mu_{O_2}$ and $\Delta\mu_{H_2O}$, respectively) on (a,d) 8MR(4NN), (b,e) 8MR(3NN), and (c,f) 6MR(3NN).

The optimized structures for $[In_2O_2]^{2+}$ at 8MR(4NN) and 8MR(3NN) sites (denoted as $[In_2O_2]^{2+}$ -8MR(4NN) and $[In_2O_2]^{2+}$ -8MR(3NN)) and for $[In(OH)]^{2+}$ at 6MR(3NN) ($[In(OH)]^{2+}$ -6MR(3NN)) are shown in Figure 9. The In–In distances for $[In_2O_2]^{2+}$ -8MR(4NN) is 2.92 Å, which is very similar to that in $[In_2O_2]^{2+}$ -8MR(3NN) (2.91 Å), despite the obvious difference in the Al–Al distances (7.88 and 7.23 Å for $[In_2O_2]^{2+}$ -8MR(4NN) and $[In_2O_2]^{2+}$ -8MR(3NN), respectively). The In–O distances range from 2.07 to 2.10 Å for both $[In_2O_2]^{2+}$ ions. These In–In and In–O distances are different from the case of $[Ga_2O_2]^{2+}$ ions in zeolites reported by Hensen *et al.*⁵⁵ where the Ga–Ga and Ga–O distances were calculated to be about 2.49–2.59 and 1.84–1.89 Å, respectively. The

In–O–In angles for $[\text{In}_2\text{O}_2]^{2+}\text{-8MR(4NN)}$ and $[\text{In}_2\text{O}_2]^{2+}\text{-8MR(3NN)}$ are about 88–89°. This value is slightly larger than the Ga–O–Ga angle in $[\text{Ga}_2\text{O}_2]^{2+}$ ions (about 84–88°). For $[\text{In}(\text{OH})]^{2+}\text{-6MR(3NN)}$, the In–O distance of $[\text{In}(\text{OH})]^{2+}$ is 2.02 Å and the Al–Al distance is 5.88 Å. The shorter Al–Al distance in 6MR(3NN) compared to those in 8MR(4NN) and 8MR(4NN) might be one of the reasons why monomeric $[\text{In}(\text{OH})]^{2+}$ ions are more stable among the other In-oxo ions. As demonstrated above, $[\text{In}_2\text{O}_2]^{2+}$ ions are expected to be the most stable In-oxo ions on paired Al sites in 8MR.

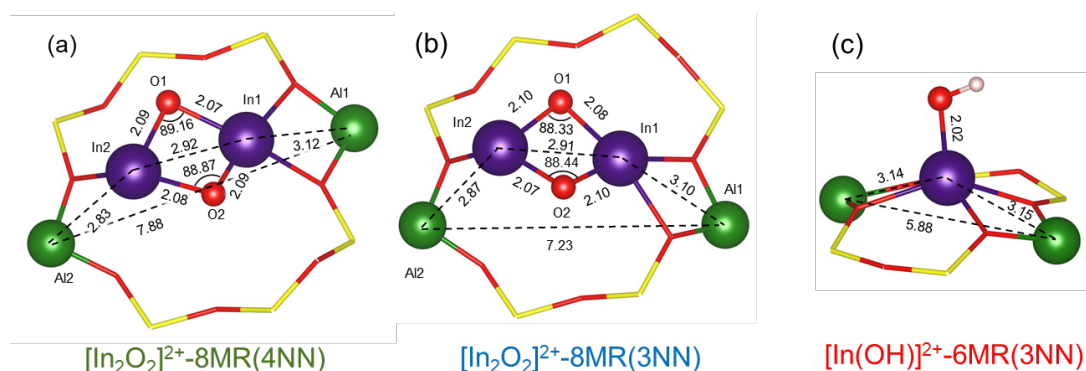


Figure 9. Optimized structures of (a) $[\text{In}_2\text{O}_2]^{2+}\text{-8MR(4NN)}$, (b) $[\text{In}_2\text{O}_2]^{2+}\text{-8MR(3NN)}$, and (c) $[\text{In}(\text{OH})]^{2+}\text{-6MR(3NN)}$.

2.3.6. Experimental and theoretical investigation for activation of CH_4 on In-oxo clusters

The development of effective catalysts for CH_4 activation under mild conditions is challenging because of the high stability of C–H bonds in CH_4 , and various experimental and theoretical studies in this research area have been carried out^{56–75}. To explore the ability to activate CH_4 of In-oxo clusters supported in CHA, the adsorbed species generated during the reaction of CH_4 on $\text{InO}_x\text{-CHA}$ at room temperature were studied by *in situ* IR measurements (Figure 10). The FT-IR spectrum contains a peak at 1379 cm^{-1} and a band around 1700 cm^{-1} after 10% CH_4 purge for 100 min followed by an N_2 purge. The first peak can be assigned to C–H bending of adsorbed formic acid⁷⁶, and the latter peak was deconvoluted into two peaks at 1710 and 1630 cm^{-1} , which can be attributed to the C=O stretching of adsorbed formic acid and water⁷⁶, respectively. The formation of formic acid was supported by the FT-IR measurement after the adsorption of formic acid on H-CHA where similar two peaks were observed (Figure S2). The CH_4 -

TPR of $\text{InO}_x\text{-CHA}$ revealed that neither CO_2 nor CO was detected at room temperature, indicating the occurrence of selective oxidation of CH_4 to formic acid. We tried to extract the adsorbed formic acid using D_2O for determination by ^1H NMR measurement according to the previous paper⁷⁷, but any peak was not observed in the NMR spectrum, which might be due to difficulty in extraction from the small pore of CHA zeolites. In the control experiments using $\text{In}_2\text{O}_3/\text{CHA}$ and In_2O_3 instead of $\text{InO}_x\text{-CHA}$, the spectra did not contain these peaks. The above results show that CH_4 was oxidized to formic acid at room temperature over the In-oxo clusters.

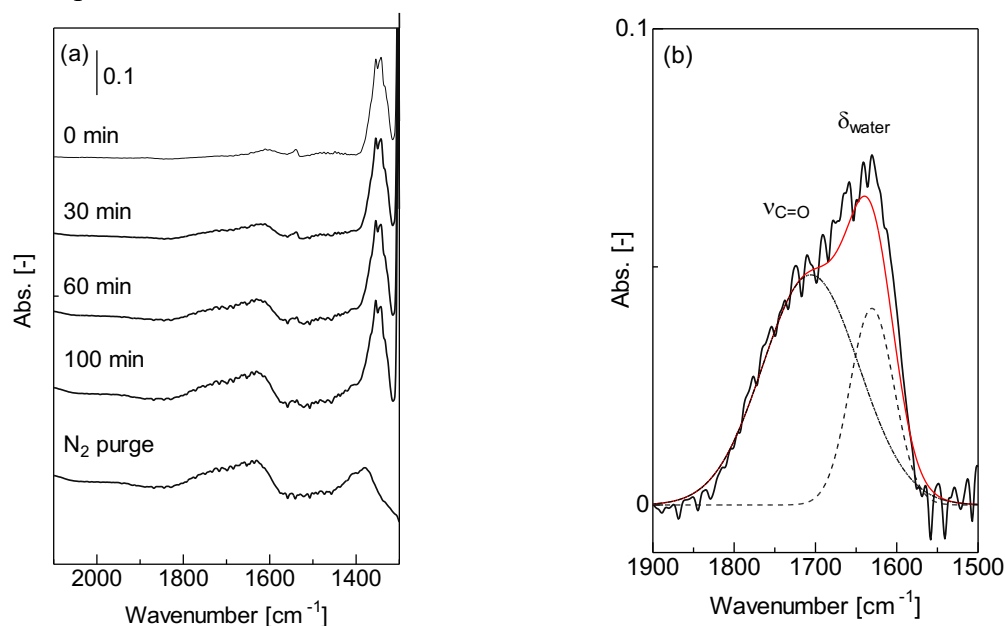


Figure 10. (a) FT-IR spectra during the reaction of CH_4 on $\text{InO}_x\text{-CHA}$ at room temperature. (b) Curve-fitting of the band around 1800–1600 cm^{-1} in the IR spectrum after N_2 purge.

We also investigated the reactivities of the possible In-oxo ions, $[\text{In}_2\text{O}_2]^{2+}\text{-8MR(4NN)}$, $[\text{In}_2\text{O}_2]^{2+}\text{-8MR(3NN)}$, and $[\text{In(OH)}]^{2+}\text{-6MR(3NN)}$, for the C–H bond cleavage of CH_4 using DFT calculations, and the reaction energy diagrams and geometrical parameters are shown in Figure 11 and Table 2, respectively. The adsorption energies of CH_4 on $[\text{In}_2\text{O}_2]^{2+}\text{-8MR(4NN)}$ and $[\text{In}_2\text{O}_2]^{2+}\text{-8MR(3NN)}$ are similar ($E_{\text{ads}} = -43.7$ and -41.8 kJ/mol, respectively) and larger than that on $[\text{In(OH)}]^{2+}\text{-6MR(3NN)}$ ($E_{\text{ads}} = -18.9$ kJ/mol). As shown in Figure 11 and Table 2, the shortest In–C distances for $[\text{In}_2\text{O}_2]^{2+}\text{-8MR(4NN)}$, $[\text{In}_2\text{O}_2]^{2+}\text{-8MR(3NN)}$, and $[\text{In(OH)}]^{2+}\text{-6MR(3NN)}$ are 2.91, 2.87, and 5.36 Å,

respectively. In contrast, the four C–H bond distances of the CH₄ molecules adsorbed on each In-oxo ions are almost the same, and the average distance is about 1.10 Å. The H–C–H angles directed toward the In cation of [In₂O₂]²⁺-8MR(4NN) and [In₂O₂]²⁺-8MR(3NN) are 114.3° and 112.4°, respectively. These values are larger than the H–C–H angle of isolated CH₄ (109.7°). These results suggest that CH₄ adsorbs on [In₂O₂]²⁺ ions in an η^2 -like fashion, which results in a distorted CH₄ structure. Similar M–H and C–H bond distances and H–C–H angles were reported by Kuroda *et al.* in their theoretical studies of CH₄ activation by Zn and Mg cations in zeolites⁷⁸. In contrast, the H–C–H angle for [In(OH)₂]²⁺-6MR(3NN) (109.0°) is very close to that in isolated CH₄.

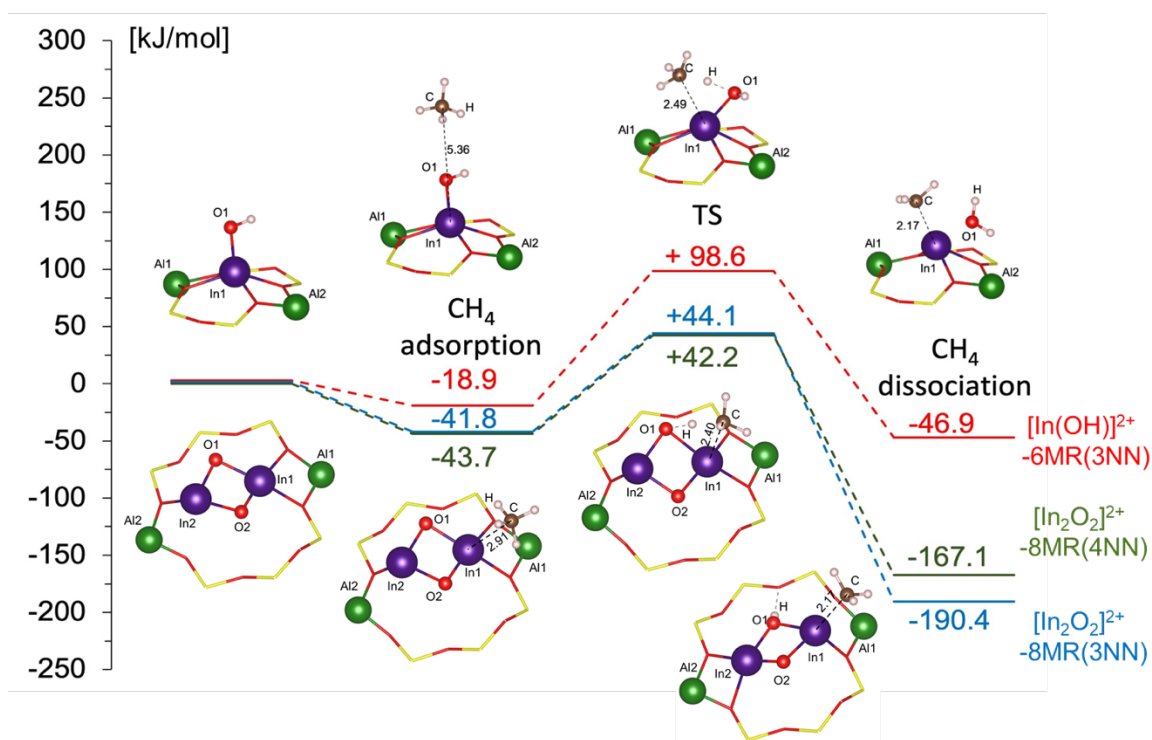


Figure 11. Reaction energy diagrams of the intermediates and transition states for the activation of CH₄ by [In₂O₂]²⁺-8MR(4NN) (green), [In₂O₂]²⁺-8MR(3NN) (blue), and [In(OH)₂]²⁺-6MR(3NN) (red). Optimized structures of the intermediates and transition states for [In₂O₂]²⁺-8MR(4NN) (bottom) and [In(OH)₂]²⁺-6MR(3NN) (top) are included in the figure.

Table 2. Geometrical parameters (distances in Å and bond angles in degrees) for adsorption (Ads), transition-state (TS), dissociation (Dis) structures of $[\text{In}_2\text{O}_2]^{2+}$ -8MR(4NN), $[\text{In}_2\text{O}_2]^{2+}$ -8MR(3NN), and $[\text{In}(\text{OH})_2]^{2+}$ -6MR(3NN).

	$[\text{In}_2\text{O}_2]^{2+}$ -8MR(4NN)			$[\text{In}_2\text{O}_2]^{2+}$ -8MR(3NN)			$[\text{In}(\text{OH})_2]^{2+}$ -6MR(3NN)		
	Ads	TS	Dis	Ads	TS	Dis	Ads	TS	Dis
In1–In2	2.94	3.04	3.17	2.92	3.03	3.15	-	-	-
In1–O1–In2	89.34	88.59	94.21	88.63	88.55	92.87	-	-	-
In1–O2–In2	89.90	94.83	100.27	88.73	94.11	99.90	-	-	-
C–H	1.10	1.38	-	1.11	1.37	-	1.10	1.35	-
O1–H	3.39	1.34	0.98	3.98	1.36	0.98	2.65	1.29	-
O1–C	4.09	2.70	3.90	4.37	2.70	3.98	3.35	2.61	3.13
In1–O1	2.10	2.26	2.18	2.08	2.24	2.22	-	-	-
In1–O2	2.09	2.06	2.11	2.11	2.08	2.11	-	-	-
In1–C	2.91	2.40	2.17	2.87	2.40	2.17	5.36	2.49	2.17
H1–C–H2	114.27	-	-	112.42	-	-	109.73	-	-

Following adsorption, CH_4 is activated by the weakening of the C–H bond via a transition state (TS). The C–H bond distances in the TS for $[\text{In}_2\text{O}_2]^{2+}$ -8MR(4NN), $[\text{In}_2\text{O}_2]^{2+}$ -8MR(3NN), and $[\text{In}(\text{OH})]^{2+}$ -6MR(3NN) are almost the same (1.38, 1.37, and 1.35 Å, respectively), whereas the activation energies for $[\text{In}_2\text{O}_2]^{2+}$ -8MR(4NN) and $[\text{In}_2\text{O}_2]^{2+}$ -8MR(3NN) are much lower than that for $[\text{In}(\text{OH})]^{2+}$ -6MR(3NN) ($E_a = 85.9$ and 85.9 vs 117.5 kJ/mol, respectively). After the dissociation of the C–H bond, an O–H bond is formed at the bridging O atom, and the resulting CH_3 group forms an In– CH_3 fragment for $[\text{In}_2\text{O}_2]^{2+}$ -8MR(4NN) and $[\text{In}_2\text{O}_2]^{2+}$ -8MR(3NN). In the case of $[\text{In}(\text{OH})]^{2+}$ -6MR(3NN), water is formed from the OH group, accompanied by the formation of an In– CH_3 bond⁷⁹. All the In–C distances are 2.17 Å, which is very similar to that in the $\text{In}(\text{CH}_3)_3$ model calculated by Gueorguiev *et al.*⁸⁰ The reactions of the C–H bond cleavage for $[\text{In}_2\text{O}_2]^{2+}$ -8MR(4NN) and $[\text{In}_2\text{O}_2]^{2+}$ -8MR(3NN) are more exothermic ($\Delta E = 123.4$ and

148.6 kJ/mol) than that of $[\text{In}(\text{OH})]^{2+}$ -6MR(3NN) (28.0 kJ/mol). These results suggest that CH_4 is likely to adsorb and react more easily on the $[\text{In}_2\text{O}_2]^{2+}$ ions rather than $[\text{In}(\text{OH})]^{2+}$ ions.

To gain some insight into the adsorption and activation mechanisms of CH_4 on $[\text{In}_2\text{O}_2]^{2+}$ -8MR(4NN), we analyzed the molecular orbitals. It is considered that there are two main interactions between the adsorbates and active metal centers: A) charge transfer interactions from the occupied orbital of the adsorbate to an empty orbital of the metal center and B) charge transfer interactions from the occupied orbital of the metal center to the empty orbital of the adsorbate^{81,82}. The energy gap between the lowest occupied molecular orbital (LUMO) of $[\text{In}_2\text{O}_2]^{2+}$ -8MR(4NN) and the highest occupied molecular orbital (HOMO) of CH_4 is 8.36 eV, which is smaller than that between the HOMO of $[\text{In}_2\text{O}_2]^{2+}$ -8MR(4NN) and the LUMO of CH_4 (10.26 eV) (Figure 12(a)), indicating that the charge transfer from the HOMO of CH_4 to the LUMO of $[\text{In}_2\text{O}_2]^{2+}$ -8MR(4NN) is more likely to occur. As shown in Figure 12(a), the LUMO of $[\text{In}_2\text{O}_2]^{2+}$ -8MR(3NN) is localized at the In1 cation where CH_4 interacts as indicated in the optimized structures (Figure 11). The charge density difference for CH_4 adsorption on $[\text{In}_2\text{O}_2]^{2+}$ -8MR(4NN) (Figure 12(b)) shows the main transfer of electron density from the C–H bonds to the region between the C–H bond and the In1 cation, indicating the heterolytic cleavage of the C–H bond^{83–85}. Heterolytic cleavage is supported by a comparison of the energy diagrams (Figure S3), which show that the activation energy for the radical intermediate is significantly larger (298.3 kJ/mol) than that for heterolytic cleavage (85.9 kJ/mol, Figure 11)⁸⁶. It is well-known that the activation of CH_4 and other light alkanes over transition metal surfaces and multinuclear Cu-oxo and Fe-oxo clusters is initiated by the homolytic cleavage of C–H bonds to give radical intermediates^{15,17,19,68,75,87,88}. Although some reports are suggesting the heterolytic cleavage of C–H bonds of those substrates by using Zn or Ga ion-exchanged zeolite materials^{83–85}, the present In-CHA system still serves as a rare example that can activate CH_4 through the heterolytic cleavage of the C–H bond.

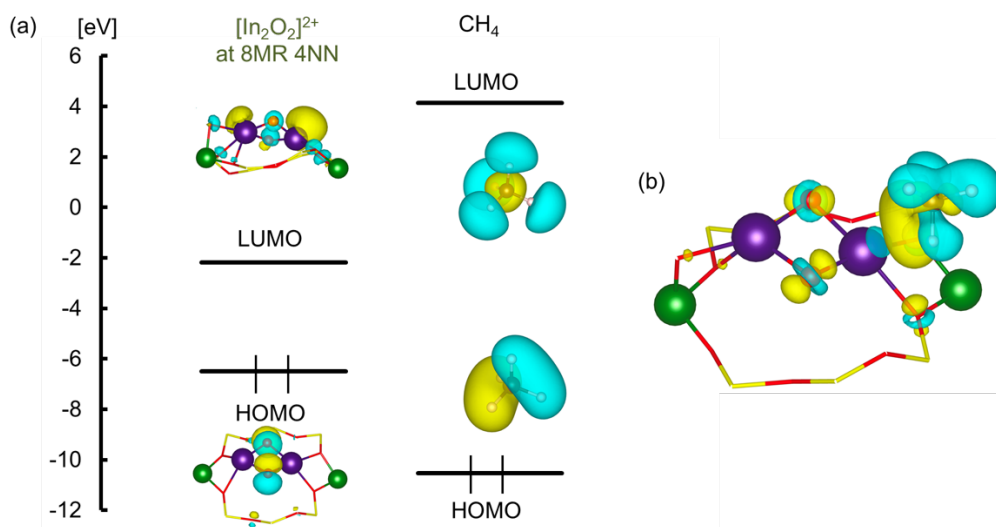


Figure 12. (a) Molecular orbitals of $[\text{In}_2\text{O}_2]^{2+}$ -8MR(4NN) and CH_4 . Only selected orbitals are depicted for clarity. (b) Isosurface plot of the charge density difference from isolated CH_4 and $[\text{In}_2\text{O}_2]^{2+}$ -8MR(4NN): yellow, negative charge accumulation; cyan, negative charge depletion.

2.3.7. XAFS and H_2 -TPR measurements for Ga-exchanged CHA zeolite

GaO_x -CHA was prepared by calcination (773 K) of a mixture of $\text{Ga}(\text{NO}_3)_3$ and NH_4 -CHA, obtained by impregnation, followed by sequential RSSIE with H_2 (973 K) and O_2 treatment (773 K). To trace the redox characteristics of Ga species formed during the preparation of GaO_x -CHA, Ga K-edge XANES spectroscopic analysis was performed. Normalized XANES spectra of a sample of Ga-modified CHA zeolites at different points in the preparative sequence, along with those of reference samples (β - Ga_2O_3 and $\text{Ga}(\text{acac})_3$, acac denotes acetylacetonate) are displayed in Figure 13(a). It is well-known that XANES spectra of gallium oxides contain two distinguishable peaks assignable to respective octahedral and tetrahedral Ga^{3+} species⁸⁹. The XANES spectrum of β - Ga_2O_3 , which contains both of these Ga^{3+} species, contains an absorption maximum at 10376 eV and a shoulder around 10373 eV, while one narrow peak at 10376 eV exists in the

spectrum of $\text{Ga}(\text{acac})_3$. The spectrum of $\text{Ga}_2\text{O}_3/\text{CHA}$ following calcination contains the two characteristic absorption peaks corresponding to octahedral and tetrahedral Ga^{3+} species. Upon H_2 treatment of the calcinated sample at 973 K, the absorption edge shifts to lower energy by 4-5 eV (Ga-CHA), indicating that the reduction of Ga species by H_2 occurs during RSSIE. This conclusion is supported by H_2 -TPR, which showed that the consumption peak for H_2 is generated from 873 to 973 K (Figure 14). Also, *in situ* XANES measurements were carried out on a sample subjected to a 5% H_2/He flow at 973 K. The *in situ* XANES spectra and corresponding ΔXANES spectra, obtained by subtraction of the spectrum of $\text{Ga}_2\text{O}_3/\text{CHA}$ at the beginning of H_2 treatment at room temperature (298 K), are given in Figure 13(c) and (d), respectively. The data show that the broad peak at 10373 eV in the ΔXANES spectrum disappears in concert with the appearance of another narrow peak at 10368 eV. The observed shift in the absorption edge in the ΔXANES spectrum is nearly the same as those observed by Hock et al⁴⁴ for H_2 reduction of Ga-modified BEA zeolite, and rationalized to correspond to the formation of a $[\text{GaH}_2]^+$ ion from gallium oxide via a $[\text{GaH}]^{2+}$ ion. Thus, it appears that a similar phenomenon is occurring with the CHA zeolite.

Upon exposure to O_2 at 773 K, the absorption edge shifts to higher energy in a manner that is similar to that of $\beta\text{-Ga}_2\text{O}_3$, and the spectrum contains mainly one peak associated with tetrahedral Ga. These results suggest that a Ga-oxo species different from Ga_2O_3 is produced. To gain more insight into the nature of the Ga-oxo species formed in the above process, extended XAFS (EXAFS) spectra were analyzed for $\beta\text{-Ga}_2\text{O}_3$ and $\text{GaO}_x\text{-CHA}$ at room temperature (Figure 13(b)). The FT-EXAFS spectrum of $\text{GaO}_x\text{-CHA}$, which is different from that of $\beta\text{-Ga}_2\text{O}_3$, contains two peaks that correspond to Ga–O and Ga–(O)–Ga shells. The intensity of a peak derived from Ga–(O)–Ga shell for $\text{GaO}_x\text{-CHA}$ was lower than that for $\beta\text{-Ga}_2\text{O}_3$. The results of curve-fitting analysis show that the coordination number (CN) and interatomic distance (R) of the Ga–(O)–Ga shell are 1.06 and 2.96 Å, respectively (Table 3). Based on these findings, we conclude that a Ga-oxo

cluster is generated in CHA zeolite by O₂ treatment of Ga-exchanged CHA, prepared by using RSSIE.

Table 3. Results of curve-fitting analysis of Ga K-edge EXAFS of GaO_x-CHA

Shell	CN ^a	R ^b (Å)	ΔE ^c (eV)	σ ^d (Å)	R ^e (%)
Ga–O	4.82 ± 1.04	1.90 ± 0.02	6.11	0.11	0.60
Ga–(O)–Ga	1.06 ± 0.84	2.96 ± 0.05	-8.07	0.08	-

^a Coordination number. ^b Bond distance. ^c Increase in the threshold energy. ^d Debye–Waller factor. ^e Residual factor.

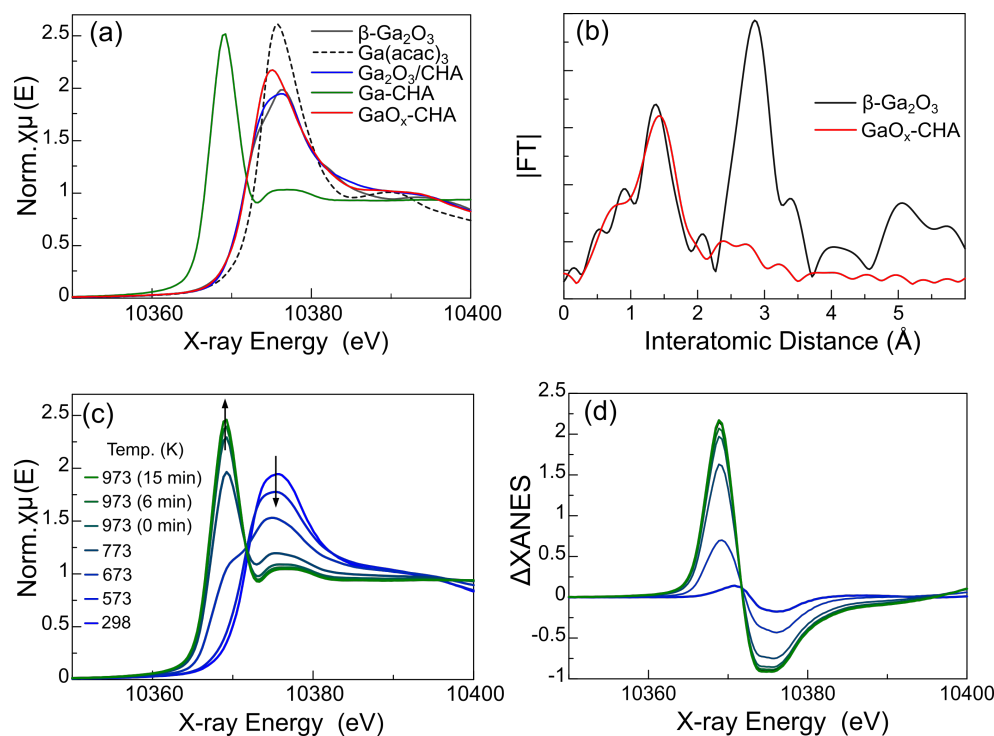


Figure 13

(a) Normalized Ga K-edge XANES spectra of β -Ga₂O₃, Ga(acac)₃, Ga₂O₃/CHA, Ga-CHA (after H₂ treatment of Ga₂O₃/CHA at 973 K), GaO_x-CHA (after O₂ treatment of Ga-CHA at 773 K). (b) FT of k^3 -weighted EXAFS oscillations measured at room temperature for β -Ga₂O₃ and GaO_x-CHA. (c) *In situ* Ga K-edge XANES spectra during H₂ treatment of Ga₂O₃/CHA. (d) Corresponding Δ XANES spectra obtained by subtraction of the spectrum of Ga₂O₃/CHA at the beginning of H₂ treatment at room temperature (298 K).

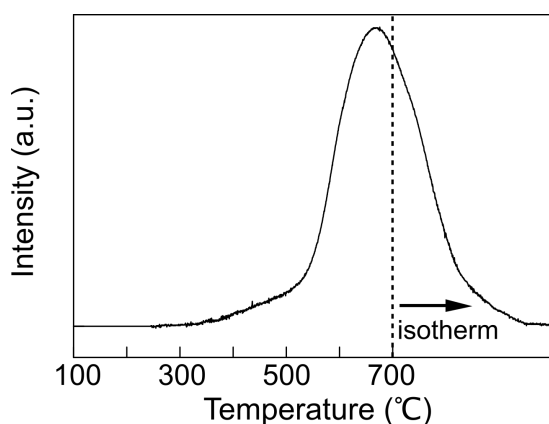
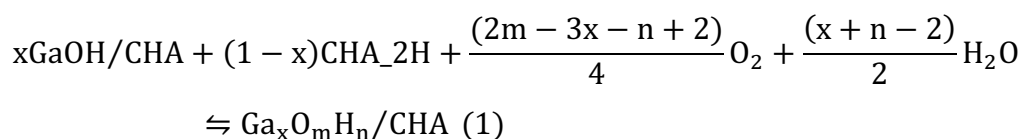


Figure 14 H₂-TPR profile of Ga₂O₃/CHA under H₂ flow.

2.3.8. *Ab initio* thermodynamics analysis for Ga species in CHA zeolite

An *ab initio* thermodynamic approach was carried out to gain information about plausible structures of the Ga-oxo species in GaO_x-CHA^{90,91}. This method has been applied to the analysis of the stabilities of multinuclear metal-oxo clusters, such as those of Cu, Al, and Fe, in zeolites^{52,53,92}. *Ab initio* thermodynamic analysis was applied to consider the effect of O₂, H₂O, and temperature on Ga-oxo ions in CHA zeolites⁵³. The relative Gibbs free energies of various Ga-oxo ions at possible coordination sites as a function of O₂ chemical potential and temperature were calculated. For this purpose, the chemical potential of H₂O was fixed so that the corresponding partial pressure is 0.001 atm (dehydration conditions). Enthalpies and entropies at each temperature and the standard state pressure (0.1 MPa) were obtained from NIST-JANAF Thermochemical Tables⁹³. The following equilibrium reaction was considered;



where the reaction energy is denoted as

$$\Delta E = E_{\text{Ga}_x\text{O}_m\text{H}_n/\text{CHA}} - xE_{\text{GaOH/CHA}} - (1-x)E_{\text{CHA}_{2\text{H}}} - \frac{(2m-3x-n+2)}{4}E_{\text{O}_2} \\ - \frac{(x+n-2)}{2}E_{\text{H}_2\text{O}} \quad (2)$$

In this way, $E_{\text{Ga}_x\text{O}_m\text{H}_n/\text{CHA}}$ represents the total energy of the CHA zeolite model containing Ga-oxo ions. $E_{\text{GaOH/CHA}}$ is that of the Ga-CHA model containing Z₂[GaOH]

($Z_2[\text{GaOH}]$ denotes the $[\text{GaOH}]^{2+}$ ion on paired Al site). $E_{\text{CHA}_2\text{H}}$, E_{O_2} and $E_{\text{H}_2\text{O}}$ represent the total energies of the unit cell of CHA zeolite possessing two protons for charge compensation, gaseous water, and oxygen molecules, respectively. The Gibbs free energy ΔG is given as

$$\Delta G(T, p) = \frac{1}{A} \left[\Delta E - \frac{(2m - 3x - n + 2)}{2} \Delta \mu_{\text{O}} - \frac{(x + n - 2)}{2} \Delta \mu_{\text{H}_2\text{O}} \right] \quad (3)$$

A represents the area of the unit cell. The change of chemical potential $\Delta \mu$ is defined as

$$\Delta \mu_{\text{O}}(T, p) = \frac{1}{2} \left[\Delta \mu_{\text{O}_2}(T, p^0) + RT \ln \left(\frac{p_{\text{O}_2}}{p^0} \right) \right] \quad (4)$$

$$\Delta \mu_{\text{H}_2\text{O}}(T, p) = \Delta \mu_{\text{H}_2\text{O}}(T, p^0) + RT \ln \left(\frac{p_{\text{H}_2\text{O}}}{p^0} \right) \quad (5)$$

Three kinds of paired Al sites, 6MR(3NN), 8MR(3NN), and 8MR(4NN) (Figure 1), were considered as coordination sites in CHA. The calculated free energies for the formation of Ga-oxo ions ((a)-(c)) and a phase diagram predicting which of Ga(-oxo) ion on paired Al sites (Z_2) is the most thermodynamically stable ((d)–(f)) are given in Figure 15. O_2 chemical potentials were translated into the O_2 partial pressures, denoted as $\log(p_{\text{O}_2})$. The phase diagram obtained for 6MR(3NN) (Figure 15(d)) shows that $Z_2[\text{Ga}_2(\text{OH})_4]$ dimer is the lowest energy Ga-oxo species below 300 K and that $Z_2[\text{GaOH}]$ monomer is the most stable one at higher temperatures. In the case of 8MR(3NN) (Figure 15(e)), the most stable species in the lower temperature region is $Z_2[\text{Ga}_2(\text{OH})_4]$ dimer, however, $Z_2[\text{Ga}_2\text{O}_2]$ dimer rather than $Z_2[\text{GaOH}]$ monomer is the lowest energy species as the temperature rises from 400 K to 600 K. It is also predicted that thermal reduction of $Z_2[\text{Ga}_2\text{O}_2]$ to form the Ga^+ cation occurs at higher temperature (1200 K) and very low p_{O_2} ($< 1 \times 10^{-6}$ atm). The existence of similar dinuclear $[\text{Ga}_2\text{O}_2]^{2+}$ ions in other zeolites was proposed by Hensen et al²⁶. Finally, in the case of 8MR(4NN) (Figure 15(f)), the nature of the lowest energy ion dependencies on $\log(p_{\text{O}_2})$ and temperature are similar to those in 8MR(3NN), although the temperature region over which $Z_2[\text{Ga}_2\text{O}_2]$ exists is wider (450–1200 K).

The calculated relative energies of other Ga-oxo clusters, such as $Z_2[\text{Ga}_2(\text{O})(\text{OH})_2]$, $Z_2[\text{Ga}_2\text{O}_2]$, and $Z_2[\text{Ga}_3(\text{O})_2(\text{OH})_3]$, at $\log(p_{\text{O}_2}) = 0.1$ and 300 K were compared to the corresponding XAFS data for a sample treated with 10% O_2 at 773 K followed by cooling

to room temperature. Figure 15(g) shows the relative energies of Ga(-oxo) ions on each paired Al site with respect to the lowest-energy Ga-oxo ions. At 6MR(3NN), $Z_2[\text{Ga}_2(\text{OH})_4]$ has a lower relative energy (ca. 0.1 eV), compared to those of other Ga-oxo clusters ($>$ ca. 0.65 eV). In the case of 8MR(3NN), $Z_2[\text{GaOH}]$ has the second lowest relative energy (ca. 0.5 eV) and the relative energies of other clusters are higher (ca. 0.7–0.8 eV). In contrast, at 8MR(4NN), $Z_2[\text{Ga}_2(\text{O})(\text{OH})_2]$, $Z_2[\text{Ga}_2\text{O}_2]$, and $Z_2[\text{Ga}_3(\text{O})_2(\text{OH})_3]$ have lower relative energies (ca. 0.25 to 0.6 eV). Note that higher oligomers, such as $Z_2[\text{Ga}_4\text{O}_4]$, have much higher relative energies ($>$ ca. 1.4 eV) at all paired Al sites. Based on these results, it is predicted that Ga-oxo clusters, such as the $Z_2[\text{Ga}_2(\text{O})(\text{OH})_2]$, $Z_2[\text{Ga}_2\text{O}_2]$, and $Z_2[\text{Ga}_3(\text{O})_2(\text{OH})_3]$, are likely to be present at 8MR(4NN) rather than 8MR(3NN), and 6MR(3NN). One of the main reasons for this is that, among the paired Al sites in CHA (Figure 1), the longest Al–Al distance exists in 8MR(4NN). Thus, 8MR(4NN) has a larger space compared to that of 8MR(3NN), and 6MR(3NN), which can effectively stabilize multinuclear metal cations. In the theoretical study of CH_4 activation (see below), we consider $Z_2[\text{GaOH}]$ at 6MR(3NN) to be a monomer model and $Z_2[\text{Ga}_2(\text{O})(\text{OH})_2]$, $Z_2[\text{Ga}_2(\text{OH})_4]$, $Z_2[\text{Ga}_2\text{O}_2]$, and $Z_2[\text{Ga}_3(\text{O})_2(\text{OH})_3]$ at 8MR(4NN) to be cluster models (Figure 16).

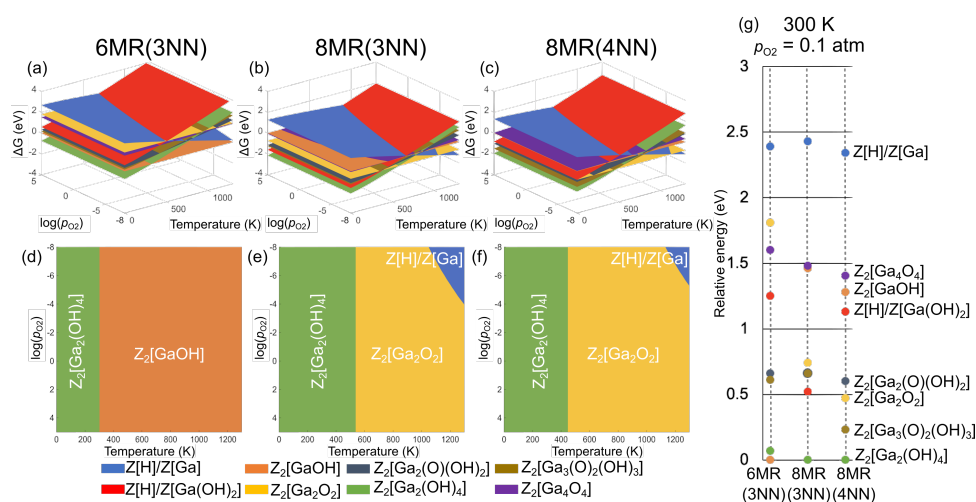


Figure 15 Free energy (ΔG) for the formation of the Ga(-oxo) ions on paired Al sites (Z_2) in CHA (top) and phase diagram showing the lowest-energy species (bottom) as a function of O_2 partial pressure ($\log(p_{\text{O}_2})$) and temperature on (a and d) 8MR(4NN), (b and e) 8MR(3NN), and (c and f) 6MR(3NN). (g) Relative energies of Ga(-oxo) ions at each paired Al sites, referenced to the lowest-energy Ga-oxo ions, O_2 partial pressure: 0.1 atm, Temperature: 300 K.

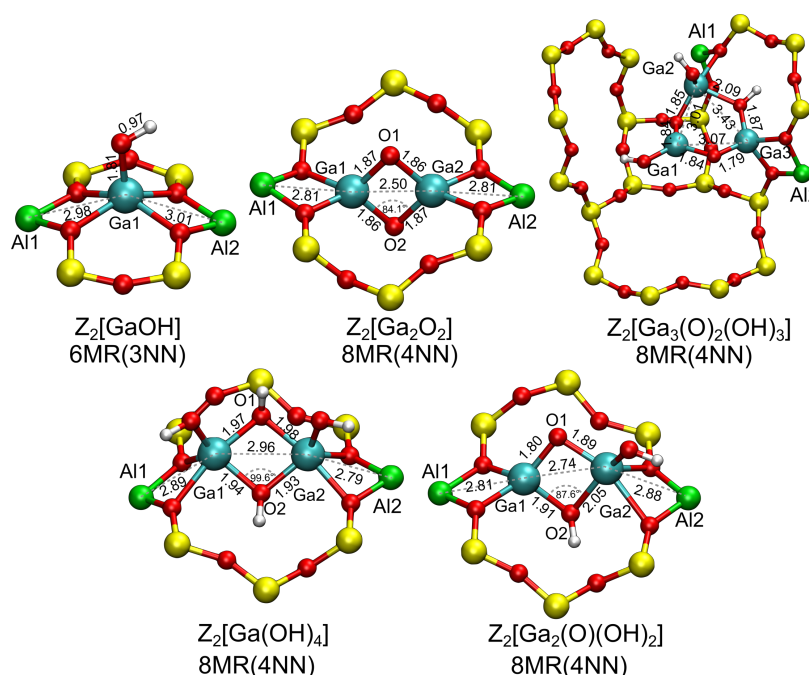


Figure 16 Plausible Ga-oxo species on paired Al sites in CHA zeolite.

2.3.9. Experimental and theoretical studies probing CH_4 activation at low temperature by Ga-CHA

Although various experimental and theoretical studies have been conducted, the activation/transformation of the highly stable C–H bond in CH_4 at low temperatures remains a formidable task. As mentioned in the Introduction, we recently showed that CHA zeolite-supported In-oxo clusters promote oxidation of CH_4 at room temperature to form adsorbed formic acid. To evaluate the abilities of Ga-oxo clusters to activate CH_4 , *in situ* FT-IR analysis was carried out on a CH_4 flow in the presence of GaO_x -CHA zeolites at room temperature (Figure 17). After purging with CH_4 for 100 min followed by N_2 purging, the GaO_x -CHA zeolite was found to display one narrow FT-IR peak at 1490 cm^{-1} and two peaks around 1700 and 1400 cm^{-1} . The peak at 1490 cm^{-1} is assignable to the scissoring of surface dioxymethylene species ($-\text{OCH}_2\text{O}-$), which correspond to adsorbed formaldehyde⁹⁴. Deconvolution of the peak around 1700 cm^{-1} revealed that it is composed of three peaks at 1719 , 1644 , and 1609 cm^{-1} , which correspond to $\text{C}=\text{O}$

stretching of H-bonded HCO_2H , Lewis-acid coordinated HCO_2H , and water, respectively⁹⁵. The band at ca. 1400 cm^{-1} can also be deconvoluted into two peaks at 1377 and 1413 cm^{-1} , which are attributable to respective C–H bending of adsorbed HCO_2H and wagging of surface $-\text{OCH}_2\text{O}-$ groups, respectively⁹⁵. The above peaks do not appear in FT-IR spectra recorded on a CH_4 flow over bulk oxides such as $\beta\text{-Ga}_2\text{O}_3$ and $\alpha\text{-Ga}_2\text{O}_3$. The absorbance derived from the adsorbed oxygenates decreased with the decrease of Ga loading while a similar IR spectrum was obtained using the $\text{GaO}_x\text{-CHA}$ with higher Ga loading (Figure S4). The combined results show that CH_4 undergoes oxidation at room temperature over Ga-oxo clusters in CHA zeolite to produce adsorbed formic acid and formaldehyde. This process is different from CH_4 oxidation by $\text{InO}_x\text{-CHA}$ where only adsorbed formic acid is produced.

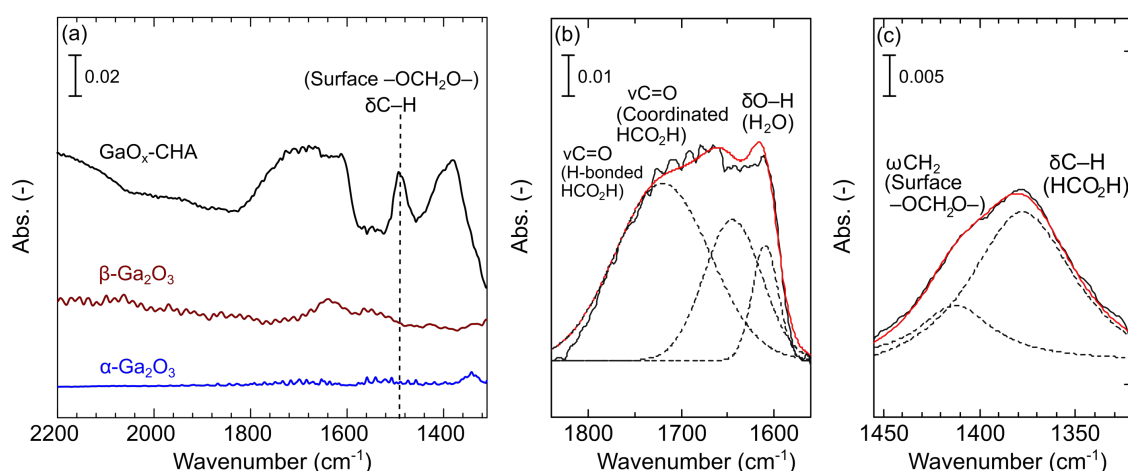


Figure 17 (a) FT-IR spectra during the reaction of CH_4 over $\text{GaO}_x\text{-CHA}$ at room temperature. Deconvolution of the bands around (b) 1700 cm^{-1} and (c) 1400 cm^{-1} .

The mechanism for the oxidation of CH_4 promoted by Ga-oxo clusters in CHA zeolite was explored by employing DFT calculations to evaluate possible transition states (TSs) for C–H bond cleavage, which is considered to be the rate-determining step in the process⁶⁵. Transition state calculation was performed to obtain activation barriers for the C–H bond cleavage in plausible models, including Ga-oxo monomer ($\text{Z}_2[\text{GaOH}]$ at

6MR(3NN)) and clusters ($Z_2[Ga_2O_2]$, $Z_2[Ga_2(OH)_4]$, $Z_2[Ga_2(O)(OH)_2]$, and $Z_2[Ga_3(O)_2(OH)_3]$ at 8MR(4NN)). The TS structures for the C–H bond cleavage step (Figure 18) and the corresponding energy diagrams (Figure 19) are displayed. The CH_4 adsorption energies for the Ga-oxo clusters are calculated to be in the range of -24.4 to -26.3 kJ/mol while that for $Z_2[GaOH]$ is slightly lower (-22.5 kJ/mol). The energies for absorption of CH_4 to the Ga-oxo clusters are much lower than those to In-oxo clusters (ca. -40 kJ/mol, given in our previous publication⁹⁶). In the context of geometric parameters, the Ga–C bond distances and H–C–H angles directed to Ga cations are calculated to be ca. 3.26-4.78 Å and 109-110°, respectively. These values are smaller than those for In-oxo clusters (2.87-2.91 Å and 112-114°, respectively), an observation that is consistent with the lower adsorption energies of Ga-oxo clusters.

Following the adsorption of CH_4 , Ga-oxo species promote cleavage of the C–H bond. Among those induced by Ga-oxo species evaluated in this effort, the C–H bond cleavage reaction promoted by $Z_2[Ga_2(O)(OH)_2]$ has the lowest calculated energy barrier ($E_a = 96.8$ kJ/mol). The respective activation barriers for processes induced by $Z_2[Ga_2(OH)_4]$ and $Z_2[Ga_3(O)_2(OH)_3]$ are 135.5 and 139.8 kJ/mol, and that for the $Z_2[Ga_2O_2]$ -catalyzed reaction is much higher than those of the other Ga-oxo clusters. Monomeric $Z_2[GaOH]$ has the highest E_a (175.2 kJ/mol), which is about twice that of the C–H bond rupture step promoted by $Z_2[Ga_2(O)(OH)_2]$. Following cleavage of the C–H bond in CH_4 , a Ga– CH_3 intermediate with Ga–C bond distances of 1.96 Å are formed from all Ga-oxo species. In the cases of $Z_2[Ga_2O_2]$, $Z_2[Ga_2(O)(OH)_2]$, and $Z_2[Ga_3(O)_2(OH)_3]$ an O–H bond is formed through reaction of a bridging O atom with a H atom derived from CH_4 , and in the $Z_2[Ga_2(OH)_4]$ and $Z_2[GaOH]$ promoted processes the H atom derived from CH_4 reacts with the OH ligand to form water. The C–H bond cleavage reactions catalyzed by the Ga-oxo species are calculated to be exothermic (-15.5 to -136.8 kJ/mol) except for the reaction promoted by $Z_2[Ga_2(OH)_4]$ which is endothermic ($\Delta E = 1.18$ kJ/mol). Based on the above results, it appears that CH_4 weakly adsorbs to all Ga-oxo species regardless of their structure and nuclearity and that C–H bond cleavage in CH_4 occurs most efficiently on $Z_2[Ga_2(O)(OH)_2]$.

The mechanism of C–H bond cleavage on $Z_2[Ga_2(O)(OH)_2]$ was subjected to further investigation. It is reported that zeolite-supported transition metal catalyst clusters cleave C–H bonds of light alkanes in a homolytic manner (Cu, Fe, Ni)^{74,97–99} while cleavage of

C–H bonds occurs heterolytically on main-group metal species (In, Ga) in zeolites^{83,96,100}. The results of calculations on the process promoted by $Z_2[Ga_2(O)(OH)_2]$ show that the energy of the intermediate methyl radical is two times larger (188.8 kJ/mol) than the activation barrier for C–H bond heterolytic cleavage (96.5 kJ/mol, Figure 20). This finding suggests that Ga-oxo-induced cleavage of a C–H bond in CH_4 occurs heterolytically.

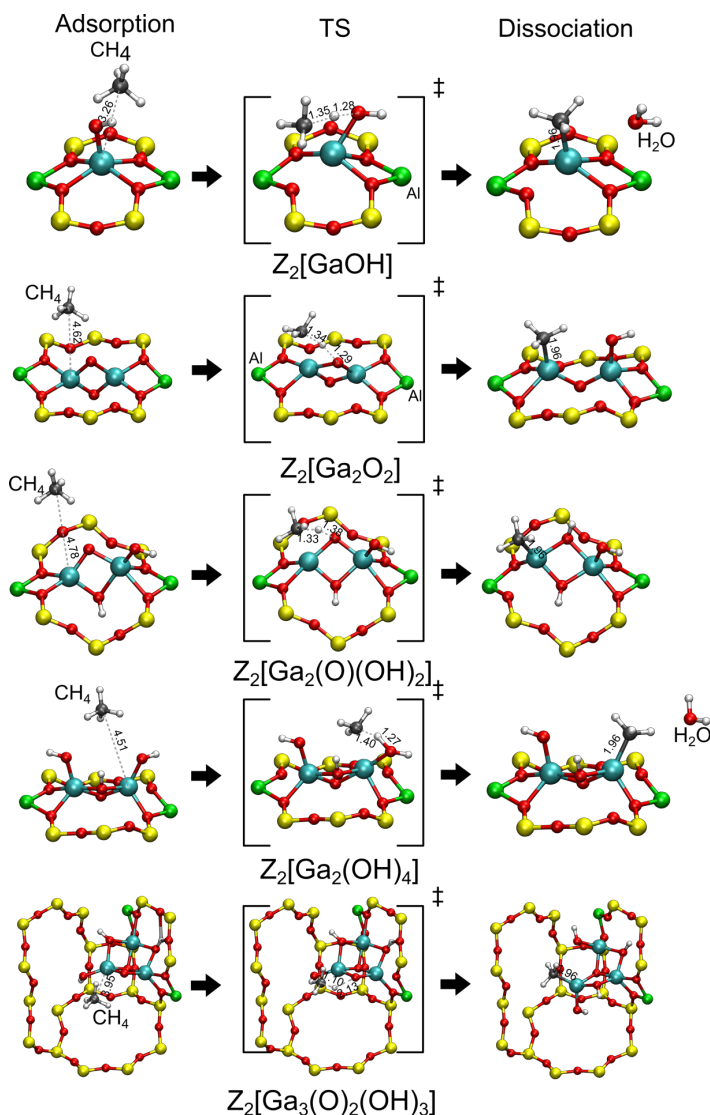


Figure 18 Optimized DFT-calculated structures of intermediates and TSs for C–H cleavage of CH_4 promoted by monomer ($Z_2[GaOH]$ at 6MR(3NN)) and clusters ($Z_2[Ga_2O_2]$, $Z_2[Ga_2(OH)_4]$, $Z_2[Ga_2(O)(OH)_2]$, and $Z_2[Ga_3(O)_2(OH)_3]$ at 8MR(4NN)) together.

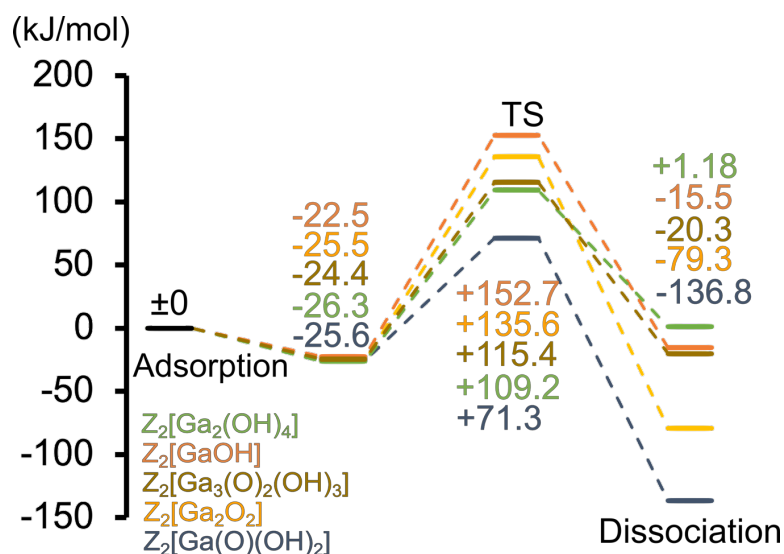


Figure 19 DFT(PBE)-calculated energy diagrams of C–H bond cleavage reaction over predicted Ga-oxo species. Energies are given in kJ/mol and include the vdW-D3 dispersive correction.

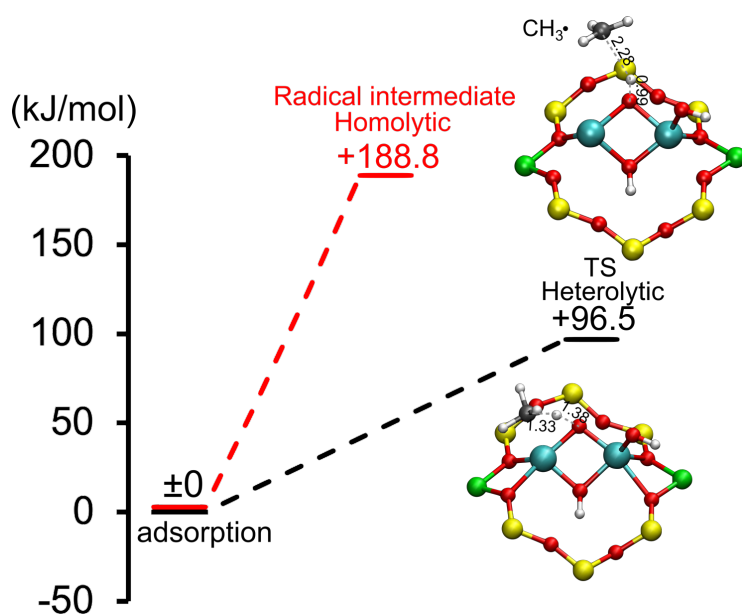


Figure 20 Comparison of energy diagrams for C–H cleavage of CH_4 promoted by $Z_2[Ga_2O_2]$ at 8MR(4NN) occurring through heterolytic (black) and homolytic pathways (red).

2.4. Conclusions

In this investigation, we demonstrated that CH₄ oxidation at room temperatures is promoted by O₂-activated In, Ga-exchanged CHA zeolite. The results of *in situ* XAFS and H₂-TPR studies suggest that multinuclear In, Ga-oxo clusters are produced by sequential RSSIE (H₂, 973 K) and oxidation (O₂, 773 K). Possible structures of In, Ga-oxo clusters responsible for this process were explored by using *ab initio* thermodynamic analysis. The results suggest that the plausible active species are the multinuclear oxo cluster (In₂O₂ and Ga₂(O)(OH)₂) under the corresponding experimental condition. The generation of adsorbed formic acid (by Ga-oxo cluster) and formaldehyde (by In-oxo cluster) in this process was demonstrated by using *in situ* IR spectroscopic monitoring of reaction of a CH₄ flow over In, Ga-oxo clusters in CHA zeolite at room temperature. The energy barriers for C–H bond cleavage over possible Ga-oxo species were calculated using DFT calculations. The results show that the process promoted by the multi-nuclear oxo-cluster has the lowest activation barrier. Finally, the results suggest that the C–H bond cleavage reaction promoted by In, Ga-oxo species proceeds through a heterolytic pathway rather than a homolytic pathway. Overall, this effort demonstrates the potential of using zeolite-supported main-group metal-oxo clusters as catalysts for CH₄ oxidation under mild conditions.

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Table S1 Specific surface areas and pore volumes of zeolites

Sample	BET surface area (m ² g ⁻¹)	Pore volume (mL g ⁻¹)
H-CHA	833	0.402
In ₂ O ₃ /CHA	785	0.378
InO _x -CHA	710	0.344

Table S2 Total energies (eV) of Ga-oxo ions on 6MR(3NN), 8MR(3NN), and 8MR(4NN)

Ga-oxo species	6MR(3NN)	8MR(3NN)	8MR(4NN)
Z[H]/Z[Ga]	-866.5	-866.4	-866.4
Z[H]/Z[Ga(OH) ₂]	-887.8	-888.4	-887.8
Z ₂ [Ga(OH)]	-874.1	-872.6	-872.7
Z ₂ [Ga ₂ O ₂]	-878.1	-880.3	-880.7
Z ₂ [Ga ₂ (O)(OH) ₂]	-895.3	-895.3	-895.3
Z ₂ [Ga ₂ (OH) ₄]	-911.7	-911.6	-911.4
Z ₂ [Ga ₃ (O) ₂ (OH) ₃]	-917.3	-917.3	-918.4
Z ₂ [Ga ₄ O ₄]	-900.3	-900.9	-900.9

Table S3 Total energies (eV) of Ga-oxo species on 8MR(4NN) with different k-point meshes (Γ , 2*2*2, and 3*3*3).

species	k-point mesh		
	Γ	2*2*2	3*3*3
Z[H]Z[Ga]	-866.43	-866.44	-866.44
Z[H]Z[Ga(OH) ₂]	-887.76	-887.77	-887.77
Z ₂ [GaOH]	-872.72	-872.74	-872.74
Z ₂ [Ga ₂ O ₂]	-880.69	-880.70	-880.70
Z ₂ [Ga ₂ (O)(OH) ₂]	-895.33	-895.35	-895.35
Z ₂ [Ga ₂ (OH) ₄]	-911.43	-911.44	-911.44
Z ₂ [Ga ₃ (O) ₂ (OH) ₃]	-918.36	-918.37	-918.37
Z ₂ [Ga ₄ O ₄]	-900.95	-900.96	-900.95

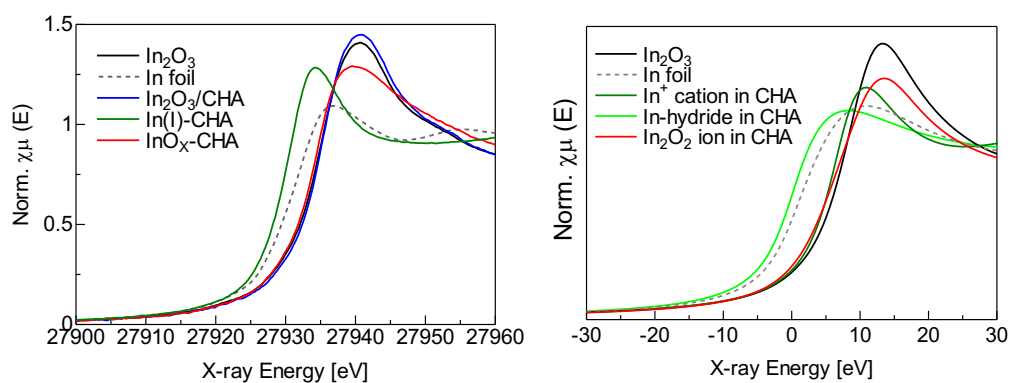


Figure S1. Comparison of experimental (left) and simulated (right) XANES spectra of a series of In-CHA and reference In compounds (In foil and In_2O_3).

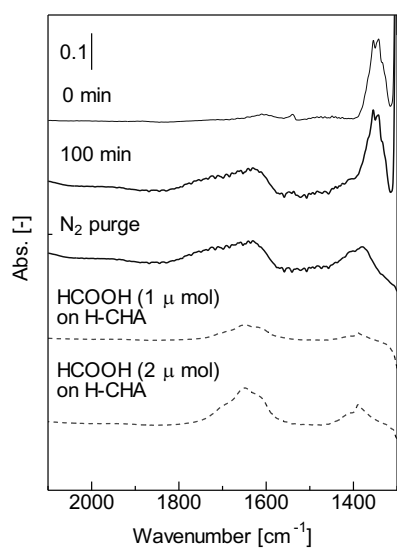


Figure S2. FT-IR spectra during reaction of CH_4 on $\text{InO}_x\text{-CHA}$ at room temperature and formic acid on H-CHA (as reference).

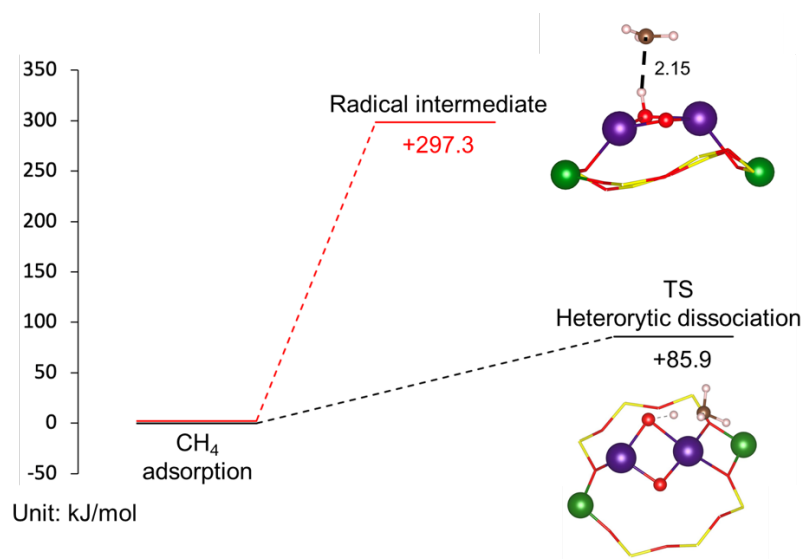


Figure S3 Comparison of energy diagrams in C–H cleavage of CH₄ on [In₂O₂]²⁺-8MR 4NN through heterolytic path (lower) and homolytic path (upper).

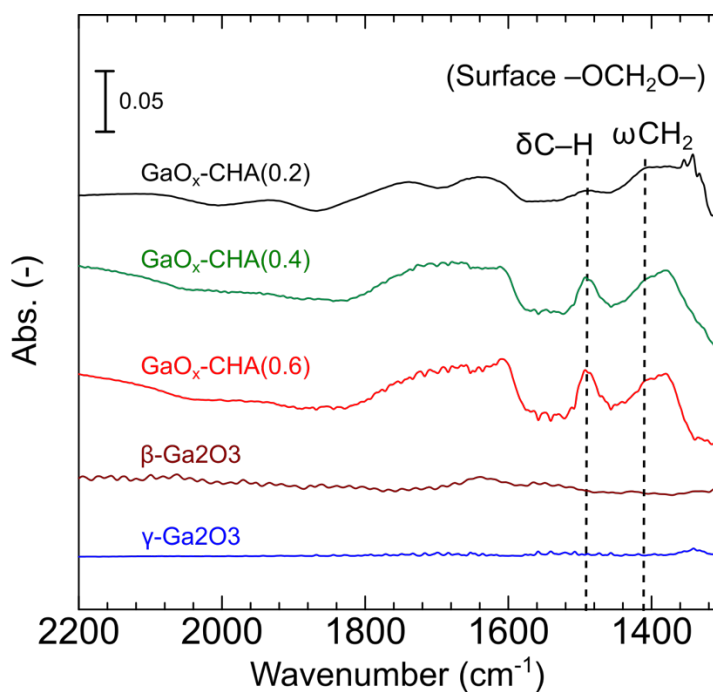


Figure S4 FT-IR spectra during reaction of CH₄ at room temperature over GaO_x-CHA (Ga/Al = 0.2, 0.4, and 0.6), β-Ga₂O₃, and γ-Ga₂O₃.

Chapter 3

Isolated Indium-hydride in CHA zeolite: speciation and catalysis for non-oxidative dehydrogenation of ethane

3.1. Introduction

Hydrides in/on solid materials have attracted significant attention in many research fields including energy engineering¹⁻⁴, electrochemistry⁵⁻⁷, and catalysis^{8,9}. In catalysis, hydrides on solid surfaces have been involved in heterogeneously-catalyzed hydrogenation, dehydrogenation, and hydrogenolysis. Hydrides on metallic surfaces exhibit high mobility, while surface hydrides on metal oxides are considered to be relatively stable due to their site isolation (isolated surface hydrides)^{8,9}. Various reports regarding the formation of surface hydrides on metal oxides¹⁰⁻¹⁶ and metals¹⁷⁻²³ have been published. Although the structures and reactivities have been discussed in some reports, studies of surface hydrides are highly complicated due to the complexity and analytical difficulty of examining solid surfaces and consequently, the details of the structures often remain unclear. As another approach, syntheses of well-regulated metal-hydrides on metal oxides via surface organometallic chemistry have been developed. This method involves the immobilization of well-defined metal complexes on oxides and subsequent reaction with H₂ to afford supported metal-hydrides. Various supported transition metal-hydride complexes of Co²⁴, Ti²⁵, Zr^{26,27}, Ru^{28,29}, Rh³⁰, Hf³¹, Ta³², W³³, Os³⁴, and Ir³⁵ were characterized using various spectroscopic techniques and exhibited unique catalytic properties. The synthesis, characterization, and catalytic function of the isolated surface hydrides are attractive but formidable research subjects.

Aluminosilicate zeolites are well-defined porous frameworks that consist of four-coordinate $[\text{SiO}_4]$ or $[\text{AlO}_4]$ subunits. Various cations can be stabilized at the framework anionic $[\text{AlO}_4]^-$ sites in their pores and the number of sites can be changed by controlling the Si/Al ratio of the zeolites^{36,37}. A few zeolite-supported metal-hydrides containing Ga, Zn, Ag, and Rh have been developed, and Ga-hydrides on ZSM-5 have been most thoroughly investigated. The formation of Ga-hydrides in ZSM-5 was first indicated by Iglesia et al. during *in situ* X-ray absorption fine structure (XAFS) measurements under an H_2 atmosphere at high temperature³⁸. Subsequently, Hensen et al. detected Ga-hydrides by diffuse reflectance infrared transform (DRIFT) measurements and proposed detailed structures that included $[\text{GaH}]^{2+}$ and $[\text{GaH}_2]^{+39,40}$. These structures were well supported by vibration frequency calculations⁴¹. Their catalytic properties for dehydrogenation/cracking of light alkanes, which are elementary steps of industrially-important dehydrocyclization reactions⁴², have been experimentally and theoretically investigated^{41,43–45}. Zn-hydrides on ZSM-5 are formed via H_2 treatment of Zn-exchanged ZSM-5^{46,47} and are considered intermediates for the dehydrogenation of alkanes⁴⁸. For Ag-exchanged zeolites, H_2 treatment afforded Ag-clustered hydride species (Ag_3H) via a multiple-step reaction⁴⁹. The synthesis of $\text{Rh}(\text{CO})(\text{H})_x$ via reaction of dealuminated Y zeolite-immobilized $\text{Rh}(\text{CO})_2$ has also been reported⁵⁰. The aforementioned studies demonstrated that zeolites have the potential as effective supports for the formation of isolated surface hydrides and catalytic applications, motivating the development of surface hydride species and unique catalysis.

Herein, we found the formation of indium(In)-hydrides by H_2 treatment of In-exchanged CHA zeolite (In-CHA). No reports regarding isolated In-hydrides in zeolites have been published although an isolated hydride on indium oxides has been reported very recently

by Ozin et al.¹⁶ The formation and detailed structure of In-hydrides in CHA zeolites was investigated by *in situ* Fourier transform IR (FTIR) and XAFS measurements as well as density functional theory (DFT) calculations. In-CHA showed high selectivity and durability for the non-oxidative dehydrogenation of ethane compared to Ga- and Zn-exchanged CHA zeolites. The mechanistic investigation based on kinetic, *in situ* spectroscopic, and theoretical studies indicated that $[\text{InH}_2]^+$ ions are potential catalytically active sites.

3.2. Experimental

3.2.1 FTIR measurement

FTIR measurements were carried out in the homemade *is situ* cell as follows. A self-supported disc of the mixture of In_2O_3 and proton-type CHA ($\text{In}_2\text{O}_3/\text{CHA}$, 40 mg) was dehydrated under He flow at 773 K and then treated with H_2 or 10% H_2/He . For measurement of In-hydrides, the obtained sample was kept at 773 K under vacuum for 2 h and a background spectrum was obtained below 153 K by cooling the cell using liquid N_2 . Next, an H_2 flow was introduced to the sample and the sample was kept under H_2 at 773 K for 2 h. After that, the temperature was decreased to below 153 K and the FTIR spectra were recorded (JASCO FT/IR-4600 equipped with a mercury cadmium telluride (MCT) detector). The reaction of In-hydrides with ethylene was carried out by treatment of In-CHA(H_2) with 10% $\text{C}_2\text{H}_4/\text{He}$ at 473 K while the *in situ* formation of In-hydrides through the reaction of In-CHA with ethane was examined at 773 K under 100% C_2H_6 . For NH_3 adsorption, the temperature was decreased to 373 K after the treatment of the disk of $\text{In}_2\text{O}_3/\text{CHA}$ under 10% H_2/He flow, and then the flow was changed to He to purge H_2 . A background spectrum under He was obtained, followed by introducing NH_3 (1%) to the sample, purging by He, and monitoring the peak derived from adsorbed NH_3 at 373 K.

3.2.2 H–D exchange reaction

For FTIR measurement, the reactions were carried out using the homemade *is situ* cell described above. Mass spectroscopic observations of the H–D exchange reaction were

conducted in a fixed-bed continuous flow system as follows. A powder of $\text{In}_2\text{O}_3/\text{CHA}$ (0.2 g) was treated under 40 mL/min of 5% H_2/N_2 at 773 K to prepare *in situ* $\text{In-CHA}(\text{H}_2)$. Next, the temperature decreased to 313 K under 40 mL/min of 5% H_2/N_2 flow, and subsequently, the gas was switched to N_2 for at least 1 h to purge H_2 from the gas phase. After the pre-treatment, the H–D exchange reaction of $\text{In-CHA}(\text{H}_2)$ with D_2 was investigated under 40 mL/min of 5% D_2/N_2 flow with increasing the temperature from 313 K to 473 K. The gas-phase products were analyzed by mass spectroscopy (Belmass, MicrotracBEL). The reverse reaction ($\text{In-CHA}(\text{D}_2)$ with H_2) was examined in a similar way.

3.2.3 XAFS measurement

An In K-edge XAFS measurement was conducted in the transmission mode in a BL14B2 station attached to a Si(311) monochromator at SPring-8 (JASRI), Japan (Proposal Nos. 2019A1614 and 2019B1686). The flow reaction system containing a flow-type cell was used for *in situ* XAFS measurements. A disc of In-CHA was prepared from a self-supported disc of $\text{In}_2\text{O}_3/\text{CHA}$ under 5% H_2/He flow at 773 K in a flow-type quartz cell with a gas mixture system using mass flow controllers. After preparation, the temperature was decreased to room temperature (ca. 298 K) and then the XAFS measurement was carried out.

3.2.4 Computational details

DFT calculations were performed by the Vienna ab-initio simulation package (VASP)^{51,52} with the periodic boundary condition under the Kohn–Sham formulation^{53,54}. All atoms were allowed to fully relax during calculations. The projected augmented wave (PAW) method^{55,56} was applied to describe the core-electron interactions and the plane wave basis set was limited to cut-off energy of 450 eV. The forces on atoms were minimized to be less than 0.03 eV/Å. Electron exchange correlation was considered by using the generalized gradient approximated Perdew-Burke-Ernzerhof (GGA-PBE) functional⁵⁷. The Γ point was used for Brillouin zone sampling. Van der Waals (vdW) dispersion corrections were included in all calculations by the semi-empirical Grimme's D3 method

^{58,59}, the lattice constants of CHA zeolite were fixed at values given in the International Zeolite Association (IZA) database ($a = b = 13.675 \text{ \AA}$, $c = 14.767 \text{ \AA}$, $\alpha = \beta = 90.0^\circ$ and $\gamma = 120^\circ$) ⁶⁰. For vibration calculation, all atoms except for In hydrides were fixed. The conjugate gradient method was used to optimize intermediate structures during the climbing-image Nudge elastic band (CI-NEB) calculations as implemented in VTST-Tools ⁶¹. The CI-NEB calculations are considered converged when the maximum forces on all atoms are less than $0.05 \text{ eV \AA}^{-1}$. For CI-NEB calculations, the spring constant between adjacent images was set to $5.0 \text{ eV/\AA}^2$. The Gibbs free energy of each species was calculated by vibrational frequency analysis based on harmonic normal mode approximation using the finite difference method in VASP. A limited set of atoms, which are determined as non-zeolite framework atoms (indium, carbon, and hydrogen atoms) in the unit cell, were used to calculate vibrational frequencies. The vibrational contribution to the free energy for each structure at 873.15 K was calculated based on the calculated frequencies. Because neglecting the spurious frequencies has the contribution to the enthalpy and entropy, spurious frequencies under 100 cm^{-1} were replaced as 50 cm^{-1} for all structures to give consistent results⁶². Ethane, ethylene, and hydrogen in the gas phase were calculated in the ideal gas approximation at 873.15 K, and their translational and rotational contribution to the free energy was evaluated in partial pressures of 0.02, 2×10^{-4} , and 2×10^{-4} atm, respectively.

3.2.5 Dehydrogenation of ethane

Non-oxidative dehydrogenation of ethane was performed in a fixed-bed continuous flow system at 933 K. The catalyst was prepared *in situ* by treatment of 0.1 g of $\text{In}_2\text{O}_3/\text{CHA}$ under 50 mL of 10% H_2/He flow at 773 K for 30 min to promote RRSIE followed by He purge for 1 h before the dehydrogenation. Ga- and Zn-exchanged zeolites were prepared through impregnation of the corresponding nitrate precursors ($\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) to CHA (Tosoh, NH_4^+ -type, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 22.3$) or ZSM5 (Tosoh, NH_4^+ -type, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 22$) followed by calcination under air at 773 K. Before the reaction, the catalysts were treated under an H_2/He flow at 993 K for Ga or at 773 K for Zn in the reactor. $\text{PtSn}/\text{Al}_2\text{O}_3$ and $\text{PtGa}/\text{Al}_2\text{O}_3$ were prepared by a conventional impregnation method of H_2PtCl_6 and $(\text{NH}_4)_2\text{SnCl}_6$ or $\text{Ga}(\text{NO}_3)_3$ to $\gamma\text{-Al}_2\text{O}_3$ (prepared by calcination of boehmite ($\gamma\text{-AlOOH}$, SASOL Chemicals) at 1173 K for 3 h) followed *in situ* reductions

of the obtained powder under an H₂/He flow at 973 K for 1 h. For all the dehydrogenation experiments, the gas from the reactor was analyzed by Shimadzu GC-14B with a SHINCARBON ST column and gas sampler (GS5100). The conversion, selectivity, and carbon balance were calculated as follows.

$$\begin{aligned}\text{Conv. [\%]} &= \frac{[\text{ethane}]_{\text{init}} - [\text{ethane}]}{[\text{ethane}]_{\text{init}}} \times 100 \\ \text{Selec. [\%]} &= \frac{[\text{ethylene}]}{[\text{ethylene}] + [\text{methane}]} \times 100 \\ \text{Carbon balance [\%]} &= \frac{([\text{ethane}] + [\text{ethylene}] + [\text{methane}])}{[\text{ethane}]_{\text{init}}} \times 100\end{aligned}$$

For the reuse experiment, the In-CHA after 90 h reaction was treated with 50 mL of 5% O₂/He at 873 K for 90 min in the reactor to calcine the coke, and then treated with 50 mL of 10% H₂/He followed by He purge for 1 h. The dehydrogenation was performed in the same reaction conditions for 20 h.

To obtain the relationship between conversion and selectivity, the reaction was carried out at 773-893 K for Ga-ZSM-5 and PtSn/Al₂O₃ and at 913-953 K, respectively.

The kinetic studies were carried out under the following conditions.

- TOF dependency on $p(\text{H}_2)$ for In-CHA (In/Al = 0.8):

$p(\text{H}_2) = 0.02\text{-}0.08$, $p(\text{C}_2\text{H}_6) = 0.02$, balanced with He (Total flow rate: 50 mL/min), 933 K.

- TOF dependency on $p(\text{C}_2\text{H}_6)$ for In-CHA (In/Al = 0.8):

$p(\text{H}_2) = 0.02$, $p(\text{C}_2\text{H}_6) = 0.02\text{-}0.08$, balanced with He (Total flow rate: 50 mL/min), 933 K.

- TOF dependency on $p(\text{H}_2)$ for Ga-CHA (Ga/Al = 0.8):

$p(\text{H}_2) = 0.02\text{-}0.08$, $p(\text{C}_2\text{H}_6) = 0.04$, balanced with He (Total flow rate: 50 mL/min), 913 K.

- TOF dependency on $p(\text{H}_2)$ for: Ga-CHA (Ga/Al = 0.8)

$p(\text{H}_2) = 0.04$, $p(\text{C}_2\text{H}_6) = 0.02\text{-}0.08$, balanced with He (Total flow rate: 50 mL/min), 913 K.

- M/Al effect on formation rate for In-CHA

$p(\text{C}_2\text{H}_6) = 0.02$, balanced with He (Total flow rate: 50 mL/min), 933 K.

- M/Al effect on formation rate for Ga-CHA

$p(\text{C}_2\text{H}_6) = 0.04$, balanced with He (Total flow rate: 50 mL/min), 913 K.

- Arrhenius plot for In-CHA (In/Al = 0.8):

$p(\text{C}_2\text{H}_6) = 0.02$, balanced with He (Total flow rate: 50 mL/min), 873-933 K.

- Arrhenius plot for Ga-CHA (Ga/Al = 0.8):

$p(\text{C}_2\text{H}_6) = 0.04$, balanced with He (Total flow rate: 50 mL/min), 873-933 K.

Temperature-programmed oxidation (TPO) measurement

TPO measurement was performed with BELCAT II (MicrotracBEL). After the 2 h reaction, 40 mg of the catalyst was used for TPO experiment. The catalyst was pretreated at 423 K for 30 min under a He atmosphere. The gas flow was switched to 50% O_2/He (40 mLmin^{-1}) and then the temperature was increased to 1073 K at 5 K/min. During the reaction, the CO_2 generated through coke oxidation ($m/e = 44$) was measured by mass spectroscopy (Belmass, MicrotracBEL).

3.3. Result and discussion

3.3.1 *In situ* FTIR measurement of In-hydride in CHA zeolite

The *in situ* FTIR measurement of In-CHA treated with H_2 at 773 K (In-CHA(H_2)) was performed. The FTIR spectrum of In-CHA(H_2) exhibited a band with a maximum at 1720 cm^{-1} (**Figure 1A**) arising from In–H stretching vibrations^{16,63}. This band remained unchanged even at 473 K, indicating the relatively-high stability of the In-hydrides. However, when ethylene was introduced at 473 K, this band disappeared and new bands with maxima at 2957, 2930, and 2875 cm^{-1} appeared (**Figure 1B and C**), corresponding to the C–H stretching vibrations of the adsorbed ethane and/or ethyl fragments⁶⁴. This

indicated that the introduced ethylene reacted with the In-hydrides. As control experiments, D_2 was used instead of H_2 for the above measurements. After D_2 treatment (denoted as In-CHA(D_2)), no bands around 1720 cm^{-1} were observed (**Figure 1A**), indicating the shift of the band at 1720 cm^{-1} . However, the expected new band at 1219 cm^{-1} was not observed because of the overlap with the strong peak derived from the zeolite framework. After the reaction of ethylene with In-CHA(D_2), the resulting spectrum showed new bands with maxima at 2208 and 2171 cm^{-1} , assignable to the C–D vibration of partially deuterated ethane (CDH_2CDH_2) and/or corresponding ethyl fragments⁶⁵ (**Figure 1(D)**), suggesting the formation of In-deuteride species after D_2 treatment. These FTIR measurements demonstrated the presence of In-hydrides in In-CHA

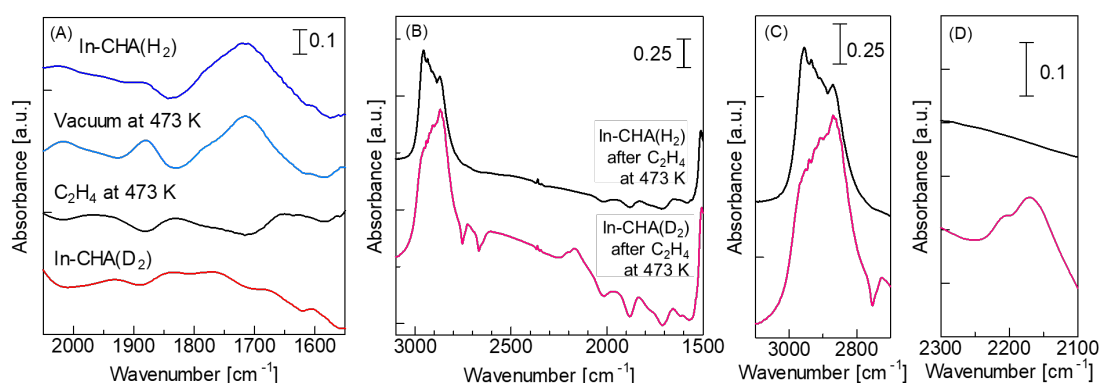


Figure 1. (A) FTIR spectra of the In-CHA after treatment with H_2 at 773 K (In-CHA(H_2)) followed by vacuum treatment or introduction of C_2H_4/He at 473 K , and the In-CHA after treatment with D_2 at 773 K (In-CHA(D_2)). (B) Spectra after the introduction of C_2H_4/He at 473 K for 20 min to the In-CHA(H_2) and In-CHA(D_2). Enlarged views of (B) at approximately (C) $3100\text{--}2700\text{ cm}^{-1}$ and (D) $2300\text{--}2100\text{ cm}^{-1}$.

To support the formation of In-hydrides, we conducted the H–D exchange reaction. In *in situ* FTIR measurement, the treatment of In-CHA(H₂) with D₂ at 373 K caused the decrease of band derived from $\nu(\text{In-H})$ and this band disappeared upon heating to 473 K (**Figure 2A**). When this D₂-treated sample was exposed to H₂ at 473 K, a band assignable to $\nu(\text{In-H})$ appeared again. The gas-phase products were also analyzed by mass spectroscopy during the H–D exchange reaction with increasing the temperature from 313 K to 473 K (For details, see the Supporting Information). The reaction of In-CHA(H₂) with D₂ afforded a positive peak for $m/z = 3$ with a negative peak for $m/z = 4$ around 373 to 473 K (**Figure 2B**) while a peak for $m/z = 2$ was hardly observed. In the reverse reaction, namely In-CHA(D₂) with H₂, a positive peak for $m/z = 3$ and a negative peak for $m/z = 2$ were observed and the signal for $m/z = 4$ did not show any peak (**Figure S1**). These results show the reversible nature of the H–D exchange reaction (In-CHA(H₂) with D₂ as well as In-CHA(D₂) with H₂) and that the gas-phase product is mainly HD rather than H₂ or D₂. A control experiment using proton-type CHA (H-CHA) instead of In-CHA (H₂-treated H-CHA with D₂) was conducted where any peak was not observed for all signals, supporting the occurrence of H–D exchange reaction between In-hydrides and D₂ (**Figure 2B**). The above results of H–D exchange reactions strongly indicate the formation of In-hydrides in In-CHA after H₂ treatment. A shoulder peak around 1660 cm⁻¹ in the FTIR spectrum after D₂ treatment of In-CHA(H₂) at 373 K (**Figure 2A**) may be assigned to the stretching vibration of In–H of partially deuterated In-hydrides. The lower wavenumber compared to that of In-hydrides was reported in the previous paper concerning InH₂ and InHD.⁶⁶ This interpretation is consistent with the formation of HD as the main product during H–D exchange reactions.

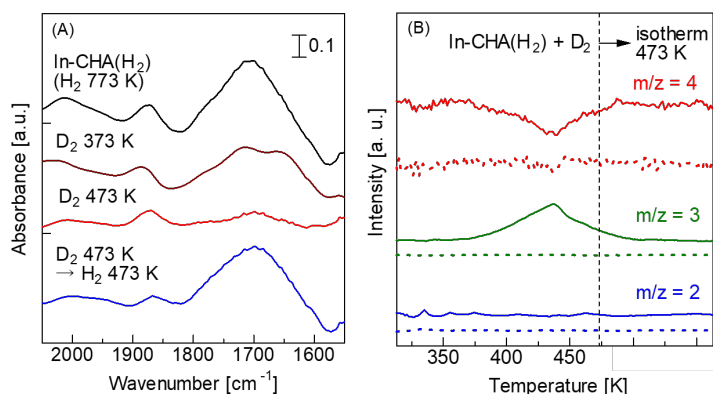


Figure 2. (A) FTIR spectra after H–D exchange reactions between In-CHA(H₂) and D₂ at 373 or 473 K as well as after the treatment of the In-CHA used for H–D exchange reaction with H₂ at 473 K. (B) Mass profiles for $m/z = 2$, 3, and 4 during the reaction between In-CHA(H₂) and D₂. The profiles for the control experiment using proton-type CHA (H-CHA) instead of In-CHA are shown in dot lines. Experimental details are described in the Supporting Information.

3.3.2 DFT calculation for frequency analysis and origin of the stability of the In-hydride

To support the formation of In-hydrides and further examine their structures, the frequencies of In–H vibrations for several In-hydride models were calculated and compared with the experimental results⁴¹. Several types of In-hydride models were considered, [InH₂]⁺ on a single [AlO₄][–] site (Z[InH₂], where Z denotes one [AlO₄][–] site), a [InH₂]⁺–H⁺ cation pair on two [AlO₄][–] sites (Z[H]/Z[InH₂]), and [InH]²⁺ on two [AlO₄][–] sites (Z₂[InH]). For the Z₂ sites, five paired sites were used as second-nearest-neighbors (2NN) in a six-membered-ring (6MR) (denoted as 6MR(2NN)), 6MR(3NN), 8MR(2NN), 8MR(3NN), and 8MR(4NN) based on previous theoretical studies for metal-exchanged CHA zeolites^{67,68} (all optimized structure files are in the Supporting Information). The

calculated frequencies of the possible $[\text{InH}_2]^+$ and $[\text{InH}]^{2+}$ ions are summarized in **Table 1**. The frequencies of $\nu_{\text{sym}}(\text{In-H})$ for $[\text{InH}_2]^+$ models are 1721–1736 cm^{-1} , in much better agreement with that for maximum absorption in the experiment (1720 cm^{-1}) compared to the frequencies of $\nu_{\text{asym}}(\text{In-H})$ (1787–1810 cm^{-1}). For $[\text{InH}]^{2+}$, the frequencies of the three models ($Z_2[\text{InH}_2]$ on 6MR(2NN), 6MR(3NN), and 8MR(2NN)) were calculated to be 1763–1793 cm^{-1} , which are similar to those of $\nu_{\text{asym}}(\text{In-H})$ for $[\text{InH}_2]^+$, while the other two models, $Z_2[\text{InH}_2]$ on 8MR(3NN) and 8MR(4NN), were not available due to the conversion of $Z_2[\text{InH}]$ affording $Z[\text{H}]/Z[\text{In}]$ during geometry optimization. The band around 1700–1800 cm^{-1} can be deconvoluted into the main peak at 1717 cm^{-1} and a minor peak at 1781 cm^{-1} (**Figure S2**). Based on the results of frequency analysis and deconvolution of the band, $[\text{InH}_2]^+$ ions are likely to be formed as main In-hydrides on both Z and Z_2 sites, and $[\text{InH}]^{2+}$ ions possibly exist as a minor species on the Z_2 sites with shorter Al–Al distances. Hereinafter, $Z[\text{InH}_2]$ was adopted as the model of In-hydrides in CHA for further calculations (**Figure 3**).

Table 1. Calculated wavenumbers $\nu(\text{In-H})$ for the possible structural models of In-hydrides in CHA zeolite. For the $[\text{InH}_2]^+$ ions on Z sites, one proton was added to compensate for cation deficiency.

model of $[\text{AlO}_4]^-$ sites	ν for $[\text{InH}]^{2+}$	$\nu_{\text{sym}}/\nu_{\text{asym}}$ for $[\text{InH}_2]^+$
Z (one $[\text{AlO}_4]^-$ site)	-	1735.6/1806.0
Z_2 in 6MR(2NN)	1773.3	1732.5/1797.4
Z_2 in 6MR(3NN)	1763.0	1735.0/1805.3
Z_2 in 8MR(2NN)	1793.0	1721.2/1787.3
Z_2 in 8MR(3NN)	n/a	1732.9/1809.7
Z_2 in 8MR(4NN)	n/a	1735.2/1806.2

n/a - not available due to the conversion of $Z_2[\text{InH}]$ to $Z[\text{H}]/Z[\text{In}]$ during geometry optimization. The scaling factor (0.969) was determined via comparison of the $\nu(\text{In-H})$ of InH_3 between the calculation performed herein (1706.0 cm^{-1}) and the previously reported experimental value (1760 cm^{-1})⁶³.

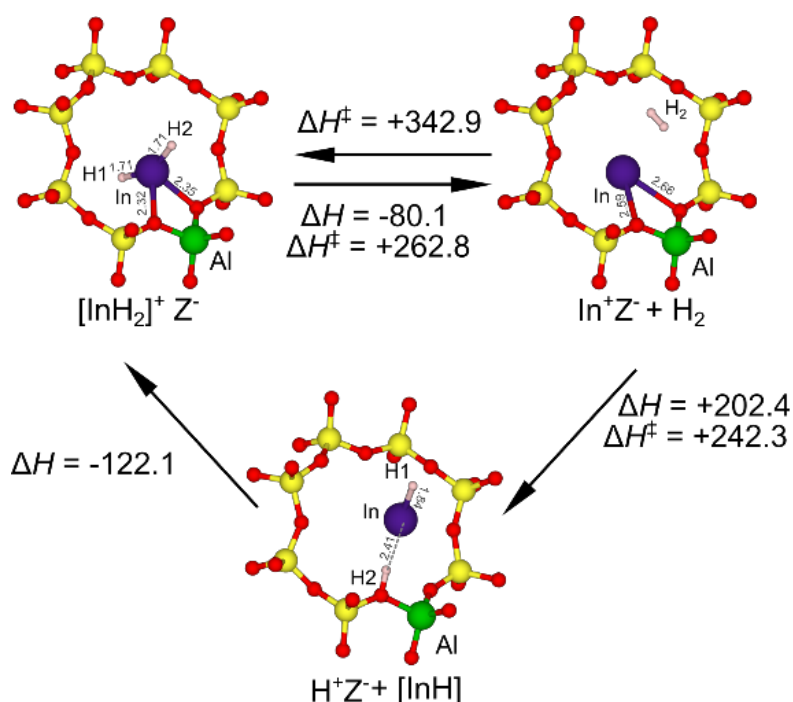


Figure 3. Optimized structure of the $[\text{InH}_2]^+$ ion $[\text{AlO}_4]^-$ site ($\text{Z}[\text{InH}_2]$) in the CHA zeolite and formation of $\text{Z}[\text{InH}_2]$ from $\text{Z}[\text{In}]$ via direct and indirect pathways as well as desorption of H_2 from $\text{Z}[\text{InH}_2]$. Activation enthalpies were estimated using TS calculations. The optimized structure files and free energies (**Figure S3**) are provided in the Supporting Information.

It is well-known that In-hydrides such as indane (InH_3) easily decompose below room temperature^{63,69}. Despite the significant effort that has been devoted to obtaining thermal stability by complexation with bulky ligands, few examples of indane complexes exhibiting room temperature stability have been reported^{70,71}. To obtain further insight regarding the formation and stability of CHA-supported In-hydrides, transition state (TS) calculations for the interconversion between $\text{Z}[\text{InH}_2]$ and $\text{Z}[\text{In}]$ were performed (**Figure 3**). The desorption of H_2 from $\text{Z}[\text{InH}_2]$ is exothermic, while the activation enthalpy ($\Delta H^\ddagger$)

was determined to be 262.8 kJ/mol. For the direct formation of $Z[\text{InH}_2]$ from $Z[\text{In}]$ with H_2 , $\Delta H^\ddagger$ was calculated to be 342.9 kJ/mol. In the indirect pathway, the heterolytic cleavage of H_2 on $Z[\text{In}]$ into $Z[\text{H}]$ and InH requires lower $\Delta H^\ddagger$ of 242.3 kJ/mol, and the generated intermediates are converted to $Z[\text{InH}_2]$ without any barrier. The free energy profiles also show lower energy values for the indirect pathway than the direct one (**Figure S3**). These TS calculations indicate that $[\text{InH}_2]^+$ ion formation requires high temperatures and the ions are thermodynamically unstable but kinetically stable. The obtained results support the formation and stability of In-hydrides at high temperatures observed in the FTIR measurements.

3.3.3 *In situ* XAFS measurement

In K-edge XAFS measurement of In-CHA under an H_2 atmosphere was conducted. It should be noted that the *in situ* XAFS measurement during RRSIE from $\text{In}_2\text{O}_3/\text{CHA}$ to In-CHA at 773 K was reported previously⁷² and the measurement for In-CHA after RSSIE under H_2 atmosphere at room temperature (298 K) was the focus herein. The XANES spectrum of In-CHA showed an absorption edge (E_0) at $E_0 = 27928.1$ eV, lower than that of $\text{In}_2\text{O}_3/\text{CHA}$ ($E_0 = 27932.1$ eV) by ca. 4 eV and different from that of In foil ($E_0 = 27929.6$ eV; **Figure 3A**). A similar edge shift after RSSIE was reported in *in situ* Ga K-edge XAFS measurement of Ga-zeolites, although the structure of Ga species after RSSIE (Ga^+ cation or Ga-hydrides) remains a topic of considerable debate. Iglesia et al. first reported the edge shift in XANES spectra ($\Delta E_0 = 4.7$ eV) during H_2 treatment of Ga-exchanged ZSM-5 zeolites obtained through impregnation of $\text{Ga}(\text{NO}_3)_3$ at a high temperature of 783 K and suggested the possibility of a monomeric Ga-hydride species at basic oxygen sites in zeolites³⁸. Other groups reported an edge shift toward lower

energies during the H_2 treatment of Ga-zeolites prepared by the impregnation method^{73,74} or chemical vapor deposition of trimethylgallium,⁷⁵ while each group indicated that the Ga species after H_2 treatment were Ga^+ cations. Hock et al. compared the XANES spectrum of Ga-exchanged BEA zeolites after H_2 treatment with those of several Ga^{3+} alkyl complexes as zeolite-coordinated Ga-hydride analogues⁷⁶. The authors proposed that the edge shift after H_2 treatment could be considered evidence of the formation of Ga-hydrides. The same group also discussed the shift of absorption edge in the In K-edge XANES spectra of SiO_2 -supported In ions during H_2 treatment by comparison with several In-alkyl complexes and claimed that the formation of In-hydrides occurred despite the unsuccessful observation of In–H groups by other spectroscopic techniques⁷⁷. As described above, the interpretation of the edge shift during H_2 treatment remains controversial for Ga-zeolites and few studies on XANES for H_2 -treated supported In ions are available.

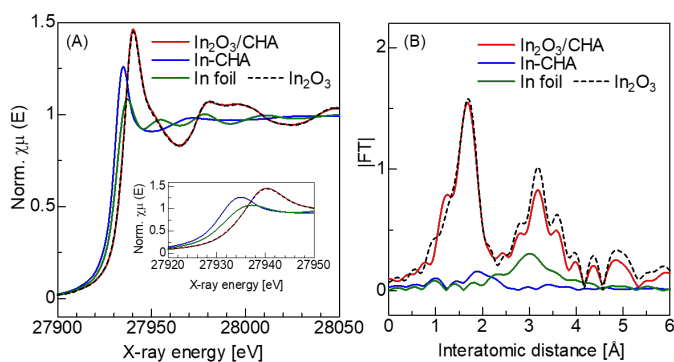


Figure 3. (A) In K-edge XAFS spectra of In-CHA after RSSIE under an H_2 atmosphere at room temperature, the corresponding precursor ($In_2O_3/H-CHA$ at room temperature), and reference samples (In_2O_3 , In foil). The inset figure shows the XANES region. (B) The corresponding FT of the EXAFS spectra.

The XAFS spectrum of In-CHA showed no scattering peak in the EXAFS region (**Figure 3A**). EXAFS analysis revealed that the scattering peak from In–O of the In–In shell was hardly observed in the FT of the EXAFS spectrum (**Figure 3B**). A similar disappearance of EXAFS features during H₂ reduction was reported in the *in situ* XAFS measurement by Iglesia et al., as mentioned above. Combined with the different adsorption edge from that of Ga metal, the authors proposed the formation of a monomeric Ga-hydride species at basic oxygen sites in zeolites³⁸. Although XAFS measurements generally do not provide direct evidence for the formation of metal-hydrides, the large energy shift in the XANES spectra and disappearance of EXAFS features clearly indicated the immobilization of reduced monomeric In species in CHA zeolites. The formation of monomeric In species was supported by the XRD measurements where the peaks derived from bulk In₂O₃ disappeared after RSSIE, while the diffraction pattern of the CHA zeolite was maintained (**Figure S1**).

3.3.4 Non-oxidative dehydrogenation of ethane

The dehydrogenation of ethane to ethylene, which is a fundamental transformation^{78,79}, was investigated using several catalysts, including In-CHA. Thermal cracking of ethane at high reaction temperatures (>1173 K) is utilized industrially, but rapid cooling of the outlet gas (<1073 K) and very short contact times are required to suppress undesired reactions of the obtained ethylene⁸⁰. Catalytic non-oxidative dehydrogenation is a promising alternative because of the absence of an oxidant and co-formation of H₂. To date, various metal catalyst systems containing Cr^{81,82}, Ga^{83–85}, and Pt-based alloys^{86–89} have been studied for the dehydrogenation of light alkanes. In this context, In has attracted significant attention as an effective additive to enhance the

activity/selectivity of Pt-based catalysts^{90–92}. However, catalyst systems utilizing In as the main active species have been rarely reported^{93,94}, and its dehydrogenation catalysis has not been fully explored.

Ethane dehydrogenation was conducted using In-CHA at 933 K and the time courses of ethane conversion and ethylene selectivity are shown in **Figure 4A** and **4B**, with the values after 0.5, 20, and 90 h provided in **Table 2**. In-CHA promoted dehydrogenation in 96.1% selectivity for ethylene in 25.9% ethane conversion at 0.5 h without co-feeding of H₂. The selectivity and conversion values were maintained for at least 90 h (27.2% conversion and 96.9% selectivity). During the reaction, CH₄ was formed as a side product in ca. 3% selectivity and the carbon balance was >98%. The effect of the In/Al ratio on the catalysis of the In-CHA was also investigated. The carbon balance increased with increasing In/Al ratio from 0.2 to 0.8 (**Figure 4C**). This dependency on the In/Al ratio was likely due to the decreased Brønsted acid sites with increasing In/Al ratio, as revealed by the NH₃ adsorption experiment monitored via FTIR spectroscopy. The FTIR spectrum for proton-type CHA (H-CHA) showed a strong peak at approximately 1470 cm⁻¹ derived from the adsorbed NH₃ on the Brønsted acid sites⁹⁵ and the absorbance decreased with increasing In/Al ratio of In-CHA. The extent of the decreased peak area was roughly proportional to the In/Al ratio (**Figure S2**) and higher loading of In ions decreased the amount of Brønsted acid sites, resulting in an improved carbon balance.

Ga- and Zn-exchanged CHA zeolites (Ga- and Zn-CHA, M/Al = 0.8) were also prepared and compared with In-CHA. Ga- and Zn-CHA exhibited much lower selectivities (**Table 2**, 76.1% and 67.3%, respectively), while the conversion values were higher at 0.5 h (57.4% and 47.6%, respectively). Their activities decreased with increasing reaction time, resulting in lower conversions than that observed for the In-CHA after 20 h. The

conversion values for In-, Ga-, and Zn-CHA at 20 h were 27.2%, 22.4%, and 18.6%, respectively. The TPO measurement of the catalysts used for the 2 h reaction (**Figure 4D**) revealed much more formation of coke for Ga- and Zn-CHA compared with In-CHA. In-CHA was also compared with Ga-exchanged ZSM-5 (Ga-ZSM-5) and Al₂O₃-supported PtSn catalysts (PtSn/Al₂O₃), which have been widely studied for the dehydrogenation of light alkanes. Both catalysts were gradually deactivated due to coke formation (**Figure 4A** and **4D**), resulting in lower conversions (22.0% for Ga-ZSM-5 at 20 h and 21.4% for PtSn/Al₂O₃ at 90 h) compared to In-CHA, although PtSn/Al₂O₃ exhibited better durability compared with Ga- and Zn-exchanged zeolites. Furthermore, the relationship between conversion and selectivity was obtained for In-CHA, Ga-ZSM-5, and PtSn/Al₂O₃ by changing the temperature and then compared (**Figure 4E**). For PtSn/Al₂O₃ and Ga-ZSM-5, the selectivity values dropped below 95% when the conversion reached above 30%. In contrast, In-CHA showed a better selectivity of 95.7% in 36.8 % conversion.

After the 90 h reaction using In-CHA, the catalyst was treated with O₂/He at 873 K, reduced using H₂/He at 873 K, and subsequently reused for catalysis of the dehydrogenation reaction (for further details, see the Supporting Information). The conversion and selectivity values remained almost constant for at least 20 h compared to the fresh In-CHA (**Figure 4A**), indicating that In-CHA was reusable. The XRD pattern of the used In-CHA exhibited a diffraction pattern similar to the fresh In-CHA and H-CHA (**Figure S1**), consistent with the good reusability observed for In-CHA. These results demonstrate the high selectivity and durability of In-CHA for the dehydrogenation of ethane at high reaction temperatures, which is advantageous from the perspective of the endothermic nature of non-oxidative dehydrogenation of alkanes^{78,79}.

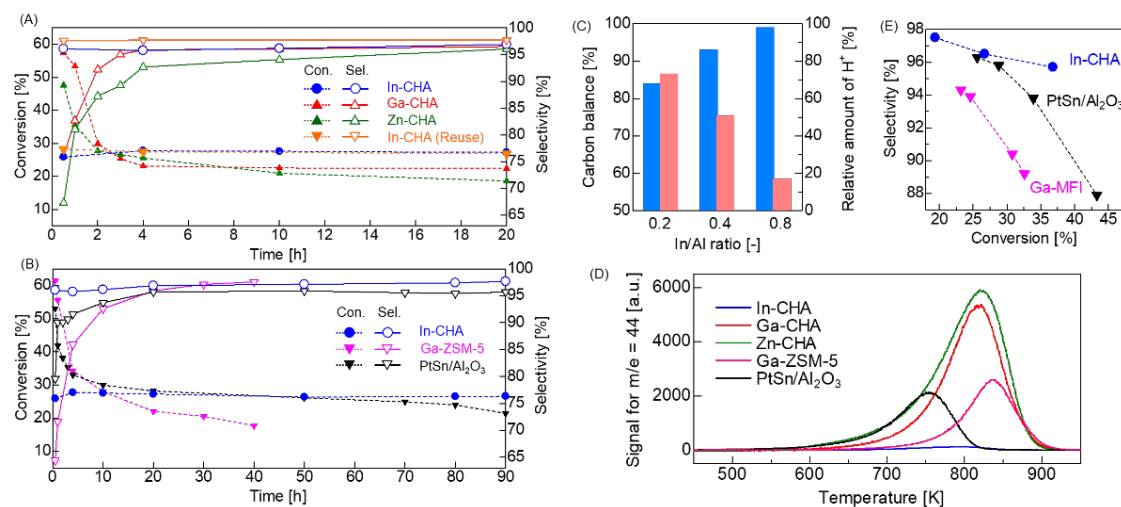


Figure 4. Time course of the non-oxidative dehydrogenation of ethane using (A) In-, Ga-, Zn-CHA for 20 h and (B) In-CHA, Al₂O₃ supported PtSn catalyst (PtSn/Al₂O₃) for 90 h and Ga-ZSM-5 for 40 h. (C) The effect of In/Al ratio on carbon balance (blue) and relative amount of Brønsted acid sites normalized to the proton-type CHA (H-CHA) (red). (D) TPO spectra of the catalysts used for 2 h reaction. (E) Relationship between conversion and selectivity for In-CHA, PtSn/Al₂O₃, and Ga-ZSM-5.

Table 2. Conversion, selectivity, and carbon balance at 0.5, 20, and 90 h.

Catalyst	Time [h]	Conv. [%] ^a	Sel. [%] ^a
In-CHA	0.5	25.9	96.1
	20	27.2	96.9
	90	26.6	97.6
Ga-CHA	0.5	57.4	76.1
	20	22.4	96.5
Zn-CHA	0.5	47.6	67.3
	20	18.6	96.0
Ga-ZSM-5 ^b	0.5	61.4	64.4
	20	22.0	95.9
PtSn/Al ₂ O ₃ ^c	0.5	53.1	79.6
	20	28.2	95.7
	90	21.4	95.7

Reaction conditions: Catalyst (0.1 g, SiO₂/Al₂O₃ = 22.3, M/Al = 0.8), 933 K, 10 mL/min of 10% C₂H₆/He. [a] Determined by GC-FID. Further detail are provided in the Supporting Information. [b] Ga-ZSM-5 (0.1 g, SiO₂/Al₂O₃ = 22, Ga/Al = 0.5). [c] PtSn/Al₂O₃ (0.1 g, Pt: 0.4 wt%, Sn: 0.8 wt%)

3.3.5 Kinetic study of ethane dehydrogenation catalyzed by In- and Ga-CHA

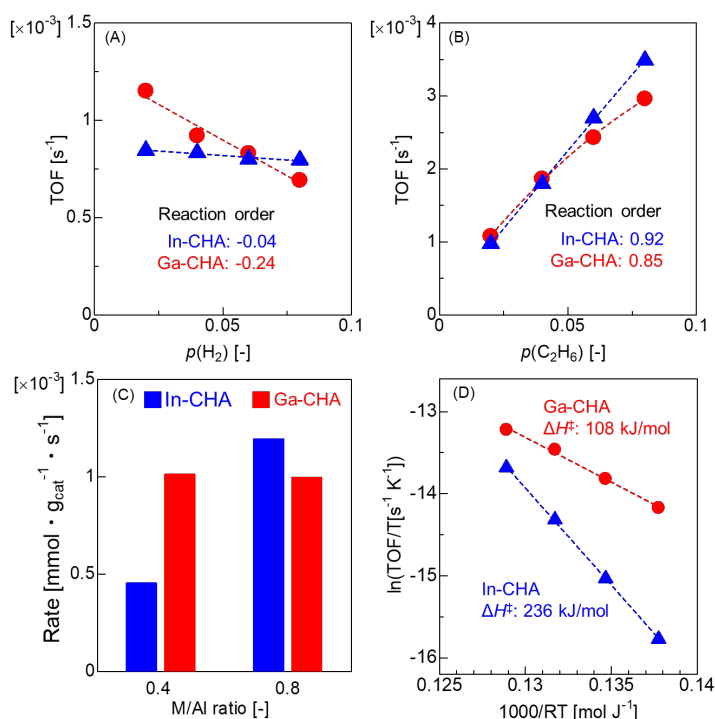


Figure 7. Kinetic studies of ethane dehydrogenation using In-CHA (blue) and Ga-CHA (red). Comparison of TOF dependency on (A) $p(\text{H}_2)$ and (B) $p(\text{C}_2\text{H}_6)$. (C) Effect of M/Al ratio on the formation rate of ethylene. Conditions: 0.1 g of catalyst, 50 mL/min of $\text{H}_2/\text{C}_2\text{H}_6/\text{He}$, 933 K for In or 913 K for Ga. (D) Eyring plot for the ethane dehydrogenation (873–933 K). The data for the kinetic studies were obtained under conditions yielding ethane conversions of <15% and the detailed conditions for each experiment are provided in the Supporting Information.

To discuss active In species for dehydrogenation, kinetic studies were performed for Ga- and In-CHA. Bell et al. recently reported mechanistic and kinetic studies of the dehydrogenation/cracking of propane using Ga-exchanged ZSM-5, indicating that the dehydrogenation reaction rate decreased with an increasing partial pressure of H_2 ($p(\text{H}_2)$) and that reaction order of $p(\text{H}_2)$ was -0.1 to -0.3⁹⁶. The authors proposed that $[\text{GaH}]^{2+}$ on

two $[\text{AlO}_4]^-$ sites were the active sites and that the inhibition by H_2 could be ascribed to the conversion of $[\text{GaH}]^{2+}$ to $[\text{GaH}_2]^+-\text{H}^+$ cation pairs via competitive adsorption of H_2 with propane. In the kinetic study described herein for the dehydrogenation of ethane using Ga-CHA (**Figure 7A** and **7B**), similar phenomena were observed. Increasing $p(\text{H}_2)$ inhibited the dehydrogenation and the reaction order of $p(\text{H}_2)$ was determined to be -0.24 (**Figure 7A**). In contrast to the Ga-zeolites, ethane dehydrogenation using In-CHA was hardly inhibited by H_2 and exhibited zero-order kinetics with respect to H_2 (the reaction order of $p(\text{H}_2)$: -0.04, **Figure 7A**), indicating that competitive adsorption of H_2 with ethane is unlikely. The reaction order of $p(\text{C}_2\text{H}_6)$ was determined to be 0.85 and 0.92 for Ga-CHA and In-CHA, respectively (**Figure 7B**). The effect of the M/Al ratio ($\text{M} = \text{In}$ or Ga) on the ethylene formation rate was also examined. The formation rate almost doubled with an increasing In/Al ratio from 0.4 to 0.8 for In-CHA, while the increased Ga/Al ratio from 0.4 to 0.8 did not increase the formation rate with the Ga-CHA catalyst (**Figure 7C**). Therefore, it is likely that the $[\text{InH}_2]^+$ ion or In^+ cation coordinated to one $[\text{AlO}_4]^-$ site, acting as plausible active sites rather than the $[\text{InH}]^{2+}$ ion coordinating to two $[\text{AlO}_4]^-$ sites. This interpretation is supported by the NH_3 adsorption experiment in **Figure S5**. The experimental activation enthalpy ($\Delta H^\ddagger_{\text{exp}}$) for In-CHA was determined to be 236 kJ/mol from the Eyring plot, which is approximately twice that obtained for Ga-CHA ($\Delta H^\ddagger_{\text{exp}} = 108$ kJ/mol; **Figure 7D**).

3.3.5 TS calculation for ethane dehydrogenation on possible In species in CHA

TS calculations for dehydrogenation on In-hydrides ($\text{Z}[\text{InH}_2]$ and $\text{Z}_2[\text{InH}]$) and In^+ cations were performed and the highest $\Delta H^\ddagger$ values and corresponding elementary steps were compared. Six mechanisms (concerted, alkyl, or σ -bond metathesis mechanism on

$[\text{InH}_2]^+$ ions, carbenium or alkyl mechanism on $[\text{InH}]^{2+}$ ions, and alkyl mechanism on In^+ cations) were considered according to previous theoretical studies regarding the dehydrogenation of light alkanes catalyzed by Ga-zeolites^{41,43,45} and the CH_4 activation on silica-supported Zr-hydride catalyst.⁹⁷ The obtained enthalpy profiles were described in solid lines in **Figures 8-10**. In the concerted mechanism on $\text{Z}[\text{InH}_2]$, as shown in **Figure 8A**, cleavage of C–H bonds and formation of dehydrogenation products (ethylene and H_2) simultaneously occur after ethane adsorption. This step is endothermic ($\Delta H = 149.4 \text{ kJ/mol}$) and $\Delta H^\ddagger$ was estimated to be 213.9 kJ/mol . The generated ethylene and H_2 desorb smoothly, regenerating $\text{Z}[\text{InH}_2]$. In the alkyl mechanism (**Figure 8B**), an $[\text{InH}_2]^+$ ion tilts from the 8MR side towards the 6MR side before the adsorption of ethane. After adsorption, the cleavage of the first C–H bond occurs to afford $[\text{InH}_2(\text{C}_2\text{H}_5)]$ and $\text{Z}[\text{H}]$ (1st step). Next, a coordinated hydride transfer from $[\text{InH}_2(\text{C}_2\text{H}_5)]$ to $\text{Z}[\text{H}]$ proceeds without barrier to yield H_2 and $\text{Z}[\text{In}(\text{H})(\text{C}_2\text{H}_5)]$ in an exothermic manner (2nd step). Finally, the second C–H bond is cleaved to form ethylene, followed by the desorption of ethylene and regeneration of $\text{Z}[\text{InH}_2]$ (3rd step). The 1st step (from $\text{Z}[\text{InH}_2]$ with ethane to $\text{Z}[\text{H}]$ with $[\text{InH}_2(\text{C}_2\text{H}_5)]$) and 3rd step (from $\text{Z}[\text{In}(\text{H})(\text{C}_2\text{H}_5)]$ to $\text{Z}[\text{InH}_2]$ with ethylene) proceeds with $\Delta H^\ddagger$ values of 239.9 and 163.1 kJ/mol , respectively. Furthermore, the σ -bond metathesis mechanism was investigated (**Figure 8C**). The C–H bond cleavage occurs in a σ -bond metathesis manner to give $\text{Z}[\text{InH}(\text{C}_2\text{H}_5)]$ with H_2 (1st step). The calculated $\Delta H^\ddagger$ is 329.2 kJ/mol , which is higher than those in concerted and alkyl mechanisms. After desorption of H_2 followed by a barrierless rotation of the coordinated C_2H_5 moiety, the cleavage of the second C–H bond proceeds $\Delta H^\ddagger$ values of 289.9 kJ/mol to give $\text{Z}[\text{InH}_2]$ and ethylene (2nd step). The desorption of the generated ethylene results in the regeneration of $\text{Z}[\text{InH}_2]$.

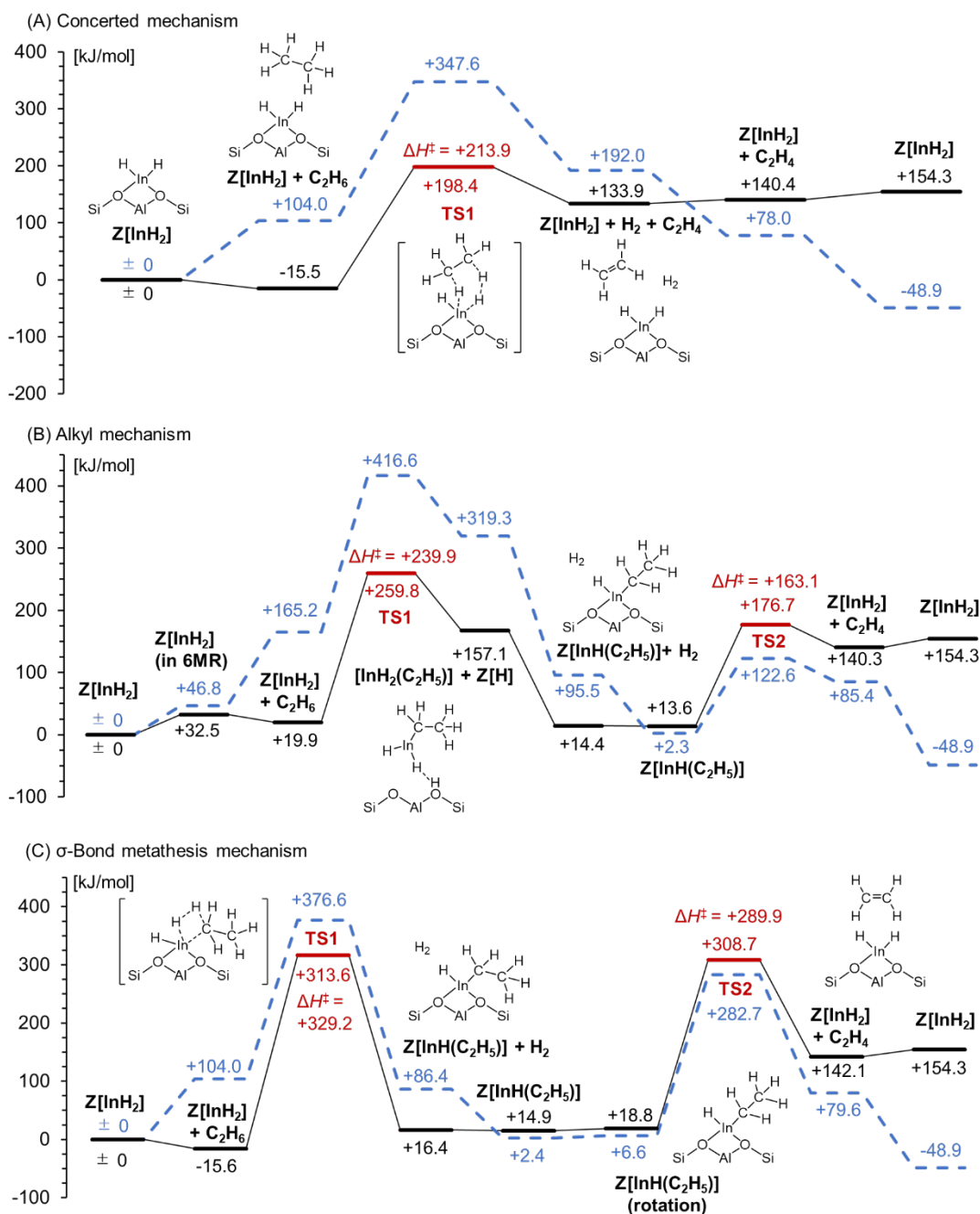


Figure 8. Enthalpy (solid lines) and free energy (dashed lines) profiles for the ethane dehydrogenation on $Z[\text{InH}_2]$ (A) via a concerted mechanism, (B) via an alkyl mechanism, and (C) via a σ -bond metathesis mechanism. The schematic illustrations of several intermediates and transition states are also described. All the optimized structures files are in the Supporting Information.

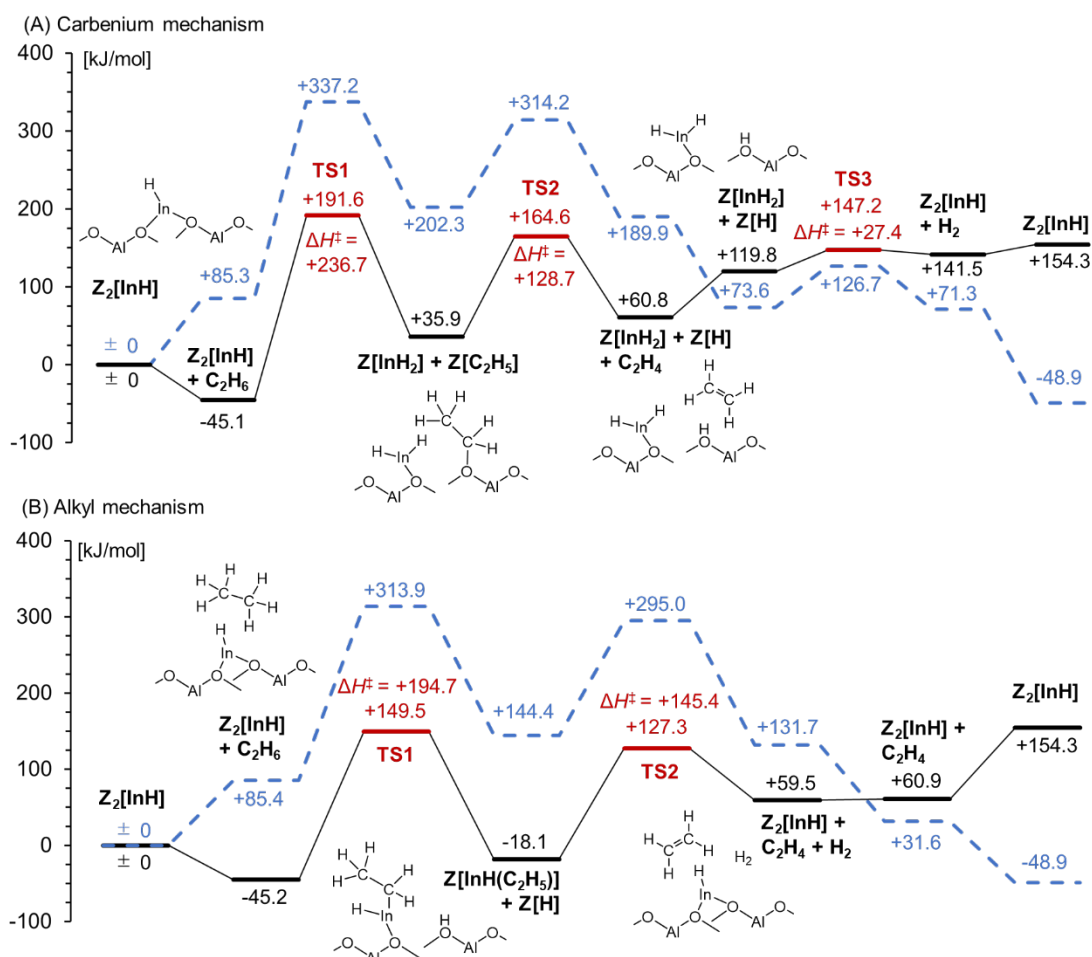


Figure 9. Enthalpy (solid lines) and free energy (dashed lines) profiles for the ethane dehydrogenation on $Z_2[InH]$ (A) via a carbenium mechanism and (B) via an alkyl mechanism. The schematic illustrations of several intermediates are also described. All the optimized structures files are in the Supporting Information.

The TS calculation for the carbenium mechanism on $Z_2[InH]$ (**Figure 9A**) indicated that the first C–H bond cleavage of the adsorbed ethane occurs via hydride transfer to afford $Z[InH_2]/Z[C_2H_5]$ (1st step) and the corresponding $\Delta H^\ddagger$ was estimated to be 236.7 kJ/mol. In the 2nd step, ethylene is generated via the second C–H bond cleavage on $Z[C_2H_5]$ with

a $\Delta H^\ddagger$ of 128.7 kJ/mol, affording $Z[\text{InH}_2]/Z[\text{H}]$. After desorption of the generated ethylene, H_2 is generated from $Z[\text{InH}_2]/Z[\text{H}]$ (3rd step; $\Delta H^\ddagger = 27.4$ kJ/mol) followed by H_2 desorption, regenerating $Z_2[\text{InH}]$. In ethane dehydrogenation on $Z_2[\text{InH}]$ via the alkyl mechanism (**Figure 9B**), the reaction proceeds via C–H bond cleavage of the adsorbed ethane (1st step) with a $\Delta H^\ddagger$ of 194.7 kJ/mol, affording $Z[\text{In}(\text{H})(\text{C}_2\text{H}_5)]$ and $Z[\text{H}]$. Ethylene and H_2 are formed from $Z[\text{In}(\text{H})(\text{C}_2\text{H}_5)]/Z[\text{H}]$ via the second C–H bond cleavage, forming $Z_2[\text{InH}]$ (2nd step). The $\Delta H^\ddagger$ value of the 2nd step was determined to be 145.4 kJ/mol and the generated H_2 desorbs smoothly while the desorption of ethylene requires a ΔH of 93.4 kJ/mol. In these reaction mechanisms on In-hydrides except for the σ -bond metathesis mechanism on $Z[\text{InH}_2]$, the rate-determining step is the first C–H cleavage and the associated $\Delta H^\ddagger$ values (194.7–239.9 kJ/mol) are in good agreement with the experimentally obtained values from the Eyring plot ($\Delta H^\ddagger_{\text{exp}} = 236$ kJ/mol; **Figure 7D**).

In contrast, dehydrogenation via the alkyl mechanism on $Z[\text{In}]$ (**Figure 10**) requires a much higher $\Delta H^\ddagger$ of 410.3 kJ/mol for the rate-determining C–H bond cleavage of the adsorbed ethane to afford $Z[\text{InH}(\text{C}_2\text{H}_5)]$ (1st step). Subsequently, ethylene and H_2 are formed from $Z[\text{InH}(\text{C}_2\text{H}_5)]$ with a relatively small activation barrier of 74.3 kJ/mol (2nd step) followed by product desorption, regenerating $Z[\text{In}]$. The above TS calculations for ethane dehydrogenation on possible In species showed that In-hydrides are more reactive than In^+ cations and are potential active sites for dehydrogenation catalyzed by In-CHA.

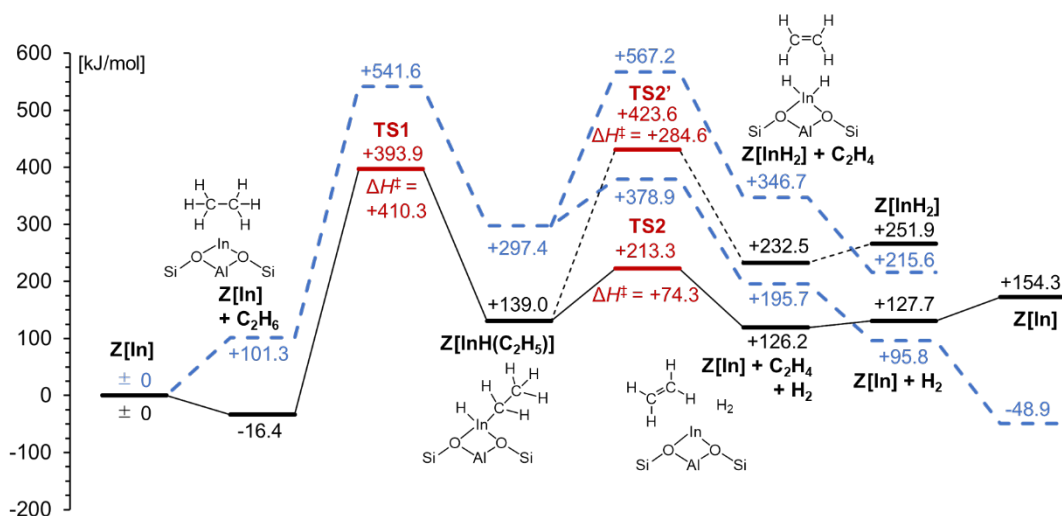


Figure 10. Enthalpy (solid lines) and free energy (dashed lines) profiles for the ethane dehydrogenation on Z[In] via an alkyl mechanism. The steps for the formation of Z[InH₂] from the intermediate Z[In(H)(C₂H₅)] via formation and desorption of C₂H₄ are included. The schematic illustrations of several intermediates are also described. All the optimized structures files are in the Supporting Information.

Furthermore, the calculations in free energy were conducted for the six mechanisms described above on different In species. The profiles are shown in dash lines in **Figures 8-10**. In all cases, the free energy barrier for the first C–H cleavage is the highest in each mechanism, which is consistent with our consideration of the rate-determining step based on enthalpy calculations. Among the mechanisms investigated for Z[InH₂] (**Figure 8**), the associated free energy for a concerted mechanism (347.6 kJ/mol) is lower than those for alkyl and σ -bond metathesis mechanisms (416.6 and 376.6 kJ/mol, respectively). For Z₂[InH] (**Figure 9**), the corresponding free energy values are relatively low for both mechanisms (337.2 and 313.9 kJ/mol for carbenium and alkyl mechanisms, respectively). However, the free energy required for Z[In] is much higher (541.6 kJ/mol, **Figure 10**)

than those for five mechanisms on In-hydrides ($Z[\text{InH}_2]$ and $Z_2[\text{InH}]$), which also evidences higher reactivity of In-hydrides than In^+ cations.

3.3.6 Active In species for selective dehydrogenation of ethane

Table 3 summarizes the results of *in situ* spectroscopic, kinetic, and theoretical studies for ethane dehydrogenation using In-CHA. The *in situ* FTIR measurement (**Figure 1**) and frequency analysis (**Table 1**) revealed that $[\text{InH}_2]^+$ ions are likely to form as main In-hydrides and $[\text{InH}]^{2+}$ ions possibly form as minor species. The kinetic studies (**Figure 7**) indicated that the catalytically active sites for ethane dehydrogenation are possibly $[\text{InH}_2]^+$ ions or In^+ cations, rather than $[\text{InH}]^{2+}$ ions, while the TS calculations (**Figures 8-10**) suggested $[\text{InH}_2]^+$ and $[\text{InH}]^{2+}$ ions as plausible active sites rather than In^+ cations. Thus, $[\text{InH}_2]^+$ ions are the most plausible catalytically active sites among the In-hydrides and In^+ cations. To further investigate the feasibility of $[\text{InH}_2]^+$ active sites during dehydrogenation, *in situ* FTIR and XAFS measurements and TS calculations of the reaction of In-CHA with ethane were performed. The FTIR spectrum of In-CHA after treatment with ethane at 773 K showed a band derived from the In–H stretching vibration of $[\text{InH}_2]^+$ ions (**Figure S6**). Note that our FTIR measurement system has a limitation where the temperature can be increased only up to 773 K. The XANES spectrum of In-CHA in the presence of ethane at 933 K was similar to that in the presence of H_2 (**Figure S7**). The TS calculation for the reaction of $Z[\text{In}]$ with ethane to form $Z[\text{In}(\text{H})(\text{C}_2\text{H}_5)]$ and successive formation of ethylene showed that $Z[\text{InH}_2]$ can be formed from $Z[\text{In}(\text{H})(\text{C}_2\text{H}_5)]$ with a $\Delta H^\ddagger$ of 284.6 kJ/mol (**Figure 10**). From the kinetic, theoretical, and *in situ* spectroscopic studies, a possible reaction mechanism of ethane dehydrogenation on $[\text{InH}_2]^+$ ions is proposed. In the presence of ethane or co-product H_2

at high reaction temperatures, an $[\text{InH}_2]^+$ ion is generated in the CHA zeolite. The generated $[\text{InH}_2]^+$ is thermodynamically unstable but kinetically trapped in the CHA pore, serving as a catalytically active site to promote the selective dehydrogenation of ethane. The concerted and alkyl mechanisms are possible rather than the σ -bond metathesis as revealed by the DFT calculations. In these two possible mechanisms, the $\Delta H^\ddagger$ for the rate-determining C–H cleavage of the adsorbed ethane is lower than that for the desorption of H_2 from an $[\text{InH}_2]^+$ ion, supporting the feasibility of dehydrogenation on $[\text{InH}_2]^+$ ions.

Table 3 Summary of results obtained in *in situ* spectroscopic and kinetic studies as well as DFT calculations for ethane dehydrogenation using In-CHA.

	$\nu(\text{In-H}) [\text{cm}^{-1}]$	In/Al [-]	$\Delta H^\ddagger [\text{kJ/mol}]$
Experimental	1720 (Maximum absorption) 1717 (Main peak), 1781 (Minor peak)	$\approx 1:1$	236
$[\text{InH}_2]^+$ ion model	1721.0 ~ 1735.6 (ν_{sym}) 1787.2 ~ 1809.7 (ν_{asym})	1:1	213.9 (Concerted), 239.9 (Alkyl), 329.2 (σ -Bond metathesis)
$[\text{InH}]^{2+}$ ion model	1763.0 ~ 1893.0	1:2	236.7 (Carbenium), 194.7 (Alkyl)
In^+ cation model	n/a	1:1	410.3 (Alkyl)

The low coke formation can be ascribed to a low abundance of *in situ*-generated protons and carbenium ions which can promote coke formation. Dehydrogenations via the concerted mechanism and the σ -bond metathesis mechanism on $[\text{InH}_2]^+$ ions do not include the generation of the above species (**Figure 8A** and **8C**), whereas, in an alkyl mechanism on $[\text{InH}_2]^+$ ions, the *in situ* generated $\text{Z}[\text{H}]$ after the 1st step smoothly reacts

with the coordinated hydride in $[\text{In}(\text{H})_2(\text{C}_2\text{H}_5)]$ without barrier, affording H_2 and $\text{Z}[\text{In}(\text{H})(\text{C}_2\text{H}_5)]$ (**Figure 8B**). For $[\text{InH}]^{2+}$ ions, ethylene formation from $\text{Z}[\text{C}_2\text{H}_5]/\text{Z}[\text{InH}_2]$ (2nd step in the carbenium mechanism; **Figure 9A**) and formation of dehydrogenation products from $\text{Z}[\text{H}]/\text{Z}[\text{In}(\text{H})(\text{C}_2\text{H}_5)]$ (2nd step in alkyl mechanism; **Figure 9B**) requires high $\Delta H^\ddagger$ values of 128.7 and 145.4 kJ/mol, respectively. The abundance of *in situ*-generated protons and carbenium ions during dehydrogenation on $[\text{InH}_2]^+$ ions is likely lower than that during dehydrogenation on $[\text{InH}]^{2+}$ ions. A similar difference of TS calculations between $[\text{GaH}_2]^+$ and $[\text{GaH}]^{2+}$ ions was indicated by Bell et al.⁴¹. Therefore, the distinction of catalytically active M-hydrides between In and Ga ($[\text{InH}_2]^+$ vs $[\text{GaH}]^{2+}$ ions) is the origin of the superior selectivity and durability of In-CHA over those of Ga-zeolites.

3.4 Conclusion

Herein, the first report of surface isolated In-hydrides in zeolites including formation, characterization, and catalysis is described. The isolated In-hydrides were formed in CHA zeolites by H_2 treatment of In-CHA at high reaction temperatures. Characterization by *in situ* FTIR measurement including isotopic experiments with D_2 and vibration calculations revealed that the $[\text{InH}_2]^+$ ions are plausible structures. The necessity of high temperature for the formation of $[\text{InH}_2]^+$ ions and their kinetic stability were also discussed in the context of TS calculations. The results of *in situ* XAFS measurement are compatible with the formation of In-hydrides. Regarding the catalysis, In-CHA exhibited high selectivity and durability for the non-oxidative ethane dehydrogenation without co-feeding H_2 . The activity and selectivity of In-CHA were maintained for at least 90 h and the catalyst was reusable without loss of its efficiency. Kinetic studies revealed that In-CHA was not

inhibited by H₂ and the formation rate increased with an increasing M/Al ratio to 0.8, which were different from those operatives in Ga-zeolites. The TS calculations for dehydrogenation on In-hydrides and In⁺ cations indicated that [InH₂]⁺ ions likely act as catalytically active sites for dehydrogenation and both concerted and alkyl mechanisms are possible. The [InH₂]⁺ ion plays a key role in selective dehydrogenation where the abundance of zeolite-coordinated protons and/or carbenium species during the dehydrogenation might be lower compared to the case of Ga-zeolites. This leads to much less coke formation, resulting in superior selectivity and durability of In-CHA. Rational studies for the formation and characterization of In-hydrides in various types of zeolites and their dehydrogenation catalysis activity remain under investigation.

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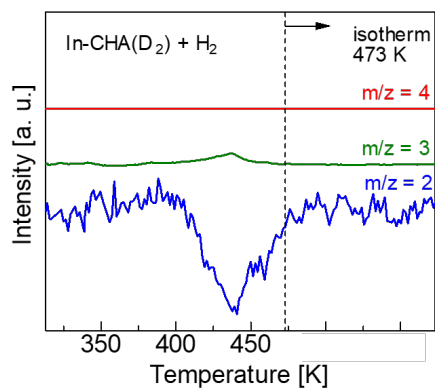


Figure S1. Mass profiles for $m/z = 2, 3$, and 4 during the reaction between $\text{In-CHA(D}_2\text{)}$ and H_2

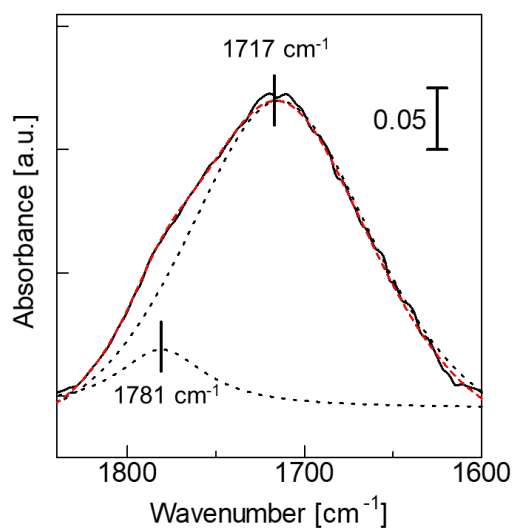


Figure S2. Deconvolution of the bands around $1700\text{--}1800\text{ cm}^{-1}$ in the FTIR spectrum of $\text{In-CHA(H}_2\text{)}$.

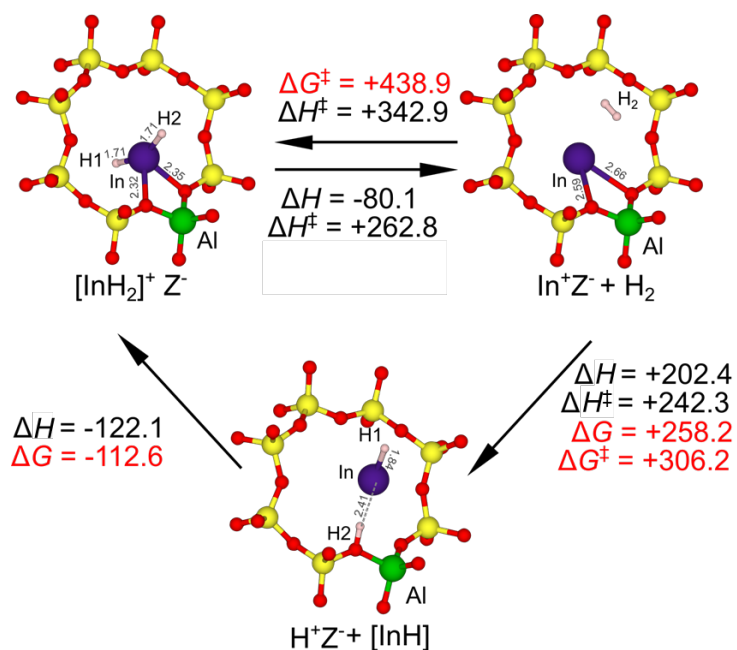


Figure S3. Enthalpy and free energy for interconversion between $\text{Z}[\text{InH}_2]$ and $\text{Z}[\text{In}]$.

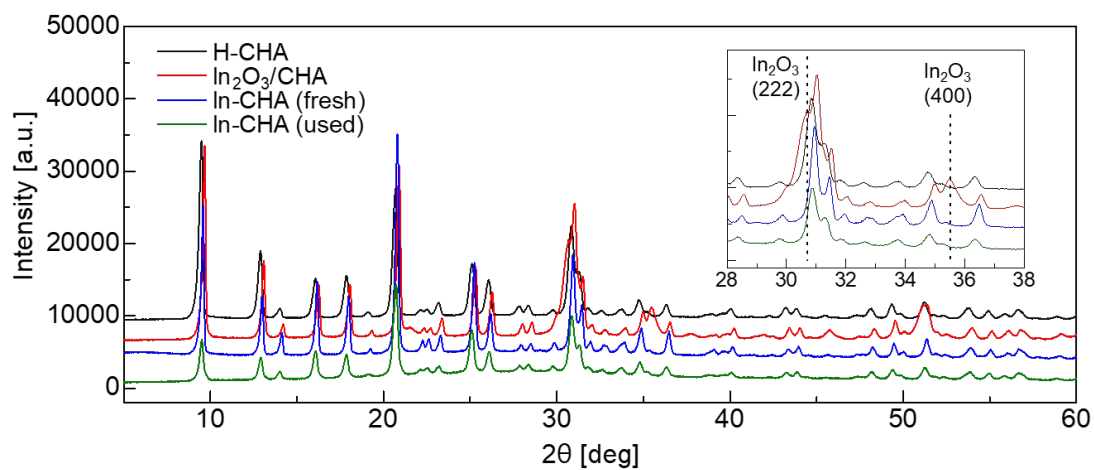


Figure S4. XRD pattern of the fresh In-CHA, the precursor material $\text{In}_2\text{O}_3/\text{CHA}$, the In-CHA used for the dehydrogenation, and H-CHA.

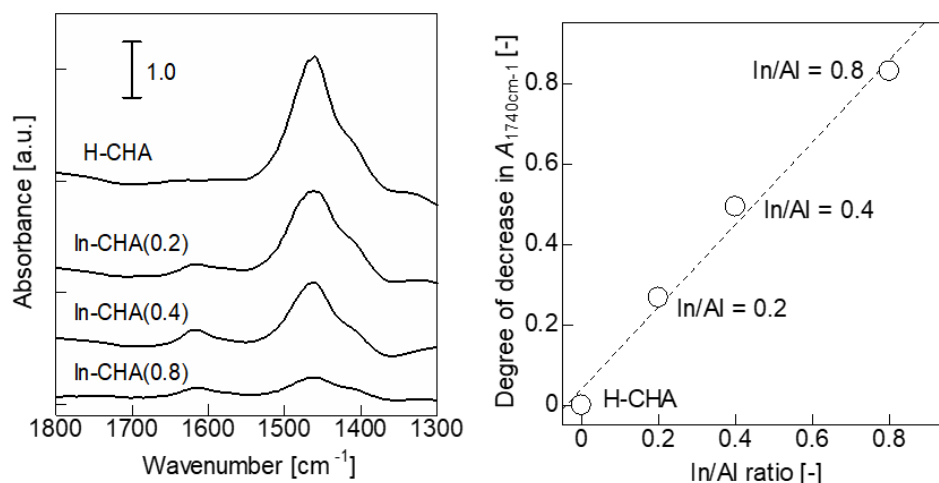


Figure S5. FTIR spectra of NH_3 adsorption experiment for In-CHA with different In/Al ratio (left). Relationship between degree of decrease in peak area around 1740 cm^{-1} ($A_{1740\text{cm}^{-1}}$) and the In/Al ratio (right).

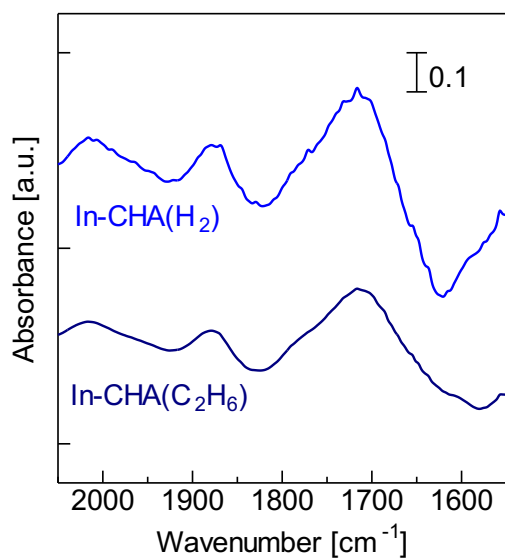


Figure S6. FTIR spectra of the In-CHA after treatment with ethane at 773 K.

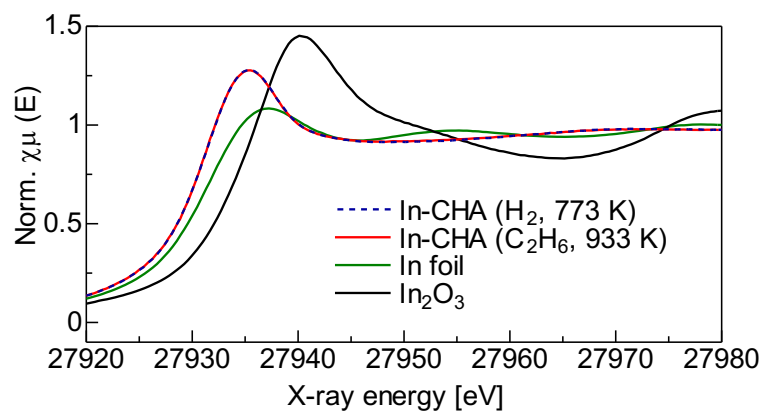


Figure S7. In situ XAFS spectra of In-CHA in the presence of H₂ (773 K) or in the presence of ethane (933 K).

Chapter 4

Preparation of high-loading Pd-CHA via oxidative dispersion by NO and the relationship between the local structure of Pd cation and NO desorption temperature

4.1. Introduction

Supported metal species have been widely utilized as heterogenous catalysts and adsorbers.¹⁻⁴ The morphology and oxidation state of immobilized metal species dynamically change with temperature and atmosphere.⁵⁻²⁰ Generally, exposure to high temperatures induces aggregation of metal species to form larger particles via particle coalescence and atomic ripening. Particle coalescence involves temperature-induced movement of metal nanoparticles, while atomic ripening occurs via the movement of atomic species on supports or in a vapor phase. As an opposite phenomenon, atomic dispersion of metal species occurs when mobile atomic species are trapped by supports.²¹⁻³⁹ Several microscopic and spectroscopic studies on atomic dispersion have appeared recently, investigating structural evolution under various reaction conditions and their effects on catalytic and adsorption properties.^{24,26,27,29,36,40,41} Atomic dispersion also has the potential to be applied to atomically-dispersed materials as well as catalyst regeneration processes, and several examples have appeared.^{32,33,38,39,42,43}

Aluminosilicate zeolites are promising oxide supports that anchor atomic metal species as cations due to their cation exchange abilities, as well as the ubiquitousness of constituent elements (Si, Al, O) with commercial availability. In the case of divalent cations, such as Pd²⁺, paired Al sites in three-dimensional zeolite frameworks serve as

anchoring sites, stabilizing through electrostatic interactions. Among them, eight-membered ring zeolites, such as CHA, have a high potential to suppress aggregation of metal cations under reaction conditions because of their small pore sizes ($3.8 \text{ \AA} \times 3.8 \text{ \AA}$) and superior stability toward hydrothermal conditions compared to medium- and large-pore zeolites.^{44–48} Even though several metal-exchanged CHA zeolites, such as Cu-CHA, can be synthesized by conventional aqueous-phase ion exchange methods, loading Pd cations into CHA zeolites is difficult owing to strong water solvation of cations, which are too bulky to access the small pores. For example, Szanyi and co-workers loaded Pd cations into several zeolites via ion exchange in an aqueous solution for use as passive NO_x adsorbers (PNAs), where isolated Pd cations are responsible for NO adsorption and aggregated PdO particles are ineffective.^{49–51} Very small amounts of Pd (1.4 %) were exchanged with cations in CHA in an aqueous solution at Pd loading amounts of 0.5 wt%, while almost all the Pd (ca. 75%) was immobilized at ion-exchange sites in BEA and ZSM-5 under similar Pd loading amounts and Si/Al ratios of zeolites.⁵² Kim and coworkers prepared Pd-modified CHA by incipient wetness impregnation and examined hydrothermal aging treatments at 700–750°C to increase the number of active Pd cations for NO adsorption.²⁹ However, bulk PdO was the main Pd species, even after treatment, as confirmed by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) measurements. Although Pd cation loading (1–3.5 wt%) has been recently achieved via a modified aqueous-phase ion exchange method by the group of Szanyi,⁵³ the development of effective methods to load Pd cations in small-pore zeolites still needs to be addressed. Pd-exchanged zeolites are considered efficient catalysts for CH₄ oxidation and the selective catalytic reduction of NO by CH₄ (CH₄-SCR).^{54–56} Recently, they were applied as passive NO_x adsorbers (PNAs) that capture NO_x in low-temperature regions (typically

< 100 °C) upstream of the NH₃-SCR system, to reduce the NO_x emission during the cold start period of a vehicle engine and, subsequently, release the stored NO_x in high-temperature regions (typically 250–400 °C) after the catalyst has reached the operating temperature.^{50,57,58} The development of efficient PNAs is highly desired because a rich regeneration process, which is required for Lean NO_x traps, can be avoided via thermal regeneration.^{49,59} Atomically dispersed Pd²⁺ cations are responsible for NO adsorption and desorption.^{60,61} Among the various Pd-exchanged zeolites, Pd-CHA has attracted attention because of its high NO_x desorption temperature and the superior hydrothermal stability of the CHA framework compared to those of other zeolites.^{61–67} Szanyi and co-workers conducted experimental and theoretical characterizations of the Pd cation in CHA zeolite and revealed that the zeolite framework can stabilize electrophilic Pd²⁺ cations.⁶¹ The same group also achieved improvements in the NO_x storage capacity and time for NO_x removal by increasing the loading of Pd cations.⁶⁸ For the NO_x desorption properties, two desorption peaks appeared in low- and high-temperature regions (around 250 and 400 °C, respectively), as demonstrated in the NO_x temperature-programmed desorption (NO_x-TPD) measurements.^{65,69} Although these peaks were indicative of the desorption from two kinds of Pd cation sites, their detailed structures and the origin of the difference in the desorption temperatures were unclear. Epling and Paolucci revealed that a bare Pd²⁺ cation at the paired Al site in the six-membered ring (6MR) of the CHA framework is the most stable and that its NO adsorption property is sensitive to reaction conditions based on a combined approach of experiments and computational modeling.⁶⁶ Additionally, Khivantsev *et al.* reported that the hydrothermal stability of loaded Pd cations was improved by the relatively high amount of paired Al sites in the CHA zeolite.⁷⁰ Gounder's group carried out a detailed speciation of the Pd cationic species in CHA zeolite and revealed Pd agglomeration and their subsequent redispersion to mononuclear Pd²⁺ ions, which prefer binding at 6MR paired Al sites in the CHA zeolite.⁷¹ Despite the aforementioned experimental and theoretical studies on Pd-CHA, the local structures of the Pd cations at different paired Al sites and their relationship with the NO adsorption/desorption properties have not been addressed yet. One of the experimental obstacles for the elucidation of this relationship is the difficulty of loading Pd cations in

concentrations of more than 1 wt% into CHA zeolites via the conventional aqueous phase ion-exchange method, which is attributed to the strong water solvation of cations that are too bulky to disperse into the small pores.⁷²

In this study, we describe the atomic dispersion of bulk Pd into CHA zeolites for the solid-state synthesis of Pd-exchanged CHA. Bulk Pd metal outside the CHA zeolites is transformed into Pd²⁺ cations on zeolite anionic sites under NO flow at 600°C. Preparation of Pd-exchanged CHA zeolites from commercially available Pd black and CHA zeolites was also achieved. Although redispersion of aggregated metal clusters in medium- and large-pore zeolites^{21,22,38,40,73,74} and the transport of metal cations/nanoparticles from the outside of CHA zeolites have been reported,^{33,75} atomic dispersion of bulk Pd from outside into small-pore zeolites has not yet been reported. Microscopic (scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM)) and spectroscopic (XRD, XAS, and Fourier transform infrared (FTIR)) characterizations revealed that atomic Pd²⁺ cations were mainly formed, and the loading amount of Pd²⁺ cations reached ca. 4 wt%. *In situ* spectroscopic studies (XAS and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)) and *ab initio* thermodynamics analysis using density functional theory (DFT) were also conducted to gain insight into atomic dispersion of bulk Pd in CHA zeolites. Furthermore, a plausible mechanism was theoretically studied to discuss the reason for the necessity of high reaction temperature. In addition, the developed method enabled the preparation of Pd-CHA zeolites with a wide loading range of Pd cations. Here, we investigated the relationship between the local structures of Pd²⁺ cations and their NO adsorption/desorption properties using a combination of theoretical and experimental approaches. First, the stabilities of the Pd²⁺ cations at different paired Al sites in 6MR/8MR and their NO adsorption energies were assessed by density functional theory (DFT) calculations. It was found that the stability of the Pd²⁺ cations strongly depends on the type of paired Al sites and that less stable Pd²⁺ cations result in increased NO adsorption strength. The NO desorption temperatures and molecular orbitals of the Pd²⁺ cations were also theoretically studied. Additionally, we experimentally investigated the NO adsorption/desorption properties of Pd-CHA with different loadings by *in-situ*

infrared (IR) and NO-TPD measurements. The increase in the Pd loading increased not only the NO adsorption capacity but also the NO desorption temperature and the adsorption energy. The dependency of the desorption temperature on the Pd loadings can be ascribed to the increase in the proportion of less stable Pd^{2+} cations. Moreover, CHA zeolites with different Al distributions and similar Si/Al ratios were prepared and subsequently applied to investigate the effect of the type of Al sites on the NO adsorption properties.

4.2. Experimental

4.2.1 Sample preparation

Pd-modified CHA zeolites were prepared through the impregnation method. In the case of Pd: 5.4 wt%, 1.0 g of CHA zeolite (Tosoh, NH_4^+ -type, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 13.7$) was suspended in an aqueous solution containing 1.14 g of $\text{Pd}(\text{NH}_3)_2(\text{NO}_3)_2$ HNO_3 solution (50 g/L, Kojima Chemicals Co., Ind.). The water was evaporated from the mixture and dried in an oven. The sample (40 mg) was pelletized into a self-supporting disk, set in a flow-type quartz cell equipped with a gas flow system, and then calcined at 600 °C under 10% O_2/He flow for 30 min to afford $\text{Pd}_{\text{imp}}/\text{CHA}$ (Pd: 5.4 wt%). The atomic dispersion experiment was conducted using the above sample. $\text{Pd}_{\text{imp}}/\text{CHA}$ was treated by 0.5% H_2/He flow (100 mL/min) at 500 °C for 30 min and then exposed to 4% NO/He flow (10 mL/min) at 600 °C for 30 min ($\text{Pd}_{\text{imp}}/\text{CHA}(\text{H}_2_ \text{NO})$).

The physical mixture of Pd black and CHA zeolites (Pd+CHA) was obtained from 0.058 g of Pd black (Nakalai Tesque, Ltd., ca 10 m^2/g determined by N_2 adsorption experiment (Bellcat)) and the 1.0 g of the CHA zeolite as mentioned above by mixing in an agate mortar. The self-supporting disk of Pd+CHA was prepared and used for atomic dispersion under 4% NO/He flow for 2 h ($\text{Pd+CHA}(\text{NO})$). Before atomic dispersion, the sample was

pretreated with 0.5% H₂/He at 300 °C to reduce the surface of Pd black.

For investigation of other zeolite framework types, the following NH₄⁺-type or H⁺-type zeolites were used; MFI (Tosoh, NH₄⁺-type, SiO₂/Al₂O₃ = 22.3) and MOR (Tosoh, H⁺-type, SiO₂/Al₂O₃ = 20.0) were directly used. NH₄⁺-type FER and Y zeolites were prepared by aqueous phase ion exchange with NH₄NO₃ with K⁺-type FER (Tosoh, SiO₂/Al₂O₃ = 18.0) and Na⁺-type Y (Catalysts & Chemicals Ind. Co., Ltd., SiO₂/Al₂O₃ = 5.3). BEA (Tosoh, organic template included, SiO₂/Al₂O₃ = 17.5) was calcined at 600°C in the air to obtain the corresponding H⁺-type BEA.

4.2.2 Characterization

Powder X-ray diffraction (XRD) patterns were recorded on Rigaku Miniflex using Cu K α radiation. FTIR spectra for CO, NO, and NH₃ adsorption experiments were recorded on a JASCO FT/IR-4600 spectrometer (triglycine sulfate (TGS) detector). After atomic dispersion under 4% NO/He flow in the cell, the remaining gas was purged with He flow and then the sample was treated under 10% O₂/He to remove the adsorbed NO. For the CO experiment, the above sample was further treated with 0.5% H₂/He at 300 °C followed by He purge. After that, the background spectrum was obtained at room temperature and the flow was changed to 0.1% CO/He followed by He purge. During the CO adsorption experiment, the spectra were continuously recorded. For the NO adsorption experiment, the above O₂-treated sample was used. After taking the background spectrum under He flow at 100 °C, the continuous FTIR measurement was started, and then 0.1% NO/He flow was introduced. The absorption coefficient value for NO adsorbed on Pd cations was determined by NO adsorption at 350 °C for

Pd_{imp}/CHA(H₂_NO) under 0.1% NO/He flow with monitoring the NO gas by a JASCO FT/IR-4600 spectrometer equipped with TGS detector and a home-made gas cell. At 350 °C, NO adsorbed Pd cations but NO⁺ was scarcely detected. The same NO adsorption experiment was repeated three times. Based on the amount of adsorbed NO, the peak area value for the NO-adsorbed Pd cations, and the amount of sample, the average absorption coefficient value was determined as 354.4 mmol⁻¹·g⁻¹. For NH₃ adsorption, the sample (20 mg) was diluted with SiO₂ (20 mg) and then palettized to make a disk. After atomic dispersion followed by He treatment at 600 °C, the temperature was decreased to 50 °C and then a background spectrum was obtained. With monitoring by FTIR measurement, 1% NH₃/He flow was introduced to the sample and then the gas phase NH₃ was purged with He. Pd K-edge XAS data were collected in quick mode and recorded in transmission mode at the BL14B2 stations attached to the Si(111) monochromator at SPring-8 (JASRI), Japan (Proposal No. 2019B1686). For *in situ* XAS measurement, a flow-type cell connected to a gas-mixing system was utilized. The XANES and EXAFS were conducted using the Athena software package⁷⁶ and REX2000 (Ver 2.5). SEM and STEM images for Pd_{imp}/CHA and Pd_{imp}/CHA(H₂_NO) were obtained using HITACHI HD-2000 (Hitachi, Ltd.) while SEM images for Pd+CHA and Pd+CHA(NO) were taken using JSM-7400F (JEOL Co., Ltd.). *In-situ* DRIFTS measurements were acquired on a JASCO FT/IR-4600 spectrometer (with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector and a diffuse reflectance cell (JASCO DR-600Ai)). The outlet line was connected to a home-made gas cell and the generated gas was monitored by another JASCO FT/IR-4600 spectrometer (TGS detector). 27 mg of Pd+CHA (Pd: 5.4 wt%) was set in the cell and pretreated by 5% H₂/He flow. The background spectrum was taken after

15 min of a He purges at 600 °C. The continuous collecting of spectra was started at the same time as the start of 4% NO/He dosing. Reflectance was converted to pseudo-absorbance using the Kubelka-Munk function.

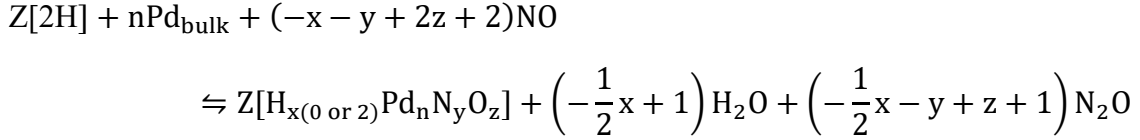
4.2.3 DFT calculation

DFT calculations were performed by means of the periodic boundary condition under the Kohn–Sham formulation^{77,78} with the Vienna ab-initio simulation package (VASP)^{79,80}. The generalized gradient approximated Perdew-Burke-Ernzerhof (GGA-PBE) functional⁸¹ was applied as an electron exchange correlation. The projected augmented waves (PAW) method was utilized for the Kohn-Sham equations^{82,83}. All atoms were allowed to fully relax during all calculations. Cut-off energy of the plane basis set was set to 500 eV. The Γ point was used for Brillouin zone sampling. The semi-empirical Grimme's D3 method implemented in VASP was used to take van der Waals (vdW) dispersion corrections into account^{84,85}. The lattice constants of the unit cell were fixed as given in the International Zeolite Association (IZA) database ($a = b = 13.675$ Å, $c = 14.767$ Å, $\alpha = \beta = 90.0^\circ$ and $\gamma = 120^\circ$) during the calculations⁸⁶.

The conjugate gradient method was used to optimize intermediate structures during the climbing-image nudge elastic band (CI-NEB) calculations as implemented in VTST-Tools.⁸⁷ For CI-NEB calculations, the spring constant between adjacent images was set to $5.0 \text{ eV}/\text{\AA}^2$; moreover, the calculations were considered converged when the maximum forces on all atoms were less than $0.05 \text{ eV } \text{\AA}^{-1}$.

Ab initio thermodynamic analysis was performed to consider the effect of partial pressure of NO, H₂O, and N₂O as well as temperature on Pd species in CHA zeolites. Enthalpies

and entropies at each temperature and the standard state pressure (0.1 MPa) were obtained from NIST thermodynamic table to utilize this analysis.⁸⁸ The following equilibrium reaction was considered for figuring the phase diagrams;



where the reaction energy is denoted as

$$\Delta E = E_{Z[H_xPd_nN_yO_z]} + \left(-\frac{1}{2}x + 1\right)E_{H_2O} + \left(-\frac{1}{2}x - y + z + 1\right)E_{N_2O} - E_{Z[2H]} \\ - nE_{Pd_{\text{bulk}}} - (-x - y + 2z + 2)E_{NO}$$

In this way, the 2Al site in the CHA zeolite is denoted as Z . $E_{Z[H_{x(0 \text{ or } 2)}Pd_nN_yO_z]}$ represents the total energy of considered CHA zeolite models containing Pd species. $E_{Pd_{\text{bulk}}}$ is that of bulk Pd, divided by the number of Pd atoms in the cell. $E_{2H/CHA}$, E_{NO} , E_{H_2O} , and E_{N_2O} represent the total energies of a unit cell of CHA zeolite containing two protons, gaseous nitrogen-monoxide, water, and nitrous oxide, respectively. The Gibbs free energy (ΔG) is described as

$$\Delta G(T, p) = [\Delta E + \left(-\frac{1}{2}x + 1\right)\Delta\mu_{H_2O} + \left(-\frac{1}{2}x - y + z + 1\right)\Delta\mu_{N_2O} \\ - (-x - y + 2z + 2)\Delta\mu_{NO}]$$

The change of the chemical potentials of H_2O and N_2O as a function of T is defined as

$$\Delta\mu_{H_2O}(T) = [\Delta\mu_{0 \text{ } H_2O}(T) + RT \ln \left(\frac{p_{H_2O}}{p_0}\right)] \\ \Delta\mu_{N_2O}(T) = [\Delta\mu_{0 \text{ } N_2O}(T) + RT \ln \left(\frac{p_{N_2O}}{p_0}\right)]$$

The pressures of H_2O and N_2O (p_{H_2O} and p_{N_2O}) are fixed as 0.001 kPa and the standard one (p_0) is fixed as 100 kPa at every temperature. The change of the chemical potential

of NO as a function of T and pressure of NO (p_{NO}) is defined as

$$\Delta\mu_{\text{NO}}(T, p) = [\Delta\mu_{0 \text{ NO}}(T) + RT \ln\left(\frac{p_{\text{NO}}}{p_0}\right)]$$

The PdO vacancy formation energy (E_{PdOvac}), where the vacancy was generated by the removal of PdO monomer from Pd(111) surface with O adatom, is defined as

$$E_{\text{PdOvac}} = (E_{\text{removed}} - E_{\text{Pdsurface}} + E_{\text{PdObulk}})/2$$

where E_{removed} , $E_{\text{Pdsurface}}$, and E_{PdObulk} are the total energy of the (111) slab model with two Pd vacancies (one vacancy on each surface), the total energy of the slab model with two O adatoms (one O adatom on each surface), and the energy of the bulk PdO (two Pd and O atoms are included in the unit cell), respectively. All optimized structures used for the calculation of E_{PdOvac} are provided in the form of CONTCAR files.

Similarly, E_{PdOvac} calculated for Pd₃₈ cluster was defined as

$$E_{\text{PdOvac}} = (E_{\text{Pd37cluster}} - E_{\text{Pd38cluster}} + \frac{1}{2}E_{\text{PdObulk}})$$

where $E_{\text{Pd37cluster}}$ and $E_{\text{Pd38cluster}}$ are the total energy of Pd₃₇ cluster (a model after the vacancy was generated from Pd₃₈ cluster) and the total energy of Pd₃₈ cluster with one O adatom, respectively. Both cluster models are calculated within a large cubic cell ($a = b = c = 40 \text{ \AA}$). The optimized structures are provided in the form of CONTCAR files.

XANES spectra were simulated by using the FDMNES software^{89,90} for the DFT-optimized structures of Pd bulk, PdO bulk, and Pd-CHA. The used structures were provided in the form of CONTCAR files. The simulated spectra were normalized based on the number of Pd atoms in each system.

4.3. Result and discussion

4.3.1 Atomic dispersion of bulk Pd in Pd-modified CHA prepared by impregnation methods

The XRD pattern of Pd_{imp}/CHA (Pd: 5.4 wt%) exhibited typical diffraction patterns of CHA zeolite with a peak derived from PdO (101) at $2\theta = 33.7^\circ$ (Figure 1a). The FTIR spectrum from the CO adsorption experiment showed peaks resulting from stretching vibrations of C=O ($\nu(\text{C=O})$) from CO-coordinated Pd cations, such as Pd²⁺(CO)₂, Pd²⁺(CO), and Pd⁺(CO), around 2220–2100 cm⁻¹ (Figure 1b).⁹¹ Note that the group of Szanyi has recently revealed that the main two peaks around 2200 cm⁻¹, which had been assigned as Pd³⁺(CO)₂,^{22,92} are derived from highly positive Pd²⁺(CO)₂ ions by experimental and theoretical approaches.^{91,93} XRD and FTIR spectroscopy from the CO adsorption experiment indicated that both bulk PdO and atomic Pd cations exist after impregnation and calcination. The coexistence of bulk PdO and atomic Pd cations is further supported by SEM and STEM results, as well as energy-dispersed X-ray (EDX) spectroscopy (Figure 2a–c).

To investigate the atomic dispersion of bulk Pd on the outside of CHA zeolite under oxidative conditions, Pd_{imp}/CHA was pretreated with 0.5% H₂/He at 500°C for 30 min and, then, exposed to 4% NO/He flow at 600°C for 30 min (Pd_{imp}/CHA(H₂_NO)). In the XRD pattern of Pd_{imp}/CHA(H₂_NO), the peak intensity derived from PdO (101) considerably decreased, while the diffraction pattern of CHA zeolite was retained (Figure 1a, the enlarged view (Figure S1) is shown in the SI). The FTIR spectrum collected from the CO adsorption experiment showed that absorptions derived from CO coordinated to Pd cations increased and peaks derived from CO adsorbed on the metallic Pd surface were

scarce (Figure 1b). STEM and EDX spectroscopy (Figure 2d–f) showed the absence of aggregated Pd species. Together, these results suggest that the outside of bulk Pd was atomically dispersed into CHA zeolite by H₂ and NO treatment.

FTIR spectroscopy of the NO adsorption experiment was further conducted. One NO molecule is known to adsorb on one Pdⁿ⁺ cation in zeolites, which exhibits a strong $\nu(\text{N-O})$ absorption band around 1800–1900 cm⁻¹. We estimated the amount of NO adsorbed based on peak areas with the absorption coefficient value (see SI), and, then, calculated the molar ratio of adsorbed NO and total Pd in the samples (hereinafter denoted as NO/Pd, the theoretical maximum is 100%) as an index of Pd dispersion. Before NO adsorption, the background spectrum was obtained after the 10% O₂/He treatment at 600°C, followed by the He purge at 100°C. The adsorption experiment was conducted under 0.1% NO/He flow at 100°C, while continuously recording IR spectra. The IR spectra for Pd_{imp}/CHA and Pd_{imp}/CHA(H₂_NO) (Figure 1c) showed strong peaks at 1861 cm⁻¹, arising from $\nu(\text{N-O})$ of Pd²⁺(NO), with shoulder peaks around 1810 cm⁻¹, assignable to Pd⁺(NO).⁵³ Note that the assignment of NO was well supported by the DFT studies in the previous paper.⁹¹ The absorbance for Pd_{imp}/CHA(H₂_NO) was much higher than for Pd_{imp}/CHA; NO/Pd increased from 32.6% to 76.1% following H₂ and NO treatment. The NO adsorption experiment showed that mainly Pd²⁺ cations formed. When Pd_{imp}/CHA was directly treated with NO without H₂ reduction (Pd_{imp}/CHA(NO)), NO/Pd was calculated to be 49.1%, which was lower compared to Pd_{imp}/CHA(H₂_NO). The metallic state is essential for efficient atomic dispersion of outside bulk Pd species into small-pore CHA zeolites.

To investigate the atomic dispersion of bulk Pd on the outside of CHA zeolite under oxidative conditions, Pd_{imp}/CHA was pretreated with 0.5% H₂/He at 500°C for 30 min and, then, exposed to 4% NO/He flow at 600°C for 30 min (Pd_{imp}/CHA(H₂_NO)). In the XRD pattern of Pd_{imp}/CHA(H₂_NO), the peak intensity derived from PdO (101) considerably decreased, while the diffraction pattern of CHA zeolite was retained (Figure 1a, the enlarged view (Figure S1) is shown in the SI). The FTIR spectrum collected from the CO adsorption experiment showed that absorptions derived from CO coordinated to Pd cations increased and peaks derived from CO adsorbed on the metallic Pd surface were scarce (Figure 1b). STEM and EDX spectroscopy (Figure 2d–f) showed the absence of aggregated Pd species. Together, these results suggest that the outside of bulk Pd was atomically dispersed into CHA zeolite by H₂ and NO treatment. FTIR spectroscopy of the NO adsorption experiment was further conducted. One NO molecule is known to adsorb on one Pdⁿ⁺ cation in zeolites, which exhibits a strong $\nu(\text{N}-\text{O})$ absorption band around 1800–1900 cm⁻¹. We estimated the amount of NO adsorbed based on peak areas with the absorption coefficient value (see SI), and, then, calculated the molar ratio of adsorbed NO and total Pd in the samples (hereinafter denoted as NO/Pd, the theoretical maximum is 100%) as an index of Pd dispersion. Before NO adsorption, the background spectrum was obtained after the 10% O₂/He treatment at 600°C, followed by the He purge at 100°C. The adsorption experiment was conducted under 0.1% NO/He flow at 100°C, while continuously recording IR spectra. The IR spectra for Pd_{imp}/CHA and Pd_{imp}/CHA(H₂_NO) (Figure 1c) showed strong peaks at 1861 cm⁻¹, arising from $\nu(\text{N}-\text{O})$ of Pd²⁺(NO), with shoulder peaks around 1810 cm⁻¹, assignable to Pd⁺(NO).⁵³ Note that the assignment of NO was well supported by the DFT studies in the previous paper.⁹¹ The

absorbance for $\text{Pd}_{\text{imp}}/\text{CHA}(\text{H}_2\text{--NO})$ was much higher than for $\text{Pd}_{\text{imp}}/\text{CHA}$; NO/Pd increased from 32.6% to 76.1% following H_2 and NO treatment. The NO adsorption experiment showed that mainly Pd^{2+} cations formed. When $\text{Pd}_{\text{imp}}/\text{CHA}$ was directly treated with NO without H_2 reduction ($\text{Pd}_{\text{imp}}/\text{CHA}(\text{NO})$), NO/Pd was calculated to be 49.1%, which was lower compared to $\text{Pd}_{\text{imp}}/\text{CHA}(\text{H}_2\text{--NO})$. The metallic state is essential for efficient atomic dispersion of outside bulk Pd species into small-pore CHA zeolites. The effect of loading amounts (1, 5.4, 6.8 wt%) on Pd dispersion was also investigated (The FTIR spectra are shown in Figure S2 in the SI). NO/Pd values were nearly the same for 1 and 5.4 wt% (78.7% and 76.1%), while the increase in loading amount to 6.8 wt% resulted in a decrease of the NO/Pd value to 63.3%. Based on the loading amount (5.4 wt%) and NO/Pd value, the contribution of Pd^{2+} cations was calculated to be 4.1 wt%. Considering that one Pd^{2+} cation is anchored by paired Al sites, the required amount of Al sites to stabilize 4.1 wt% of Pd^{2+} cations is theoretically estimated to be 0.76 mmol/g, which is lower than 50% of the total Al content of CHA ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 13.7$) (2.1 mmol/g). Therefore, we can consider that all the Pd cations exist on Al sites.

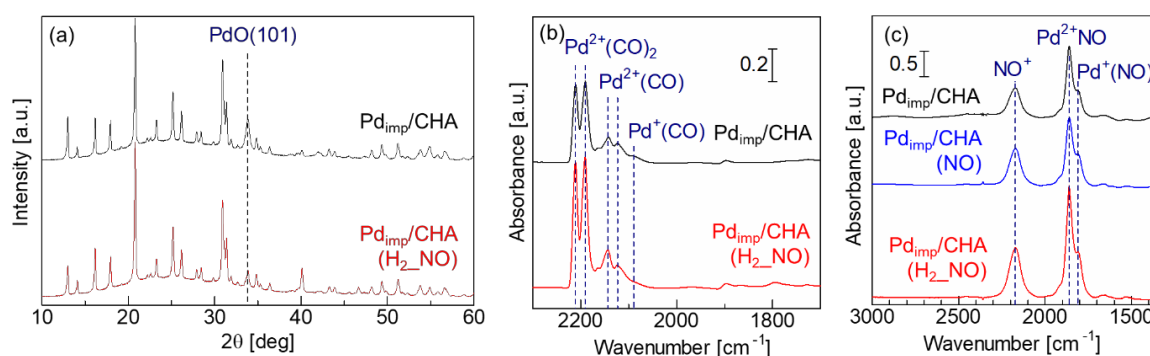


Figure 1. (a) XRD patterns and FTIR spectroscopy of (b) CO and (c) NO adsorption experiments for a series of $\text{Pd}_{\text{imp}}/\text{CHA}$. The CO adsorption experiment was conducted at

room temperature under 0.1% CO/He flow, followed by a He purges, while the NO adsorption experiment was investigated at 100°C under 0.1% NO/He flow. Before adsorption experiments, the sample was treated with 10% O₂/He to remove NO adsorbed during atomic dispersion. Detailed procedures are described in the SI.

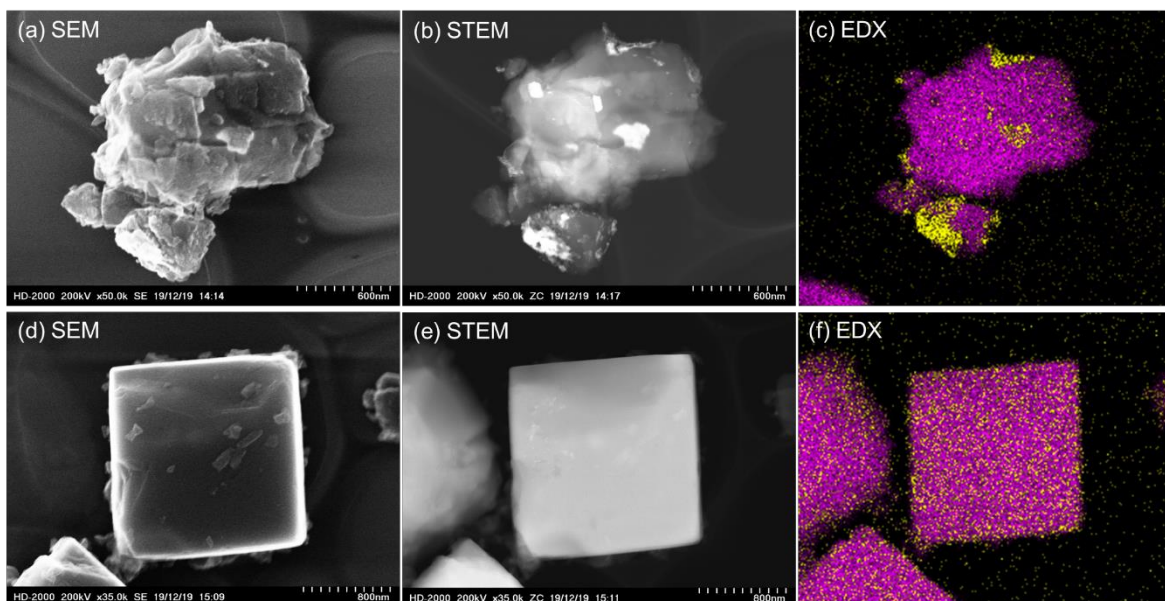


Figure 2. SEM (a and d), high-angle annular dark field STEM images (b and e), and elemental mapping of Pd (yellow) and Si (purple), obtained by EDX spectroscopy (c and f), for Pd_{imp}/CHA (a–c) and Pd_{imp}/CHA(H₂_NO) (d–f).

To support the formation of Pd cations in CHA zeolites, an *ex situ* XAS measurement was carried out. The normalized XAS spectrum of Pd_{imp}/CHA(H₂_NO) after O₂ treatment exhibited an absorption edge similar to that of PdO, rather than Pd black (Figure 3a). In the FT of the extended X-ray absorption fine structure (EXAFS) spectra of Pd_{imp}/CHA and O₂-treated Pd_{imp}/CHA(H₂_NO), the peak derived from the Pd–(O)–Pd shell drastically decreased in intensity by H₂ and NO treatment (Figure 3b). The coordination

number of the Pd–O shell for O₂-treated Pd_{imp}/CHA(H₂_NO) was estimated at 3.5 (Table S2). These results are consistent with the formation of Pd cations.

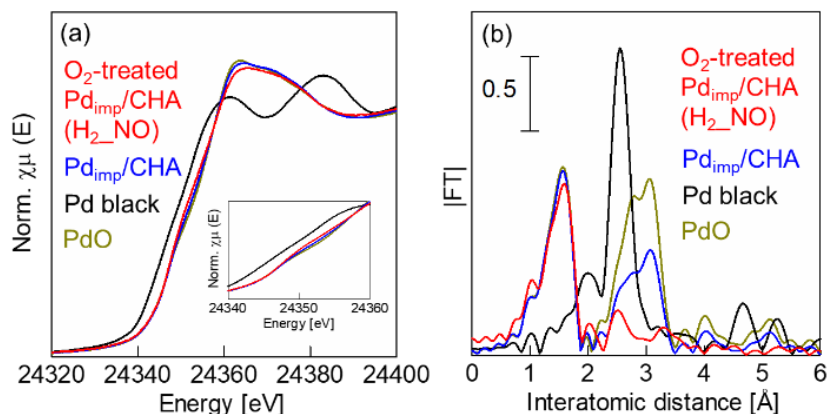


Figure 3. (a) *Ex situ* XANES and (b) FT of EXAFS spectra of Pd_{imp}/CHA, O₂-treated Pd_{imp}/CHA(H₂_NO), and reference samples (Pd Black and PdO) obtained under ambient conditions (air at room temperature).

Furthermore, FTIR spectroscopy of NH₃ adsorption was conducted to investigate the coordination of Pd cations for the O₂-treated Pd_{imp}/CHA(H₂_NO) with different Pd loading amounts (1, 3, and 5.4 wt%). The spectrum of H-CHA after NH₃ adsorption exhibited a strong absorption band arising from NH₃ on protons at zeolite Al sites (Figure 4a).⁹⁴ The peak area of this band monotonically decreased with increasing loading amounts from 1 to 5.4 wt% (Figure 4a and 4b), indicating Pd²⁺ cations were immobilized at Al sites in CHA zeolites. To support this consideration, SiO₂-supported Pd (Pd_{imp}/SiO₂, 5.4 wt%) was prepared and, then, treated with 0.5% H₂/He flow, followed by 4% NO/He treatment, similarly. However, the NO adsorbed on atomic Pd cations was hardly detected,

and NO/Pd was about 1% (Figure S3), showing that anchoring sites are necessary for atomic dispersion.

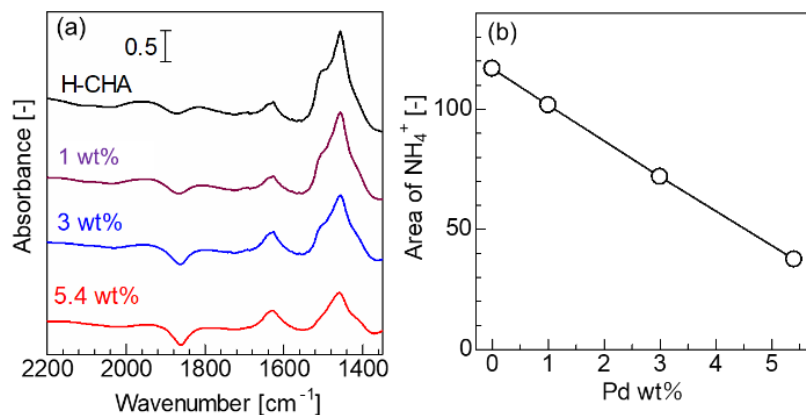


Figure 4. (a) FTIR spectra of NH_3 adsorption for H-CHA and O_2 -treated $\text{Pd}_{\text{imp}}/\text{CHA}(\text{H}_2\text{NO})$ with different Pd loading amounts (1, 3, and 5.4 wt%). The adsorption experiment was conducted at 50°C under 1% NH_3/He flow, followed by a He purge. Before the adsorption experiments, the sample was treated by He flow at 600°C . The detailed procedures are described in the SI. (b) Relationship between the peak area of the absorption band, derived from NH_4^+ and Pd loading amount.

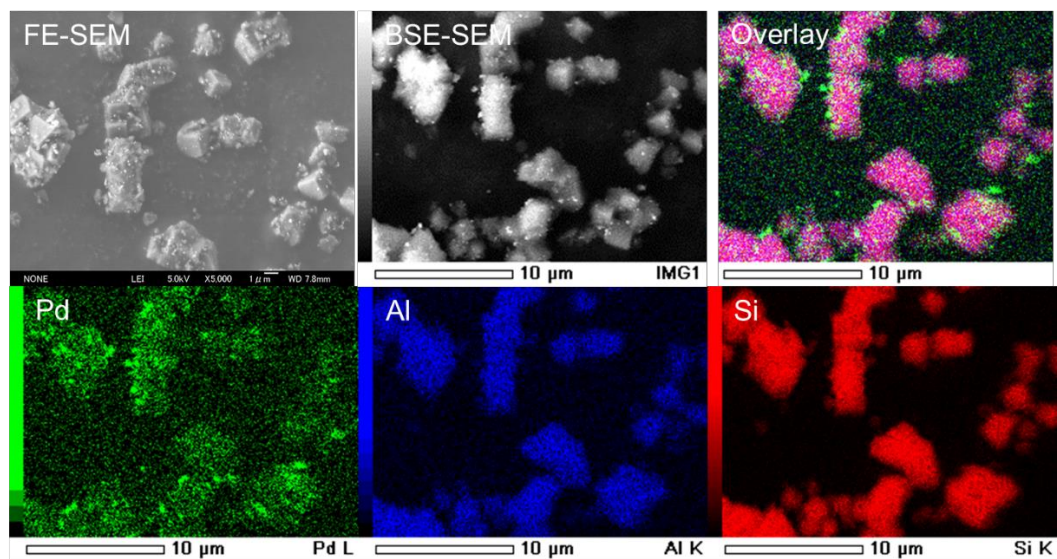
4.3.2 Preparation of Pd-exchanged CHA from Pd black and CHA zeolites

Encouraged by the above results, we envisioned that NO-induced atomic dispersion of outside bulk Pd can be utilized for a physical mixture of Pd black and CHA zeolites (Pd+CHA, Pd: 5.4 wt%). This solid-state reaction would be another preparation method for Pd-exchanged CHA zeolites with high Pd cation loading amounts. Sub-microsized bulk Pd and microsized cubic zeolites were observed by field-emission- and backscattered-electron SEM (FE- and BSE-SEM) and EDX mapping (Figure 5a).

Pd+CHA was pretreated under 0.5% H₂/He flow at 300°C, followed by treatment with 4% NO/He flow at 600°C for 2 h (Pd+CHA(NO)). SEM micrographs with EDX mapping of Pd+CHA(NO) revealed that highly dispersed Pd species were immobilized in CHA zeolites, whereas sub-microsized Pd species were hardly observed (Figure 5b). In the XRD spectra, the diffraction peak derived from Pd(111), around $2\theta = \text{ca. } 40^\circ$, disappeared after NO treatment, while the diffraction pattern of CHA zeolite was maintained (Figure 6a).

Atomic dispersion of Pd black was evaluated by FTIR spectroscopy of CO and NO adsorption experiments for Pd+CHA and Pd+CHA(NO). The FTIR spectrum from the CO adsorption experiment revealed the formation of atomic Pd cations by NO treatment. The spectrum of NO adsorption showed that the NO/Pd value significantly increased from 9.9% to 76.3%. The results in the CO and NO adsorption experiments for Pd+CHA(NO) and Pd_{imp}/CHA(H₂_NO) are almost the same. As control experiments, O₂ and CO were used instead of NO for the treatment of Pd+CHA (Pd+CHA(O₂) and Pd+CHA(CO)), and then, their Pd dispersions were evaluated by NO adsorption experiments. The resulting NO/Pd values were 21.4% and 15.4%, respectively. NO treatment was most effective for atomic dispersion of bulk Pd.

(a) Pd+CHA



(b) Pd+CHA(NO)

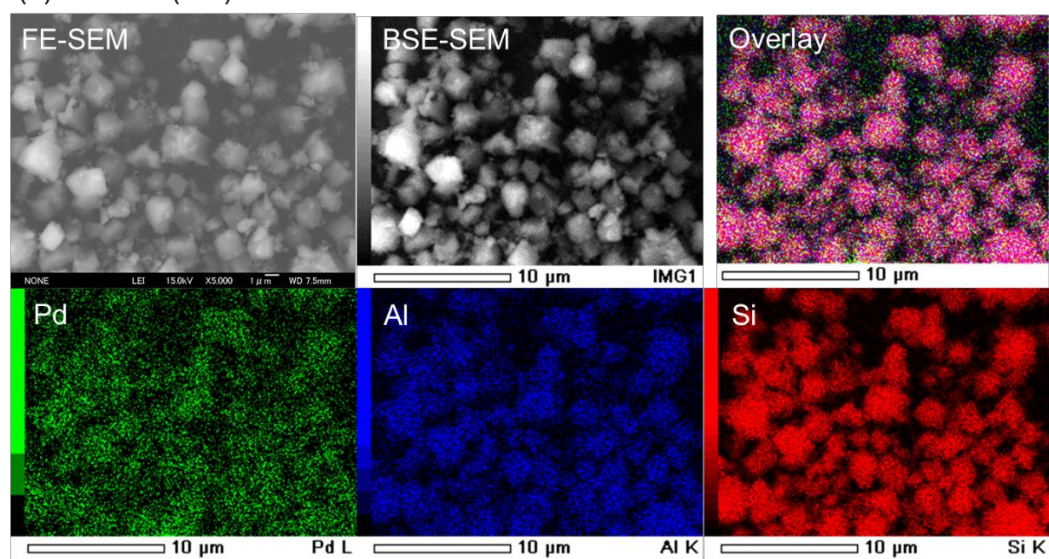


Figure 5. SEM images and elemental mapping of (a) Pd+CHA obtained by physical mixing of commercially available Pd black and CHA zeolites, and (b) Pd+CHA(NO) obtained by H₂ pretreatment and NO treatment of Pd+CHA.

The recent study on the preparation of Pd-loaded CHA zeolites via a modified ion-exchange method reported by Szanyi has achieved a complete atomic dispersion (NO/Pd = 100%) for 1–1.9 wt% of total Pd loading whereas the increase of Pd loading amount resulted in the decrease of atomic dispersion (NO/Pd = 90% and 70% for 3 wt% and 5 wt% of Pd loading, respectively).⁵³ In our case using NO-facilitated atomic dispersion of Pd black, a comparable NO/Pd (76.1%) was obtained for 5.4 wt% of Pd loading although complete atomic dispersion was not achieved for lower Pd loading amount (NO/Pd = 86.2% and 89.5% for 1 wt% and 3 wt% of Pd loading, respectively. See below). The literature comparison of the loading amount of Pd²⁺ cations is summarized in Table S1 in the SI.

Atomic dispersion of Pd black was evaluated by FTIR spectroscopy of CO and NO adsorption experiments for Pd+CHA and Pd+CHA(NO). The FTIR spectrum from the CO adsorption experiment revealed the formation of atomic Pd cations by NO treatment. The spectrum of NO adsorption showed that the NO/Pd value significantly increased from 9.9% to 76.3%. The results in the CO and NO adsorption experiments for Pd+CHA(NO) and Pd_{imp}/CHA(H₂_NO) are almost the same. As control experiments, O₂ and CO were used instead of NO for the treatment of Pd+CHA (Pd+CHA(O₂) and Pd+CHA(CO)), and then, their Pd dispersions were evaluated by NO adsorption experiments. The resulting NO/Pd values were 21.4% and 15.4%, respectively. NO treatment was most effective for atomic dispersion of bulk Pd (Table 1).

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resulted in the decrease of atomic dispersion ($\text{NO}/\text{Pd} = 90\%$ and 70% for $3 \text{ wt}\%$ and $5 \text{ wt}\%$ of Pd loading, respectively).⁵³ In our case using NO-facilitated atomic dispersion of Pd black, a comparable NO/Pd (76.1%) was obtained for $5.4 \text{ wt}\%$ of Pd loading although complete atomic dispersion was not achieved for lower Pd loading amount ($\text{NO}/\text{Pd} = 86.2\%$ and 89.5% for $1 \text{ wt}\%$ and $3 \text{ wt}\%$ of Pd loading, respectively. See below). The literature comparison of the loading amount of Pd^{2+} cations is summarized in Table S1 in the SI.

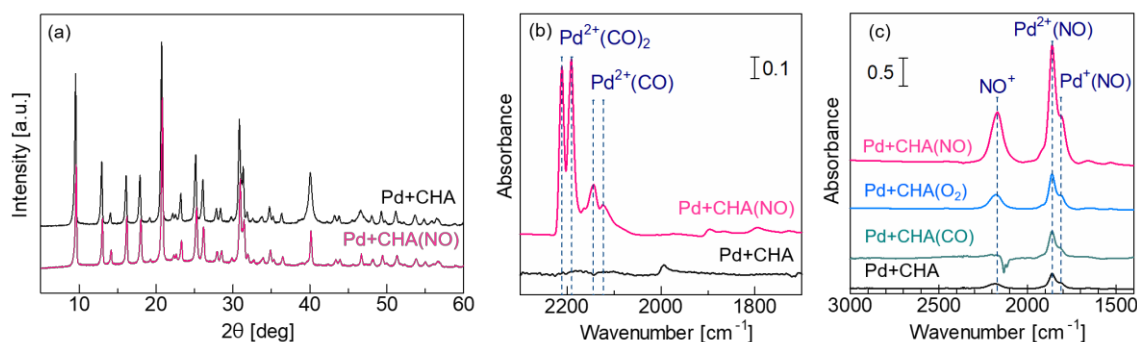


Figure 6. (a) XRD patterns and FTIR spectroscopy of (b) CO adsorption at room temperature and (c) NO adsorption at 100°C for a series of Pd+CHA. Detailed procedures are described in the SI.

Table 1 Comparison of NO/Pd values determined by NO adsorption experiments at 100°C for a series of Pd-modified CHA or SiO₂ under different treatments.^a

Sample	Treatment	NO/Pd	Pd cation ^d
		[%]	[wt%]
Pd _{imp} /CHA ^b	None	32.6	1.76
	H ₂ followed by NO (30 min)	76.1	4.11
	NO (30 min)	49.1	2.65
Pd+CHA ^b	None	9.9	0.53
	NO (2 h)	76.3	4.12
	O ₂ (2 h)	21.4	1.16
	CO (2 h)	15.4	0.83
Pd _{imp} /SiO ₂ ^c	None	1.7	0.09
	H ₂ followed by NO (30 min)	1.5	0.08

^aThe details of NO adsorption experiments and adsorption coefficient are described in the SI. ^bTotal Pd loading amount: 5.4 wt%. ^cTotal Pd loading amount: 5.0 wt%. ^dEstimated from the reported total Pd loading amount and NO/Pd value.

4.3.3 Atomic dispersion of bulk Pd into other zeolites with different framework types

The dispersion of Pd nanoparticles (NPs) in zeolites under oxidative reaction conditions has been studied by several research groups.^{21,22,73} Primet and coworkers first demonstrated the dispersion of small Pd NPs in zeolites to afford Pd²⁺ cations.²¹ They prepared Pd²⁺-exchanged Y zeolites by aqueous phase ion exchange method followed by the reduction treatment by H₂, affording the 2 nm Pd(0) NPs occluded in the zeolites. Subsequently, the oxidative redispersion of Pd NPs in the zeolite cages was conducted by NO at room temperature. Bell and Okumura independently reported the redispersion of small Pd NPs in MFI zeolites obtained by the H₂ reduction of Pd²⁺-exchanged MFI zeolites in similar manners.^{22,73} The redispersion of aggregated Pd by NO treatment has also been extensively utilized in the industry for catalyst regeneration.³⁸ However, the oxidative dispersion of bulk Pd, such as commercially available Pd black, was not investigated in the aforementioned studies. To investigate the effect of zeolite framework types and the difference between small Pd NPs and bulk Pd in atomic dispersion, the reaction of a physical mixture of Pd black (Pd: 1 wt%) and several zeolites, such as FER, MFI, MOR, BEA, and Y, with NO and then NO/Pd values were compared by NO adsorption experiment (Table 2). Note that Al contents in zeolites (0.9–3.2 mmol/g) are much higher than that required to stabilize 1 wt% of Pd²⁺ cations (ca. 0.19 mmol/g) in all cases (The details are described in the SI). For FER, MFI, and MOR zeolites, high NO/Pd values were achieved (73.0–93.7%), while a moderate NO/Pd value was obtained in the case of BEA (48.9%). The use of Y zeolites resulted in an extremely low NO/Pd value (5.1%). These results showed that the present method utilizing atomic dispersion of bulk Pd was applicable to other zeolites tested (CHA, FER, MFI, MOR, and BEA) except for

Y zeolites. In all the cases, the XRD patterns obtained after the NO treatment showed that the diffraction peak derived from Pd(111) decreased in intensity (Figure S4), indicating that the reaction of bulk Pd with NO occurred for all the zeolites. Taking into account the report on redispersion of small Pd NPs by NO in Y zeolites at room temperature,²¹ Y zeolites are unlikely to stabilize atomic Pd cations in high reaction temperatures.

Table 2 NO/Pd values determined by NO adsorption experiments at 100°C for the reaction of physical mixture of Pd black and other zeolites with different framework types under NO at 600°C.^a

Zeolites	SAR ^b	Total loading [wt%]	Pd NO/Pd [%]	Pd cation ^c [wt%]
CHA	13.7	5.4	76.3	4.12
CHA	13.7	3.0	89.5	2.69
CHA	13.7	1.0	86.2	0.86
FER	18.0	1.0	93.4	0.93
MFI	22.3	1.0	93.7	0.94
MOR	20.0	1.0	73.0	0.73
BEA	17.5	1.0	48.9	0.49
Y	5.5	1.0	5.1	0.05

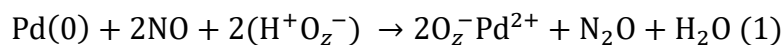
^aThe details of NO adsorption experiments and adsorption coefficient are described in the SI.

^bSiO₂/Al₂O₃ ratio. ^cEstimated from the reported total Pd loading amount and NO/Pd value.

To investigate the effect of zeolite framework types and the difference between small Pd NPs and bulk Pd in atomic dispersion, the reaction of a physical mixture of Pd black (Pd: 1 wt%) and several zeolites, such as FER, MFI, MOR, BEA, and Y, with NO and then NO/Pd values were compared by NO adsorption experiment (Table 2). Note that Al contents in zeolites (0.9–3.2 mmol/g) are much higher than that required to stabilize 1 wt% of Pd²⁺ cations (ca. 0.19 mmol/g) in all cases (The details are described in the SI). For FER, MFI, and MOR zeolites, high NO/Pd values were achieved (73.0–93.7%), while a moderate NO/Pd value was obtained in the case of BEA (48.9%). The use of Y zeolites resulted in an extremely low NO/Pd value (5.1%). These results showed that the present method utilizing atomic dispersion of bulk Pd was applicable to other zeolites tested (CHA, FER, MFI, MOR, and BEA) except for Y zeolites. In all the cases, the XRD patterns obtained after the NO treatment showed that the diffraction peak derived from Pd(111) decreased in intensity (Figure S4), indicating that the reaction of bulk Pd with NO occurred for all the zeolites. Taking into account the report on redispersion of small Pd NPs by NO in Y zeolites at room temperature,²¹ Y zeolites are unlikely to stabilize atomic Pd cations in high reaction temperatures.

4.3.4 Spectroscopic and theoretical elucidation of plausible reaction in atomic dispersion of bulk Pd into CHA zeolites described results for Pd_{imp}/CHA, Pd+CHA, and Pd_{imp}/SiO₂ and those after different treatments (Table 1) 20, 60, 120, and 145 min are shown in Figure 7a. Before the measurement, Pd+CHA was treated with 0.5% H₂/He, followed by purging under He flow. The spectrum after pretreatment showed a peak unique to Pd(0) metal around 24388 eV with an absorption edge (E_0) at 24344.7 eV. When NO/He was

introduced, the peak around 24388 eV decreased, with the concomitant appearance of a new peak derived from Pd²⁺ species around 24365 eV, while the absorption edge shifted toward higher energy. After 120 min of treatment with NO, the peak around 24388 eV disappeared, and the absorption edge remained unchanged ($E_0 = 24349.0$ eV). The XANES spectrum at 120 min resembled O₂-treated Pd_{imp}/CHA(H₂_NO) under He flow at 100°C, implying the formation of Pd²⁺ cations primarily. These changes are shown more clearly in the Δ XANES spectra (Figure 7b). The peak derived from Pd(0) species steeply decreased in intensity with the appearance of the peak assignable to Pd²⁺ species in the initial stage ($t = 0$ –20 min) and, then, continuously decreased until $t = 120$ min. From these results, Pd black was atomically dispersed by oxidation of Pd(0) species toward Pd²⁺. *In situ* DRIFTS measurements were also conducted by monitoring the produced gas. The background spectrum was taken after the pretreatment of Pd+CHA with H₂/He, followed by a He purge. After that, the gas was changed to 4% NO/He, while recording the spectra continuously. A negative band was observed around 3600 cm⁻¹ upon exposure to NO, and its absorbance became more negative with extended treatment times (Figure 8a). This phenomenon can be ascribed to the consumption of protons on Al sites (H⁺ O_z⁻) of CHA zeolites, owing to a cation-exchange reaction with Pd²⁺ cations. Further, NO adsorbed on *in situ* generated Pd²⁺ cations was detected. The gas product analysis revealed that N₂O was generated as a main gas product (Figure 8b). Plots of N₂O concentration and IR area for H⁺ O_z⁻ versus time (Figure 8c) showed that N₂O formation and consumption of H⁺ O_z⁻ occurred simultaneously. Combined with *in situ* XAS results, the atomic dispersion of bulk Pd can be described by the following equation (eq.1).



A similar equation was proposed by Perimet and co-workers²¹. The amount of generated N_2O was estimated to be $328 \mu\text{mol/g}$, which was ca. 65% of the total molar amount of Pd ($508 \mu\text{mol/g}$), supporting that the above equation (eq.1) is the most plausible reaction of atomic dispersion. However, HNO_3 was detected instead of H_2O . The generated H_2O may react with NO_2 derived from a decomposition reaction of NO under high temperature,⁹⁵ yielding HNO_3 .

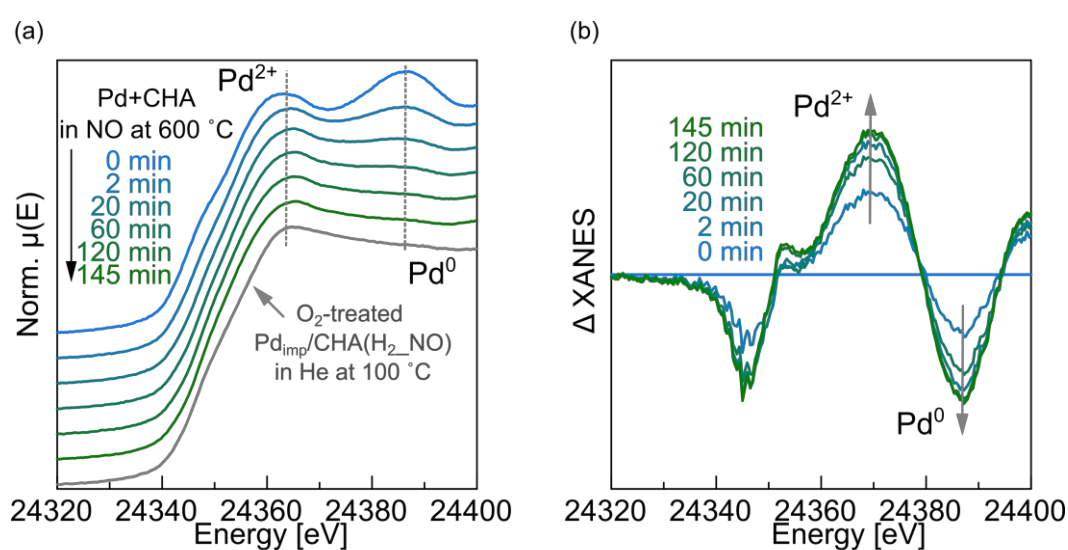


Figure 7. (a) *In situ* XANES spectra during the reaction of Pd+CHA under 4% NO/He flow at 600°C and O₂-treated Pd_{imp}/CHA(H₂_NO) under He flow at 100°C. (b) The corresponding ΔXANES spectra. The data were obtained by subtraction with the spectrum taken at 0 min.

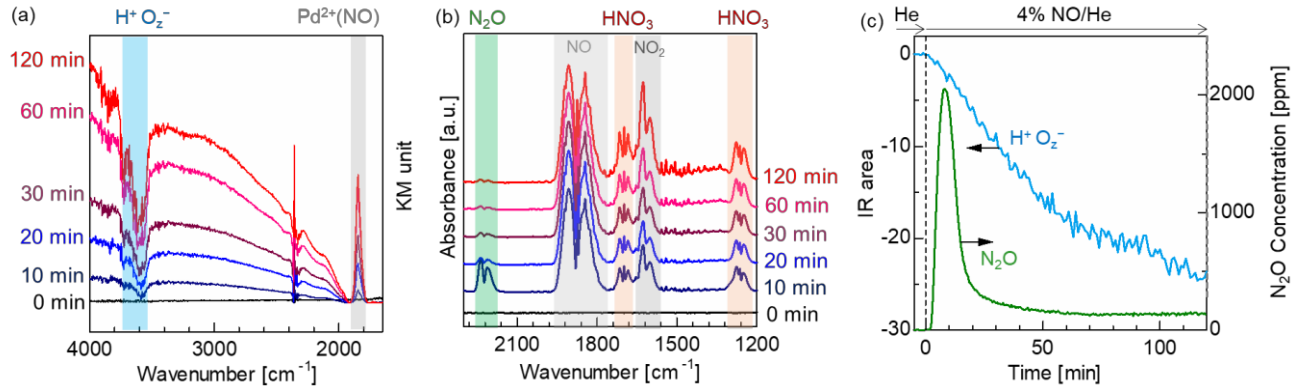
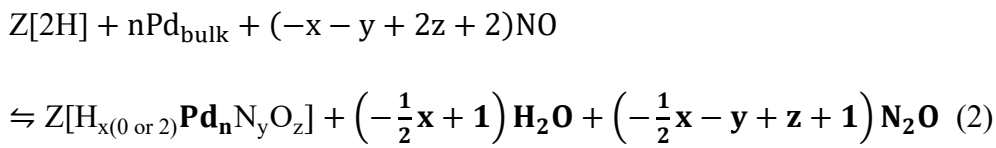


Figure 8. (a) *In situ* DRIFTS spectra during the reaction of Pd+CHA under 4% NO/He flow at 600°C. (b) Spectra for NO_x gases monitored by IR with a gas cell. (c) Plots of N₂O concentration and IR area for H⁺O_z⁻.

Furthermore, the atomic dispersion of bulk Pd in CHA zeolites was theoretically studied. Periodic DFT calculations, combined with *ab initio* thermodynamics analysis, were used to figure out a phase diagram to predict plausible Pd species at relevant partial pressures and temperatures.^{96,97} The following equilibrium reaction was considered (eq. 2):



Paired Al sites possessing two O_z⁻ are denoted as Z. Detailed definitions for relative Gibbs free energies (ΔG) of Z[H_xPd_nN_yO_z], and the chemical potentials of gaseous molecules are described in the SI. The third-nearest-neighbor site in the eight-membered-ring is considered as Z, where the Al–Al distance is moderate (7.18 Å) among paired Al sites in

CHA zeolite.⁹⁸ Proton-type CHA zeolite, in which two protons are possessed at Z for charge compensation, is treated as the reference model. This model is denoted as Z[2H], meaning that Pd species remain as bulk Pd. For divalent cationic species, a Pd²⁺ cation (Z[Pd]), NO-adsorbed Pd²⁺ cation (Z[PdNO]), and cationic Pd tetramer (Z[Pd₄]) are taken into account. A PdO monomer (Z[2H]_PdO), Pd atom (Z[2H]_Pd) and Pd tetramer (Z[2H]_Pd₄) are evaluated as uncoordinated neutral species. Note that Z[Pd₄] and Z[2H]_Pd₄ have been applied as representative models of small Pd clusters in previous papers.^{99,100} The structural information (CONTCAR files) of all the considered structures can be found in the SI. Note that the simulated XANES spectrum for the optimized Z[Pd] structure is similar to the experimental one for Pd_{imp}/CHA(H₂_NO) (Figure S5), confirming that our model is reasonable as Pd²⁺ cations in CHA zeolites.

Figure 9a shows the phase diagram as a function of the partial pressure of NO ($\log(p_{\text{NO}}/p_0)$) and temperature. Z[PdNO] (Figure 9c) is the lowest species in free energy over a wide range of lower temperature conditions ($< 300^\circ\text{C}$). With an increase of temperature at $\log(p_{\text{NO}}/p_0) > -4$, Z[Pd] (Figure 9d) becomes the most stable Pd species, while Z[2H] is predicted as the most stable structure under low NO concentrations in the high-temperature region. Figure 9b shows the calculated ΔG as a function of $\log(p_{\text{NO}}/p_0)$ at 627°C . In the lower concentration region, ΔG values, for all considered Pd species, are higher than for Z[2H]. With increasing NO concentration, ΔG for Z[PdNO], Z[Pd], Z[2H]_PdO, and Z[Pd₄] decrease. At $\log(p_{\text{NO}}/p_0) = -1.4$, corresponding to experimental conditions employed in this study (4% NO/He), Z[PdNO] and Z[Pd] are thermodynamically more favorable than Z[2H].

To confirm the requirement of high temperature for atomic dispersion of bulk Pd, the

physical mixture of Pd black (5.4 wt%) with CHA zeolites was treated by NO at a different temperature from 30–600°C. The results are summarized in Figure S6 and Table S3 in the SI. The atomic dispersion scarcely occurred at room temperature even by extending the time to 48 h ($\text{NO/Pd} < 1\%$) and 600°C was required to obtain high NO/Pd values (76.1 %). Furthermore, the reason for the necessity of high temperatures was theoretically studied. Several previous studies on atomic dispersion of Pd NPs under oxidative conditions proposed that the formation of mononuclear Pd species, including PdO,²¹ Pd(OH)₂,²⁶ and Pd-nitrosyl complexes,¹⁰¹ play key roles in the dispersion. In our experiments for the atomic dispersion of Pd black into CHA zeolites, the use of O₂ instead of NO-induced the formation of bulk PdO, as indicated by XRD (Figure S7), and resulted in the significant decrease of Pd²⁺ cations (Table 1) while any mobile Pd-nitrosyl complex was not detected during the dispersion process using NO, unfortunately (confirmed by FTIR). Therefore, the formation of mononuclear PdO from partially oxidized Pd surfaces was considered a simple calculation model to discuss the difference between bulk Pd and Pd NPs in NO-induced atomic dispersion. A Pd(111) surface slab and a Pd₃₈ cluster¹⁰² with surface atomic O species were applied as representative models for Pd bulk surface and Pd NPs, respectively, and the formation energy of PdO vacancy (E_{PdOvac}) was compared (the used models and detailed definition can be found in the SI). The E_{PdOvac} for the Pd(111) surface is highly endothermic (168.7 kJ/mol) while that for the Pd₃₈ cluster is relatively small (4.3 kJ/mol) (Figure S8a). Furthermore, the diffusion of generated PdO species in CHA zeolite pores was also investigated by transition state calculation, resulting in the small diffusion barrier through the eight-membered ring (28.3 kJ/mol, Figure S8b).¹⁰³ Considering the previous studies on the reaction of metallic Pd with

NO ,^{104,105} a plausible mechanism can be proposed as follows. A surface Pd atom is oxidized by the atomic O species generated by the dissociation of a NO molecule on Pd metal surface.¹⁰⁴ A N_2O molecule is concomitantly generated from the remaining N and another NO.¹⁰⁵ Subsequently, a mononuclear PdO is formed from the oxidized Pd surface. This step is highly endothermic and thus requires high temperature. The generated PdO species can easily diffuse and access paired Al sites in CHA zeolites, and finally, isolated Pd^{2+} cations are placed at ion-exchange sites with the concomitant formation of H_2O . The paired Al sites in CHA zeolites can serve as anchoring sites of Pd^{2+} cations even under high reaction temperatures, enabling NO-facilitated atomic dispersion of bulk Pd.

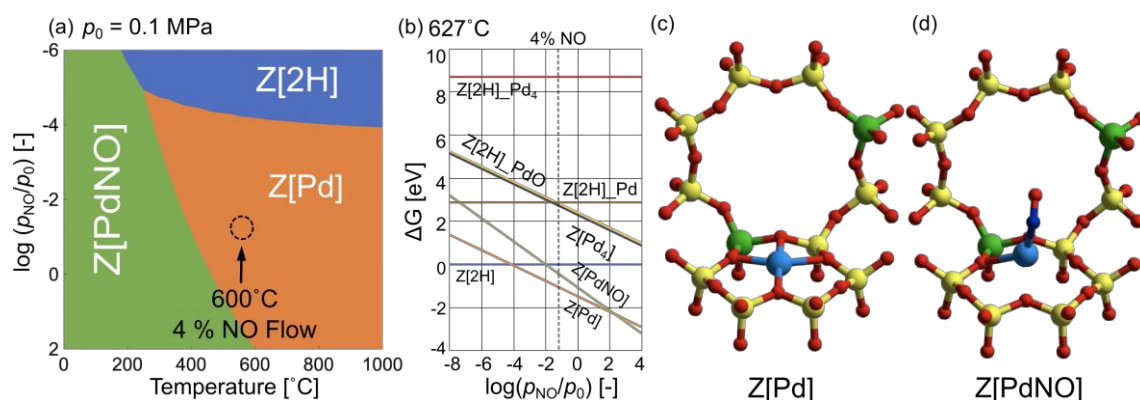


Figure 9 (a) Relative Gibbs free energy (ΔG) of the Pd species on paired Al sites (denoted as Z) in CHA zeolite, and a phase diagram showing the lowest-energy species as a function of NO partial pressure ($\log(p_{\text{NO}}/p_0)$) and temperature. (b) ΔG of Pd species on Z in CHA zeolite as a function of $\log(p_{\text{NO}}/p_0)$ at 627°C. The optimized structures

4.3.5. Formation of Pd^{2+} cations at different paired Al sites in CHA zeolite

A CHA zeolite is composed of a rhombohedral unit cell with two cage sizes, forming four-, six-, and eight-membered rings (4MR, 6MR, and 8MR, respectively). Several kinds of two Al sites were considered as the exchange sites for bare divalent cations regardless

of different descriptions, such as paired and close unpaired Al sites.^{66,106–112} For the theoretical investigation in the present study, five paired Al sites: 6MR(3NN), 8MR(2NN), 8MR(3NN), 8MR(4NN), and 5NN, were considered as the model sites for the stabilization of Pd²⁺ cations. These models are also considered as possible two Al sites in the recent theoretical studies.^{66,112,113} Although the valence states of Pd cations on the considered models (especially on 5NN) are still controversial^{66,112,113}, these models were applied to explore the effect of Al–Al distance on the NO adsorption. The model sites can be distinguished by the type of sharing ring and the number of Si centers connecting two Al sites (Figure 10). For example, the paired Al site with a connectivity distance of 3 (Al–O–(Si–O)₂–Al) in 6MR is labeled as 6MR third-nearest-neighbor, i.e., 6MR(3NN). For 5NN, each Al site exists in 6MR and 8MR and is connected by a distance of 5 (Al–O–(Si–O)₄–Al). The Al–Al distances are different in the range of 5.74–9.71 Å among the five paired Al sites.

The stability of the Pd cations at different paired Al sites was theoretically evaluated. Figure 11 shows the optimized structures, and Table 3 summarizes the distance between the Pd²⁺ cation and each Al site (Al1 and Al2 denote the close Al site and the far Al site, respectively). For 6MR(3NN), a Pd²⁺ cation is located at almost the center of 6MR to minimize both the distances of Pd–Al1 and Pd–Al2 for charge compensation.^{66,114} For 8MR(2NN), (3NN), (4NN), and 5NN sites, the Pd²⁺ cations are located at the center of 6MR to maintain suitable distances with Al1 (ca. 2.86 Å), while the distance from Al2 is greater (5.43–8.51 Å). Other examined configurations of Pd²⁺ cations on each paired Al site are provided (Figure S10). The relative formation energies of the Pd cations (ΔE_f) are listed in Table 3. We also calculated ΔE_f for the Pd²⁺ cations at 8MR in 8MR(2NN), 8MR(3NN), 8MR(4NN), and 5NN sites and then compared with the above results (Figure S10). The ΔE_f value of the Pd²⁺ cation at 6MR is lower than one at 8MR in all cases. The ΔE_f value for 6MR(3NN) is the lowest among all the models (2.06 eV), which is consistent with the calculation results reported by Epling and Paolucci.⁶⁶ The ΔE_f value increased in the order of 6MR(3NN) < 8MR(2NN) < 8MR(3NN) < 8MR(4NN) < 5NN. As the Pd–Al2 distance increases (2.92–8.51 Å), ΔE_f increases, which indicates that a long Pd–Al2 distance is unfavorable for the stabilization of the Pd²⁺ cation due to the

difficulty of charge compensation with Al sites.^{66,114}

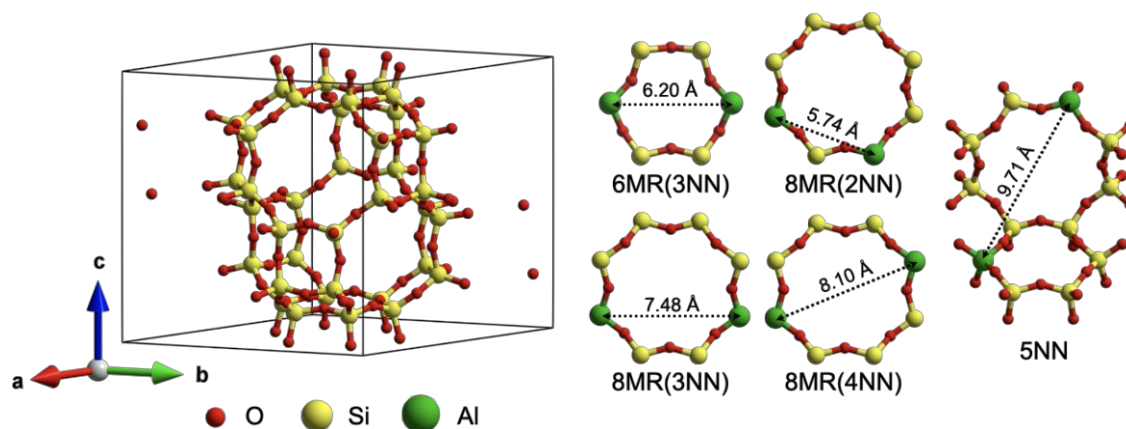


Figure 10 A unit cell of CHA zeolite and the considered paired Al sites in periodic DFT calculations.

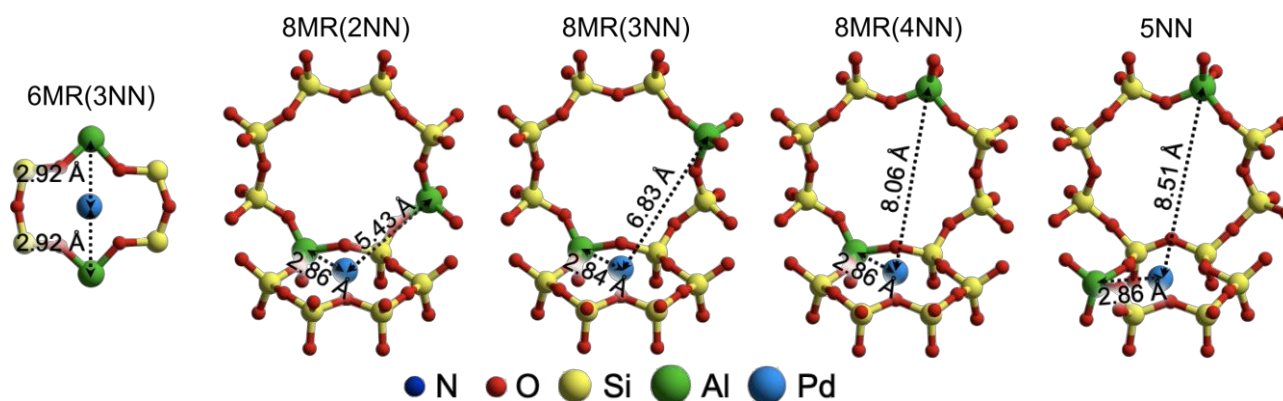


Figure 11 Optimized structures of Pd cations at different paired Al sites in CHA zeolites. Al1 and Al2 denote the close and far Al sites, respectively. Only the atoms around the Pd cation are shown for clarity. The structural information (CONTCAR files) of all the considered structures are provided in ESI.

Table 3 Pd–Al distances and relative formation energy of the Pd cations at different paired Al sites.

Paired Al sites	Pd–Al1 (Å)	Pd–Al2 (Å)	Relative formation energy (ΔE_f) ^a (eV)
6MR(3NN)	2.92	2.92	2.06
8MR(2NN)	2.86	5.43	3.18
8MR(3NN)	2.84	6.83	3.63
8MR(4NN)	2.86	8.06	3.67
5NN	2.86	8.51	3.75

4.3.6 NO adsorption on each Pd²⁺ cation at different paired Al sites

The NO adsorption on Pd²⁺ cations was also theoretically investigated for different paired Al sites. Figure 12 shows the optimized structure of the NO-adsorbed Pd cations. Their adsorption energies (E_{ad}) and geometric parameters (Pd–N bond length and Pd–N–O angle) are listed in Table 5. E_{ad} negatively increases from -1.04 to -1.74 eV in the following order: 6MR(3NN) < 8MR(2NN) < 8MR(3NN) < 8MR(4NN) < 5NN. This order is the same as the order of increase in ΔE_f . As the NO adsorption energy increases negatively, the Pd–N bond length decrease in the range of 1.77–1.92 Å. The adsorption geometry was bent in all the considered structures (Pd–N–O angles: 121.1–158.1°). Similar adsorption structures were reported in a previous study on Pd–MOR, where the NO molecule preferentially adsorbed at a Pd–N–O angle of ca. 130°, due to the electronic interaction of the $d\sigma$ and $d\pi$ orbitals of the Pd²⁺ cation with a singly occupied antibonding π^* molecular orbital (SOMO) of the NO molecule.¹¹⁴

Raybaud *et al.* theoretically investigated the NO adsorption on the Pd²⁺ cations in Pd–MOR, where the adsorption strength of NO depends on the empty Pd electronic levels just about the Fermi energy level, inducing the transfer of electrons from the SOMO of NO to the d states of Pd.¹¹⁴ Inspired by their study, the correlation between the lowest

unoccupied molecular orbital (LUMO) energy level of the Pd cation and the corresponding NO adsorption energy was further investigated in this study. The levels of the LUMO of the Pd cation and the SOMO of the NO molecule were calculated using the Gaussian 16 software. The cluster models used for this analysis were prepared by cutting out from the optimized periodic models (Figure S11). As shown in Figure 13a, the energy level of the LUMO of the Pd cation becomes low as the stability of the Pd²⁺ cation decreases. The NO adsorption energies for all considered models are plotted as a function of the energy difference between the LUMO of the Pd cation and the SOMO of the NO molecule (ΔE_{dif}) to assess their interaction (Figure 13b). A linear correlation was observed between E_{ad} and ΔE_{dif} ($R^2 = 0.9861$), indicating that the strong NO adsorption with few stable Pd cations is derived from the strong interaction between the LUMO of the Pd cation and the SOMO of the NO molecule.¹¹⁵ This consideration was supported by the orbital interaction diagram depicted by CDA¹¹⁶ in which the main component of the SOMO of the NO-adsorbed Pd cation in CHA zeolite is the LUMO of Pd (76%), indicating the transfer of electrons from the SOMO of NO into the empty orbital of the Pd cation (Figure 13c).

The vibration analysis of the adsorbed NO species revealed that the vibration frequencies were red-shifted (1861.0–1869.5 cm⁻¹) in comparison with the gas-phase value (1904 cm⁻¹) in all considered structures, except for the unstable Pd cation at 5NN (1906.1 cm⁻¹). The calculated frequencies are comparable with reported theoretical values^{66,114,117}, as well as experimental values.^{55,66,118} Note that the stretching frequency of the NO molecule on unstable Pd cations was calculated to be too high, possibly due to the exchange splitting of Pd d-states.¹¹⁴ Furthermore, to assess the effects of the experimental conditions, including temperature and partial pressures of gaseous molecules,⁶⁶ a thermodynamic analysis was performed to obtain the phase diagrams predicting the NO desorption temperature for the considered Pd cationic sites (Figure S12). It was demonstrated that the NO desorption temperatures varied depending on the sites, and the difference in the temperature was estimated to be approximately 300 °C between 6MR(3NN) and 5NN. In summary, the type of paired Al site strongly affects the stability of Pd cations, as well as the NO adsorption toward high desorption temperatures, where

strong NO adsorption occurs on a few stable Pd cations. This is attributed to the strong interaction between the LUMO of the Pd cation and the SOMO of the NO molecule.

Table 4 The geometric parameters, adsorption energies for the NO structure, and calculated stretching frequency.

Configuration of paired Al sites	Pd–N (Å)	Pd–N–O (°)	Adsorption energy (E_{ad}) (eV)	Vibrational frequency ^a (cm ⁻¹)
6MR(3NN)	1.92	121.1	–1.04	1861.5
8MR(2NN)	1.90	124.6	–1.36	1869.5
8MR(3NN)	1.87	127.1	–1.54	1861.0
8MR(4NN)	1.79	143.8	–1.68	1864.1
5NN	1.77	158.1	–1.74	1906.1
Gas-phase	–	–	–	1904

^a The calculated frequencies were scaled by a factor of 0.9908. This value was defined from the experimental value (1904.1 cm⁻¹)^{119,120} and the calculated frequency of the gas-phase NO molecule (1921.8 cm⁻¹).

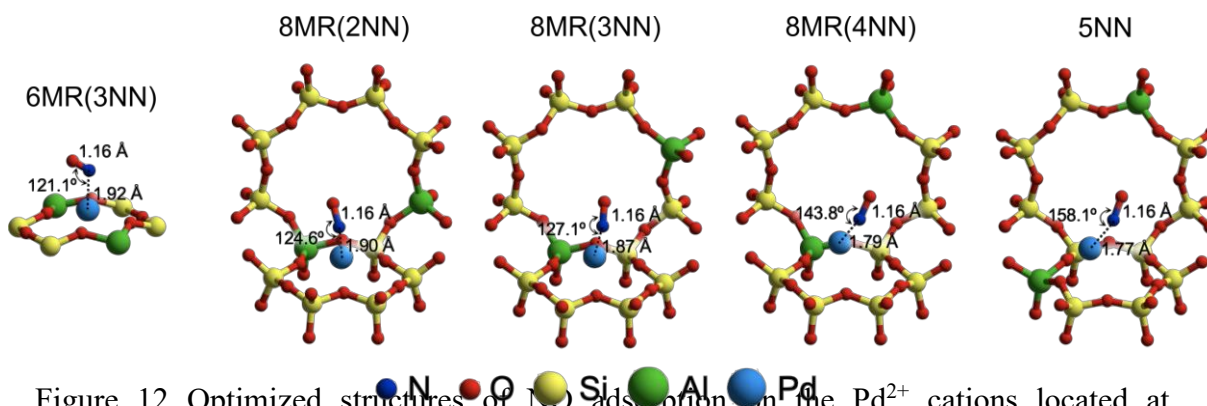


Figure 12 Optimized structures of NO adsorption on the Pd²⁺ cations located at 6MR(3NN), 8MR(2NN), 8MR(3NN), 8MR(4NN), and 5NN sites in CHA zeolite (Only the atoms around the Pd cation are shown for clarity).

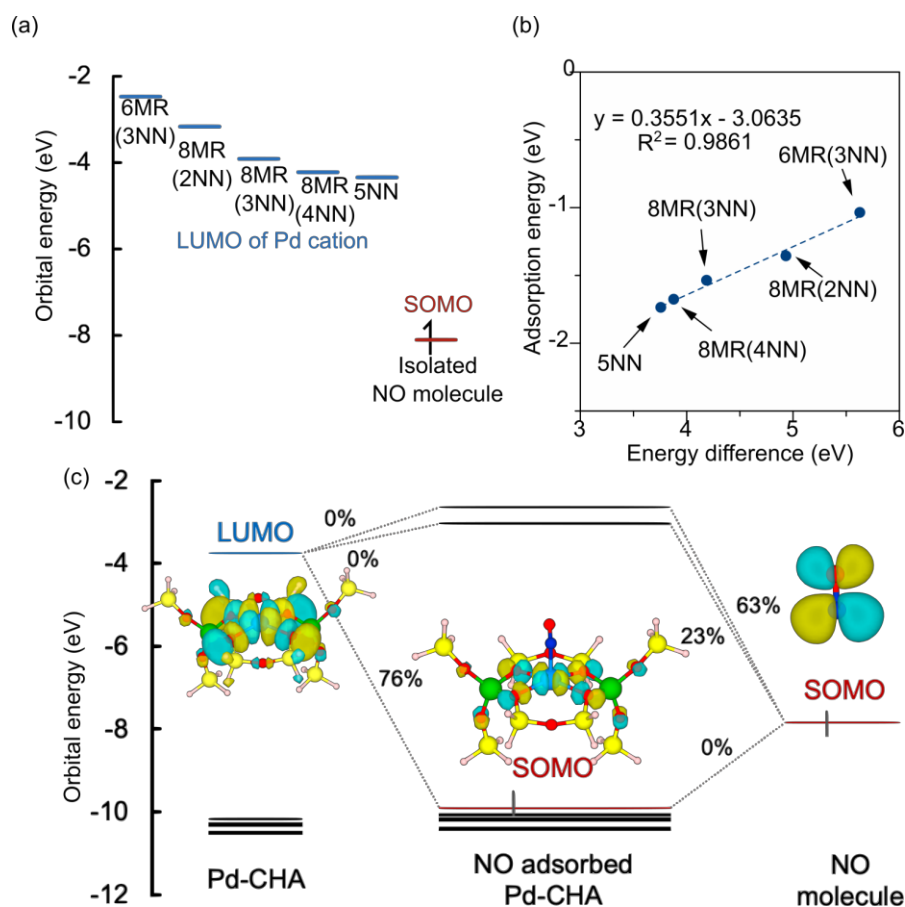


Figure 13 (a) Energy levels of the LUMO of Pd at different paired Al sites and the SOMO of an isolated NO molecule. Blue lines and a red line represent the LUMO of Pd and the SOMO of NO, respectively. (b) The correlation of the NO adsorption energy and the energy difference between the LUMO of Pd and the SOMO of NO. (c) Orbital interaction diagram of α -spin, determined by CDA for the cluster model of the NO-adsorbed Pd cations at 6MR(3NN). (Yellow: Si, Red: O, Green: Al, Blue: N, Cyan: Pd, White: H).

4.3.7 *In-situ* IR measurement for NO adsorption on Pd-CHA with different Pd loadings

To experimentally investigate the relationship between the stability of Pd cations and the NO adsorption properties, a series of Pd-CHAs with different Pd loadings (0.5–5.4 wt%) were prepared through our preparation method, which utilizes a NO-facilitated solid-state ion-exchange reaction.¹²¹ The prepared Pd-CHAs were used for static NO adsorption experiments monitored by *in-situ* IR spectroscopy. The IR spectra were collected after the intensity of the band derived from NO on the Pd²⁺ cation (NO-Pd²⁺) around 1860 cm⁻¹

reached equilibrium under a flow of 0.1% NO. The IR spectra obtained at different temperatures for 0.5 and 5.4 wt% Pd-CHA are shown in Figure 14a and 5b, respectively (the IR spectra for the samples with other loadings are shown in ESI (Figure S13)). The IR peak area of NO-Pd²⁺ over 5.4 wt% Pd-CHA was significantly higher than that over 0.5 wt% Pd-CHA. Based on the absorption coefficient,¹²¹ the amounts of adsorbed NO species over 0.5 and 5.4 wt% Pd-CHAs are determined as 0.04 and 0.41 mmol/g, respectively, corresponding to NO/Pd = 0.86 and 0.77 (NO/Pd denotes the molar ratio of the adsorbed NO to the total Pd amount). This indicates that c.a. 80% of the introduced Pd species are present in a cationic state. In this way, large Pd particles were not observed by XRD and STEM measurements.¹²¹ The IR band was clearly observed even at 400 °C over 5.4 wt% Pd-CHA, while the band was scarcely observed in the same temperature region over 0.5 wt% Pd-CHA. The peak top positions were varied depending on the Pd loading amount and temperature in the range of c.a. 1850–1870 cm⁻¹, which agreed with our theoretical results. Figure 14c shows the normalized areas of the IR band around 1860 cm⁻¹ over Pd-CHA with different Pd loadings (0.5–5.4 wt%) as a function of temperature. The IR band areas were normalized by those obtained at 100 °C. Note that the shoulder peak around 1810 cm⁻¹, which is assignable to NO on the Pd⁺ cation, is included in the calculation of the area.^{61,72} In all cases, the normalized areas decreased with the increase in the adsorption temperature. The areas for the 0.5 and 1 wt% Pd-CHAs drastically decreased in the region from 100 °C to 300 °C and nearly reached zero in the high-temperature region. In contrast, the IR bands were still noticeably observed at 400 °C for 2–5.4 wt% Pd-CHAs. To compare the stability of NO adsorption in the high-temperature region, the normalized areas at 400 °C were plotted as a function of the corresponding Pd/Al ratio in Figure 14d. The normalized area increased with the loading. This dependency implies that the increase in the Pd loading induces the formation of less stable Pd cations, which increases the NO adsorption strength.

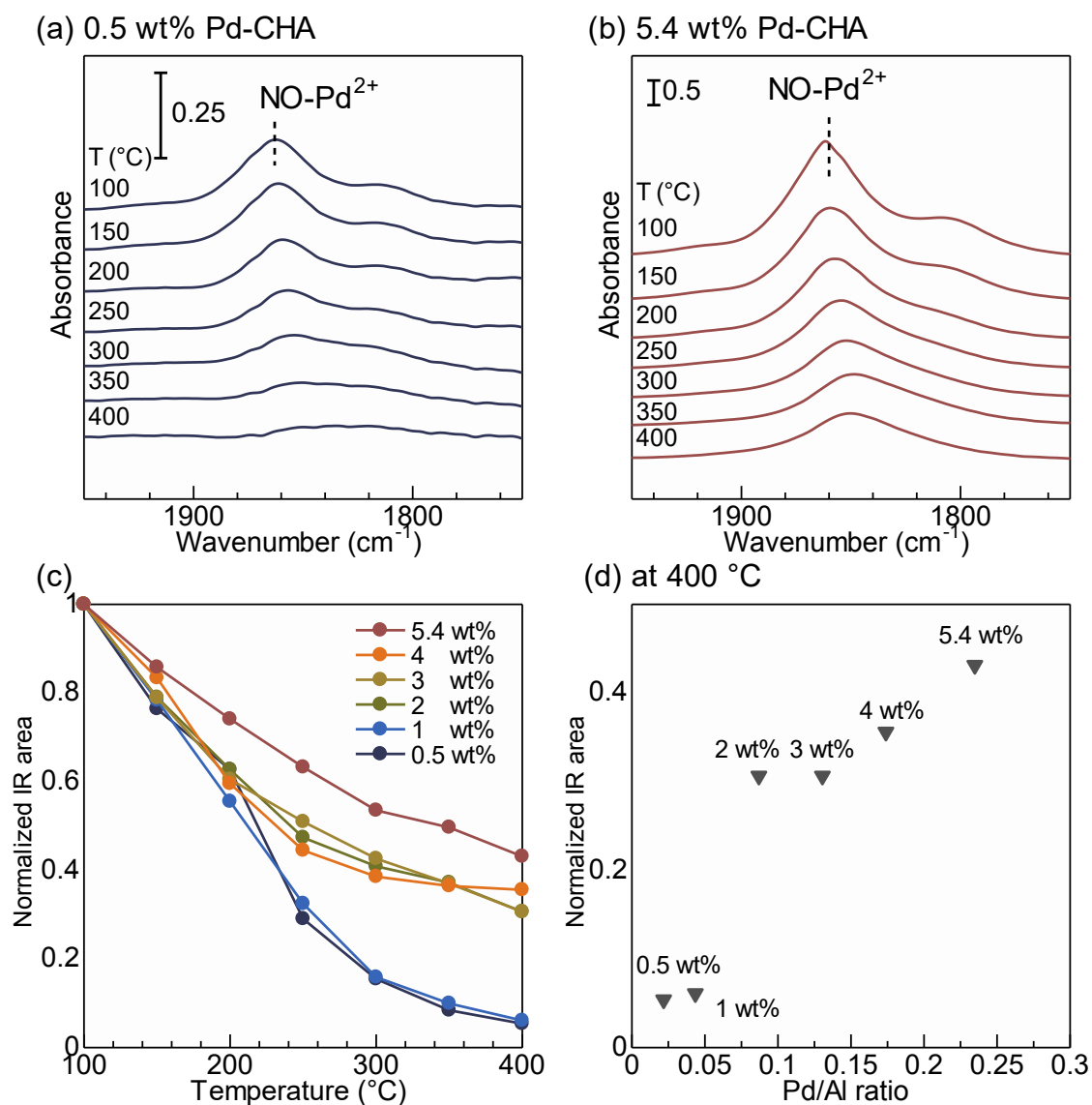


Figure 14 *In-situ* IR spectra of NO-Pd²⁺ species over (a) 0.5 wt% and (b) 5.4 wt% Pd-CHAs under a flow of 0.1% NO (total flow: 100 mL/min). The background spectra were recorded under He flow at each measuring temperature before introducing the NO flow. (c) Temperature dependency of the normalized IR band area around 1860 cm⁻¹ for different Pd loadings (0.5–5.4 wt%). (d) The normalized IR band area around 1860 cm⁻¹ at 400 °C as a function of the Pd/Al ratio.

4.3.8 The dependency of the NO adsorption on the proportion of paired Al sites in 6MR Gounder's group reported that the proportion of paired Al sites in 6MR of CHA zeolite can be tuned by controlling the ratio of inorganic and organic templates during hydrothermal synthesis.¹²² To investigate the effects of the differences in the proportion of paired Al sites, three kinds of CHA zeolites having different proportions of paired Al sites in 6MR (0.7%, 2.2%, and 7.1% in the total Al site) with a similar Si/Al ratio (Si/Al = 12.0–16.5) were synthesized according to the previous papers mentioned above. Thereafter, they were applied to prepare 1 wt% Pd-CHA($\text{Al}_{6\text{MR pair}}/\text{Al}$) ($\text{Al}_{6\text{MR pair}}/\text{Al}$ denotes the relative portion of paired Al sites in 6MR) for NO adsorption. The $\text{Al}_{6\text{MR pair}}/\text{Al}$ values were determined by an aqueous-phase ion-exchange reaction of the corresponding H^+ -CHA with Co^{2+} cations (details are provided in ESI). Note that the actual ion-exchange sites for Co^{2+} cations are still controversial because the experimental conditions possibly affect the amount of exchanged Co^{2+} cations and their sites. Sklenak et al. investigated Co^{2+} ion-exchange into Na^+ - and NH_4^+ -CHA where both paired and close unpaired Al sites accommodate bare and hydrated Co^{2+} ions.^{110,111} The peak areas at 100 °C were similar among three 1 wt% Pd-CHA(0.7), (2.2), and (7.1) (Figure S14), indicating that the Si/Al ratio does not significantly affect the NO adsorption at low temperatures. Despite using the same Pd loadings, the normalized areas in the high-temperature region above 300 °C increased with the decrease in $\text{Al}_{6\text{MR pair}}/\text{Al}$ (Figure 15a). A linear correlation between the normalized IR area at 300 °C and $\text{Al}_{6\text{MR pair}}/\text{Al}$ was observed (Figure 15b). This result indicates that the paired Al sites in 6MR, such as 6MR(3NN), are responsible for the weak NO adsorption, owing to the formation of stable Pd cations; it also supports the occurrence of strong NO adsorption on Pd cations in paired Al sites in 8MR (8MR(2NN), (3NN), and (4NN)) or those between 6MR and 8MR (5NN).

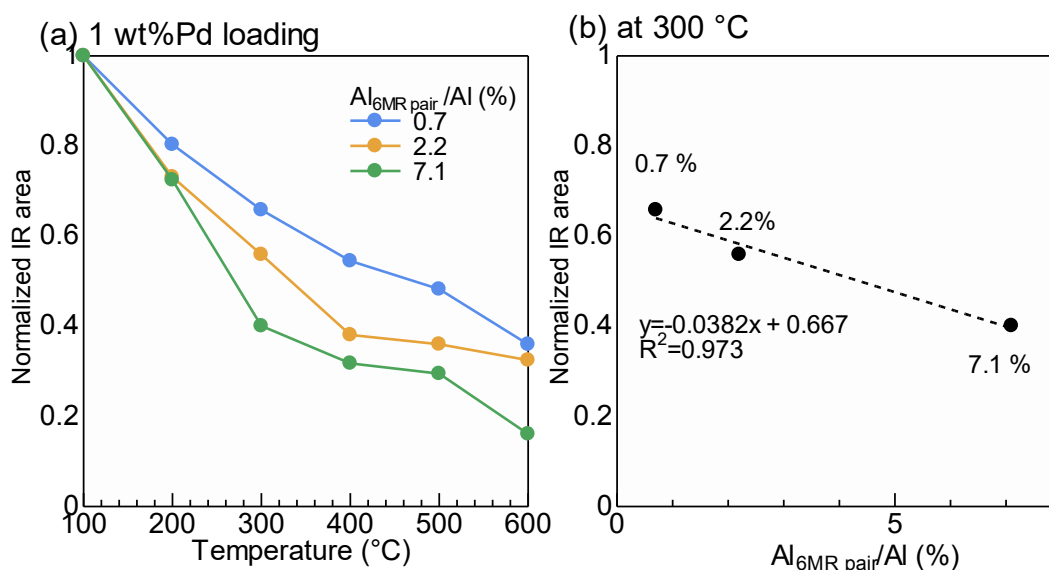


Figure 15 (a) Temperature dependence of the normalized IR band area around 1860 cm⁻¹ over 1 wt% Pd-CHA with different Al_{6MR pair}/Al values (0.7, 2.2, 7.1 %), under a flow of 0.1% NO (total flow: 100 mL/min). (b) The normalized IR band areas around 1860 cm⁻¹ at 300 °C as a function of Al_{6MR pair}/Al.

4.3.9 NO-TPD measurement of Pd-CHA with different Pd loadings

Finally, the NO desorption properties of Pd-CHA with high loadings (2–5.4 wt%) were examined by TPD measurements using a fixed-bed continuous flow system.^{62,68,123} After the solid-state ion-exchange reaction was performed *in-situ* as explained above, the temperature of the reactor was set to 350 °C for NO adsorption. Note that the formation of NO⁺ species at zeolite anions is unlikely to occur at 350 °C.¹²⁴ The obtained TPD profiles are shown in Figure 16. Once the feed was switched to the reactor, a negative peak was observed for all the Pd-CHAs, corresponding to the NO adsorption. The area of the negative peak increased with the Pd loading, confirming that more NO species were captured. During the temperature increase, two positive peaks were observed, attributed to NO desorption. For the 2 wt% Pd-CHA, the main desorption peak was observed around 350–450 °C, while the second peak area, observed at a higher temperature of approximately 450 °C, was relatively small. With an increase in the Pd loading, the second desorption peak shift toward high temperatures, indicating that increasing the Pd loading increases the NO adsorption strength. The amounts of NO adsorption/desorption

determined by the peak areas increase with the increase in Pd loading amount (Table S2). These results are consistent with those obtained by static NO adsorption experiments using *in-situ* IR spectroscopy.

To specify the Pd cations responsible for the NO desorption in the low- and high-temperature regimes, the adsorption energies corresponding to the observed NO desorption peaks were experimentally evaluated using the Redhead equation¹²⁵ (see ESI) and subsequently compared with the theoretically estimated values by DFT calculation (Table 6). The adsorption energies for the low-temperature desorption (E_{low}) were determined to be approximately 1.40 eV, whereas those for the high-temperature desorption (E_{high}) ranged from -1.57 to -1.83 eV. Compared with the theoretical values (Table 6), the low- and high-temperature NO desorption can be ascribed to the Pd cations on 8MR(2NN) ($E_{\text{ad}} = -1.36$ eV) and those on other paired Al sites, i.e., 8MR(3NN), 8MR(4NN), and 5NN ($E_{\text{ad}} = -1.54$ to -1.74 eV), respectively, demonstrating that strong NO adsorption likely occurs on unstable Pd cations.

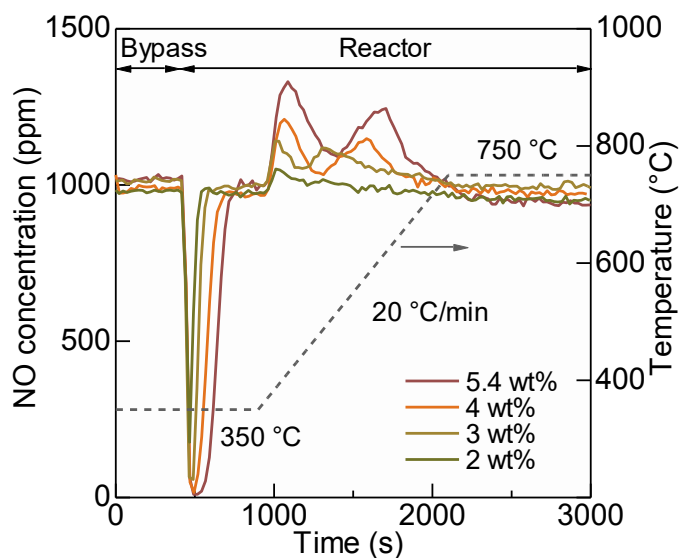


Figure 16 NO adsorption at 350 °C for 600 s, followed by TPD (20 °C/min up to 750 °C) under a flow of 0.1% NO (He balance, total flow: 100 mL/min). The flow passed through a bypass line in the first 400 s.

Table 5 Comparison of the experimental and theoretical NO adsorption energies.

		NO adsorption energy (eV)	
		$E_{\text{low}}^{\text{a}}$	$E_{\text{high}}^{\text{b}}$
Exptl.	2 wt% Pd-CHA	-1.36	-1.57
	3 wt% Pd-CHA	-1.36	-1.57
	4 wt% Pd-CHA	-1.38	-1.76
	5.4 wt% Pd-CHA	-1.40	-1.83
		E_{ad}^{c}	
Theor.	8MR(2NN)	-1.36	
	8MR(3NN)	-1.54	
	8MR(4NN)	-1.68	
	5NN	-1.74	

^a Experimental adsorption energy of NO desorption at low temperatures. ^b Experimental adsorption energy of NO desorption at high temperatures. ^c Theoretical adsorption energy of Pd cations at different paired Al sites.

4.4 Conclusion

We have shown that bulk Pd can be atomically dispersed into small pores of CHA zeolite with 4% NO flow at 600°C. The microscopic (SEM, STEM, EDX) and spectroscopic (XRD, FTIR, XAS) characterizations showed that Pd²⁺ cations on zeolite anionic sites were mainly formed. The amount of Pd²⁺ cations reached 4.1 wt%, which is higher than the highest value reported previously. The solid-state synthesis of Pd-exchanged CHA from commercially available Pd black and CHA zeolites was also demonstrated, where

NO was the most effective among other reactive gases tested, such as O₂ and CO. The present method utilizing atomic dispersion of Pd black was applicable to other zeolites with different framework types. From *in situ* XAS and DRIFTS, combined with online gas monitoring, atomic dispersion occurs through oxidation of Pd metal by NO, yielding Pd cations on Al sites with concomitant formation of N₂O and H₂O (as HNO₃). The phase diagram, determined by *ab initio* thermodynamics analysis, showed that divalent Pd cations on paired Al sites are thermodynamically favored under the experimental conditions (4% NO and 600°C), consistent with the occurrence of atomic dispersion of bulk Pd. The DFT calculations suggest that the generation of mononuclear Pd species from bulk Pd is a highly endothermic reaction and thus requires high reaction temperature. The generated mononuclear Pd species can easily diffuse into small-pore CHA zeolites to afford Pd²⁺ cations on paired Al sites. The paired Al sites in CHA zeolites stabilize atomic Pd cations even under severe reaction conditions, allowing the preparation of Pd²⁺-loaded CHA zeolites from commercially available Pd black and CHA zeolites. This work demonstrates the potential of atomic dispersion for the preparation of metal cation-exchanged small-pore zeolites that cannot be obtained by conventional aqueous-phase cation-exchange methods. It is noteworthy that the present method can be combined with conventional methods. The NO adsorption/desorption properties and hydrothermal stability of Pd-loaded CHA zeolites with high loading of Pd²⁺ cations are now under investigation for PNA applications.

Additionally, we revealed the relationship between the atomic-scale structure of the Pd²⁺ cations in CHA zeolite and the NO adsorption/desorption property by a combined approach of DFT calculations, *in-situ* IR spectroscopy, and NO-TPD measurement. First, the stability of the Pd²⁺ cations and the strength of the NO adsorption over Pd species

located at five different 2Al sites were assessed using DFT calculations, which revealed that less stable Pd^{2+} cations afforded strong NO adsorption. As expected from the theoretical investigation, *in-situ* IR and NO-TPD measurements revealed that the NO desorption temperature increased with the Pd loading amount (up to 5.4 wt%). It was also observed that the amount of NO adsorbed in the high-temperature region increased upon decreasing the proportion of paired Al sites in 6MR in the CHA zeolite support, despite using the same Pd loading, indicating that weak NO adsorption is likely to occur on Pd cations at 6MR(3NN). For strong NO adsorption, the experimental adsorption energies of the NO desorption at low (350–450 °C) and high (> 450 °C) temperatures agree reasonably with the theoretically estimated values of the moderately stable Pd cations at 8MR(2NN) and the relatively unstable ones at 8MR(3NN), 8MR(4NN), and 5NN. This study not only revealed the dependency of the local structure and NO adsorption/desorption properties of Pd cations on the structure of the Al sites in CHA zeolites but also demonstrated the tunability of Pd-CHA functions as PNAs by controlling the Pd loading amount and the distribution of Al sites.

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Table S1. Comparison of loading amount of Pd²⁺ cations between this work and previous reports on Pd-modified zeolites including SSZ-13.

Sample	Total Pd Loading [wt%]	NO/Pd [-]	Pd cations [wt%]	Reference
Pd _{imp} /CHA(H ₂ _NO) (Si/Al = 6.85)	5.4	0.761 ^a	4.1 ^c	This work
Pd+CHA(NO) (Si/Al = 6.85)	5.4	0.763 ^a	4.1 ^c	This work
	3.0	0.895 ^a	2.7 ^c	
	1.0	0.862 ^a	0.86 ^c	
Pd/H-SSZ-13 (Si/Al = 6)	5	0.7 ^b	3.5 ^c	Angew. Chem. Int. Ed. 2018 , <i>57</i> , 16672–16677
	3	0.9 ^b	2.7 ^c	
	1.9	1.0 ^b	1.9 ^c	
Pd/SSZ-13_0.50% (Si/Al = 12.5)	0.5	-	0.007 ^d	J. Phys. Chem. C 2017 , <i>121</i> , 15793–15803

Pd/ZSM-5_0.48%	0.48	-	0.354 ^d	J. Phys. Chem. C
(Si/Al = 15)				2017, 121, 15793–15803
Pd/Beta_0.50%	0.5	-	0.375 ^d	J. Phys. Chem. C
(Si/Al = 12.5)				2017, 121, 15793–15803
Pd/SSZ-13	2.28	0.122 ^b	0.278 ^c	Cat. Today
(Si/Al = 22.4)				2019, 320, 175–180
HTA Pd/SSZ-13	1	0.23 ^b	0.23 ^c	Appl. Catal. A, General
(Si/Al = 22.4)				2019, 569, 28-34
Pd/SSZ-13	1	0.43 ^b	0.43 ^c	Emiss. Control Sci. Technol.
(Si/Al = 12)				2020, 6, 126-138
Pd(2)/SSZ-13(35)	2	0.41 ^b	0.82 ^c	Catal. Sci. Tech.
750C HTA				2019, 9, 163-173
(Si/Al = 17.5))				
(Continued)				
Pd05/BEA	0.5	0.80 ^b	0.4 ^c	Top. Catal.
(Si/Al = 17)				2018, 61, 2021
Pd05/FER	0.5	0.52 ^b	0.26 ^c	Top. Catal.
(Si/Al = 12)				2018, 61, 2021
Pd05/MOR	0.5	0.42 ^b	0.21 ^c	Top. Catal.
(Si/Al = 6)				2018, 61, 2021

Pd(2)/SSZ-13 (Si/Al = 17.5)	2	0.133 ^b	0.266 ^c	Appl. Environmemntal	Catal.	B,
2020, 277, 119190						

^aDetermined by NO adsorption experiment monitored by IR. ^bEstimated from the reported total Pd loading and NO adsorption capacity. ^cEstimated from NO/Pd value.

^dEstimated from the reported total Pd loading amount and the ratio of Na-exchangeable Pd.

Table S2. Curve-fitting analysis of Pd K-edge EXAFS of Pd_{imp}/CHA(H₂_NO_O₂)

Shell	CN ^a	R ^b (Å)	ΔE ^c (eV)	σ ^d (Å)	R ^e (%)
Pd–O	3.48 ± 0.48	1.99 ± 0.01	0.04	0.065	1.11

^aCoordination numbers. ^bBond distance. ^cIncrease of the threshold energy. ^dDebye–Waller factor. ^eResidual factor.

Table S3. Effect of NO treatment temperature on NO/Pd values for Pd+CHA(NO).^a

Temperature [°C]	Time [h]	NO/Pd ^b [%]	Pd cations [wt%]
600	2	76.3	4.1
500	2	53.3	2.9
400	2	21.4	1.2
200	2	11.2	0.6
100	2	2.6	0.1

30 48 <1 n.a.^c

^aTotal Pd loading amount: 5.4 wt%. ^bNO/Pd values were determined by NO adsorption experiments at 100°C after the dispersion process. ^cNot available.

Table S4 Synthesis conditions and characterizations of CHA zeolites with different amount of paired Al sites in 6MR.

Sample	NaOH/SiO ₂	TMAOH/SiO ₂	Si/Al ^a	Loaded Co cation ^a	Al _{6MR} pair/Al ^b
CHA(0.7)	-	0.50	12.0	4.2 μmol/g	0.7%
CHA(2.2)	0.10	0.40	15.4	11.2 μmol/g	2.2%
CHA(7.1)	0.20	0.30	16.5	34.1 μmol/g	7.1%

Synthesis conditions: Si/Al = 20, H₂O/SiO₂ = 44, Temp. 160 °C, Time = 6 days, Rotation speed = 30 rpm. ^a Determined by ICP-AES. ^b Estimated from Si/Al values and amounts of loaded Co cations.

Table S5 The amount of NO adsorption/desorption determined by the NO adsorption and the following TPD measurement (Figure 16).

	NO adsorption (mmol/g)	NO desorption (mmol/g)
2 wt% Pd-CHA	0.034	0.018
3 wt% Pd-CHA	0.069	0.05
4 wt% Pd-CHA	0.111	0.085
5.4 wt% Pd-CHA	0.171	0.13

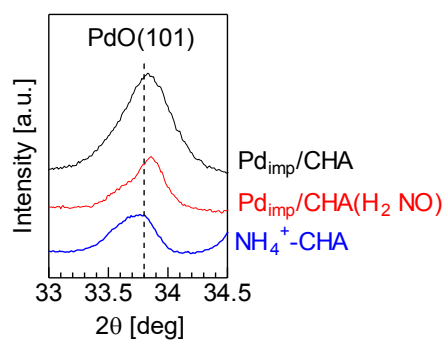


Figure S1. Enlarged view of XRD patterns for Pd_{imp}/CHA, Pd_{imp}/CHA(H₂_NO), and NH₄⁺-CHA.

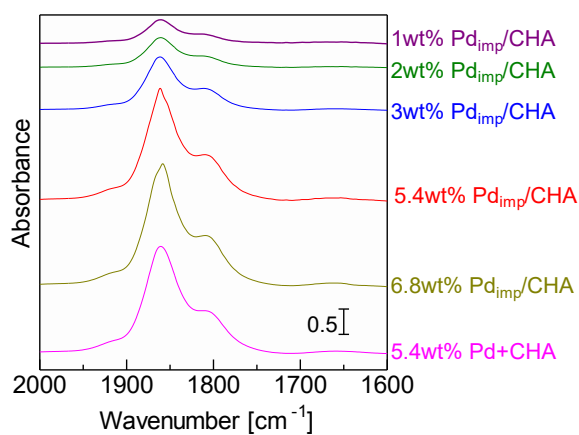


Figure S2. FTIR spectra for NO adsorption on Pd_{imp}/CHA(H₂_NO) with different Pd loading.

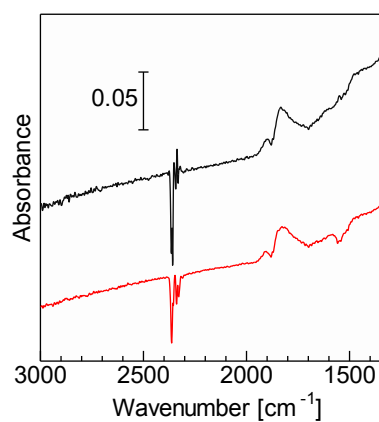


Figure S3. FTIR spectra for NO adsorption of Pd_{imp}/SiO₂ and Pd_{imp}/SiO₂(H₂_NO).

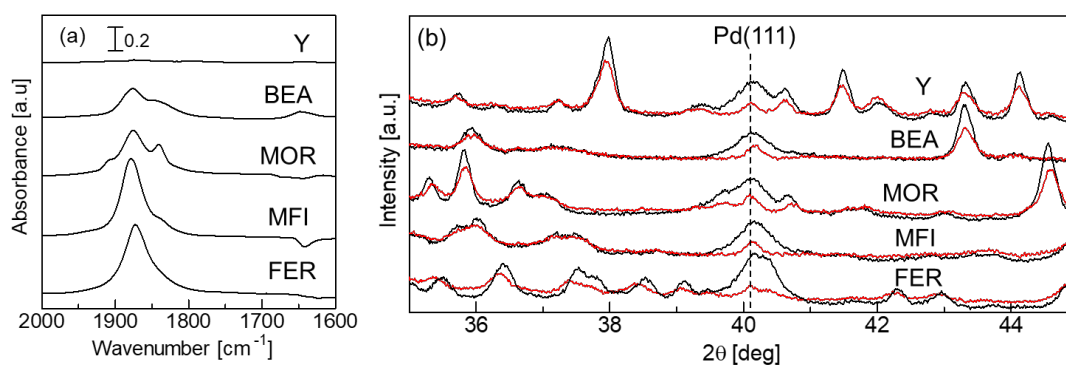


Figure S4. (a) FTIR spectra for NO adsorption after the reaction of physical mixture of Pd black (1 wt%) and other zeolites (FER, MFI, MOR, BEA, and Y) with NO at 600°C followed by O₂ treatment. (b) XRD patterns before (black) and after (red) the NO treatment.

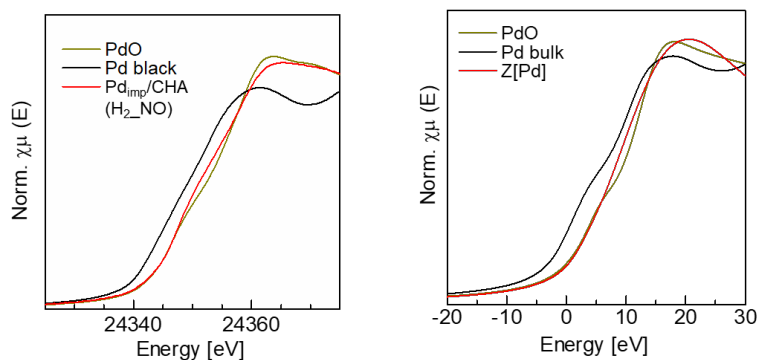


Figure S5. Comparison of experimental (left) and simulated (right) XANES spectra for Pd_{imp}/CHA(H₂_NO) (after O₂ treatment), Pd metal, and PdO. The structure models were optimized using DFT calculations prior to the simulation.

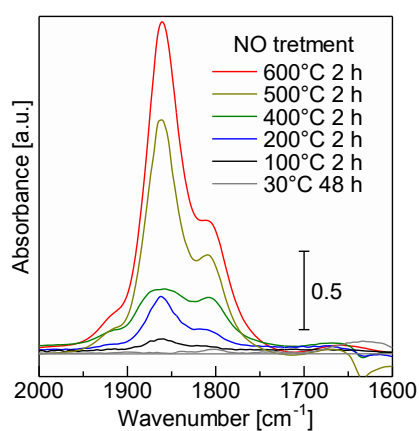


Figure S6. FTIR spectra for NO adsorption on Pd+CHA(NO) prepared at different temperature.

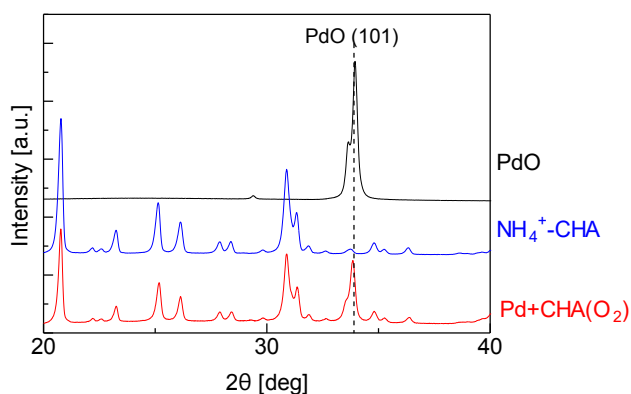


Figure S7. XRD patterns for Pd+CHA(O₂), NH₄⁺-CHA, and PdO.

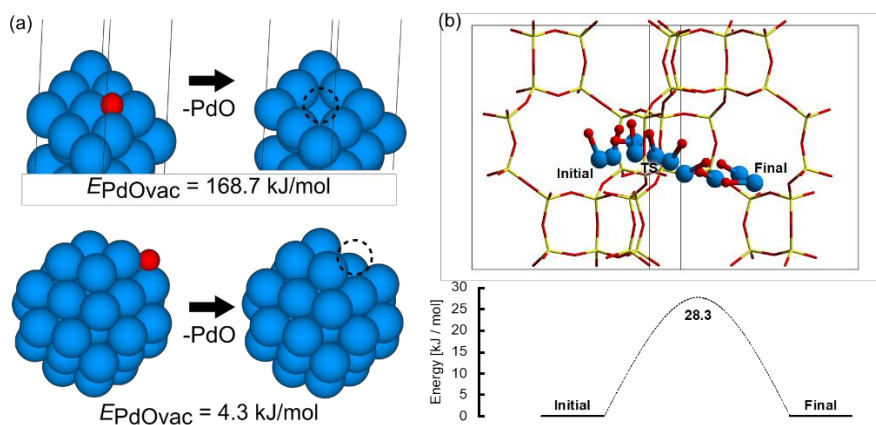


Figure S8. (a) Optimized structures of oxidized Pd surface by atomic O (left) and after the formation of mononuclear PdO species (right) for Pd(111) surface (upper row) and Pd₃₈ cluster model (lower row). A dashed circle shows a PdO vacancy. (b) Diffusion barrier of PdO monomer across an 8 membered ring in CHA zeolite. Cyan: Pd, Red: O. Only PdO moiety is shown with the stick and ball style for clarity.

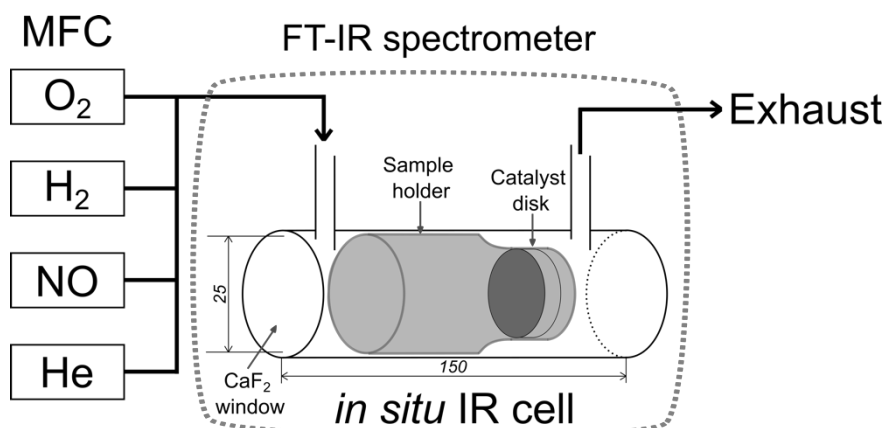


Figure S9. Schematic view of the used setup for *in-situ* IR measurement. Inner diameter and length of the cell are provided with a unit of mm.

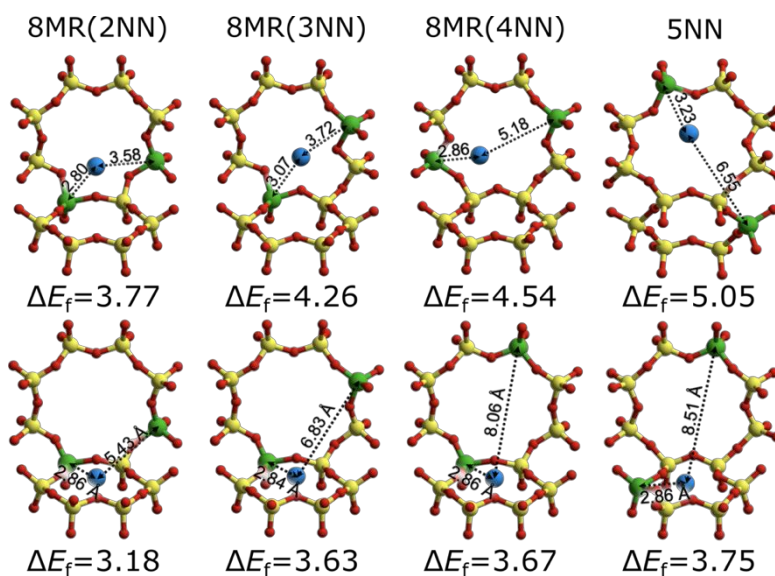


Figure S10 The optimized structure of considered models with relative formation energies (ΔE_f , the definition is described in the experiential section). Yellow: Si, Red: O, Green: Al, Blue: N, Cyan: Pd. Only atoms around Pd are shown for clarity.

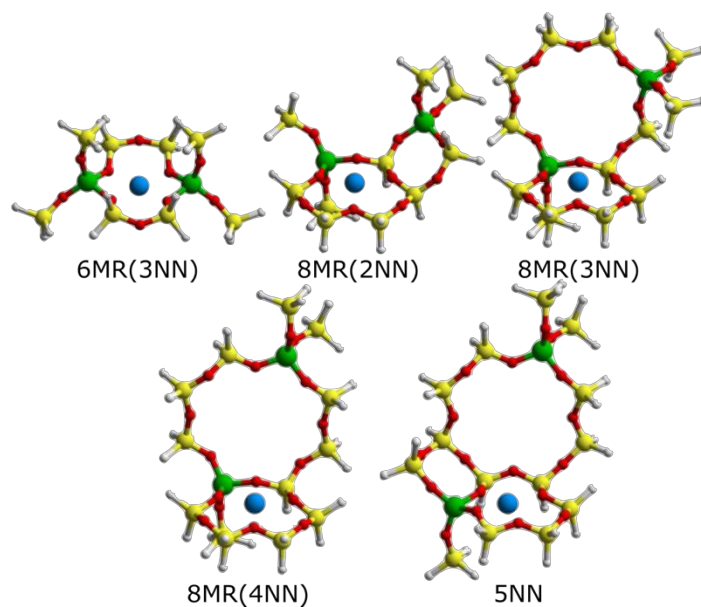


Figure S11 The cluster models used for the molecular orbital analysis. Yellow: Si, Red: O, Green: Al, Blue: N, Cyan: Pd, White: H.

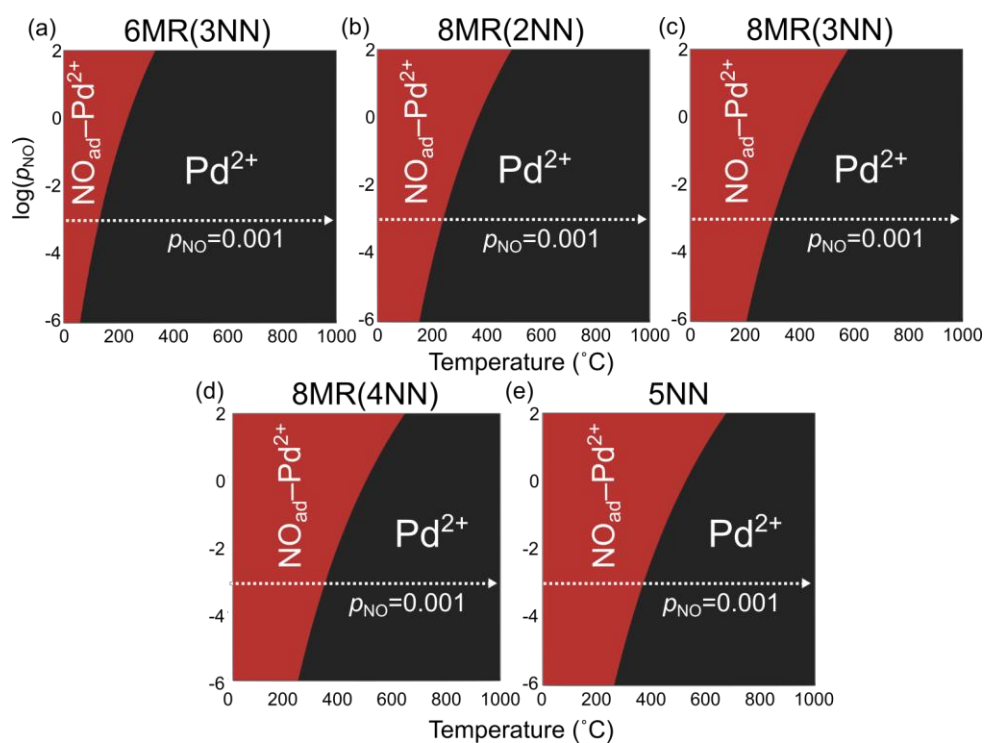


Figure S12 Thermodynamic phase diagrams for bare Pd^{2+} cation (Pd^{2+}) and NO adsorbed one ($\text{Pd}^{2+}-\text{NO}_{\text{ad}}$) at each paired Al site as a function of temperature and partial pressure of NO

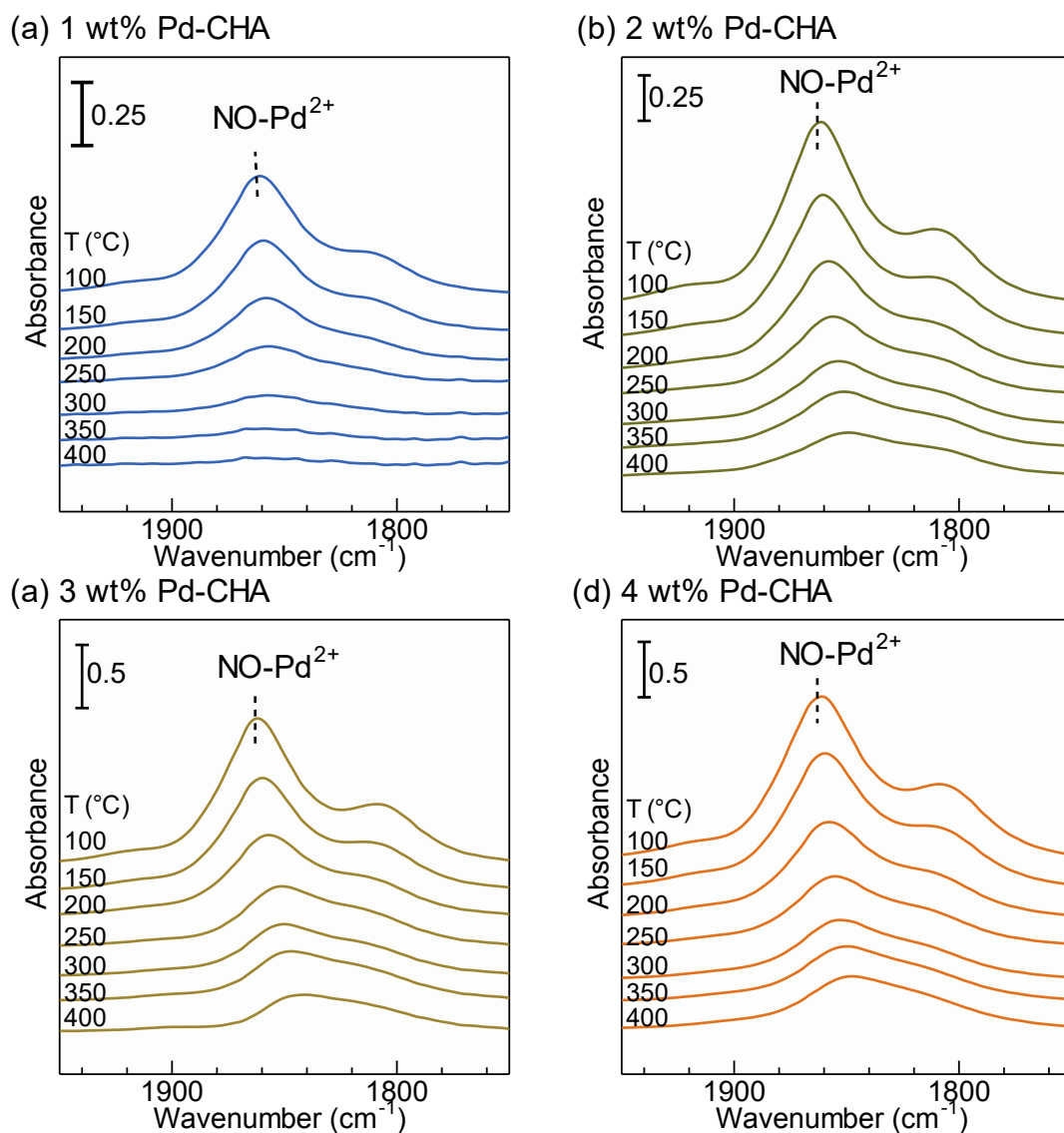


Figure S13 *In-situ* IR spectra of NO-Pd²⁺ species over (a) 1 wt%, (b) 2 wt%, (c) 3 wt%, and (d) 4 wt% Pd-CHA under a flow of 0.1% NO (total flow: 100 ml/min). The background spectra were taken under He flow at each measuring temperature before subjecting to NO.

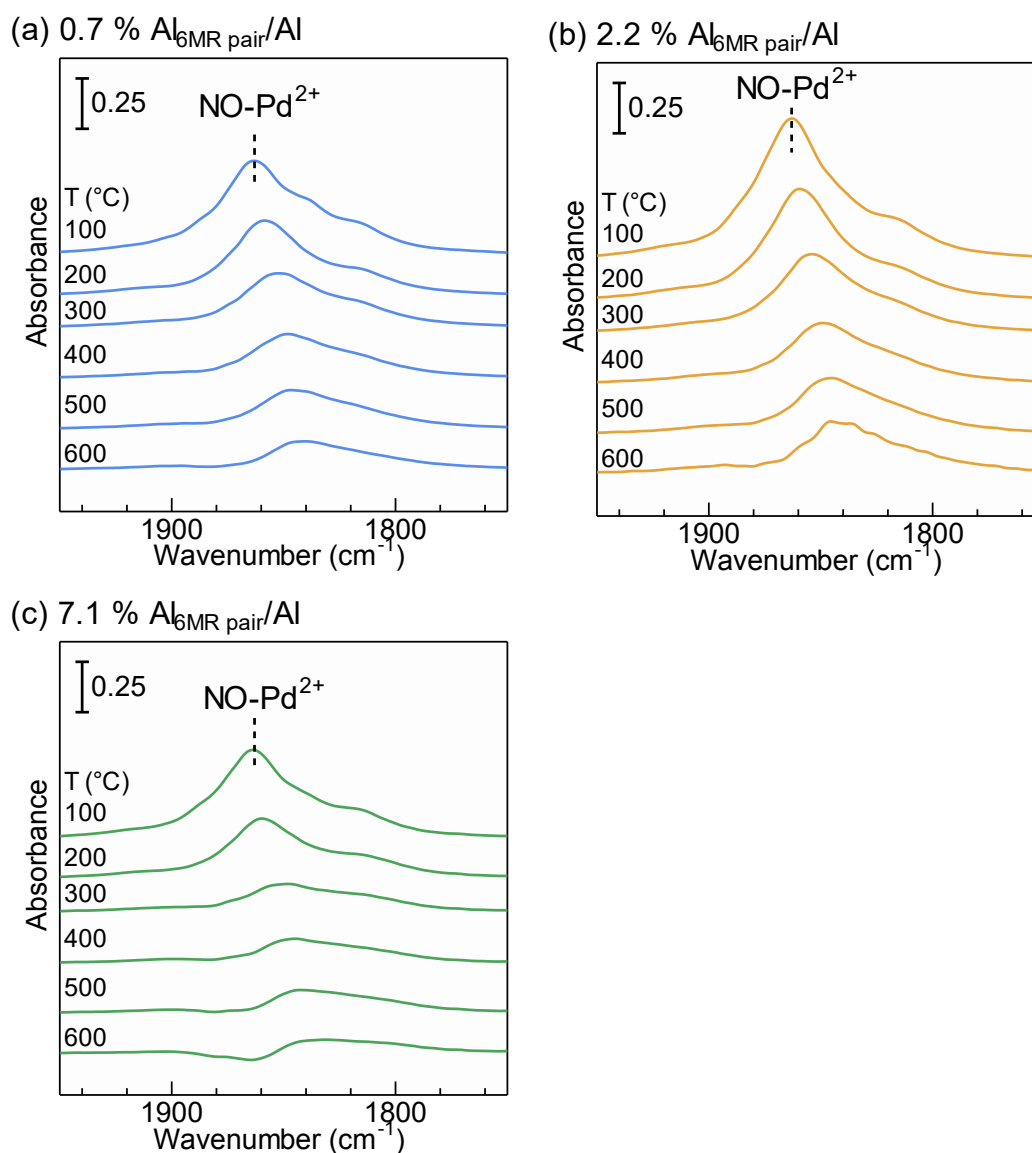


Figure S14 *In-situ* IR spectra of NO-Pd²⁺ species over prepared 1 wt% Pd-CHA with different ratios of 6MR paired Al sites ($\text{Al}_{6\text{MR pair}}/\text{Al}$) (a) 0.7%, (b) 2.2%, and (c) 7.1%) under a flow of 0.1% NO (total flow: 100 ml/min). The background spectra were taken under He flow at each measuring temperature before subjecting to NO.

Chapter 5

Rh-exchanged zeolites for transient de-NO_x under periodic lean/rich conditions and dynamic structural evolution of Rh species

5.1. Introduction

The sizes, shapes, and oxidation states of active sites in heterogeneous catalysts change dynamically depending on the reaction temperature, atmosphere, and adsorbent.^{1–6} Owing to recent progress in *in situ/operando* spectroscopic techniques and density functional theory (DFT) calculations, structural changes in the active species during catalytic cycles have been observed under the working states, leading to a molecular-scale understanding of the reaction mechanism.^{7–19} The molecular-level understanding of heterogeneous catalysis is reported to be less than that of homogeneous catalysis because of the nonuniformity in the structure of the solid surfaces. Well-defined metal complexes or clusters in zeolites are rare examples of structurally uniform heterogeneous catalysts.^{20–29} Rhodium complexes and clusters anchored in zeolites are among the successful examples of well-defined active species.^{30–36} Reversible changes in their oxidation states and nuclearities (isolated complexes ↔ metal clusters) depending on the reaction conditions have been characterized using *in situ/operando* spectroscopic techniques.^{37–45} Fang et al. investigated the dynamic structural evolution of Rh species in zeolites using *in situ* IR and X-ray absorption spectroscopy (XAS) and revealed that [Rh(CO)₂]⁺ complexes anchored at zeolitic anion sites were reversibly converted into Rh₄(CO)₁₂ and Rh₆(CO)₁₆ clusters depending on the reaction temperature under a flow of CO + H₂O or CO₂ + H₂.^{37,40} Amiridis et al. conducted XAS, high-resolution scanning transmission

electron microscopy (HRSTEM), IR, and DFT calculations to clarify the detailed structure of isolated $[\text{Rh}(\text{NO})_2]^+$ complexes in the zeolite and their catalysis for the hydrogenation and dimerization of hydrocarbons.³⁴ Although previous studies have focused on the *in situ/operando* characterization of well-defined Rh species under steady-state conditions, only a few studies have reported unsteady-state catalysis of anchored Rh complexes driven by their reversible structural changes.³⁷

The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) using NH_3 (NH_3 -SCR) on Cu-exchanged chabazite (Cu-CHA) is used in the state-of-the-art urea-SCR system as a current NO_x purification process for diesel emission control.^{46–48} Although high NO_x conversions are achieved by the urea-SCR system using temperatures that are typically above 200 °C, the urea injection temperature (normally above 180 °C) and the low catalytic activity of the Cu-CHA limit the application of the system at low temperatures.⁴⁹ Additionally, the urea-SCR system requires an expensive reductant (i.e. urea solution) and a high initial cost because of the requirement of a large urea tank; its complicated NH_3 injection system limits its use for a lean-burn gasoline direct injection engine (lean GDI) in a small fuel-efficient vehicle.⁵⁰ A passive NO_x adsorber (PNA) attached to the urea-SCR system can improve NO_x conversions at low temperatures.^{51–55} Pd^{2+} -exchanged zeolites, one of the most promising PNAs, trap NO_x at temperatures below 100 °C and release NO_x at high temperatures (above 250 °C), where the downstream urea-SCR system shows high NO_x conversions.²² However, once Pd-zeolites are exposed to reductant-rich conditions, isolated Pd^{2+} cations undergo irreversible deactivation as NO adsorption sites due to the reductive aggregation of Pd^{2+} to metal particles on the external surface of zeolites.^{54,56} In this context, an NO_x adsorber workable under rich conditions,

in which the adsorbed NO_x can be reduced without deactivation, is required.

NO_x storage and reduction (NSR; also known as the lean NO_x trap (LNT)) systems have been commercialized for removing NO_x under lean (excess oxygen) conditions.⁵⁷ The NSR system reduces NO_x to N₂ through a two-step cyclic operation. The NO_x trapped on the catalyst during the lean period is released and reduced to N₂ as the engine is switched to a fuel-rich condition (rich period). Major limitations of NSR technology include the use of large quantities of expensive platinum group metals (PGM), deactivation by strong SO_x adsorption on NO_x adsorption sites (basic oxides), a narrow temperature range for NO_x reduction, and slipping of the generated toxic byproduct (i.e., NH₃). Recently, a combination of NSR and NH₃-SCR (NSR-SCR)^{58–65} has been studied for ways to overcome the individual limitations of NSR and NH₃-SCR. During the rich period, the NH₃ formed on an NSR catalyst is trapped by acid sites on a zeolite-based NH₃-SCR catalyst placed downstream and is thereafter utilized to reduce the NO_x slipped from the NSR in the subsequent lean period. An alternative lean de-NO_x approach recently proposed by a General Motors study is the combination of a three-way catalyst (TWC) with NH₃-SCR called passive SCR. In passive SCR, NH₃ generated over a TWC in a rich period is stored on a downstream SCR catalyst (Cu-zeolites), and NH₃-adsorbed Cu-zeolites reduce the NO_x slipped from the upstream TWC in a lean period.^{50,66–70} The TWC component has to produce sufficient NH₃ for the reduction of the slipped NO_x in the downstream NH₃-SCR catalyst. Thus, a drawback of the passive SCR is the requirement of strict N₂/N₂O/NH₃ selectivity control in the TWC over a wide range of conditions coupled with a complicated mathematical model for lean/rich cyclic engine operations.⁶⁸

Previous studies on $\text{NO} + \text{H}_2$, $\text{NO} + \text{CO} + (\text{H}_2\text{O})$, TWC, and the rich period of NSR show that the $\text{N}_2/\text{N}_2\text{O}/\text{NH}_3$ selectivity is significantly affected by the reaction conditions and the nature of the catalytic sites.^{26–39} The NO reduction using the conventional PGM particle-based TWC and NSR catalysts generally affords a mixture of $\text{N}_2/\text{N}_2\text{O}/\text{NH}_3$. Recently, Christopher *et al.*⁸⁵ and Wang *et al.*⁸⁶ independently reported that atomically dispersed (single atom) Rh sites on Al_2O_3 and CeO_2 show high selectivity for NH_3 in the $\text{NO} + \text{CO} + \text{H}_2\text{O}$ reaction. These studies suggested that single-atom Rh sites catalyze NH_3 formation via the reduction of NO with H_2 produced by the water gas shift ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) reaction. In 2001, Nakatsuji *et al.* developed a lean de-NO_x system catalyzed by Rh-loaded β zeolites under periodic lean/rich cycles.⁸⁷ This catalytic system was highly resistant to SO_x poisoning because of the absence of basic sites on the zeolite-based catalyst. The authors proposed an NO reduction mechanism through the reduction of NO to N_2 by Rh^0 , in preference to the formation of NH_3 . This was followed by the reduction of the oxidized Rh species to regenerate the Rh^0 sites. Subsequently, Nakatsuji *et al.* reported a novel de-NO_x system under lean/rich cycles using Pt/ CeO_2 and H-MOR. Based on the *in situ* infrared (IR) results, the NO_x adsorbed on the basic sites of CeO_2 in a lean period is thereafter reduced, in a rich period, to selectively produce NH_3 adsorbed on the acid sites of H-MOR. In the subsequent lean period, the adsorbed NH_3 reacts with NO_x to afford N_2 .⁸⁸

Consequently, considering the well-known fact that NO adsorption on Rh sites in zeolites produces $[\text{Rh}(\text{NO})_2]^+$ complexes,^{34,89–91} we hypothesized that Rh-exchanged zeolites can act as NO_x adsorbers in a lean period. Subsequently, in a rich period, these zeolites catalyze the selective reduction of adsorbed NO by H_2 to give NH_3 adsorbed on a

Brønsted acid site (BAS) in the zeolites. The use of Al-rich β zeolites^{92–95} as a host material may be effective in designing an isolated Rh site adjacent to the BAS. In the present study, *in situ* IR experiments were performed with a second IR gas cell and mass spectrometry (MS) to simultaneously monitor the surface species and gas-phase products (*operando* IR). Herein, we propose a new lean de-NO_x system (an “active” NO_x adsorber) that functions in four ways on the same catalyst: (i) NO_x storage (by Rh), (ii) NH₃ formation (by Rh), (iii) NH₃ storage (by BASs), and (iv) NH₃–SCR. First, the structure of the Rh species in the Rh-exchanged Al-rich β zeolites was explored by H₂-temperature-programmed reduction (TPR), X-ray absorption near-edge structure (XANES), extended X-ray absorption fine structure (EXAFS), and IR measurements. Afterward, the formation, storage, desorption, and reaction of the NO_x and NH₃ ad-species were investigated by *operando* IR experiments under transient or temperature-programmed surface reaction (TPSR) conditions. In addition, we have investigated the molecular-level mechanism of the periodic NO_x storage/reduction system over Rh-loaded mordenite zeolite (RhMOR) with low Rh loading. First, reversible structural changes in the Rh species have been studied using *operando* IR and *in situ* XAS. Combined with a thermodynamic discussion using *ab initio* thermodynamic calculations, we have shown that Rh metal clusters are oxidized by NO to afford [Rh(NO)₂]⁺ complexes in the zeolite, which are then reduced by H₂ to afford Rh metal clusters and NH₃ in the zeolite. The activation barriers for NH₃ formation on an isolated Rh⁺ cation and Rh metal cluster have been investigated using transition-state calculations. The proposed reaction pathway for NH₃ formation shows a lower activation barrier than that for N₂ and N₂O formation on both active sites. The detailed speciation of Rh species provided in this study sheds a light

on the importance of understanding the dynamic structural evolution under working conditions to design heterogeneous catalysts with unique properties.

5.2. Experimental

5.2.1 Sample preparation

The NH_4^+ -form of MOR zeolite with Si/Al ratio of 10, denoted as NH_4^+ -MOR was supplied from Catalysis Society of Japan (JRC-Z-M20). Rh(0.6 wt%)-exchanged MOR (RhMOR) was prepared by ion-exchange of NH_4^+ -MOR (Si/Al = 10) with 0.002 M aqueous solution of RhCl_3 at 80 °C for 12h, followed by filtering, washing with distilled water (200 cm^3) three times, drying at 100 °C for 20 h, and by calcination in the air at 500 °C for 0.5 h. Rh(10 wt%)-impregnated Al_2O_3 was prepared by impregnation of Al_2O_3 , by aqueous HNO_3 solution of $\text{Rh}(\text{NO}_3)_3$, followed by drying at 100 °C, calcination at 500 °C, and reduction under H_2 at 500 °C. Rh loadings were determined by X-ray fluorescence spectroscopy (Shimadzu, EDX-700HS).

5.2.2 IR measurement

In situ IR measurements were carried out within transmission mode using a JASCO FT/IR-4200 spectrometer equipped with a triglycine sulfate (TGS) detector. A home-made *in situ* IR cell, set in the IR spectrometer, was connected to a conventional flow reaction system (total flow: 100 mL min^{-1}). The sample disk was obtained by pelletizing into a 40 mg self-supported disk and placed in the *in situ* IR cell (made by pyrex) with CaF_2 windows. IR spectra were recorded by accumulating 20 scans at a resolution of 4 cm^{-1} . The reference spectrum of the sample disk was collected under a He

flow at the measuring temperature (200 °C). The gas line from the IR cell was directly connected to a homemade gas cell equipped with KBr windows to monitor the generated gases (NO, N₂O, and NH₃) using a JASCO FT/IR-4600 spectrometer (equipped with a TGS detector). To monitor outlet N₂, a mass spectrometry (BELMass, MicrotracBEL Corp.) was connected downstream of the IR gas cell. The schematic view of the used setup is shown in **Figure S6**.

5.2.3. X-ray absorption spectroscopy

Rh K-edge XAS data were collected in quick mode and recorded in transmission mode at the BL14B2 station attached to the Si(311) monochromator at SPring-8 (JASRI), Japan (Proposal No. 2021A1615 and 2021B1840). 700 mg of the RhMOR (ϕ : 7 mm) and 50 mg of Rh10Al₂O₃ (ϕ : 7 mm) catalysts were pelletized into self-supported disks which were then introduced into a quartz *in situ* cell equipped with Kapton film windows. The catalyst was pretreated under a flow of 2% H₂/He (500 cm³ min⁻¹) at 200 °C for 0.5 h. After purging with He, the reaction gas was fed at a total flow rate of 500 cm³ min⁻¹. The XANES and EXAFS as well as curve-fitting analysis were conducted using the Athena and Artemis software package⁹⁶. For the curve-fitting analysis of NO-treated RhMOR, the structure model of [Rh(NO)₂]⁺, optimized by DFT calculation, was applied as a reference. The used structure is provided in xyz format.

5.2.3 Catalytic test

A catalytic test under lean/rich cycles was performed using a fixed continuous flow system (a fixed-bed reactor). A 40 mg of sample was put into a glass reactor with

quartz wool as a bed. The outlet gas from the reactor was directly connected to a home-made IR gas cell to monitor the concentration of NO, NO₂, and N₂O by IR equipment. The rich gas (0.1% NO + 2% H₂; 60 s) and lean gas (0.1% NO + 2% O₂; 120 s) were repeatedly fed to a fixed-bed flow type reactor at measuring temperatures (100, 200, and 300 °C).

5.2.4 DFT calculation

DFT calculations were performed by the periodic boundary condition under the Kohn–Sham formulation^{97,98} with the Vienna ab-initio simulation package (VASP)^{99,100}. The generalized gradient approximated Perdew-Burke-Ernzerhof (GGA-PBE) functional¹⁰¹ was applied as electron exchange correlation. The projected augmented waves (PAW) method was utilized for the Kohn-Sham equations^{102,103}. All atoms were allowed to fully relax during all calculations. Cut-off energy of the plane basis set was set to 400 eV. The Γ point was used for Brillouin zone sampling. The DFT-D3 dispersion correction with Becke–Johnson damping was employed for all calculations^{104,105}. The lattice constants of the unit cell were fixed as given in the International Zeolite Association (IZA) database ($a = 18.2560$ Å, $b = 20.5340$ Å, $c = 15.0840$ Å, and $\alpha = \beta = \gamma = 90.0^\circ$) during the calculations¹⁰⁶. Among distinct T sites in MOR framework, T4 site was applied as the Al replacement site.^{107,108} A $1 \times 1 \times 2$ of supercell was used in this study. The conjugate gradient method was used to optimize intermediate structures during the climbing-image nudge elastic band (CI-NEB) calculations as implemented in VTST-Tools.^{109,110} For CI-NEB calculations, the spring constant between adjacent images was set to 5.0 eV Å⁻²; moreover, the calculations were considered converged when the

maximum forces on all atoms were less than 0.05 eV Å⁻¹. VESTA is used for visualizing the structures.¹¹¹

5.3 Result and discussion

5.3.1 Structural Evolution of Rh Species during the Preparation of the Rh-loaded β zeolite

Rh(4 wt%)-exchanged β zeolite (Rh4 β 5) was prepared by the ion exchange of NH₄⁺- β 5 (Si/Al = 5) with an aqueous solution of RhCl₃ (more details can be found in supporting Information (SI)). Figure 1 (left) shows the XANES spectra of Rh4 β 5 with the spectra of reference compounds recorded under ambient conditions (SI). The absorption edge for the as-calcined Rh4 β 5 is close to that of the reference compound of Rh³⁺ (Rh(NO₃)₃-loaded SiO₂). The Fourier transforms (FTs) of the k^3 -weighted Rh K-edge EXAFS of the as-calcined Rh4 β 5 are shown in Figure 1 (right), and the results of the curve fitting analysis are summarized in Table 1. The as-calcined Rh4 β 5 shows an Rh–O bond at a distance (R) of 2.03 Å with a coordination number (CN) of 5.3 and a weak Rh–O–Rh shell (2.81 Å) with a CN of 1.4. The fractions of the Rh metal/Rh⁺/Rh³⁺ species over the as-calcined sample were analyzed by a linear combination fitting (LCF) analysis of the XANES spectrum (Figure S1 (left)). The main component in the fraction is Rh³⁺ species (84%), indicating that Rh³⁺ species are the dominant Rh species in the as-calcined Rh4 β 5.

The absorption edge for Rh4 β 5 reduced by H₂ at 500 °C for 15 min (H₂-reduced Rh4 β 5) was close to those of the reference compounds Rh⁺ (Rh(CO)₂(acac)) and Rh foil (Figure 1 (left)). The LCF analysis of XANES for the H₂-reduced Rh4 β 5 (Figure S1 (right)) shows the presence of Rh metal as the main component (60%) and the copresence of Rh³⁺ (21%)

and Rh^+ (19%) species. The EXAFS of H_2 -reduced $\text{Rh4}\beta 5$ shows an Rh–Rh shell of Rh metal and an Rh–O shell, even after H_2 reduction at 500 °C. The fitting analysis shows that the Rh–O bond distance (2.01 Å) of H_2 -reduced $\text{Rh4}\beta 5$ is close to that of the as-calcined $\text{Rh4}\beta 5$ (2.03 Å), while its CN (2.5) of the H_2 -reduced sample is lower than that of the as-calcined one (5.3). As for the Rh–Rh shell, the CN (4.6) and bond distance (2.68 Å) of H_2 -reduced $\text{Rh4}\beta 5$ are lower than those of the Rh foil (CN = 12, R = 2.72 Å). Besides, the obtained CN and bond distance are very close to the reported values for Rh small cluster in NaY (CN = 4.5, R = 2.67 Å), implying the presence of small Rh metal clusters, possibly in the zeolitic pores.⁴³ Combined with the results of the XANES analysis, it was observed that Rh^{3+} species are reduced by H_2 to afford Rh metal clusters and Rh^+ cations, possibly at the cation exchange site of zeolite. A TPR profile with H_2 (H_2 -TPR) on the as-calcined $\text{Rh4}\beta 5$ (Figure 2) shows that Rh^{3+} species are reduced below 200 °C. This indicates that a reduction temperature of 500 °C is sufficient for the reduction of the Rh^{3+} species. For comparison, a 4 wt% Rh-loaded $\beta 5$ catalyst was prepared by the impregnation method, followed by calcination and H_2 reduction at 500 °C (H_2 -reduced $\text{Rh4}\beta 5\text{imp}$). The EXAFS analysis of this sample shows a higher CN of the Rh–Rh shell (7.6) than the H_2 -reduced $\text{Rh4}\beta 5$, indicating the presence of larger Rh metal nanoparticles over the H_2 -reduced $\text{Rh4}\beta 5\text{imp}$.

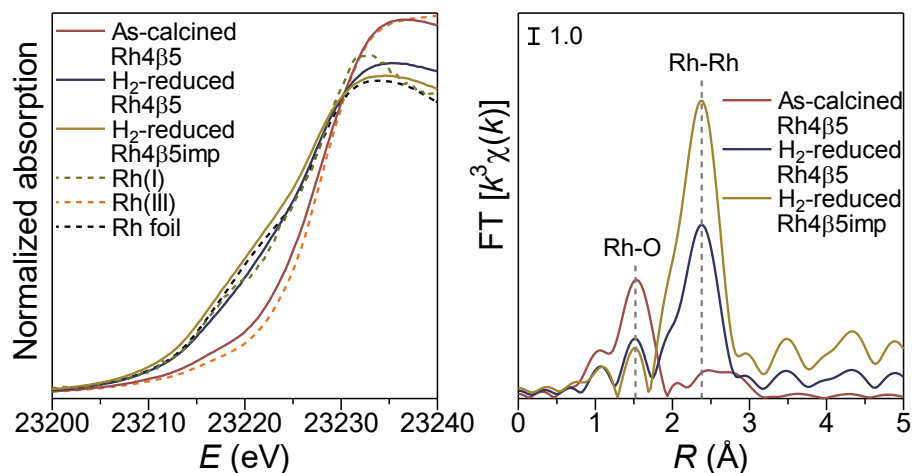


Figure 1. Rh K-edge X-ray absorption near-edge structure (XANES) (left) and Fourier transforms of extended X-ray absorption fine structure (FT-EXAFS) (right) of Rh4 β 5 pretreated under different conditions and reference Rh compounds.

Table 1. Curve fitting analysis of Rh K-edge extended X-ray absorption fine structure (EXAFS) for Rh4 β 5 under different conditions.

Conditions	Shell	CN ^a	$R/\text{\AA}$ ^b	$\sigma/\text{\AA}$ ^c	R ^d
As-calcined Rh4 β 5	Rh–O	5.3	2.03	0.074	0.004
	Rh–O–Rh	1.4	2.81	0.089	
H ₂ -reduced Rh4 β 5	Rh–O	2.5	2.01	0.094	0.004
	Rh–Rh	4.6	2.68	0.072	
H ₂ -reduced Rh4 β 5imp	Rh–Rh	7.6	2.68	0.069	0.005
Rh ₂ O ₃ ^e	Rh–O	6	2.07	-	-
	Rh–O–Rh	3	3.09	-	-
Rh foil ^e	Rh–Rh	12	2.72	-	-

^a Coordination numbers. ^b Bond distance. ^c Debye–Waller factor. ^d R-factor.

^e Crystallographic data of Rh₂O₃ and Rh metal.

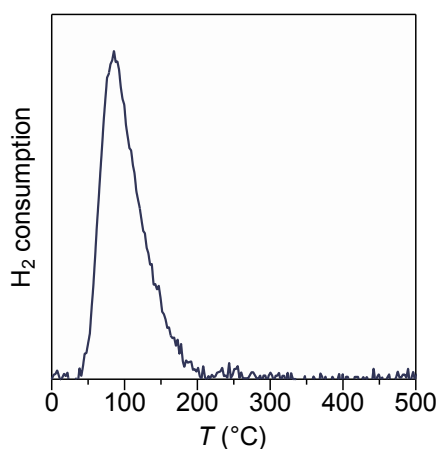


Figure 2. H₂-temperature-programmed reduction (TPR) (20 °C min⁻¹) profile of as-calcined Rh4β5 preoxidized in 2% O₂ at 500 °C

5.3.2 Storage of NH₃ and NO_x and Thermal Desorption

To investigate the thermal stability of the adsorbed NH₃ species, temperature-programmed desorption (TPD) of NH₃ was performed, combined with IR observations of adsorbed NH₃ species. Before the measurement, the catalyst powder was pelletized into 40 mg of self-supporting IR disks, which were subsequently exposed to 0.1% NH₃/He at 100 °C (600 s), followed by purging under a He flow for 600 s. Changes in the IR spectra of the adsorbed NH₃ were monitored as a function of temperature under He flow with ramping temperature (20 °C min⁻¹). Simultaneously, the outlet NH₃ concentration was quantified by the IR gas cell downstream of the first IR cell (a schematic view of the used IR setup is shown in Figure S2). Figure 3a and b (left) show the IR spectra of the adsorbed NH₃ species on Hβ5 and the as-calcined Rh4β5. At 100 °C, the IR spectrum for Hβ5 shows a band at 1450 cm⁻¹ assignable to NH₃ adsorbed on the Brønsted acid sites (B-NH₃)¹¹² whereas that for Rh4β5 shows a band for B-NH₃ (1450 cm⁻¹) and a band at 1620

cm^{-1} due to NH_3 coordinated to $\text{Rh}^{\text{n+}}$ Lewis acid sites (L-NH_3). The peak heights of B- and L- NH_3 and outlet NH_3 concentrations are plotted as a function of temperature in Figure 3a and b (right). H β 5 exhibits a B- NH_3 desorption peak ($> 200\text{ }^\circ\text{C}$), while Rh4 β 5 shows a low-temperature ($< 200\text{ }^\circ\text{C}$) desorption of L- NH_3 and high-temperature desorption of B- NH_3 . The higher thermal stability of B- NH_3 than that of L- NH_3 implies that Brønsted acid sites can act effectively as NH_3 storage sites over a wide temperature range (100–400 $^\circ\text{C}$).

Operando IR was conducted under TPD conditions (Figure 4) to investigate the nature of the adsorbed NO_x species on the H_2 -reduced Rh4 β 5. When the H_2 -reduced Rh4 β 5 was exposed to $\text{NO} + \text{O}_2$ at 200 $^\circ\text{C}$, two strong bands at 1780 and 1860 cm^{-1} assignable to $[\text{Rh}(\text{NO})_2]^+$ ^{34,89–91} were observed (Figure 4 (left)). After cooling the IR cell to 50 $^\circ\text{C}$ under a He purge, IR spectra were collected under 2% O_2 flow during temperature ramping (20 $^\circ\text{C min}^{-1}$), and the outlet NO_x was monitored by MS. The surface concentration of $[\text{Rh}(\text{NO})_2]^+$ (peak heights of the band at 1780 cm^{-1}) and the MS intensity for outlet NO_x were plotted as a function of temperature in Figure 4 (right). The NO_x desorption curve shows two maxima at 240 $^\circ\text{C}$ and 420 $^\circ\text{C}$, accompanying a corresponding decrease in the IR band height of $[\text{Rh}(\text{NO})_2]^+$. Above 300 $^\circ\text{C}$, other bands at 1910 and 1956 cm^{-1} derived from cationic mononitrosyl species on cationic Rh sites ($\text{Rh}^{\delta+}-\text{NO}^+$)^{113,114} were observed. The amount of $\text{Rh}^{\delta+}-\text{NO}^+$ increased through temperature ramping, indicating that some of the adsorbed NO molecules on the Rh^+ sites remained and formed thermally stable $\text{Rh}^{\delta+}-\text{NO}^+$ species at high temperatures. The NO-TPD results revealed that Rh^+ sites act as effective NO storage sites over a wide temperature range (100–500 $^\circ\text{C}$), even in the presence of O_2 . Figure 5 (left) shows the *in*

situ IR spectra of the adsorbed species on the H₂-reduced Rh4β5 under a NO flow at 200 °C. Figure 5 (right) shows the time courses for the surface concentration of [Rh(NO)₂]⁺ (peak height of the band at 1780 cm⁻¹) and concentration of outlet NO and N₂O (another IR equipped with a gas cell). Initially, NO adsorbed on Rh⁰ metal sites (1680 cm⁻¹)^{113,114} and a small amount of N₂O in the gas phase were generated; subsequently, their amounts gradually decreased. This implies that the Rh⁰ metal species are dispersed into [Rh(NO)₂]⁺ species via an oxidative dispersion by using NO as the oxidant. A similar phenomenon was reported that NO can cause the oxidative dispersion of supported Rh species via the formation of thermodynamically stable [Rh(NO)₂]⁺ species.^{44,115,116}

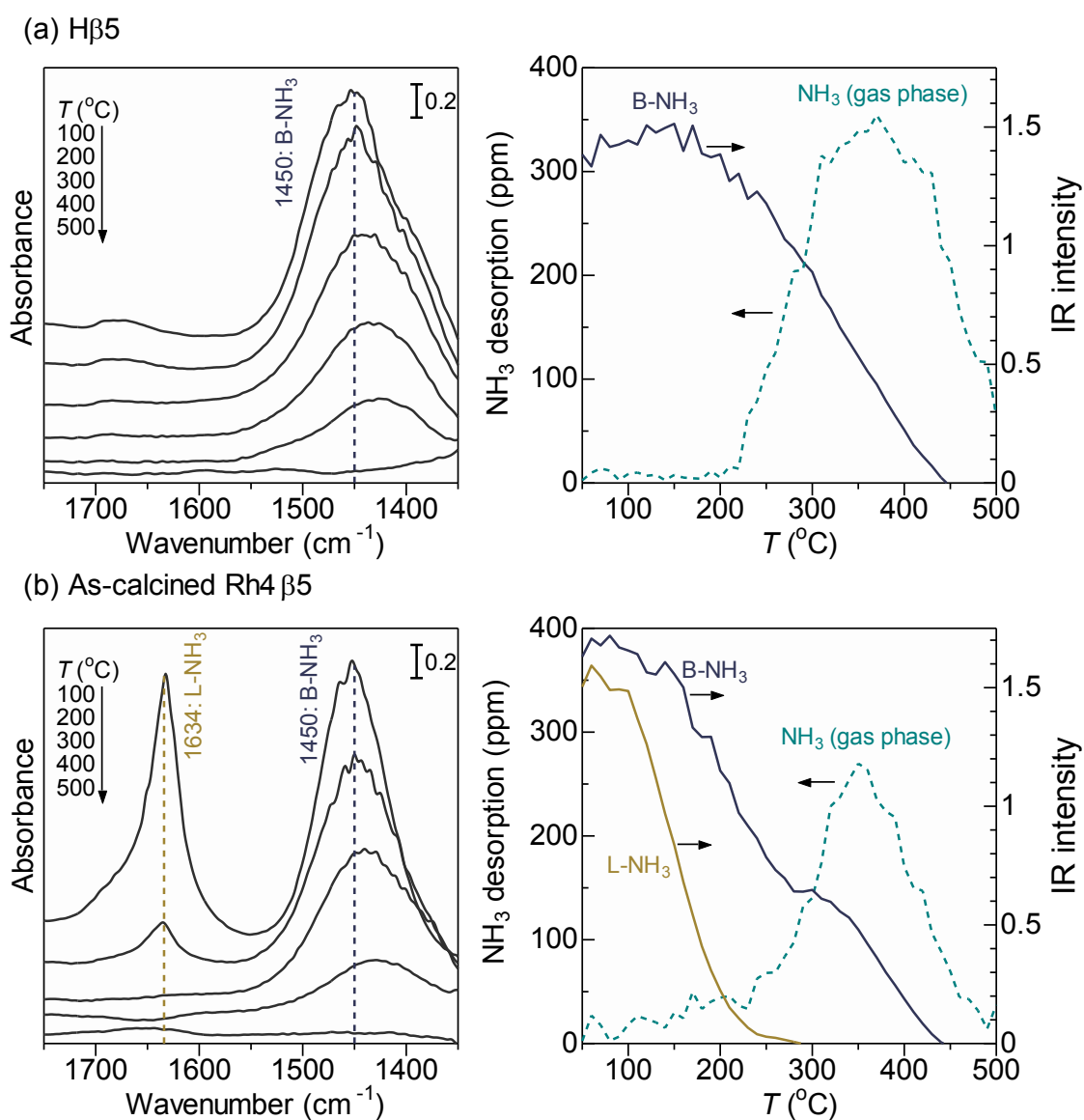


Figure 3. NH_3 -temperature-programmed desorption (TPD) ($20\text{ }^{\circ}\text{C min}^{-1}$) under He flow for (a) $\text{H}\beta 5$ and (b) as-calcined $\text{Rh4}\beta 5$. Both samples were preexposed to 0.1% NH_3 at $100\text{ }^{\circ}\text{C}$ (600 s), followed by a He purge (600 s): IR spectra of adsorbed species at different temperatures (left), infrared (IR) intensity of adsorbed NH_3 (B-NH_3 and L-NH_3), and concentration of desorbed NH_3 versus temperature (right).

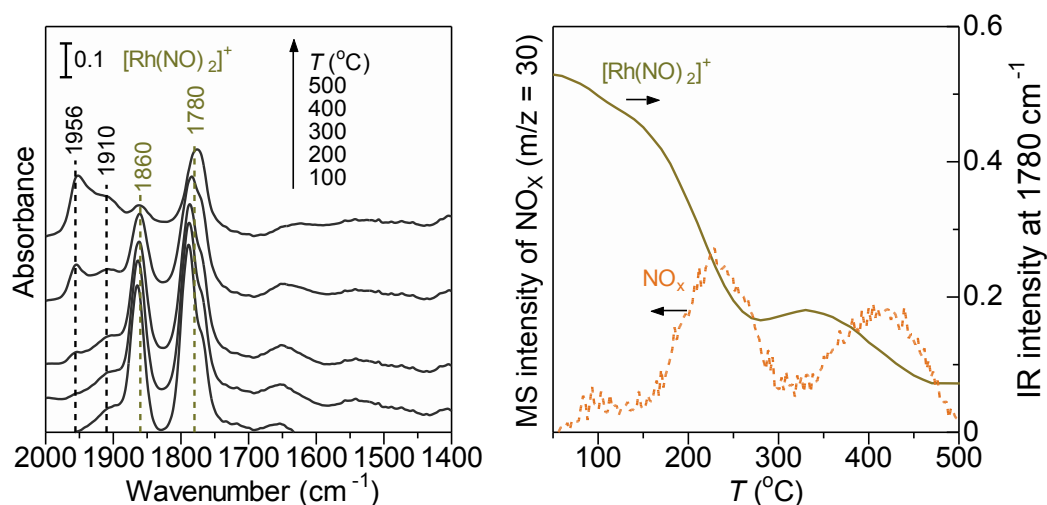


Figure 4. NO_x-temperature-programed desorption (TPD) ($20\text{ }^{\circ}\text{C min}^{-1}$) under 2% O₂ flow over H₂-reduced Rh4β5, preexposed to 0.1% NO + 2% O₂ at 200 °C (600 s), followed by cooling to 50 °C under He flow: IR spectra of adsorbed NO_x species at different temperatures (left), infrared (IR) peak height of $[\text{Rh}(\text{NO})_2]^+$, and desorbed NO_x as a function of temperature (right).

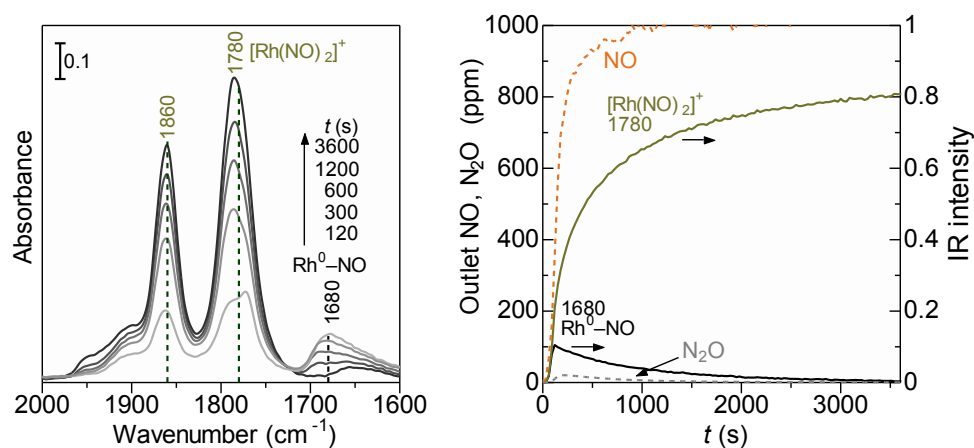


Figure 5. *In situ* infrared (IR) spectra of adsorbed species on H₂-reduced Rh4β5 under flowing 0.1% NO at 200 °C (left) and time course of IR intensities and concentration of outlet NO and N₂O analyzed by an IR gas cell (right).

5.3.3 *In situ* Formation of NH_3 by the Reaction of $[\text{Rh}(\text{NO})_2]^+$ with H_2

The reduction of $[\text{Rh}(\text{NO})_2]^+$ with H_2 was studied by a TPSR while recording the surface reaction by IR (Figure 6). The IR disk of the H_2 -reduced $\text{Rh4}\beta\text{5}$ was heated from 50 °C to 500 °C (20 °C min^{-1}) under a flow of $\text{NO} + \text{H}_2$ while monitoring the gas-phase products by online IR (gas cell) and MS (a schematic view of the used IR setup is shown in Figure S2). Upon exposure to $\text{NO} + \text{H}_2$, $[\text{Rh}(\text{NO})_2]^+$ was rapidly generated on the surface at 50 °C. The concentration of gas-phase NO and $[\text{Rh}(\text{NO})_2]^+$ sharply decreased above 200 °C, with the generation of B-NH_3 on the surface. Above 300 °C, B-NH_3 was desorbed, and gas-phase NH_3 was subsequently observed. Importantly, N_2 formation was not observed below 380 °C, and the N_2O formation was lesser than the NH_3 formation. The N_2 formation above 380 °C could be caused by the $\text{NO} + \text{NH}_3$ reaction.¹¹⁷ This result indicates that the $\text{Rh4}\beta\text{5}$ catalyst selectively promotes NO reduction by H_2 toward NH_3 in place of N_2 and N_2O over a wide temperature range.

To examine the stability and reactivity of the $[\text{Rh}(\text{NO})_2]^+$ complexes under oxidative or reductive atmospheres at 200 °C, the $[\text{Rh}(\text{NO})_2]^+$ complexes generated on the surface were sequentially subjected to He , 2% O_2 , and 2% H_2 flows (Figure 7). The results show that the $[\text{Rh}(\text{NO})_2]^+$ complexes are thermally stable under He flow and are gradually oxidized to $\text{Rh}^{\delta+}-\text{NO}^+$ (1956 cm^{-1}) under a flow of 2% O_2 . These adsorbed NO species were quickly reduced by a flow of 2% H_2 to produce B-NH_3 . These results indicate that $[\text{Rh}(\text{NO})_2]^+$ complexes and $\text{Rh}^{\delta+}-\text{NO}^+$ species, which are considerably stable under oxidative (lean) conditions, are highly reactive under reductive conditions. This property is suitable for lean de- NO_x under cyclic lean/rich operations.

Next, we attempted to optimize the catalysts suitable for this de- NO_x process.

Figure 8 (left) shows the effect of Rh loading and the Si/Al ratio of zeolites on the reaction rates for the reduction of $[\text{Rh}(\text{NO})_2]^+$ by H_2 at 200 °C. The IR peak of the $[\text{Rh}(\text{NO})_2]^+$ complexes in the catalyst disappeared within 300 s, and B-NH₃ was generated as the sole N-containing product. The B-NH₃ formation rates depended strongly on the Rh loading; Rh4β5 exhibited a higher rate than the low Rh loading catalyst (Rh0.5β5). In addition, Rh0.5β5 showed higher rates for the consumption of $[\text{Rh}(\text{NO})_2]^+$ and B-NH₃ formations than the low Al content catalyst (Si/Al = 20) with low Rh loading (Rh0.5β20), indicating that more BAS is expedient for a NO reduction. As shown in Figure 8 (right), all samples were pretreated by NO + H₂ flow for 600 s to generate B-NH₃ on their IR disks, followed by purging with He. When the flowing gas was switched to NO + O₂, B-NH₃ was consumed accompanied by the formation of N₂, which indicates that B-NH₃ acts as a reductant for the selective reduction of NO to N₂ under lean conditions.¹¹² The initial rate of this transient reaction, estimated by the height of the N₂ peak, depends on the catalyst composition, and large amounts of Rh and Al, resulting in high rates of NO reduction to N₂ in the lean de-NO_x system.

Finally, to test the de-NO_x performance of the catalysts under periodic lean/rich conditions, lean/rich cycling measurements were conducted over Rh4β5, Rh0.5β5, Rh0.5β20, and Rh4β5imp. The rich gas (0.1% NO + 2% H₂; 120 s) and lean gas (0.1% NO + 2% O₂; 600 s) were repeatedly fed to a fixed-bed flow type reactor at 200 °C while monitoring the NO, NO₂, and N₂O concentrations in the outlet gas by an IR gas cell. After the cycling experiment shown in Figure 9, Rh4β5 exhibited a slightly higher NO_x conversion than Rh0.5β5. Compared with the results of Rh0.5β20, which was prepared by using a β zeolite with a low Al content, the use of Al-rich β (Rh0.5β5) results in a high

NO_x conversion. In addition, the standard Rh4β5 catalyst prepared by the ion-exchange method showed a higher NO_x conversion than Rh4β5imp. Adsorption measurements were carried out to examine the storage capacities of NO and NH₃ (Figure S3) and the obtained values as well as NO_x conversion were plotted as a function of Rh loading amount (Figure S4). Among the tested samples, Rh4β5 and Rh0.5β5 show the highest NO and NH₃ adsorption capacities, respectively, while their NO_x conversions were comparable (48% vs 41%, respectively). These results indicate that the cooperation of NO storage sites (highly dispersed Rh species) and NH₃ storage sites (Brønsted acid sites) are important for the design of de-NO_x catalysts under periodic lean/rich conditions. In addition, the lean/rich cycle test was carried out with the lean (0.1% NO + 2% O₂; 600s) and O₂-added rich condition (0.1%NO + 2% O₂ + 2% H₂; 120s) using Rh4β5 (Figure S5), resulting in less NO_x conversion (31%) than the result above (48%).

Under the same periodic lean/rich condition, a Pd-loaded CHA zeolite (Pd0.5CHA7) was prepared to assess its de-NO_x performance (Figure 10), resulting in a low NO_x conversion, possibly due to the aggregation of Pd species using H₂ as a strong reductant. The results of Pd-CHA highlight the importance of dispersed Rh species for selective NO reduction toward NH₃, which is suitable for lean de-NO_x systems under cyclic lean/rich operations.

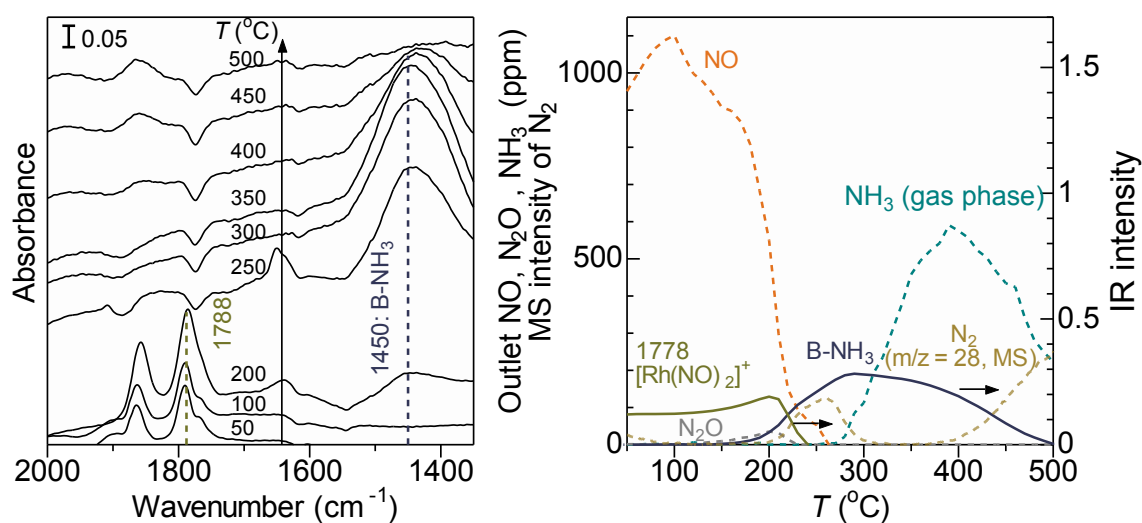


Figure 6. Temperature-programmed surface reaction (TPSR) ($20\text{ }^{\circ}\text{C min}^{-1}$) under flowing 0.1% NO + 0.5% H₂ over H₂-reduced Rh4 β 5: infrared (IR) spectra of adsorbed species at different temperatures (left) and IR intensities ($[\text{Rh}(\text{NO})_2]^+$ and B-NH₃), MS intensity of N₂ (arbitrary unit), and concentration of outlet NO, N₂O and NH₃ versus temperature (right).

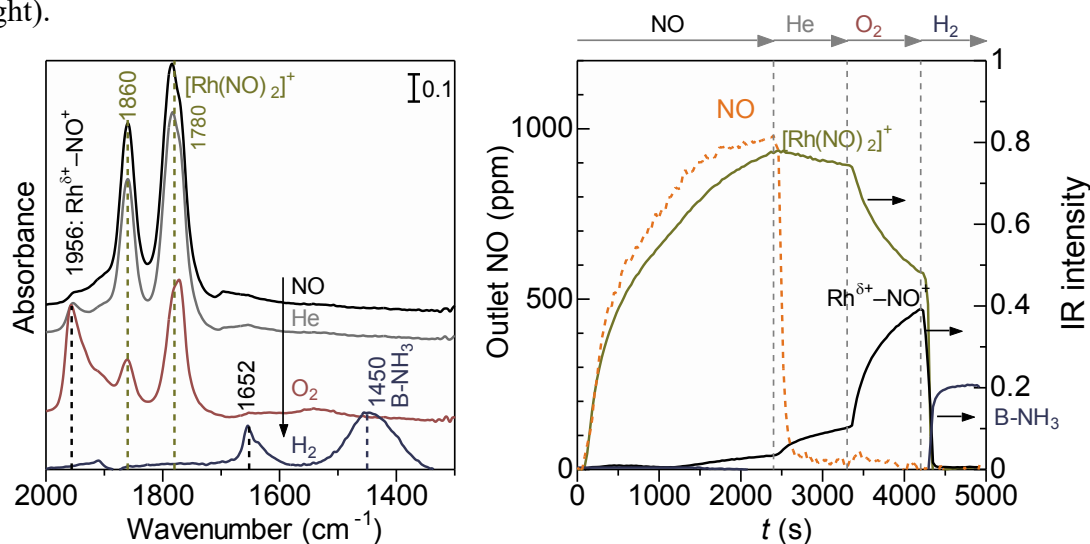


Figure 7. *In situ* infrared (IR) spectra of adsorbed species on Rh4 β 5 at $200\text{ }^{\circ}\text{C}$ under flowing 0.1% NO (2400 s), He (900 s), 2% O₂ (1200 s), and 2% H₂ (left), successively, and time course of the height of the IR peaks and concentration of outlet NO (right).

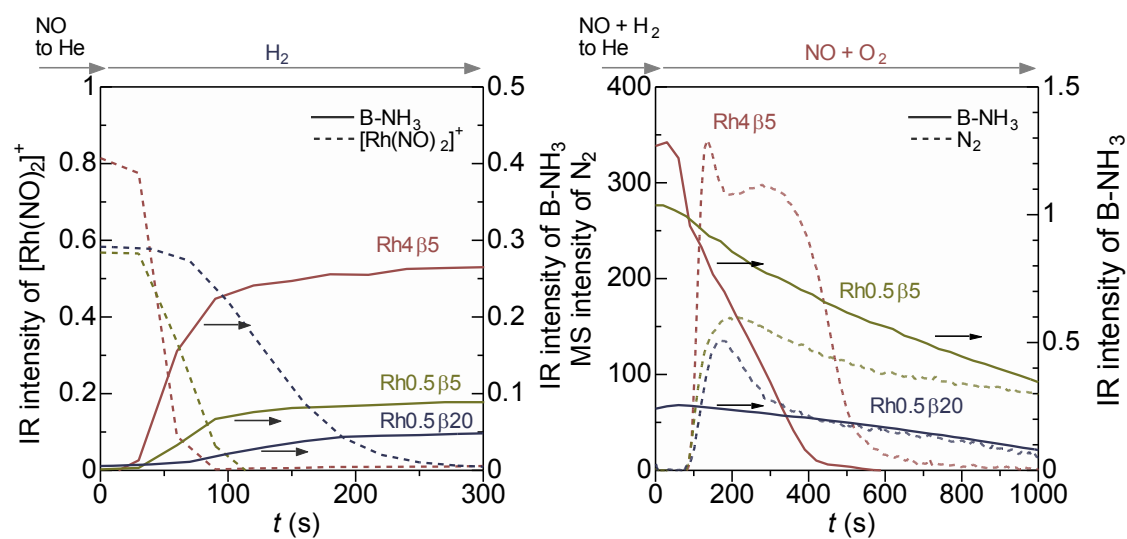


Figure 8. Time-resolved infrared (IR)/ mass spectrometry (MS) data at 200 °C for the reduction of adsorbed NO on the Rh catalysts under 2% H₂ (left) and reaction of B-NH₃ under 0.1% NO + 2% O₂ (right).

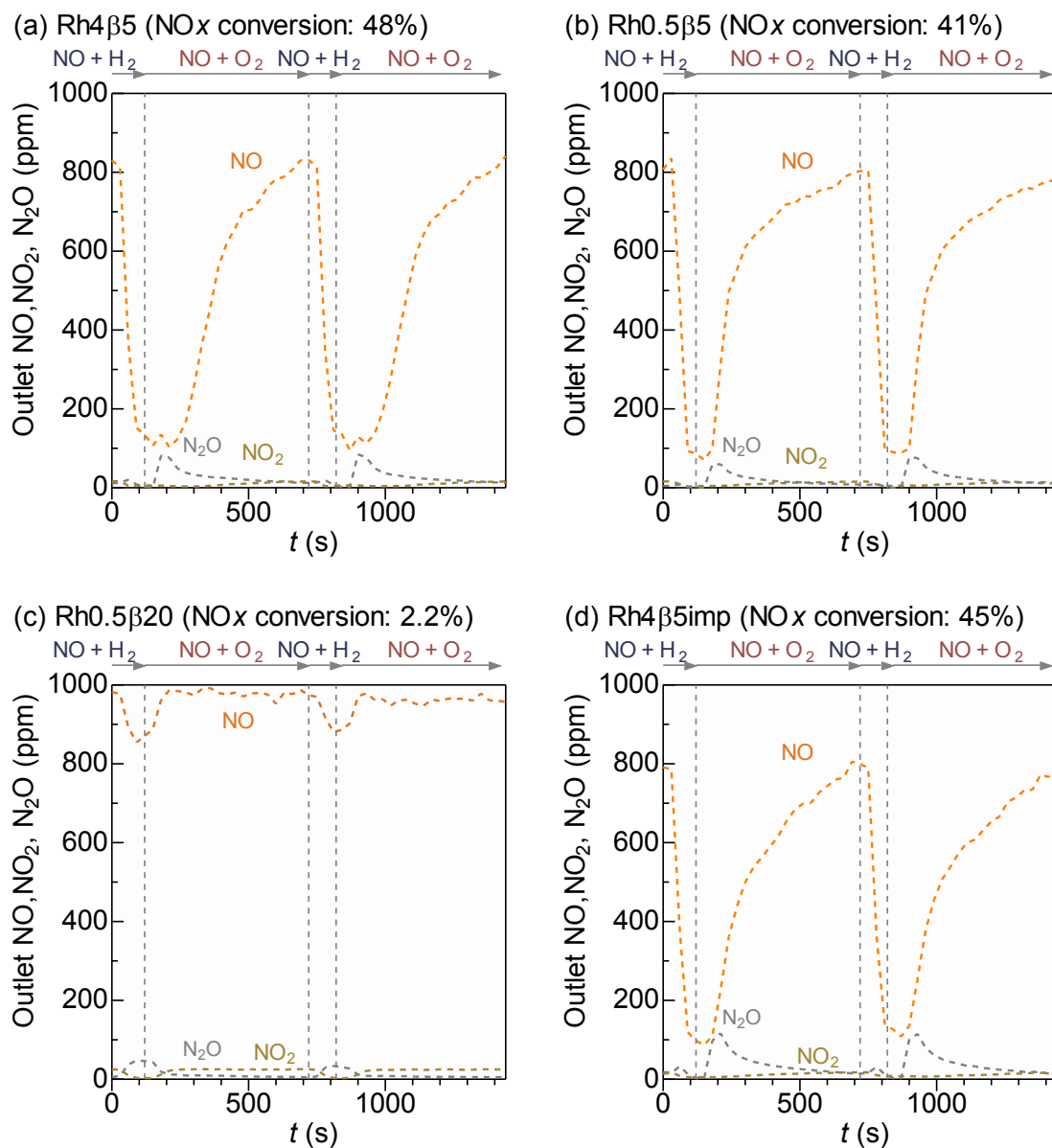


Figure 9. Concentration profile of NO, NO₂, and N₂O determined by infrared (gas cell) data under the periodic lean (0.1% NO+ 2% O₂; 600 s) and rich (0.1% NO + 2% H₂; 120 s) operations at 200 °C using various Rh-zeolite catalysts.

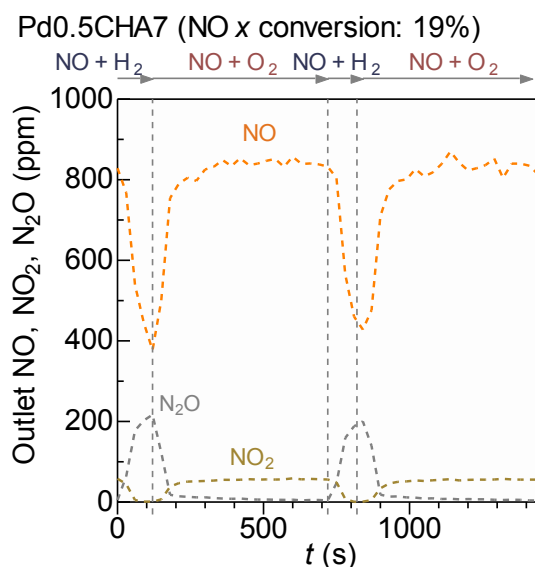
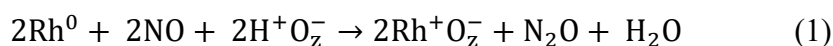
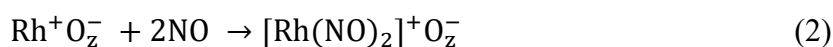


Figure 10. Concentration profile of NO, NO₂, and N₂O determined by infrared (gas cell) data under the periodic lean (0.1% NO + 2% O₂; 600 s) and rich (0.1% NO + 2% H₂; 120 s) operations at 200 °C using the Pd0.5CHA07 zeolite.

5.3.4 Investigation of the dynamic structural evolution of Rh species

0.6wt% Rh-loaded MOR zeolite (RhMOR) was pretreated by ion exchange using 0.002 M aqueous solution of RhCl₃, followed by calcination at 500°C and reduction under 2% H₂ flow at 200°C. Then, the sample was exposed to 0.1% NO flow at 200°C while recording IR spectra of adsorbed species by *operando* IR (more details of the used setup are shown in Figure S6). Figure 11a shows the IR spectra (left) and the time course of IR intensities of the observed ad-species together with the concentration of N₂O and NH₃ analyzed by the IR gas cell and mass spectrum (MS) intensity of N₂ (right). Initially (t = 90s), a peak at 1670 cm⁻¹ ascribed to the NO adsorbed on Rh⁰ sites of metal clusters (Rh⁰-NO) was observed^{113,114,118}. The peak intensity of Rh⁰-NO decreased with increasing NO

flow time, while the IR peaks at 1862 and 1786 cm^{-1} assignable to the $[\text{Rh}(\text{NO})_2]^+$ complexes increased^{89–91,119}. This indicated that the metallic Rh^0 species were oxidized by NO to afford isolated Rh^+ species ($[\text{Rh}(\text{NO})_2]^+$). Considering N_2O formation in the outlet gas during the initial period, the following schemes are the most likely reactions that account for the results in Figure 11a.



Initially, the metallic Rh species reacted with the BASs of the zeolite ($\text{H}^+\text{O}_\text{Z}^-$) and NO to afford Rh^+ cations at the anionic oxygen sites of the zeolite ($\text{Rh}^+\text{O}_\text{Z}^-$) as well as H_2O and N_2O (reaction 1). Then, two NO molecules were coordinated to the Rh^+ site to afford the $[\text{Rh}(\text{NO})_2]^+$ complex stabilized at the anionic oxygen site of the zeolite ($[\text{Rh}(\text{NO})_2]^+\text{O}_\text{Z}^-$; reaction 2).

For comparison, 2.4 mg of 10wt% Rh-loaded Al_2O_3 ($\text{Rh10Al}_2\text{O}_3$) and 37.6 mg of proton-type MOR zeolite (HMOR) were physically mixed and pelletized into 40 mg of IR disk (Rh loading amount of the mixture ($\text{Rh10Al}_2\text{O}_3 + \text{HMOR}$) is 0.6 wt%). The sample disk pre-reduced under 10% H_2 flow at 500°C, was exposed to NO at 200°C while monitoring IR spectra of adsorbed species. As shown in Figure 11b (left), a band due to $\text{Rh}^0\text{--NO}$ (1660 cm^{-1}) was observed and its maximum IR intensity was comparable to that of RhMOR, although the $\text{Rh}^0\text{--NO}$ did not decrease with increasing NO flow time (Figure 11b (right)). Broad IR bands at 1786 cm^{-1} and 1862 cm^{-1} , possibly corresponding to $[\text{Rh}(\text{NO})_2]^+$ complex, were observed while its IR intensity was very weak and the complex did not increase under NO flow. An online analysis of the components in the outlet gas (Figure 11b (right)) showed that the formation rates of N_2 and N_2O over the

Rh10Al₂O₃ + HMOR mixture were much higher than those over RhMOR.

To explore the dynamic structural changes of the Rh species in RhMOR, an *in situ* XAS measurement was conducted. Figure 12 (left) shows the Rh K-edge spectra obtained through X-ray absorption near edge structure (XANES) of RhMOR, along with the spectra of the reference compounds recorded under ambient conditions (the spectra in a wider range are shown in Figure S7). The absorption edge of the RhMOR calcined under a flow of 10% O₂ at 500°C (as-calcined RhMOR) was close to that of the reference compound, Rh(III) oxides (Rh₂O₃). After He purge and the following 2% H₂ treatment at 200°C, the absorption edge of the RhMOR shifted to lower energy and reached the energy of Rh foil (reference compound of Rh metal). When the H₂-reduced RhMOR was subjected to a flow of 0.1% NO, the absorption edge shifted to higher energy and reached the energy of Rh(CO)₂(acac) (reference compound of Rh(I) complexes). Figure S7 and S3 show that the white line intensity of the NO-treated sample becomes higher than that of the H₂-reduced sample (before the NO treatment), indicating that Rh species in the NO-treated sample have more oxidic states^{45,120}. Figure 13 shows the evolution of the XANES spectra of RhMOR (top) and the change in energy at 0.5 of normalized $\chi\mu(E)$ (norm. $\chi\mu(E)$) as a function of the exposure time (bottom; the spectra in a wider range are shown in Figure S8)¹²¹. NO treatment of the H₂-reduced RhMOR resulted in a gradual shift in the edge energy (Figure 13a (bottom)). These results indicate that the Rh species were oxidized by NO into Rh⁺ species. After He purges, RhMOR was further subjected to a flow of 2% H₂ while recording the XANES spectra (Figure 13b (top)). The energy at 0.5 of the norm. $\chi\mu(E)$ (Figure 13b (bottom)) decreased rapidly with increasing time of H₂ flow. Note that the adsorption edge shifted toward lower energy than that of Rh metal,

possibly due to the presence of Rh–H species.^{30,122}

This indicates that the $[\text{Rh}(\text{NO})_2]^+$ species were reduced to the Rh^0 species, which is consistent with the *operando* IR results (Figure 11).

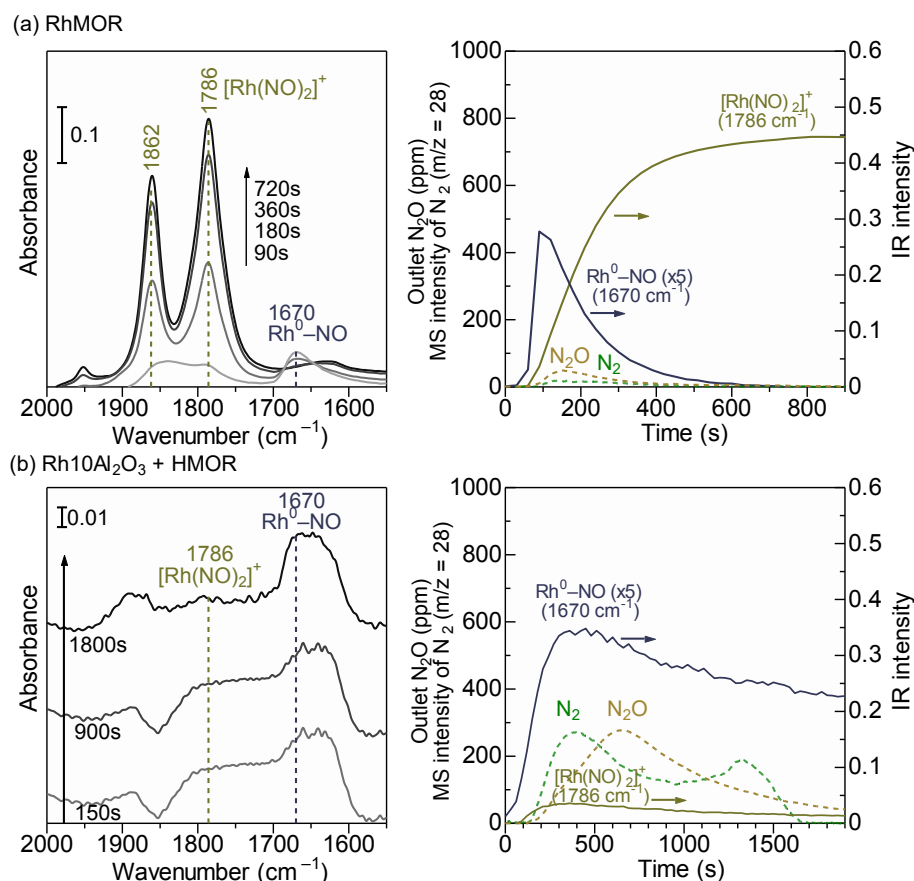


Figure 11 *operando* IR spectra (left) of adsorbed species under flowing 0.1% NO at 200°C on (a) RhMOR, pre-reduced by 2% H₂ at 200°C and (b) physical mixture of Rh10Al₂O₃ and HMOR (Rh loading of the mixture = 0.6wt%), pre-reduced by 10% H₂ at 500°C. The time course of IR intensities as well as concentrations of outlet N₂O and NH₃ analyzed by an IR gas cell and MS intensity of N₂ ($m/z = 28$, right). The times courses of IR intensities and gaseous components (analyzed by gas cell and MS) were described by solid and dashed lines, respectively.

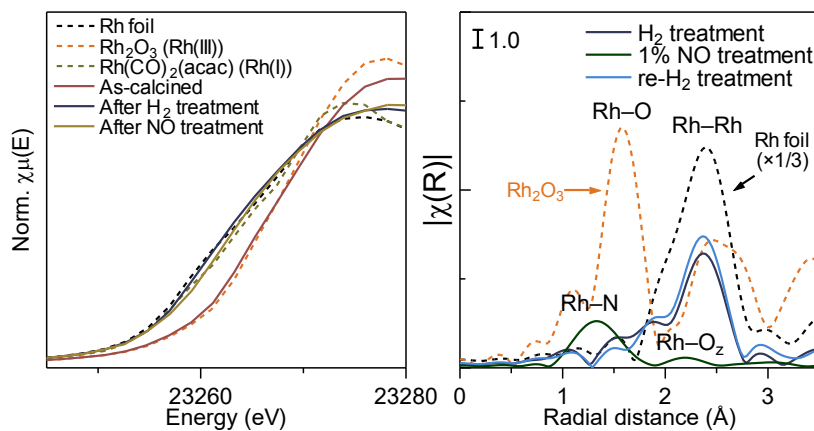


Figure 12 *In situ* Rh K-edge XANES (left) and EXAFS Fourier transforms (right) of RhMOR under different conditions and *ex situ* spectra of reference Rh compounds measured at room temperature. As-calcined RhMOR (red) was successively exposed to 2% H_2 (blue), 0.1% NO (dark yellow), 1% NO (dark green), and 2% H_2 (light blue) at 200°C.

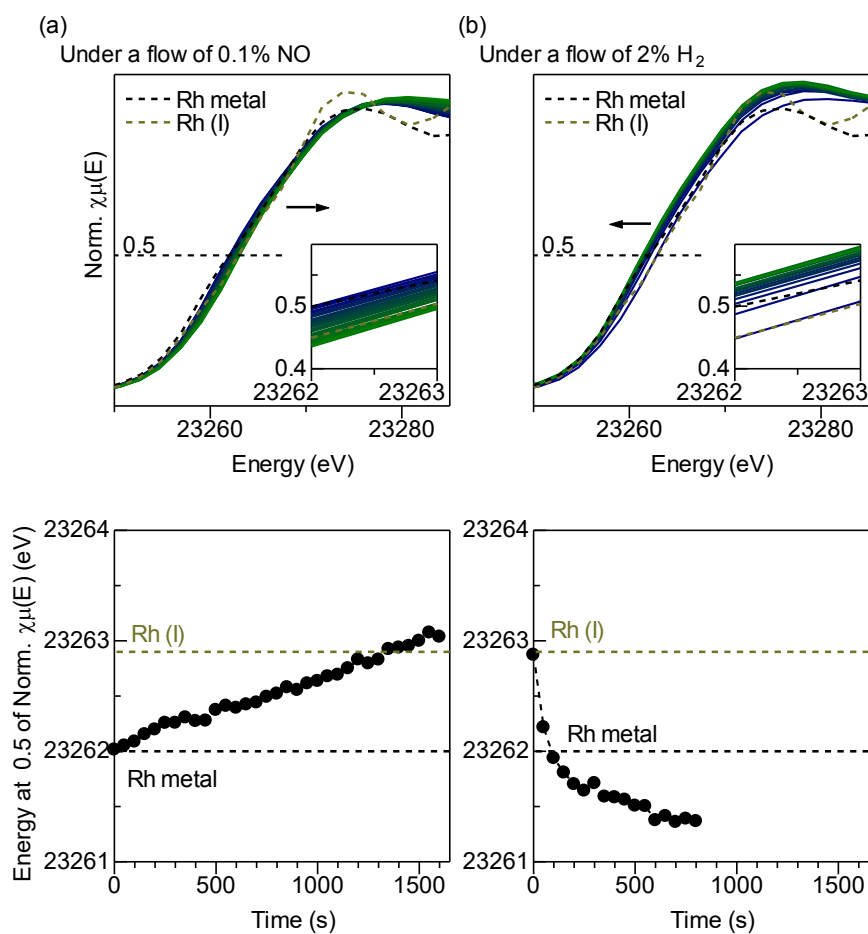


Figure 13 Evolution of Rh K-edge XANES spectra (top) of RhMOR for each 100 s, pre-reduced by 2% H₂ at 200°C, and changes in the energy for the normalized $\chi\mu(E)$ of 0.5 (bottom) during successive feed of (a) 0.1% NO (1700 s) and (b) 2% H₂ (800 s) at 200°C. The reaction gas was purged by He before each transient experiment. The spectra of Rh(CO)₂(acac) and Rh foil are shown together as references for Rh(I) and Rh metal species

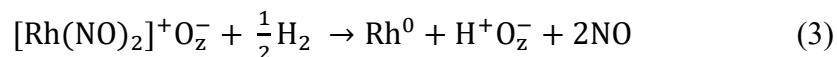
Table 2. Curve-fitting analysis of *in situ* Rh K-edge EXAFS for RhMOR and Rh10Al₂O₃ at 200°C.

Sample/Condition	Shell	CN ^a	R / Å ^b	σ^2 / Å ² ^c	R- factor
RhMOR					
H ₂ -reduced	Rh–O	1.4 ±	2.11 ±	0.00751 ±	0.009
		0.80	0.044	0.0060	
	Rh–Rh	3.8 ±	2.65 ±	0.00774 ±	
		0.80	0.008	0.0012	
NO-treated	Rh–N	1.0 ±	1.79 ±	0.00057 ±	0.026
		0.44	0.038	0.0027	
	Rh–O _z ^d	0.4 ±	2.29 ±	0.00241 ±	
		0.50	0.071	0.0098	
H ₂ -reduced aft. NO treatment	Rh–Rh	4.2 ±	2.64 ±	0.00730 ±	0.022
		0.71	0.007	0.0010	
Rh10Al ₂ O ₃					
NO-treated	Rh–Rh	8.4 ±	2.66 ±	0.00821 ±	0.006
		0.52	0.003	0.0003	
	Rh–O	2.1 ±	2.01 ±	0.00810 ±	0.010
		0.66	0.025	0.0029	
	Rh–Rh	4.8 ±	2.66 ±	0.00853 ±	
		0.62	0.005	0.0007	
Rh ₂ O ₃ ^e	Rh–O	6	2.07	-	-
	Rh–O–Rh	3	3.09	-	-
Rh foil ^e	Rh–Rh	12	2.72	-	-

^a Coordination number. ^b Bond distance. ^c Debye-Waller factor. ^d Oxygen atom of zeolite framework. ^e Crystallographic data of Rh₂O₃ and Rh metal.

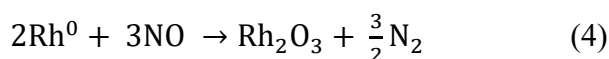
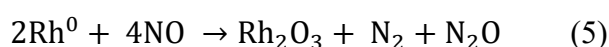
The Fourier transforms (FTs) of the k^3 -weighted Rh K-edge extended X-ray absorption fine structure (EXAFS oscillations with the result of fitting and their imaginary parts are shown in Figure S9 and S10, respectively) are shown in Figure 12 (right), and the results of the curve-fitting analysis are summarized in Table 2. The H₂-reduced RhMOR shows an Rh–O shell ($R = 2.11 \text{ \AA}$) with CN of 1.4 and an Rh–Rh shell ($2.65 \text{ \AA}$) with CN of 3.8, indicating the co-presence of small Rh metal clusters and Rh_xO_y species in the zeolite.^{43,123} Exposure of the reduced sample to 0.1% NO significantly decreased the CN of the Rh–Rh shell. The concentration of NO was subsequently increased to 1% to improve the quality of EXAFS (Figure 12 (right)). Curve-fitting analysis for 1%NO-treated RhMOR using DFT optimized structure of [Rh(NO)₂]⁺ in MOR zeolite as a reference shows CN of 1.0 for Rh–N bond ($1.79 \text{ \AA}$) and CN of 0.4 for Rh–O_z (oxygen atom of zeolite framework) bond ($2.29 \text{ \AA}$)³⁴. These EXAFS features are similar to those of the [Rh(NO₂)]⁺ species in zeolites as previously reported by Konstantin et al.³⁴, although the values of CN are relatively small because of the difference in measuring temperature (200°C and liquid nitrogen temperature). Figure S9b displays EXAFS oscillation of NO-treated RhMOR and Rh(NO₃)₃-loaded SiO₂ (mainly showing the contribution of Rh–O bond on EXAFS Fourier transforms), showing different features of their EXAFS spectra. The EXAFS results suggested the reaction of small Rh metal clusters with NO to afford the dispersed Rh species (probably [Rh(NO)₂]⁺ species) in the zeolite. To confirm the reversibility of the process, the NO-treated RhMOR was exposed to a flow of 2% H₂. The H₂-reduction of the NO-treated RhMOR resulted in the disappearance of the Rh–N shell (Figure 12 (right)) and the appearance of the Rh–Rh shell ($R = 2.64$, CN = 4.2). The EXAFS results confirm the reversibility of the reductive

aggregation/oxidative dispersion process. Combined with the IR (Figure 11) and XANES results, the reductive aggregation $[\text{Rh}(\text{NO})_2]^+$ species in the zeolite can be described by the following reaction (3):



A more detailed mechanism is discussed in the following section based on the results of *operando* IR and DFT calculations.

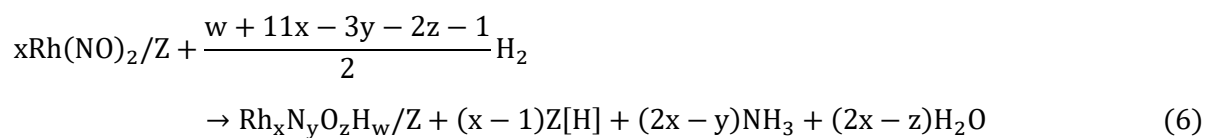
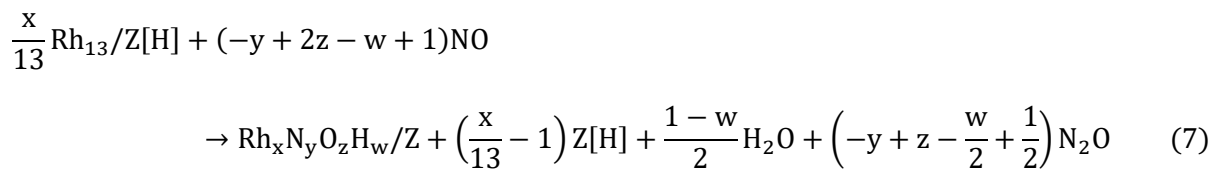
To discuss the effect of the zeolitic anion sites (i.e., Al sites) on the reversible structural changes in the Rh species, the same *in situ* XAS measurements were performed for Rh10Al₂O₃. After the H₂-reduction of Rh10Al₂O₃ at 200°C, the absorption edge was located at similar energy to the Rh foil (Figure S7). By the subsequent oxidation by NO + O₂ flow, the edge position shifted to a higher position than that of the reference Rh₂O₃. Curve-fitting analysis (Table 2) of EXAFS (Figure S12) showed an Rh–Rh bond at 2.66 Å with a CN of 8.4, indicating the presence of Rh metal particles on the Al₂O₃ support (EXAFS oscillations with the result of fitting are shown in Figure S13).¹²⁴ When the H₂-reduced Rh10Al₂O₃ was exposed to 0.1% NO (Figure S11a (top)), the absorption edge shifted to higher energy and reached a similar value to Rh₂O₃ (Figure S11a (bottom)), which indicates that Rh metal species were oxidized by NO. Curve-fitting analysis of EXAFS of the NO-treated Rh10Al₂O₃ showed an Rh–O bond (CN = 2.1, R = 2.01 Å). Considering the results in Figure 11b, reactions (4) and (5) account for the oxidation of the Rh metal particles on Al₂O₃ to Rh₂O₃.



A comparison of the RhMOR results indicates that the zeolite, probably a cation exchange site (H^+O_2^-) of the zeolite, is indispensable for the reaction of Rh metal with NO to form $[\text{Rh}(\text{NO})_2]^+$ complexes. The Rh_2O_3 species on NO-treated $\text{Rh10Al}_2\text{O}_3$ was gradually reduced to metallic Rh under H_2 (Figure S11b), although the rate of reduction was lower than that for NO-treated RhMOR. This indicates that the Rh_2O_3 species on $\text{Rh10Al}_2\text{O}_3$ was less reducible than that on RhMOR.

5.3.5 *Ab initio* thermodynamics analysis for Rh species under oxidative/reductive conditions

To gain thermodynamic insight into the reductive aggregation/oxidative dispersion of Rh species in zeolite, *ab initio* thermodynamic analysis was performed to compute the phase diagrams.^{115,125–128} The thermodynamic stabilities of plausible Rh species under experimental conditions were theoretically assessed in terms of Gibbs free energy (ΔG). Equilibrium reactions (6) and (7) were considered for reductive and oxidative conditions, respectively.



The T4 site of the MOR framework, generally regarded as a preferable Al replacement site facing the 12 membered-ring, was used as a representative Al site.^{107,108} The definition

of the Gibbs free energy (ΔG) of Rh species and the chemical potentials of gaseous molecules can be found in the SI. For the isolated Rh species, a bare Rh^+ cation ($\text{Z}[\text{Rh}]$), mononitrosyl Rh cation ($\text{Z}[\text{Rh}(\text{NO})]$), and dinitrosyl Rh cation ($\text{Z}[\text{Rh}(\text{NO})_2]$) were considered. An Rh_{13} cluster weakly bound to BAS ($\text{Rh}_{13}/\text{Z}[\text{H}]$) was considered a representative metallic Rh cluster while the Rh_6 cluster ($\text{Rh}_6/\text{Z}[\text{H}]$) was also considered a relatively small Rh cluster.⁴³ In this study, the icosahedral shape, which was determined the most stable and reactive with NO ^{129,130}, was adopted for the Rh metal cluster. All used models are provided in the xyz format (see SI). Figure 14(left) shows the phase diagram as a function of the partial pressure of H_2 (p_{H_2}) and temperature. The diagram for reductive conditions shows that $\text{Rh}_{13}/\text{Z}[\text{H}]$ is the most stable species among the examined structures, whereas $\text{Rh}_6/\text{Z}[\text{H}]$ is less stable. The average Rh–Rh bond length for $\text{Rh}_{13}/\text{Z}[\text{H}]$ (2.64 Å) was closer to the experimental value (2.65 Å) of H_2 -reduced RhMOR (Table 2) than that of $\text{Rh}_6/\text{Z}[\text{H}]$ (2.53 Å). These results indicate that $\text{Rh}_{13}/\text{Z}[\text{H}]$ is a plausible structure for the metallic Rh species under H_2 . Figure 14(right) shows the phase diagram as a function of the partial pressure of NO (p_{NO}) and temperature. In the presence of NO below 600 K, $\text{Z}[\text{Rh}(\text{NO})_2]$ is the most stable species. It is also the most stable under the experimental conditions for *operando* IR and EXAFS ($\log(p_{\text{NO}}) = -3$ and $T = 473$ K), where the experimental results show that $[\text{Rh}(\text{NO})_2]^+$ is the dominant Rh species under NO . By increasing temperature along with $\log(p_{\text{NO}}) = -3$, the most stable species is shown to be $\text{Z}[\text{Rh}(\text{NO})]$, followed by $\text{Z}[\text{Rh}]$. Under low p_{NO} ($\log(p_{\text{NO}}) < -4$) at high temperatures (> 800 K), the thermal reduction of Rh(I) species results in the formation of $\text{Rh}_{13}/\text{Z}[\text{H}]$. These results indicate that the small Rh metal cluster and $\text{Z}[\text{Rh}(\text{NO})_2]$ species are the

most plausible species under H_2 and NO, respectively, which is consistent with the experimental results at 200°C.

For comparison, a phase diagram of bulk Rh metal and Rh_2O_3 (in the absence of zeolite) is shown in Figure 15 as a function of p_{NO} and temperature (details can be found in the SI). The results show that bulk Rh_2O_3 is the most stable Rh species under NO below 800 K, which is consistent with the results of *in situ* XAS (Figure S11); the Rh species was overoxidized owing to the absence of proper anchoring sites (i.e., Al sites in zeolite). The results of the phase diagram calculations indicate that the driving force for reversible structural evolution under H_2 and NO is the thermodynamic stability of the Rh species in the zeolite cage.

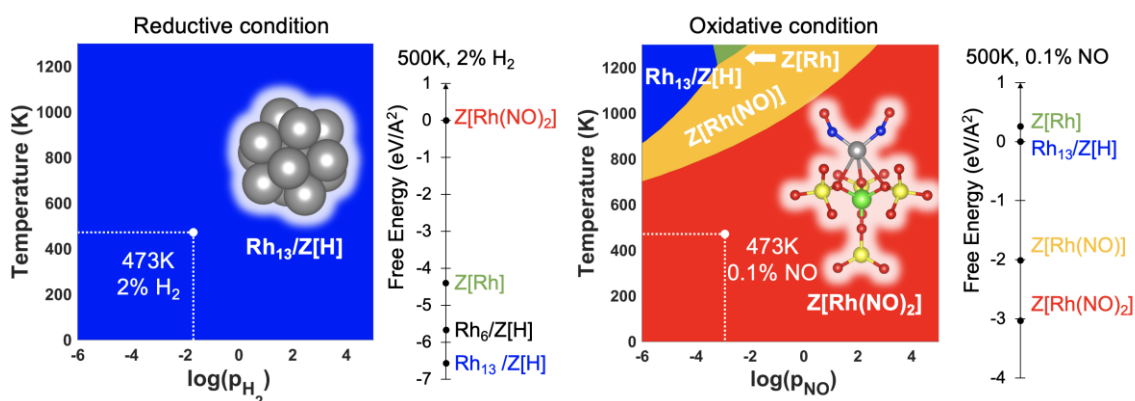


Figure 14. Calculated phase diagrams showing the most stable Rh species as a function of partial pressures of H_2 (left) and NO (right) ($\log(p_{H_2})$ as well as $\log(p_{NO})$) and temperature. Relative Gibbs free energies (ΔG) of the examined Rh species on Al site (denoted as Z) at 2% H_2 and 0.1% NO are shown together ($T = 500$ K). The representative structures (visualized by VESTA¹¹¹) are shown in the figures. Green: Al, Red: O, Blue: N, Gray: Rh, Yellow: Si. Only atoms around Z are shown for clarity.

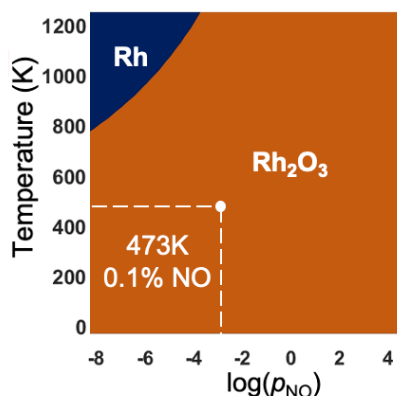
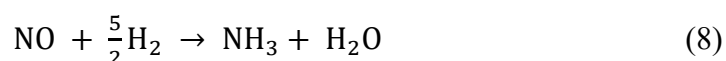


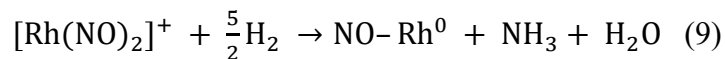
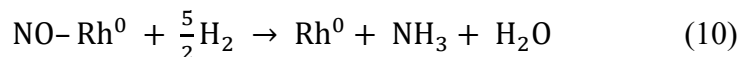
Figure 15. Calculated phase diagram showing the most stable Rh species among bulk Rh metal and Rh_2O_3 as a function of NO partial pressure ($\log(p_{\text{NO}})$) and temperature.

5.3.6 NH_3 formation from NO and H_2 on Rh^+ cation and Rh metal cluster

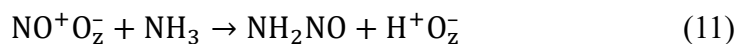
NO capture by RhMOR under lean conditions and the subsequent reduction of the captured NO into NH_3 under rich conditions were experimentally explored by *in situ* IR at 200°C (more details can be found in the SI). The H_2 -reduced RhMOR was exposed to a flow of 0.1% NO + 2% O_2 followed by He purging, and the sample was subjected to a flow of 2% H_2 (Figure 16 (left)). On the IR spectrum at 0 s (i.e., before the exposure to 2% H_2 flow), two IR bands at 1785 and 1860 cm^{-1} assignable to $[\text{Rh}(\text{NO})_2]^+$ species were observed, indicating that the NO was captured as $[\text{Rh}(\text{NO})_2]^+$ species even in the presence of excess O_2 . When the sample was subjected to a flow of 2% H_2 , the IR intensity of $[\text{Rh}(\text{NO})_2]^+$ rapidly decreased, while IR bands attributed to NH_3 adsorbed on Brønsted acid sites ($\text{B}-\text{NH}_3$) appeared at 1433 cm^{-1} ^{113,114}. This observation can be explained by the reductive aggregation of (reaction (3)), followed by the reduction of NO to NH_3 by the Rh sites (reaction (8)).¹³¹



Considering the formation of the NO–Rh⁰ species (1660 cm⁻¹) under H₂ (Figure 16), an alternative pathway is a reaction of [Rh(NO)₂]⁺ with H₂ to yield NO–Rh⁰ and NH₃ (reaction (9)), followed by the reduction of NO–Rh⁰ by H₂ to yield NH₃ (reaction (10)).



After He purge, the IR disk was further exposed to a flow of 0.1% NO + 2% O₂. As shown in Figure 16 (bottom), the regeneration of [Rh(NO)₂]⁺ complexes and consumption of B–NH₃ were observed by IR, and N₂ formation was confirmed by mass spectrometry, indicating the re-dispersion of Rh species (reaction (1)) as well as the reduction of NO by NH₃ on the Brønsted acid site (H⁺OZ⁻), where NO⁺OZ⁻, which further reacts with NH₃ to afford N₂ via catalyst-free decomposition of NH₂NO, forms with a low barrier (E_a = 38 kJ/mol; reaction (11) and (12)).¹³²



Summarizing the above discussions, a mechanism for lean deNO_x under lean/rich cycles is shown in Figure 17, in combination with the dynamic structural changes in the Rh sites. The de-NO_x performance of the catalysts was examined under periodic lean/rich conditions. The lean gas (0.1% NO + 2% O₂; 120s) and rich gas (0.1% NO + 2% H₂; 60s) were repeatedly fed and the outlet gas was analyzed by IR equipped with a gas cell (detailed explanation is in SI). After the cycling experiment shown in Figure 18, RhMOR exhibited approximately 60% of NO_x conversion above 200°C, demonstrating its

capability of NO capture and subsequent reduction under practical lean/rich conditions. $[\text{Rh}(\text{NO})_2]^{2+}$, which can work as NO capturing site under lean conditions, was scarcely observed over $\text{Rh10Al}_2\text{O}_3$ under NO flow (Figure 1b). This result implies that $\text{Rh10Al}_2\text{O}_3$ is not workable under periodic lean/rich conditions due to the absence of NO capturing site. The NH_3 formation route was not experimentally verified; thus, we carried out a theoretical study on the NH_3 formation pathways in the following section.

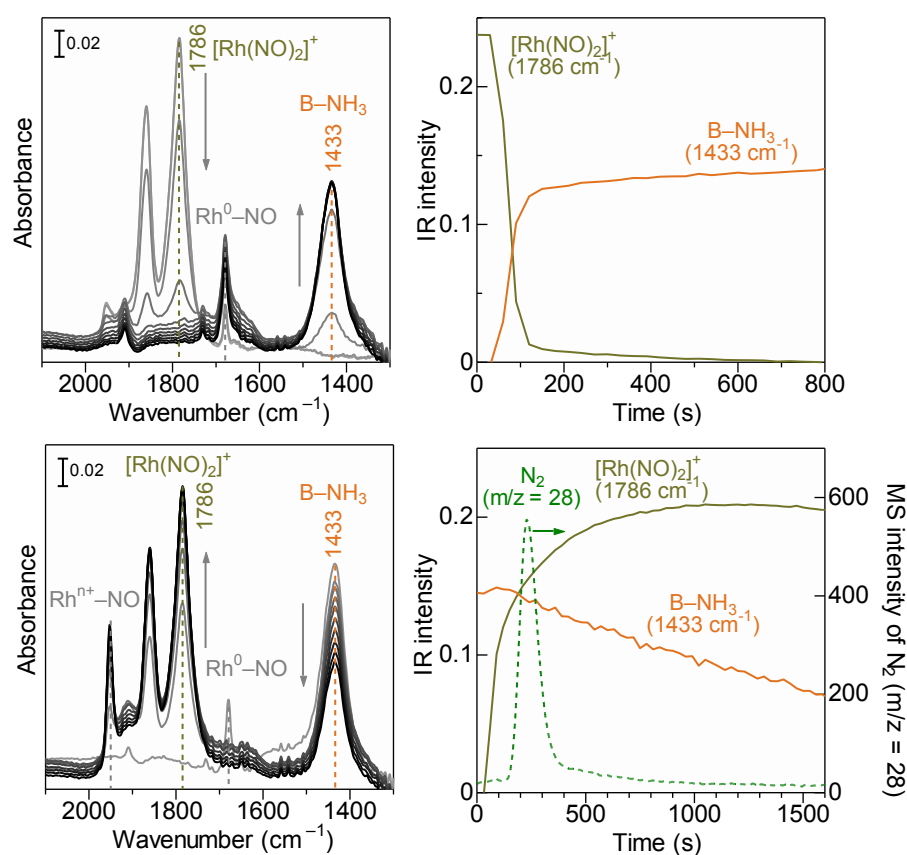


Figure 16 In situ IR spectra of NO_x species adsorbed on RhMOR (left) pre-exposed to a flow of 2% H_2 (top) and subsequent a flow of $\text{NO} + \text{O}_2$ (bottom). Time dependence of IR intensity of surface species and MS intensity of N_2 (right)

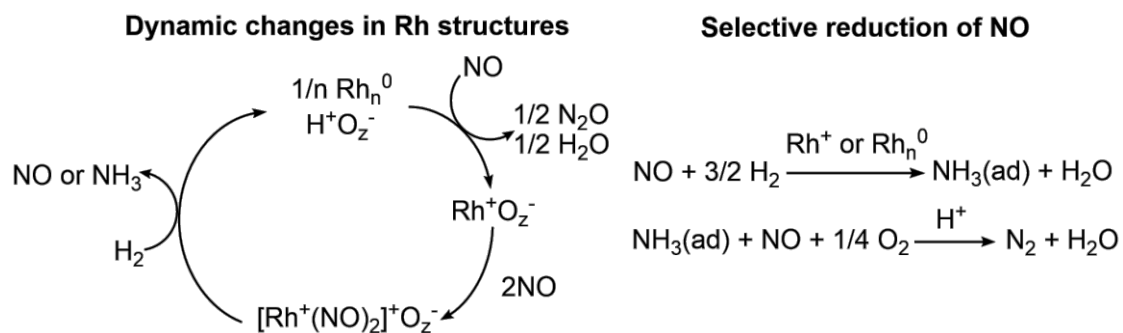


Figure 17. Dynamic structural changes in Rh sites in zeolite and selective reduction of adsorbed NO by H₂ via NH₃.

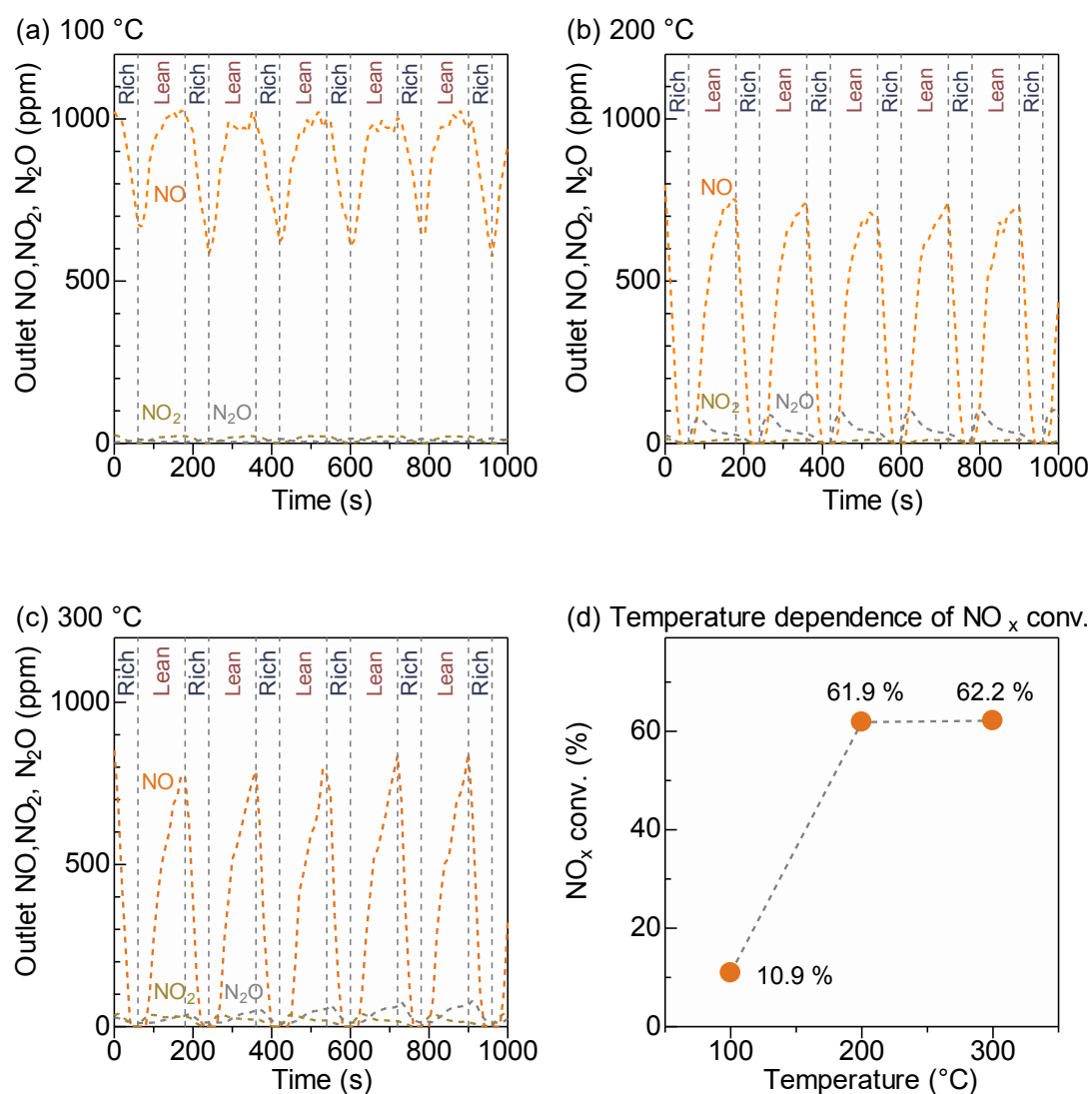


Figure 18. Concentration profile of NO, NO₂, and N₂O, determined by infrared (gas cell) data under the periodic lean (0.1% NO + 2% O₂; 120 s) and rich (0.1% NO + 2% H₂; 60 s) operations at (a) 100, (b) 200, and (c) 300 °C using the RhMOR catalyst (total flow: 100 ml/min, He balance). (d) Temperature dependence of NO_x conversion.

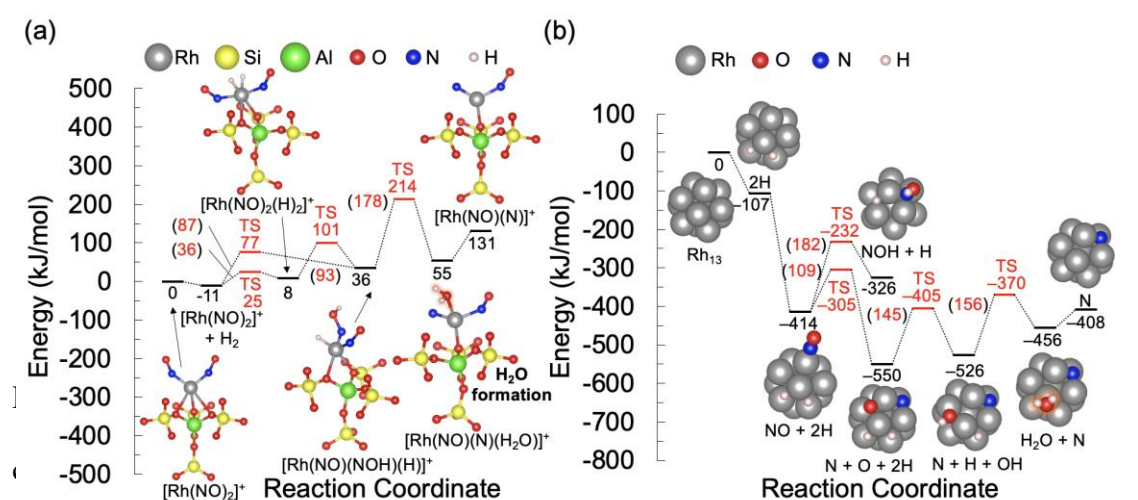
5.3.7. Transition state calculation for selective reduction of NO toward NH₃

Transition state calculations were carried out to theoretically verify the reaction mechanism of NH₃ formation by H₂-reduction of the [Rh(NO)₂]⁺ complex or NO ad-species on the Rh₁₃ cluster. Figure 19a shows the energy profile for the H₂-reduction of one NO molecule in [Rh(NO)₂]⁺ to yield an N atom and an H₂O molecule on the Rh⁺ site. First, an H₂ molecule is weakly adsorbed on the [Rh(NO)₂]⁺ complex, and then H₂ dissociation occurs with an activation barrier (E_a) of 36 kJ/mol to give a [Rh(NO)₂(H)₂]⁺ complex. One of the dissociated H atoms transfers to the O atom of the NO molecule to give a [Rh(NO)(NOH)(H)]⁺ intermediate (E_a = 93 kJ/mol). An alternative route via the direct formation of the [Rh(NO)(NOH)(H)]⁺ intermediate through H₂ dissociation between an Rh atom and the O atom of the NO molecule was also assessed, and the E_a value (87 kJ/mol) of the direct route was comparable to that of the stepwise process. The OH group formed in the NOH fragment then interacted with the H atom on the Rh⁺ site to afford an H₂O molecule and an N atom on the Rh⁺ site ([Rh(NO)(N)(H₂O)]⁺). This process exhibited a high E_a value (178 kJ/mol). Finally, a [Rh(NO)(N)]⁺ intermediate was formed by desorption of the H₂O molecule. Figure 20a shows the hydrogenation process of the N atom in the [Rh(NO)(N)]⁺ intermediate to produce the NH₃ molecule. Note that TS calculations were not conducted here because every step in the hydrogenation process is a highly exothermic reaction. This indicates that once the N atom was formed on the Rh cation, NH₃ formation by H₂ occurred easily; in contrast, the formation of N₂O on the Rh cation ([Rh(N₂O)]⁺) from the [Rh(NO)(N)]⁺ intermediate was highly endothermic (363 kJ/mol). This result indicates that N₂O formation is energetically unfavorable in this process. The [Rh(NO)(H)] intermediate was converted to a Rh(NO) neutral species via a

barrierless route with 47 kJ/mol of endothermicity (Figure S14), implying that a portion of the isolated Rh species was converted into neutral Rh(NO) species toward the formation of Rh metal cluster.

The reaction coordinates for the H₂-reduction of the NO ad-species on the Rh₁₃ cluster were also explored (Figure 19b). Since the considered Rh₁₃ cluster is smaller than the pore size of MOR zeolite, the TS calculations of the Rh₁₃ cluster were performed in a large cubic cell (25 Å) without the zeolite structure to reduce computational costs. Similar to the case of isolated Rh cations, the dissociative adsorption of H₂ molecules was calculated to be a barrierless reaction. After NO adsorption, the reaction of H with NO can occur via two possible pathways: (i) the reaction of H with NO to provide NOH species, and (ii) the dissociation of NO, followed by the reaction of N and O atoms with H atoms. The calculation results show that the latter route ($E_a = 109$ kJ/mol) occurs more frequently than the former ($E_a = 182$ kJ/mol). Sasaki and co-workers reported that the higher energy of the 4d band center of the smaller Rh cluster is more favorable for NO dissociation, which is in agreement with our result of the facile dissociation of NO molecules on the Rh₁₃ cluster. Thus, the O atom reacted with two H atoms to give H₂O molecules in two steps with E_a values of 145 and 156 kJ/mol. Next, the remaining N atom was hydrogenated in a stepwise manner to provide NH₃ with 180 kJ/mol of exothermicity (Figure 20b). In this process, the formation of NH + H from N + 2H resulted in the highest E_a (129 kJ/mol). In addition, the formation of N₂O and N₂ were examined (Figure 21a and b, respectively). The calculated endothermicity for N₂O formation (206 kJ/mol) and E_a values for N₂ (254 kJ/mol) formation were higher than those for NH₃ formation (129 kJ/mol). The above theoretical study shows that the highest E_a for the Rh₁₃ cluster (156

kJ/mol) is slightly lower than that for isolated Rh species (178 kJ/mol), suggesting that the Rh₁₃ cluster is a more plausible active site for selective NH₃ formation under NO + H₂ flow. Combined with the experimental results, the roles of isolated Rh⁺ species and Rh metal clusters under lean/rich conditions can be proposed: the isolated Rh⁺ sites act as NO-capturing sites under lean (NO + O₂) conditions, and Rh metal clusters act as NH₃ formation sites under rich (NO + H₂) conditions.



clarity. Black and red values are relative energies of each optimized structure and transition state, respectively. The values in brackets show activation barrier of each elementary step. (Unit: kJ/mol)

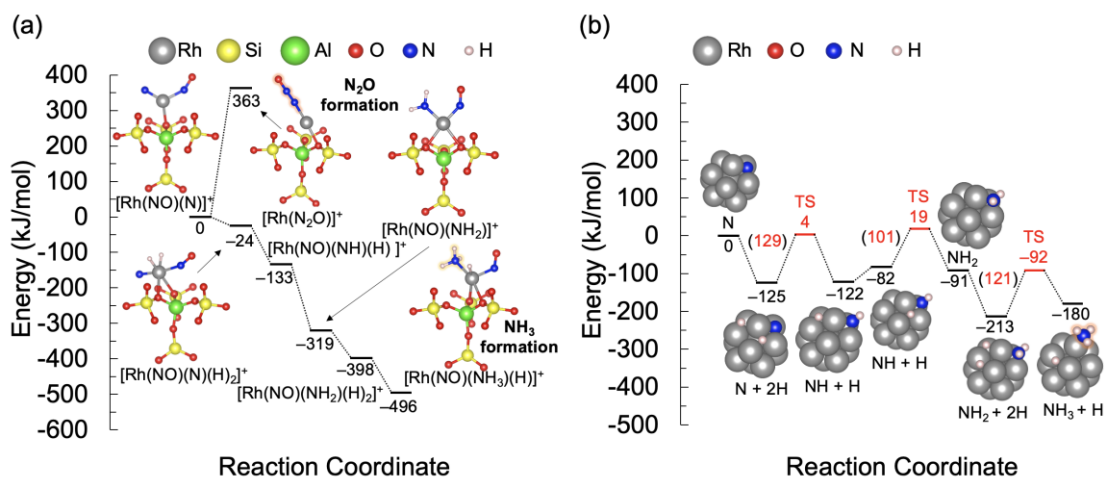


Figure 20 Energy profiles for the hydrogenation of N atom on (a) Rh⁺ site and (b) Rh₁₃ cluster. For the model of Rh⁺ site, only atoms around the Rh species are shown for clarity. Black and red values are relative energies of each optimized structure and transition state, respectively. The values in brackets show activation barrier of each elementary step. (Unit: kJ/mol).

Figure 21 Energy profiles for the formation of (a) N₂O and (b) N₂ over Rh₁₃ cluster. Black and red values are relative energies of each optimized structure and transition state, respectively. The values in brackets show activation barrier of each elementary step. (Unit: kJ/mol).

5.4 Conclusion

To rationally design the new de-NO_x system (an “active” NO_x adsorber) workable under periodic lean (NO + O₂) and rich (NO + H₂) cycle conditions, we studied transient reactions over an Rh-loaded Al-rich β zeolite. The structural results indicate that a part of the H⁺ sites in the β zeolite is exchanged by Rhⁿ⁺, which is subsequently reduced using H₂ to the Rh⁺ and Rh⁰ metal sites. Under lean (NO + O₂) conditions, the Rh⁺ site captures NO in the form of [Rh(NO)₂]⁺ over a wide temperature range (100–400 °C), while the coexisting Rh⁰ metal sites have low NO storage capacity. The NO captured by the oxidized Rh cation, which is stable under oxidative (lean) conditions, is reduced by H₂ above 200 °C to afford NH₃ in preference to N₂ and N₂O over a wide temperature range (200–500 °C). The *in situ*-generated NH₃ was captured by Brønsted acid sites (NH₃ storage sites). When the NH₃-captured catalyst is switched to a lean (NO + O₂) condition, the captured NH₃ acts as a reductant for the selective reduction of NO to N₂. NO_x reduction was applied to the system under periodic lean (NO + O₂) and rich (NO + H₂) cycle conditions. The NO_x trapped on the catalyst in the lean period was selectively reduced to NH₃ on the same catalyst during the rich period. The trapped NH₃ is stored, and it is used to selectively reduce NO to N₂ in the next lean period. Our results demonstrate a new de-NO_x system that utilizes an “active” NO_x adsorber in which the adsorbed NO is not desorbed; however, it is directly reduced to and stored as NH₃ under rich conditions. The cooperation of NO storage sites (isolated Rh⁺ ions) and NH₃ storage sites (Brønsted acid sites) is key to new de-NO_x catalysis under periodic lean/rich conditions. The dynamic structural evolution of Rh species in MOR zeolite was investigated by *in situ/operando* spectroscopy (IR and XAS) and DFT calculations, and

the following conclusions were drawn. Under NO flow, metallic Rh species are oxidized and dispersed into $[\text{Rh}(\text{NO})_2]^+$ species at the Al sites in the zeolite, which thermodynamically stabilizes the isolated Rh^+ species and thus prevents their overoxidation to Rh_2O_3 . The isolated Rh complexes are reduced/aggregated to small Rh clusters under subsequent flow of H_2 . The calculated phase diagram theoretically identified $[\text{Rh}(\text{NO})_2]^+$ and $\text{Rh}_{13}/\text{Z}[\text{H}]$ species as the plausible Rh species under NO and H_2 at 200°C . This system is applicable to unsteady-state de-NO_x under periodic lean-rich cycles via an NH_3 intermediate. Under lean ($\text{NO} + \text{O}_2$) conditions, NO is captured as a $[\text{Rh}(\text{NO})_2]^+$ complex, which is reduced by H_2 to afford adsorbed NH_3 and Rh metal clusters under rich conditions. The $[\text{Rh}(\text{NO})_2]^+$ complexes are regenerated by the subsequent exposure of the reduced catalyst to $\text{NO} + \text{O}_2$, accompanied by the selective reduction of NO by the adsorbed NH_3 to form N_2 . Transition state calculations show the activation barrier for NO reduction to NH_3 on $[\text{Rh}(\text{NO})_2]^+$ (178 kJ/mol) is higher than that on Rh_{13} (156 kJ/mol), suggesting that Rh metal clusters are preferable NH_3 formation sites. The reaction of NO adsorbed by H atoms on Rh_{13} to produce N atoms and H_2O is a rate-limiting step. NH_3 formation from the surface N and H atoms has a lower barrier than the N_2O and N_2 formation pathways, which accounts for the negligible formation of N_2O and N_2 under NO. The reversible dynamic structural evolution of the Rh species, $[\text{Rh}(\text{NO})_2]^+ \leftrightarrow \text{Rh metal clusters}$, under lean and rich conditions, is a key mechanistic feature for unsteady-state de-NO_x via NO capture by Rh^+ sites, selective reduction of NO to afford adsorbed NH_3 on Rh metal clusters, and selective reduction of NO with adsorbed NH_3 on zeolite.

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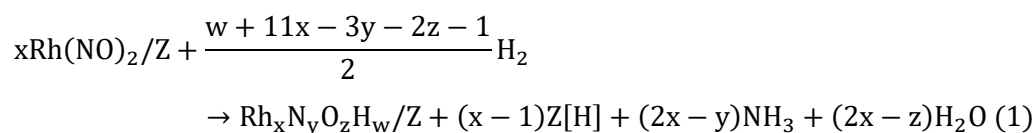
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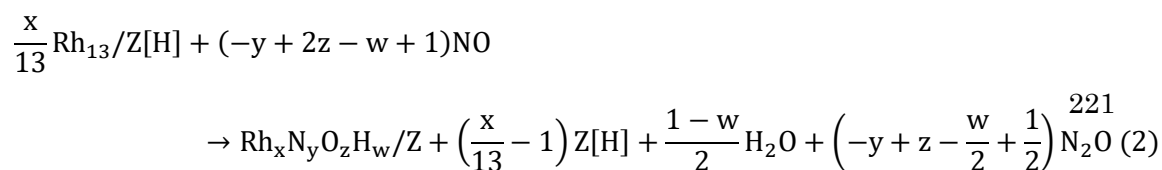
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Ab initio thermodynamic analysis was performed to consider the effect of partial pressure of H₂ and NO as well as temperature on Rh species in MOR zeolites. Enthalpies and entropies at each temperature and at the standard state pressure (0.1 MPa) were obtained from NIST thermodynamic table to utilize this analysis.¹ The following equilibrium reactions were considered to figure the phase diagrams for (1) reductive condition and (2) oxidative condition;

(1) Reductive condition



(2) Oxidative condition



where the reaction energy is denoted as

For reductive condition

$$\Delta E = E_{\text{Rh}_n\text{N}_y\text{O}_z\text{H}_w} + (x - 1)E_{\text{Z}[\text{H}]} + (2x - y)E_{\text{NH}_3} + (2x - z)E_{\text{H}_2\text{O}} \\ - xE_{\text{Rh}(\text{NO})_2/\text{Z}} - \left(\frac{w + 11x - 3y - 2z - 1}{2} \right) E_{\text{H}_2}$$

For oxidative condition

$$\Delta E = E_{\text{Rh}_n\text{N}_y\text{O}_z\text{H}_w} + \left(\frac{x}{13} - 1 \right) E_{\text{Z}[\text{H}]} + \left(\frac{1 - w}{2} \right) E_{\text{H}_2\text{O}} + \left(-y + z - \frac{w}{2} + \frac{1}{2} \right) E_{\text{N}_2\text{O}} \\ - \frac{x}{13} E_{\text{Rh}_{13}/\text{Z}[\text{H}]} - (-y + 2z - w + 1)E_{\text{NO}}$$

In this way, the 2Al site in the MOR zeolite is denoted as Z. $E_{[\text{Rh}_n\text{N}_y\text{O}_z\text{H}_w]}$ represents the total energy of considered MOR zeolite models containing Rh species. $E_{\text{Rh}(\text{NO})_2/\text{Z}}$ and $E_{\text{Rh}_{13}/\text{Z}[\text{H}]}$ are that of MOR zeolite structure having Rh mono-nitrosyl species at Al site and Rh_{13} metal cluster with Brønsted acid site, respectively. $E_{\text{Z}[\text{H}]}$ represent the total energies of a unit cell of MOR zeolite containing one proton. E_{NH_3} , $E_{\text{H}_2\text{O}}$, E_{H_2} , $E_{\text{N}_2\text{O}}$, and E_{NO} represent the total energies of the unit cell ($a = 18.2560 \text{ \AA}$, $b = 20.5340 \text{ \AA}$, $c = 15.0840 \text{ \AA}$, and $\alpha = \beta = \gamma = 90.0^\circ$) containing one molecular ammonia, water, hydrogen, nitrous oxide, and nitrogen-monoxide, respectively. The Gibbs free energies (ΔG) are described as

For Oxidative condition

$$\Delta G(T, p) = [\Delta E + (2x - y)\Delta\mu_{\text{NH}_3} + (2x - z)\Delta\mu_{\text{H}_2\text{O}} \\ - \left(\frac{w + 11x - 3y - 2z - 1}{2} \right) \Delta\mu_{\text{H}_2}]$$

For Reductive condition

$$\Delta G(T, p) = [\Delta E + (2x - y)\Delta\mu_{\text{NH}_3} + (2x - z)\Delta\mu_{\text{H}_2\text{O}} - \left(\frac{w + 11x - 3y - 2z - 1}{2}\right)\Delta\mu_{\text{H}_2}]$$

The change of the chemical potentials of H₂O and N₂O as a function of T are defined as

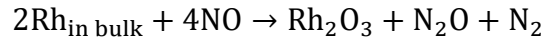
$$\Delta\mu_{\text{H}_2\text{O}}(T) = [\Delta\mu_{0 \text{ H}_2\text{O}}(T) + RT \ln \left(\frac{p_{\text{H}_2\text{O}}}{p_0}\right)]$$

$$\Delta\mu_{\text{N}_2\text{O}}(T) = [\Delta\mu_{0 \text{ N}_2\text{O}}(T) + RT \ln \left(\frac{p_{\text{N}_2\text{O}}}{p_0}\right)]$$

The pressures of H₂O and N₂O ($p_{\text{H}_2\text{O}}$ and $p_{\text{N}_2\text{O}}$) are fixed as 0.001 kPa and the standard one (p_0) is fixed as 100 kPa at every temperature. The change of the chemical potential of NO as a function of T and pressure of NO (p_{NO}) is defined as

$$\Delta\mu_{\text{NO}}(T, p) = [\Delta\mu_{0 \text{ NO}}(T) + RT \ln \left(\frac{p_{\text{NO}}}{p_0}\right)]$$

Similarly, the analysis for bulk Rh metal and Rh₂O₃ was carried out by considering the following equilibrium reaction,



where the reaction energy is denoted as

$$\Delta E = E_{\text{Rh}_2\text{O}_3} + E_{\text{N}_2\text{O}} + E_{\text{N}_2} - 2E_{\text{Rh}_{\text{in bulk}}} - 4E_{\text{NO}}$$

$E_{\text{Rh}_2\text{O}_3}$ represents the total energy of the unit cell of bulk Rh₂O₃ (containing 8 of Rh and 12 of O atoms), divided by 4. $E_{\text{Rh}_{\text{in bulk}}}$ describes that of Rh metal bulk, divided by the number of Rh atoms in the cell.

The Gibbs free energies (ΔG) are described as

$$\Delta G(T, p) = [\Delta E + \Delta\mu_{\text{N}_2\text{O}} + \Delta\mu_{\text{N}_2} - 4\Delta\mu_{\text{NO}}]$$

The change of the chemical potentials of H₂O and N₂O as a function of T are defined as

$$\Delta\mu_{\text{N}_2\text{O}}(T) = [\Delta\mu_{0\text{N}_2\text{O}}(T) + RT \ln \left(\frac{p_{\text{N}_2\text{O}}}{p_0} \right)]$$

$$\Delta\mu_{\text{N}_2}(T) = [\Delta\mu_{0\text{N}_2}(T) + RT \ln \left(\frac{p_{\text{N}_2}}{p_0} \right)]$$

The pressures of N_2O and N_2 ($p_{\text{N}_2\text{O}}$ and p_{N_2}) are fixed as 0.001 kPa and the standard one (p_0) is fixed as 100 kPa at every temperature. The change of the chemical potential of NO as a function of T and pressure of NO (p_{NO}) is defined as

$$\Delta\mu_{\text{NO}}(T, p) = [\Delta\mu_{0\text{NO}}(T) + RT \ln \left(\frac{p_{\text{NO}}}{p_0} \right)]$$

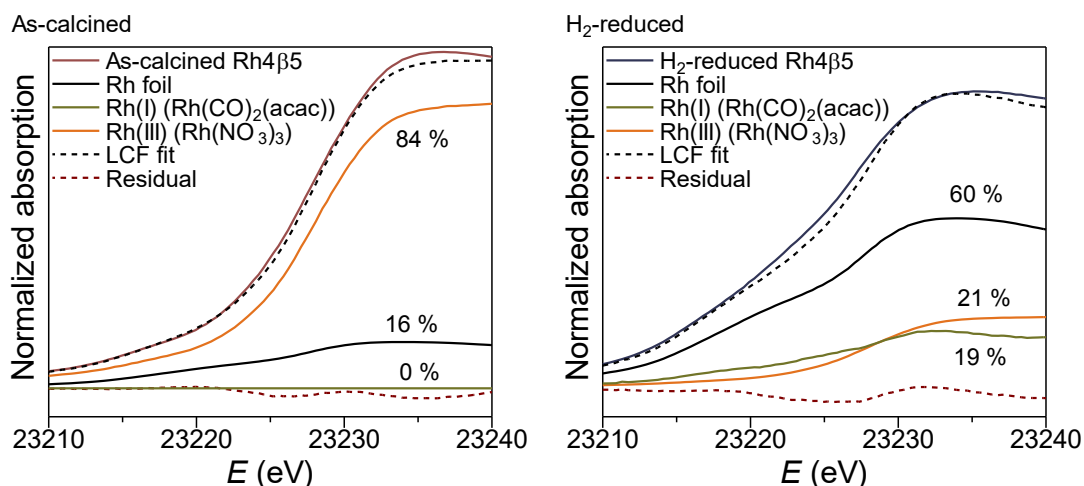


Figure S1 LCF fitting for as-calcined (left) and H_2 -reduced (right) Rh4 β 5 by using Athena software package.

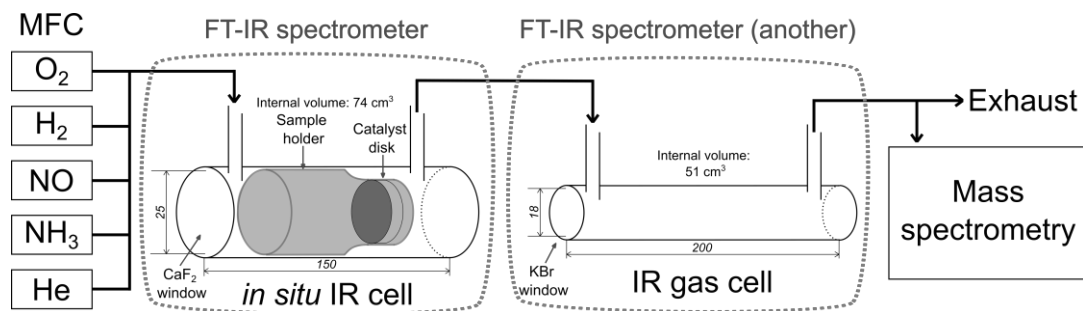


Figure S2 Schematic view of the used setup for *in situ* IR measurement including *in situ* IR cell and IR gas cell. An inner diameter and length of the cell are provided with a unit of mm.

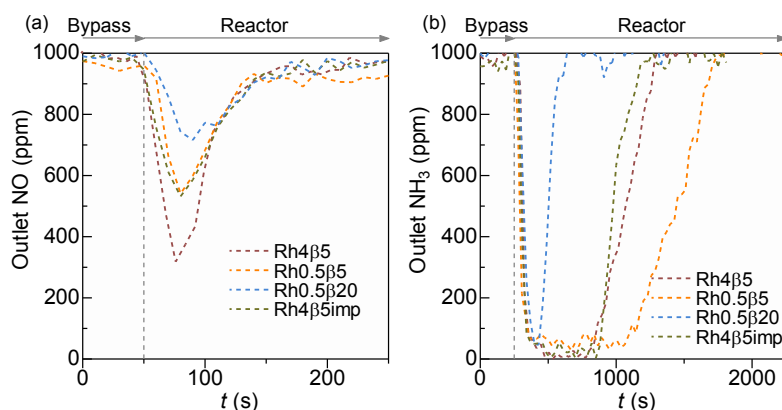


Figure S3 Adsorption measurement of different Rh-loaded β zeolite catalysts (40 mg) at 200 °C under a flow of (a) 0.1% NO + 2% O₂ and (b) 0.1% NH₃ (He balance, total flow: 100 mL min⁻¹). The flow passed through a bypass line in the first 50 s and 250 s for (a) NO and (b) NH₃ adsorption measurement, respectively.

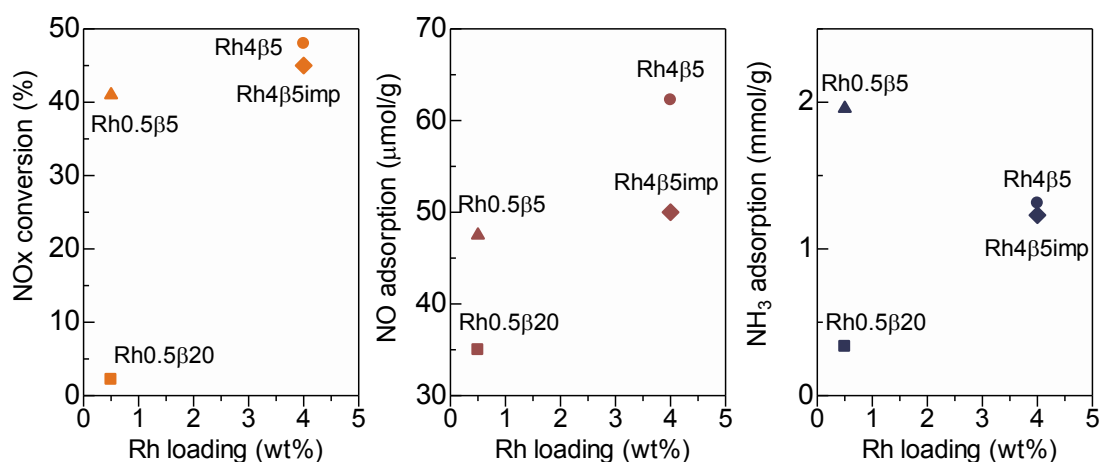


Figure S4 NO_x conversion during lean/rich test (left), NO adsorption amount (middle), and NH₃ adsorption amount (right) of different Rh-loaded β zeolite catalysts (40 mg) as a function of the Rh loading amount (wt%).

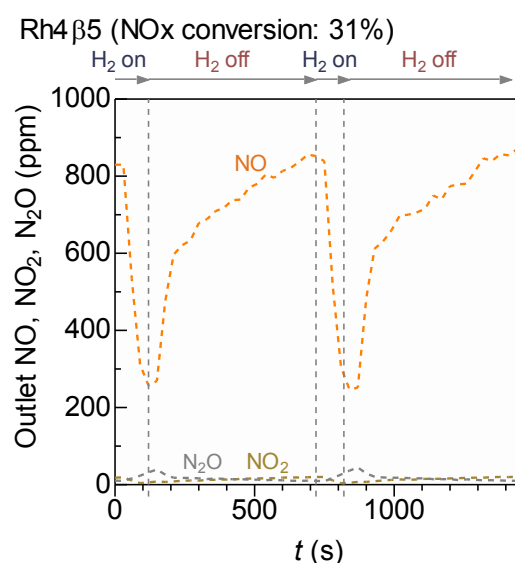


Figure S5 Concentration profile of NO, NO₂, and N₂O determined by infrared (gas cell) data under the periodic lean (0.1% NO + 2% O₂; 600 s) and O₂-added rich (0.1% NO + 2% O₂ + 2% H₂; 120 s) operations at 200 °C using the Rh4β5 catalyst.

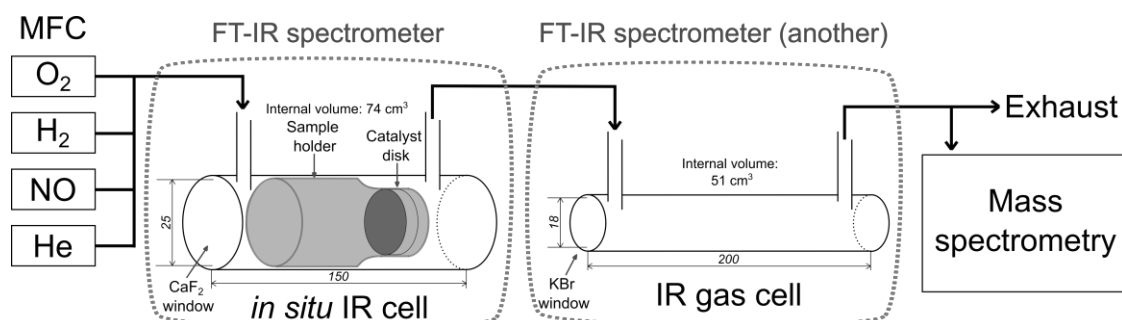


Figure S6 Schematic view of the used setup for *in situ* IR measurement including *in situ* IR cell, IR gas cell, and mass spectrometry. An inner diameter and length of the cell are provided with a unit of mm.

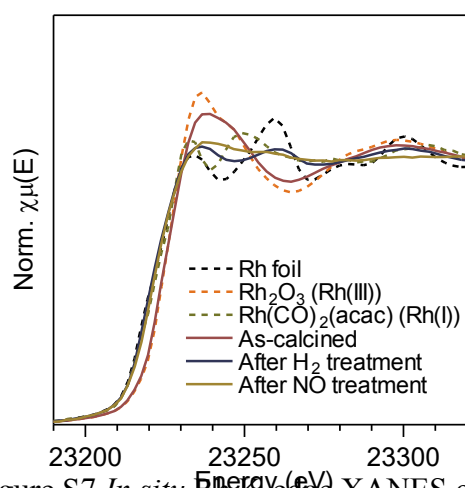


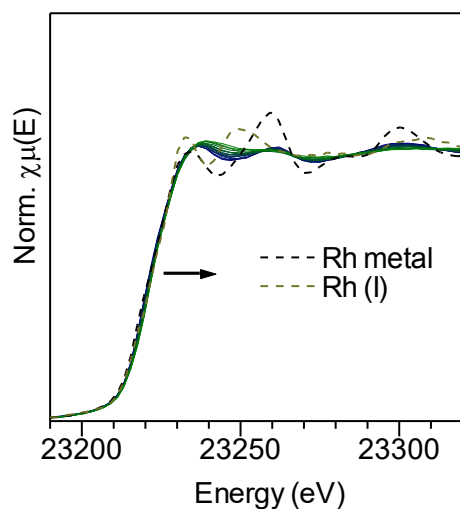
Figure S7 *In situ* Rh K-edge XANES of RhMOR under different conditions and *ex situ*

spectra of reference Rh compounds, measured at room temperature, in a wider range.

As-calcined RhMOR (red) was successively exposed to 2% H₂ (blue) and 1% NO at 200°C (orange).

(a)

Under a flow of 0.1% NO



(b)

Under a flow of 2% H₂

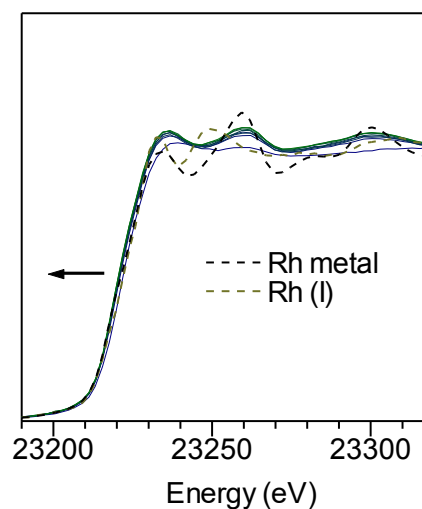


Figure S8 Evolution of Rh K-edge XANES spectra of RhMOR in a wider range, pre-reduced by 2% H₂ at 200°C during successive feed of (a) 0.1% NO (1700 s) and (b) 2% H₂ (800 s) at 200°C. The reaction gas was purged by He before each transient experiment. The spectra of Rh(CO)₂(acac) and Rh foil, measured at room temperature, are shown together as references for Rh(I) and Rh metal species

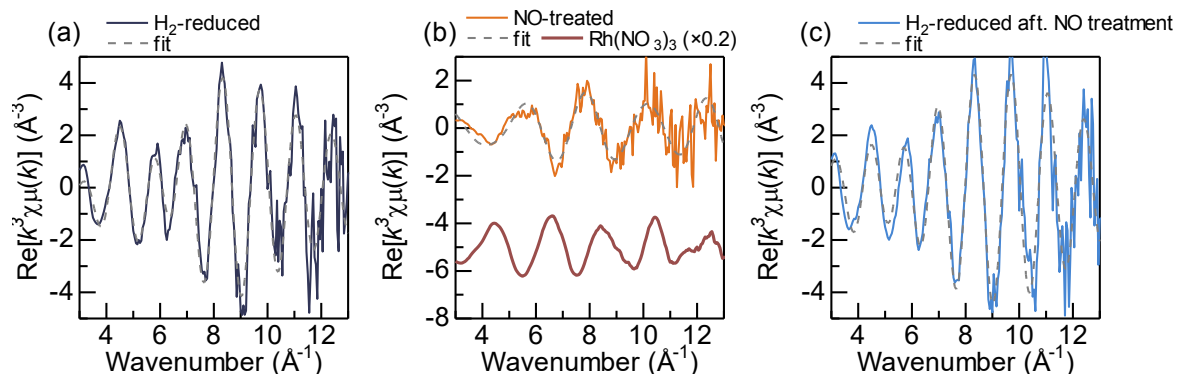


Figure S9 Rh K-edge k^3 -weighted raw EXAFS oscillations of RhMOR after (a) H_2 reduction, (b) NO treatment, and (c) re- H_2 reduction at $200^\circ C$ (corresponding spectra are shown in Figure 12). The result of $Rh(NO_3)_3$ -loaded SiO_2 is shown in (b) for comparison with NO-treated sample. Corresponding curve-fitting results of the k^3 -weighted EXAFS oscillations (dashed lines) are overlapped with the raw oscillations. The fitting range was $\Delta k = 3-12 \text{ \AA}^{-1}$ and $\Delta r = 1.1-3 \text{ \AA}$.

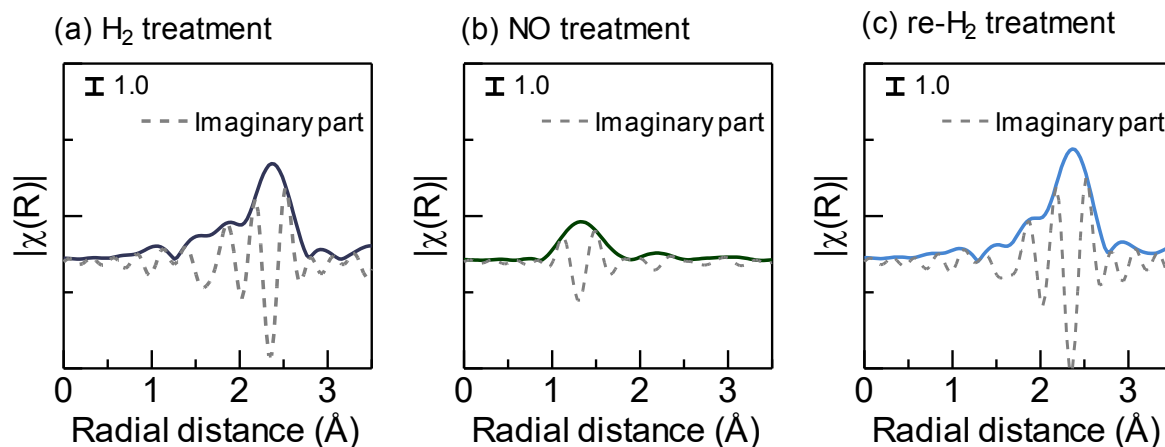


Figure S10 Rh K-edge k^3 -weighted EXAFS Fourier transforms of RhMOR under different conditions. As-calcined RhMOR was successively exposed to (a) 2% H_2 (blue), (b) 0.1% NO, 1% NO (dark green), and (c) 2% H_2 (light blue) at $200^\circ C$. Each imaginary part was shown together with dashed lines (grey).

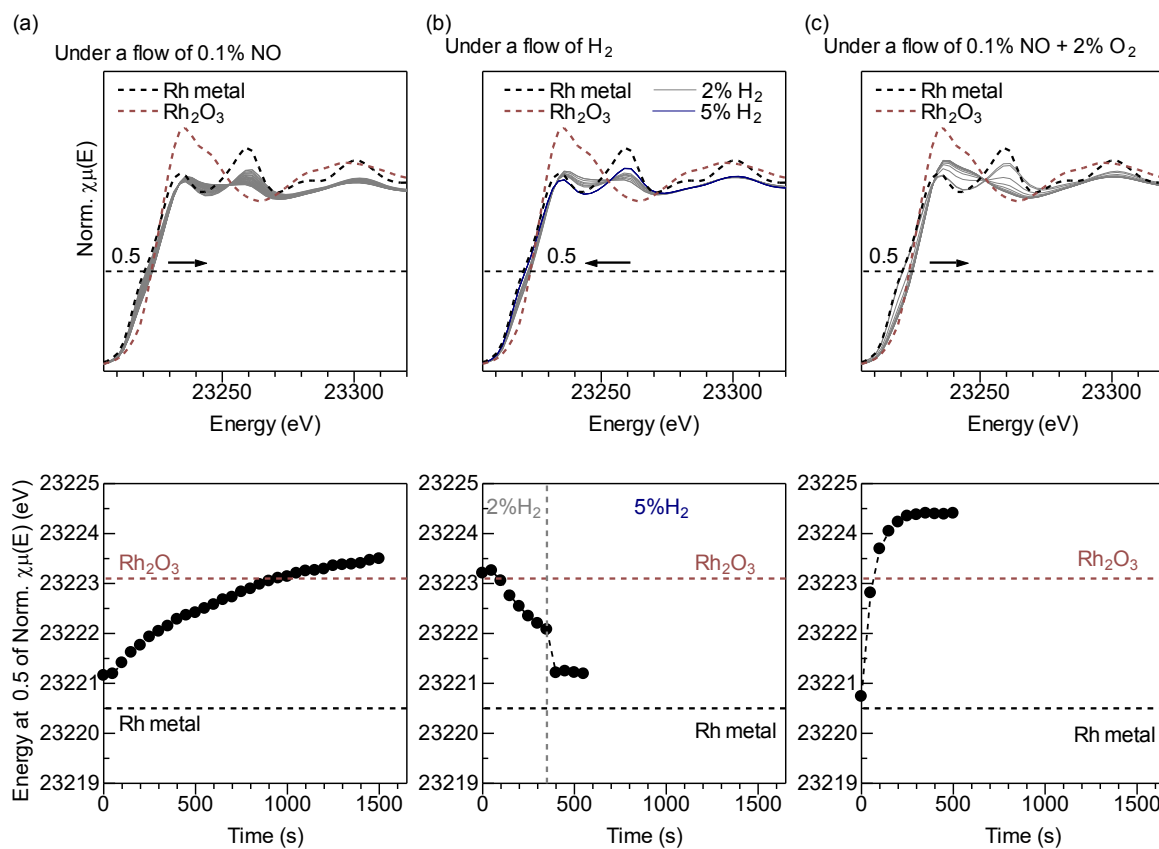


Figure S11 Evolution of Rh K-edge XANES spectra of Rh₁₀Al₂O₃ during successive feed of (a) 0.1% NO (1500s), (b) 2% H₂, He (600 s), and (c) 0.1% NO + 2% O₂ (600s) at 200 °C. The reactive gas was purged by He flow before the flow switched to the next one. Prior to the measurement, the sample was pretreated under a flow of 2% H₂ at 200 °C. Changes in the XANES energy at 0.5 are shown together (bottom).

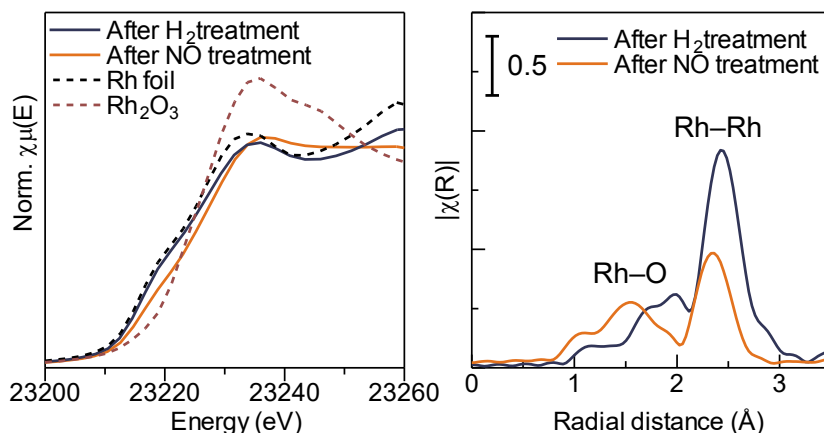


Figure S12 *In situ* Rh K-edge XANES (left) and EXAFS Fourier transforms (right) of Rh10Al₂O₃ after 2% H₂ (blue) and 0.1% NO (orange) treatments at 200 °C. *Ex situ* spectra of reference Rh compounds, measured at room temperature, were shown together.

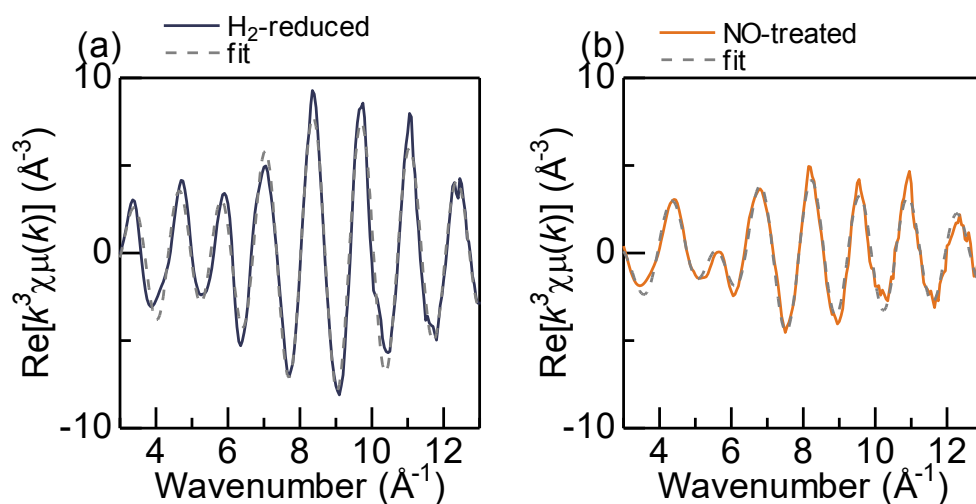


Figure S13 Rh K-edge k^3 -weighted raw EXAFS oscillations of Rh10Al₂O₃ after (a) H₂ reduction and (b) NO treatment at 200 °C. Corresponding curve-fitting results of the k^3 -weighted EXAFS oscillations (dashed lines) are overlapped with the raw oscillations. The fitting range was $\Delta k = 3\text{--}14 \text{ Å}^{-1}$ and $\Delta r = 1\text{--}3 \text{ Å}$.

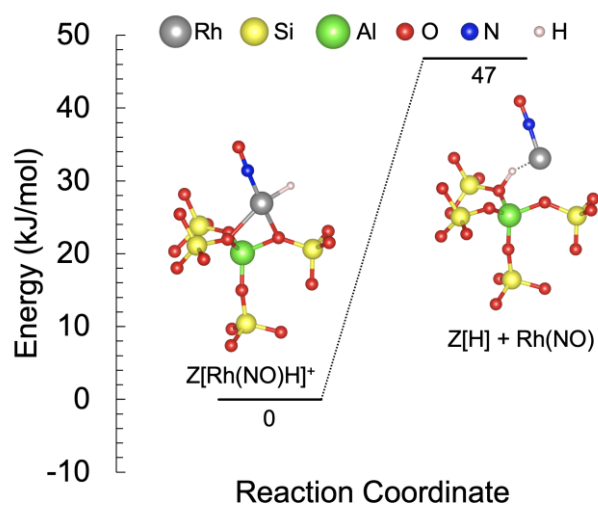


Figure S14 Energy profiles for the formation of $\text{Rh(NO)}/\text{Z[H]}$ from Z[Rh(NO)(H)] . Black values are relative energies of each optimized structure. (Unit: kJ/mol).

Chapter 6

Computational design of main-group catalysts for low-temperature methane combustion by ozone

6.1. Introduction

The past decades have witnessed the widespread utilization of natural gas as a clean fuel for vehicles and power plants. The catalytic combustion of methane (CH_4) into carbon dioxide (CO_2) is becoming an increasingly valuable strategy for addressing the emissions of unburned CH_4 , which exerts a greenhouse gas effect that is 22 times higher than that of CO_2 .^{1–3} Different types of heterogeneous catalysts, such as platinum-group-metal (PGM)-^{4–7} and metal-oxide-based catalysts,^{8–10} have been reported. Among them, PGM-based catalysts, such as Pd- and Pt-loaded Al_2O_3 , exhibited the highest catalytic activities.¹¹ However, the Pd-based catalysts suffer from high operating temperatures ($>500\text{ }^\circ\text{C}$) under humidity conditions, as well as irreversible deactivation by sulfation during the co-feeding of steam and SO_2 .^{2,12–14} Moreover, large amounts of PGMs (200–266 g) must be utilized to achieve the combustion of CH_4 in a natural-gas-fueled heavy-duty vehicle.¹⁵ Additionally, the mining and purification of PGMs extensively impact the environment (the productions of 1 kg each of Pt and Pd generate 12,500 and 3880 kg of CO_2 equivalents, respectively). Conversely, the production of main-group elements generates significantly lower CO_2 equivalents (e.g., 8.2 kg of Al).^{16,17} Thus, it is highly desirable (economically and ecologically) to develop main-group catalysts that can function at $<200\text{ }^\circ\text{C}$ in the co-presence of steam and SO_2 .

Conventional catalyst screening, which is based on trial-and-error experiments, may not

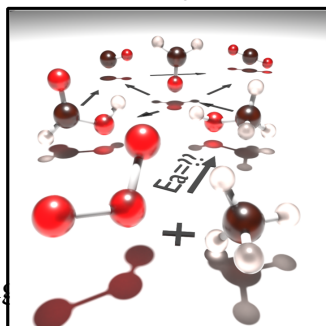
yield discontinuous discoveries, such as the main-group-facilitated catalytic combustion of CH_4 at low temperatures. The computational reaction route mapping of the unexplored chemical reaction space can benefit the discovery of different catalytic reactions.^{18–23} Generally, the computations of the elementary steps in combustion reactions are considered challenging because of the abundant intermediates and products that exhibit similar formation energies and activation barriers (E_a).²⁴ To comprehensively explore the various reaction routes, density functional theory (DFT)-based automated methods for predicting reaction pathways are promising because they link the theoretical prediction to the practical designs of catalysts.^{25–30} Maeda et al. developed an efficient automated path-searching method, namely the artificial force-induced reaction (AFIR) method, which involves pressing the atoms in given reactant molecules together by applying artificial force to form new structures (products) and assigning their transition states (TS).^{30–41} Via AFIR, they elucidated the entire reaction pathways of uncatalyzed reactions.^{32,37,39,40} The automated reaction route mapping of heterogeneous catalysis systems is still formidable owing to the complexity of the surface reactions on solid materials, where the adsorption/desorption of the reactants and products, diffusion/migration of the adsorbates, and bond rearrangements proceed simultaneously.^{35,36,41}

Ozone (O_3), a strong oxidant⁴², is generated onsite by a commercial ozonizer. O_3 has been employed to enhance the catalytic performance of the gas-phase combustion of volatile organic compounds (VOCs), including toluene,^{43–45} acetone,^{46,47} and benzene.^{48,49} Regarding the combustion of CH_4 with O_3 ,^{50–52} zeolite-based catalysts, such as Pd^{53-} , Fe^{54-} , Co^{55-} , and proton⁵⁶-type zeolites, have demonstrated efficiencies at low temperatures. However, the reported studies only considered the catalytic performance;

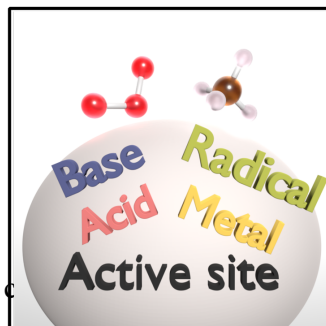
thus, the strategy for designing the catalysts based on the detailed mechanism and elementary steps must still need to be addressed.

Herein, based on a computational design concept employing the AFIR method, we report a main-group catalyst for driving catalytic combustion of CH₄ with O₃ at low temperatures. First, we explored the CH₄ + O₃ reaction network toward generating CO₂ (Figure 1a), confirming that the formation of methanol (CH₃OH), CH₄ + O₃ → CH₃OH + O₂, was the rate-determining step (RDS) of CH₄ combustion. Thereafter, we performed the virtual screening of the active sites for RDS to propose the following concept: stronger Brønsted acid sites (BASs) exhibit higher catalytic activities (Figure 1b). This concept was experimentally verified via CH₄ combustion tests employing O₃ at 200 °C in the presence of different BAS catalysts exhibiting different acid strengths (Figure 1c). Finally, we demonstrated that a proton-type beta zeolite with Si/Al = 8.5 (Hβ8.5) exhibited a reaction rate that was three orders of magnitude higher than that of a PGM-based benchmark catalyst, 5wt% Pd-loaded Al₂O₃ (Pd5Al₂O₃). The developed catalyst exhibited very high resistance to steam and SO₂ poisoning during the 170-h reaction test.

(a) Reaction route mapping for non-catalytic reaction



(b) Virtual screening of active site



(c) Experimental testing

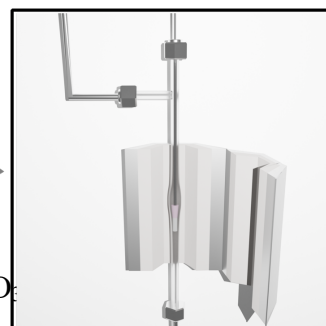


Fig.

concept for c

H₄ with O₃

single-component (SC)-AFIR, CH₄ combustion with O₃ was comprehensively explored to determine the key intermediates and elementary steps. (b) Different active sites were evaluated regarding the decrease in *E_a* of the key elementary step. (c) Heterogeneous catalyst comprising the predicted active site was tested experimentally.

6.2 Experimental

6.2.1 DFT calculations

Spin-polarized DFT calculations were performed employing the generalized-gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) functional,⁵⁷ as implemented in the Vienna Ab Initio Simulation Package^{58,59} (VASP), and the projected augmented waves^{60,61} (PAW) method was employed for the Kohn–Sham equations with cut-off energy of 500 eV. The Γ point was employed for the Brillouin-zone sampling⁶². DFT-D3 dispersion correction with the Becke–Johnson damping was employed for all the calculations⁶³. To simulate the gas-phase reaction, calculations were conducted within a large cubic cell ($a = b = c = 15$ Å). The structure of the β zeolite was obtained from the International Zeolite Association (IZA) database,⁶⁴ and the lattice constants were fixed at initial values ($a = b = 12.632$ Å, $c = 26.186$ Å, $\alpha = \beta = \gamma = 90.0^\circ$) during the calculations.

The SC-AFIR method, as implemented in the GRRM17 program,³⁸ was applied for reaction route mapping with a model collision energy parameter of 1000 kJ/mol. Only a positive force was applied for the AFIR calculations. The H, O, and C atoms in the CH₄ and O₃ molecules were considered the targets of SC-AFIR. The locally updated plane (LUP) method availed the path top (PT) points, which were subsequently optimized as TS structures and determined by the following intrinsic reaction coordinate (IRC) calculation.⁶⁵ To calculate for the β zeolite, the atoms of the zeolitic framework, except for the Al atom, as well as the Si atoms adjacent to the Al and O atoms connecting to the adjacent Si, and H atoms of BAS were fixed at the crystallographic position (Figure 5b). The stabilization energy of C₅H₅N was defined, as follows:

$$E_{\text{pyr}} = (E_{\text{C}_5\text{H}_5\text{N on BAS}} - E_{\text{BAS}} - E_{\text{C}_5\text{H}_5\text{N}})$$

Thus, the total energies of the models including a C₅H₅N molecule, acid molecules, and C₅H₅N interacting with the acid molecules were described as $E_{\text{C}_5\text{H}_5\text{N}}$, E_{BAS} , and $E_{\text{C}_5\text{H}_5\text{N on BAS}}$, respectively.

6.2.2. Experiment

Proton-type (H) β zeolite with a Si/Al ratio of 8.5 (H β 8.5) was obtained via the calcination of an NH₄⁺-type β zeolite that was purchased from Tosoh Co. (HSZ-920NHA) in the air at 500 °C. The H β zeolites with Si/Al ratios of 20 and 255 (HSZ-940HOA and HSZ-980HOA, respectively) were supplied by Tosoh Co., and another with a Si/Al ratio of 12.5 was supplied by the Catalysis Society of Japan (JRC-Z-HB25). Acid-load SiO₂ was prepared via impregnation method. SiO₂ (CARiACT Q-10, Fuji Silysia) was

suspended in an aqueous solution of H_2SO_4 , HClO_4 , H_3PO_4 , and HNO_3 . The water was evaporated from the mixture and dried in an oven. Al_2O_3 was prepared by calcining γ - AlOOH (Catapal B Alumina, Sasol) for 3 h at 900 °C. Next, 5 wt% Pd-loaded Al_2O_3 was prepared by impregnating Al_2O_3 with an aqueous HNO_3 solution of $\text{Pd}(\text{NH}_3)_2(\text{NO}_3)_2$. The catalytic test was conducted in a fixed-bed reactor under in 0.1% CH_4 + 0.7% O_3 + 5.95% O_2 (He balance, total flow: 100 ml/min) as a typical condition. The outlet was directly connected to a JASCO FT/IR-4600 spectrometer that was equipped with a triglycine sulfate (TGS) detector, in which a homemade infrared (IR) gas cell, which was equipped with KBr windows, was placed to monitor the concentrations of CH_4 and O_3 . The IR area of O_3 was calibrated employing an O_3 analyzer (EG-550, EcoDesign Inc.) to convert the area into concentration. To feed O_3 into the system, an O_2 flow was passed through an ozonizer (F0G-AC5G, EcoDesign Inc.) that was placed before the mainstream. The whole view of the employed setup is shown in Supplementary Figure S7. The NH_3 -adsorption measurement was carried out by Infrared spectroscopy (JASCO FT/IR-4200 spectrometer using a home-made *in situ* IR cell. The catalyst disc of the zeolite sample (40 mg.) was dehydrated under He flow at 500 °C before a background spectrum was recorded under a flow of He at 200 °C. Then, NH_3 (1%) flowed to the sample, followed by He purging before IR spectrum was taken at 200 °C.

6.3 Result and discussion

6.3.1 Computation of the reaction pathways toward CH₄ combustion by O₃

We explored the reaction pathway of CH₄ and O₃ (CH₄ + O₃) via SC-AFIR, which was an automated method for searching for reaction paths, as implemented in the GRRM program. Employing this method, the reaction routes of the non-catalytic oxidation of CH₄ into CO₂ by O₃ are automatically mapped. Figure 2a shows the reaction pathways with the corresponding values of their relative energies (ΔE) and E_{as} . In the first reaction, CH₄ is oxidized by O₃ to yield CH₃OH and O₂ with strong exothermicity (243.0 kJ/mol). In the TS structure, one O atom of O₃ extracts one H atom of CH₄ to yield CH₃ and OOOH fragments, where the evaluated E_a is 142.7 kJ/mol. This value is comparable to the reported experimental value for gas-phase CH₄ combustion by O₃ (148 kJ/mol).⁶⁶ Next, the reactivity of CH₃OH with O₃ is assessed by exploring the reaction pathway via the SC-AFIR method (see Supplementary Figure S1). Although CH₃OH is oxidized into formaldehyde (CH₂O), H₂O, and O₂ by O₃, CH₃OH + O₃ → CH₂O + H₂O + O₂, via an exothermic reaction (210.1 kJ/mol), the process requires a very high E_a (255.1 kJ/mol). Alternatively, the oxidation of CH₃OH by O₂ produces CH₂O and H₂O₂, CH₃OH + O₂ → CH₂O + H₂O₂, via a low E_a of 76.1 kJ/mol (Figure 2a). The subsequent oxidation of CH₂O by H₂O₂ yields formic acid (CH₂O₂) and H₂O, CH₂O + H₂O₂ → CH₂O₂ + H₂O, with an E_a of 124.2 kJ/mol. The decomposition of the produced CH₂O₂ yields CO₂ and H₂, CH₂O₂ → CO₂ + H₂, or CO and H₂O molecules, CH₂O₂ → CO + H₂O. However, these decomposition processes require high E_{as} to produce CO₂ and CO (264.3 and 296.3 kJ/mol, respectively) because of the high stability of CH₂O₂. As an alternative reaction path, we explored the oxidation of CH₂O by O₂, which was abundantly present in the

practical systems, via SC-AFIR (see Supplementary Figure S2). Thus, the oxidation of CH_2O by O_2 represents a facile process for producing CO and H_2O_2 via an E_a of 113.7 kJ/mol. The CO was oxidized into $\text{CO}_2 + \text{O}_2$ by O_3 through an E_a of 84.9 kJ/mol (see Supplementary Figure S3). For comparison, Nitrous oxide (N_2O) and H_2O_2 were assessed as alternative oxidants to oxidize CH_4 into CH_3OH (see Supplementary Figure S4). The evaluated E_a s of the $\text{CH}_4 + \text{N}_2\text{O}$ and $\text{CH}_4 + \text{H}_2\text{O}_2$ reactions are 269 and 177 kJ/mol, respectively, indicating that O_3 is the most efficient oxidant for producing CH_3OH .

Employing the explored reaction pathways (Figure 2b), the reaction, $\text{CH}_4 + \text{O}_3 \rightarrow \text{CH}_3\text{OH} + \text{O}_2$, was determined as the crucial process, with the highest E_a in the CH_4 oxidation reaction (the RDS). To further elucidate the TS structure of this reaction, Bader charge analysis was performed to investigate the distribution of charge on each atom in the TS structure (Figure 2b). The total atomic charges in the CH_3 fragment are almost neutral (+0.12), indicating that it is a radical-like fragment. Regarding the OOOH fragment, the structure is divided into two parts: (I) the part comprising the H and O atoms that are closer to the CH_3 fragment (denoted as O1) and (II) that comprising the other two O atoms (denoted as O2 and O3). In the former part, the determined atomic charges of the H and O1 atoms are +0.56 and -0.58, respectively, while those of the O2 and O3 atoms in the latter part are +0.06 and -0.12, respectively. This charge distribution indicates that the OOOH fragment comprises a OH radical and O_2 molecular species.

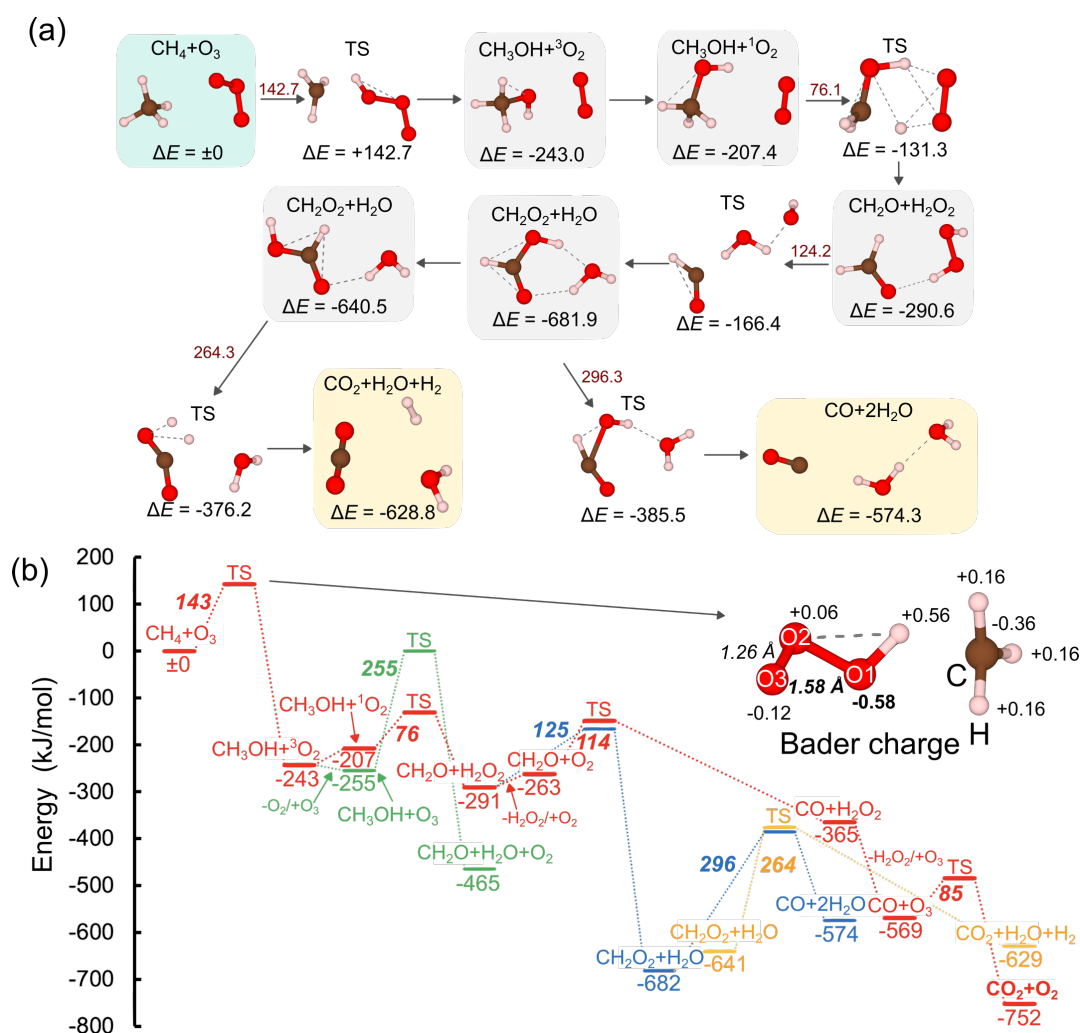


Figure 2 (a) Calculated reaction pathway of $\text{CH}_4 + \text{O}_3$, as well as the values of relative energies (ΔE s). The values written in dark red represent E_a . (b) Energy profile of CH_4 combustion to yield CO_2 . The reaction path shown by the red lines is the most plausible for CO_2 formation. The result of the Bader charge analyses of the TS structures of $\text{CH}_4 + \text{O}_3$ and $\text{CH}_3\text{OH} + \text{O}_3$ is shown together. ΔE s are provided under each bar, and the E_a s are described employing the bold italic style (Unit: kJ/mol)

6.3.2. Virtual screening of catalytic sites for the reaction of $\text{CH}_4 + \text{O}_3$ to produce $\text{CH}_3\text{OH} + \text{O}_2$

The oxidation of CH_4 by O_3 into CH_3OH and O_2 was determined as the key reaction during CH_4 combustion (Section 2.1). To conduct the virtual screening of the catalytically active sites that effectively decrease the E_a , we carried out SC-AFIR calculations for the $\text{CH}_4 + \text{O}_3$ reaction on the following model active sites: (a) a $\text{Cu}(0)$ atom as a redox site, (b) an NO molecule as a radical species, (c) pyridine ($\text{C}_5\text{H}_5\text{N}$) as a base site, and (d) sulfuric acid (H_2SO_4) as an acid site (Figure 3). Figure 3a shows the reaction path of $\text{CH}_4 + \text{O}_3$ over $\text{Cu}(0)$. First, the C–H bond of CH_4 is cleaved by the O atom of O_3 over the Cu atom to yield OH and CH_3 groups on the $\text{Cu}(\text{II})$ cation ($\text{Cu}(\text{OH})(\text{CH}_3)$), as well as adsorbed O_2 molecules through a high E_a (318.2 kJ/mol). Subsequently, the adsorbed O_2 molecule interacts with the neighboring CH_3 group to form CH_3OO species on the $\text{Cu}(\text{II})$ cation ($\text{Cu}(\text{OH})(\text{CH}_3\text{OO})$) via an E_a of 115.4 kJ/mol, while the extraction of the H atom of the OH group ($\text{Cu}(\text{O})(\text{OOH})(\text{CH}_3)$) is determined as an unfavorable path. Finally, the $\text{Cu}(\text{OH})_2$ species and CH_2O are produced with a moderate barrier (108.7 kJ), although the $\text{Cu}(\text{II})$ cation was not reduced back into the $\text{Cu}(0)$ atom. The maximum barrier was higher than that of the uncatalyzed reaction (142.7 kJ/mol). Hence, the $\text{Cu}(0)$ atom was not a suitable catalyst for the $\text{CH}_4 + \text{O}_3$ reaction. Further, the NO molecules as a representative radical site reacted with O_3 to yield O_2 and NO_2 , where the H atom of CH_4 was subsequently extracted to yield the CH_3 radical species that were bound to the nitrous acid (HONO) species (Figure 3b). Although the evaluated E_a of this step was relatively low (122.7 kJ/mol), that of the reverse reaction ($\text{CH}_3\cdot + \text{HONO} \rightarrow \text{CH}_4 + \text{NO}_2$) was very low (2.0 kJ/mol). Additionally, the reaction, $\text{NO}_2 + \text{CH}_4$, to yield $\text{CH}_3\text{OH} + \text{O}_2$ shows

only a low exothermicity (-21.1 kJ/mol). These results indicate that NO is also an inefficient catalyst for the $\text{CH}_4 + \text{O}_3$ reaction. In the case of $\text{C}_5\text{H}_5\text{N}$ as a base site, O_3 slightly interacted with the basic site (the N atom) of $\text{C}_5\text{H}_5\text{N}$ before reacting with CH_4 ; thus, O_3 was not decomposed by the active site (Figure 3c). Thereafter, CH_3OH was produced through a similar TS structure to the gas-phase one, and the product, which was weakly bound to the base site, was slightly more stable than that in the gas phase ($\Delta E = -264$ kJ (on the base site) vs -243 kJ (in the gas phase)), while their E_{as} were comparable ($E_{\text{a}} = 134.9$ vs 142.7 kJ/mol). Finally, H_2SO_4 was assessed as an acid site. CH_3OH was produced via an E_{a} of 126.2 kJ/mol, which was lower than that of the gas-phase reaction (142.7 kJ/mol), with very high exothermicity ($\Delta E = -279.3$ kJ/mol; Figure 3d). Consequently, we predicted that BASs were the most effective among the virtually screened active sites for $\text{CH}_4 + \text{O}_3$. In the next section, we discussed the preferable property of BAS, as well as the detailed mechanism of decreasing E_{a} .

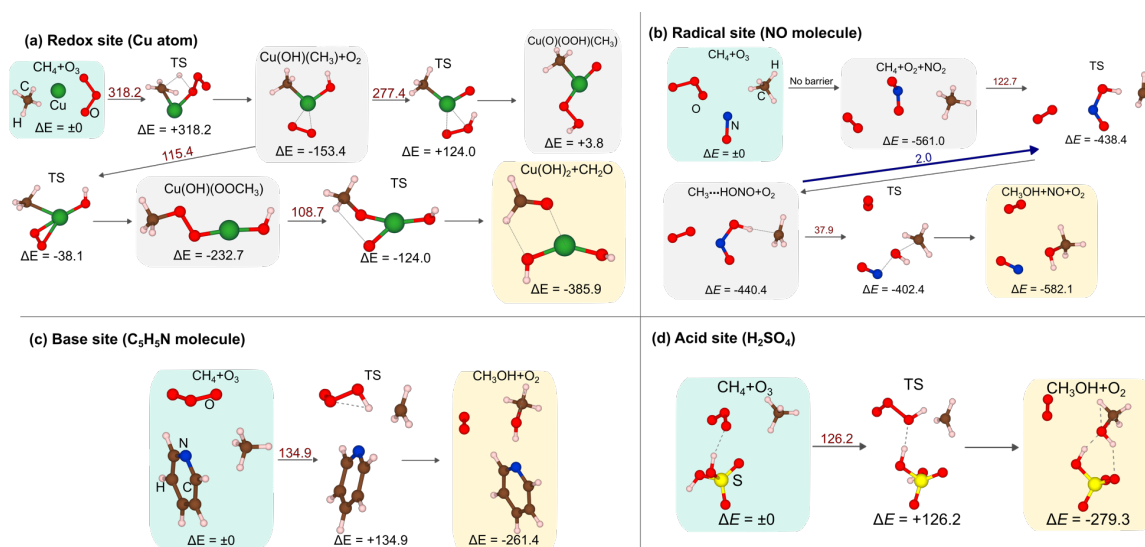


Figure 3 Calculated reaction pathways of CH₄ + O₃ on (a) Cu(0) atom, (b) NO molecule, (c) C₅H₅N molecule, and (d) H₂SO₄ molecule. The values of Δ*E* and the *E_a* (dark red) are shown together (Unit: kJ/mol)

6.3.3. Promotion effect of BAS on the CH₄ + O₃ reaction

We investigated the effect of the acid strength of BASs of the mineral acids on the *E_a* of CH₄ + O₃. H₂SO₄, perchloric acid (HClO₄), nitric acid (HNO₃), and phosphoric acid (H₃PO₄) were evaluated as BASs exhibiting different acidities. The initial structure (IS), final structure (FS), and TS are shown in Supplementary Figure S5. The *E_a*s of the strong acids (128.4 and 126.2 kJ/mol for HClO₄ and H₂SO₄, respectively) are lower than that of the uncatalyzed reaction (142.7 kJ/mol), which is close to the value for a weak acid (142.2 and 138.8 kJ/mol for H₃PO₄ and HNO₃, respectively).

To quantitatively evaluate the impact of the acid strength, the *E_a*s of the CH₄ + O₃ reaction are plotted as a function of the stabilization energy of C₅H₅N on BASs (*E_{pyr}*), as

determined by DFT calculations. Notably, the adsorption of C_5H_5N on BAS of solid material has been widely applied to experimentally and theoretically analyze its acidity.^{67–}

⁶⁹ The values of E_{pyr} for $HClO_4$, H_2SO_4 , HNO_3 , and H_3PO_4 are -94.3 , -91.1 , -70.9 , and -76.2 kJ/mol, respectively, indicating that the stronger acids ($HClO_4$ and H_2SO_4) avail a more stable structure than the weaker acids (HNO_3 and H_3PO_4), corresponding to their experimentally obtained deprotonation enthalpies (see Supplementary Table S1). Figure 4d shows that the Eas of the $CH_4 + O_3$ reaction on BASs decreased with the increasing acid strengths, indicating that stronger BASs correspond to higher reaction rates for the $CH_4 + O_3$ reaction. Bader charge analysis was performed on the TS structures of the examined acids (see Supplementary Figure S6). The charge of the O atom in the OH species of the strong acids (-0.70) is more negative than those of the two weak acids (-0.66 and -0.62). Regarding the bond distance in the TS structure, the more negative charge of the O atom elongates the O–O bond in the OOOH fragment (1.69 vs. 1.66 Å for $HClO_4$ and H_3PO_4 , respectively), thereby decreasing Ea .

Inspired by the newly gained insight into BASs as active sites, a proton-type zeolite (β -type) was theoretically examined for the adsorption of C_5H_5N (Figs. 4a and b). The result indicates the higher acid strength of the zeolite ($E_{pyr} = -199.8$ kJ/mol) than that of H_2SO_4 (-91.1 kJ/mol). The extrapolation of the linear relationship between E_{pyr} and Ea of the mineral acids indicates that the zeolite might achieve an extremely low Ea (~ 60 kJ/mol). To verify this hypothesis, we conducted TS calculations for the $CH_4 + O_3$ reaction on the BAS of the zeolite. Figure 4c shows the optimized structures of IS, TS, and FS. As expected from the strong acidity of the zeolite, the computed Ea (71.2 kJ/mol) is considerably lower than those for the mineral acids (126.2 – 142.2 kJ/mol).

Next, we experimentally verified the theoretically predicted relationship between the E_a and acid strength (E_{pyr}) of the $\text{CH}_4 + \text{O}_3$ reaction. The mineral acid (3 wt% H_2SO_4 , HClO_4 , HNO_3 , or H_3PO_4) was loaded onto an SiO_2 support and tested for the reaction in a 0.1% $\text{CH}_4 + 5.95\% \text{O}_2 + 0.7\% \text{O}_3 + 3\% \text{H}_2\text{O}$ flow (total flow: 100 ml/min, He balance) at 200 °C employing a fixed-bed flow reactor. The concentrations of CH_4 and O_3 in the outlet gas were monitored by a gas cell that was equipped with an infrared spectroscope (Supplementary Figure S7 shows the illustration of the experimental setup). The observed conversions of CH_4 are plotted as a function of E_{pyr} (Figure 4e). Interestingly, the observed conversions of CH_4 correlate moderately with E_{pyr} . Next, an H β zeolite with a relatively low Si/Al ratio (8.5) (H β 8.5) was tested via the same reaction. Therein, H β 8.5 achieves an extremely higher conversion of CH_4 (97%) than HClO_4 (23%), demonstrating the highest CH_4 conversion among the tested catalysts. The above results demonstrate that the high CH_4 -combustion activity of a strong BAS-based catalyst, H β 8.5, could be rationally predicted based on computational mapping of the reaction network, as well as TS calculations. In the next section (2.4), we experimentally demonstrate the superior performance of H β 8.5 by comparing it with $\text{Pd5Al}_2\text{O}_3$ as a conventional catalyst.

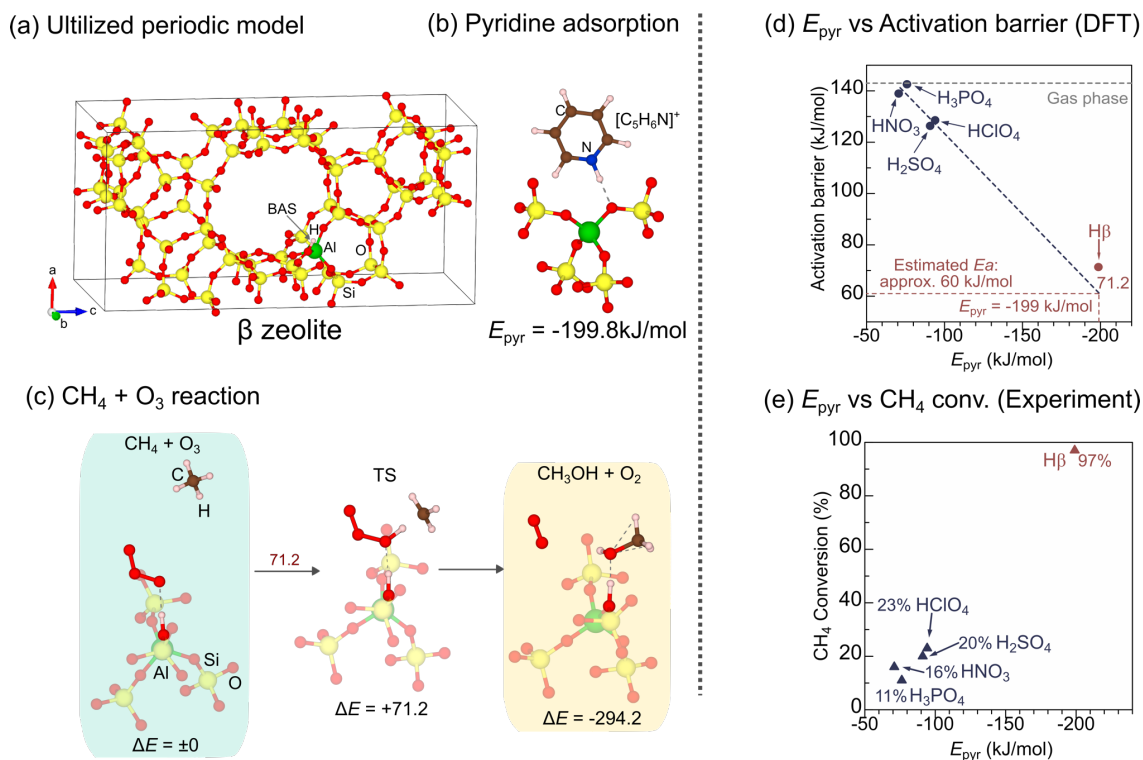


Figure 4 (a) Employed periodic model of the β zeolite. (b) Structure of the adsorption of $\text{C}_5\text{H}_5\text{N}$ on BAS of β zeolite. (c) TS calculations of the $\text{CH}_4 + \text{O}_3$ reaction on BAS of the β zeolite. ΔE is reported in the kJ/mol unit. E_a is shown in dark red. (d) Plot of E_a of the $\text{CH}_4 + \text{O}_3$ reaction as a function of the $\text{C}_5\text{H}_5\text{N}$ -stabilization energy (E_{pyr}) of the acids. (e) CH_4 conversion of 40 mg of the samples in 0.1% $\text{CH}_4 + 5.95\% \text{O}_2 + 0.7\% \text{O}_3 + 3\% \text{H}_2\text{O}$ at 200 °C (He balance, total flow: 100 ml/min) as a function of E_{pyr}

6.3.4. Performance of the H β -catalyzed CH₄ combustion with O₃

We conducted catalytic tests to experimentally demonstrate the catalytic performance of H β 8.5. Figure 5a shows the conversions of CH₄ over H β 8.5 and a benchmark catalyst (Pd5Al₂O₃) in a flow of 0.1% CH₄ + 5.95% O₂ + 0.7% O₃ at different temperatures. In 0.1% CH₄ + 10% O₂, H β 8.5 did not achieve CH₄ conversion in the entire temperature range, indicating the necessity of O₃ as the oxidant. In 0.1% CH₄ + 5.95% O₂ + 0.7% O₃, H β 8.5 achieved the high conversion of CH₄ at 200 °C, while Pd5Al₂O₃ required a temperature of >400 °C to achieve comparable performance. At >250 °C, the conversion of CH₄ over H β 8.5 decreased because O₃ conversion had reached 100% via self-decomposition (Figure 5b). The effect of BAS on the self-decomposition of O₃ into O₂ (2O₃ → 3O₂) was theoretically investigated because this reaction represented an obstacle to the practical application of O₃ as an oxidant. Supplementary Figure S8 shows the comparison between the optimized TS structures of the uncatalyzed and H β -catalyzed decompositions of O₃. The calculated *E_a* of the uncatalyzed and H β -catalyzed reactions are 42.3 and 69.5 kJ/mol, respectively, indicating that BAS in zeolite do not promote the self-decomposition of O₃. This property is desirable in catalysts for CH₄ combustion by O₃. Dissimilar to H β 8.5, Pd5Al₂O₃ exhibited high activity toward O₃ decomposition (complete conversion even at 50 °C); hence, the addition of O₃ did not increase the CH₄ combustion activity of Pd5Al₂O₃.

Figure 5c shows a plot of the conversions of CH₄ and O₃, as well as the BAS amounts, as evaluated by NH₃-adsorption measurement as a function of the Si/Al ratio of the utilized β zeolites (Si/Al = 8.5, 12.5, 20, and 255). Evidently, the Al-rich β zeolites with more BASs exhibited higher CH₄ conversions. The Arrhenius plot of the H β 8.5-catalyzed CH₄

combustion with O₃ (Figure 5d) revealed an apparent barrier (E_a) of 75 kJ/mol, which agrees with the theoretical value of the CH₄ + O₃ reaction to yield CH₃OH (E_a = 71.2 kJ/mol). The E_a of H β 8.5 was considerably lower than that of Pd5Al₂O₃ (E_a = 95 kJ/mol) in 0.1% CH₄ + 10% O₂. Supplementary Figure S9 shows the results of the kinetic analyses for estimating the reaction orders. The reaction orders of CH₄ (0.2) and O₃ (0.2) were positive. Further, the reaction rates per weight of the catalyst (for H β 8.5 and Pd5Al₂O₃) for CH₄ conversion (V_{CH_4}) at 190 °C were compared, and the result indicated that V_{CH_4} of H β 8.5 (57.5 mmol h⁻¹ g_{cat}⁻¹) was 442 times higher than that of Pd5Al₂O₃ (0.13 mmol h⁻¹ g_{cat}⁻¹), demonstrating that the designed main-group catalyst (H β 8.5) exhibited considerably higher activity toward CH₄ combustion than the PGM-based benchmark catalyst.

Further, H β 8.5 and Pd5Al₂O₃ were tested for CH₄ combustion in the co-presence of H₂O and SO₂ to compare their resistance to steam and SO_x poisoning. Figure 5f shows the time course of CH₄ combustion over 40 mg of H β 8.5 (5.95% O₂ + 0.7% O₃ at 200 °C) and Pd5Al₂O₃ (10% O₂ at 400 °C) in 0.1% CH₄ + 3% H₂O + 40 ppm SO₂. By feeding H₂O and SO₂, the CH₄ conversion at 400 °C over Pd5Al₂O₃ decreased with the reaction time, reaching almost zero after 10 h. Conversely, the CH₄ conversion over H β 8.5 did not decrease at 200 °C even after 15 h, indicating that H β 8.5 was highly resistant to steam and SO₂ poisoning. Finally, 10 mg of H β 8.5 was examined for the long-term reaction test in 0.1% CH₄ + 5.95% O₂ + 0.7% O₃ + 3% H₂O + 40 ppm SO₂ at 200 °C, and the result indicated that the catalyst did not significantly decrease the CH₄ conversion for 170 h of reaction time.

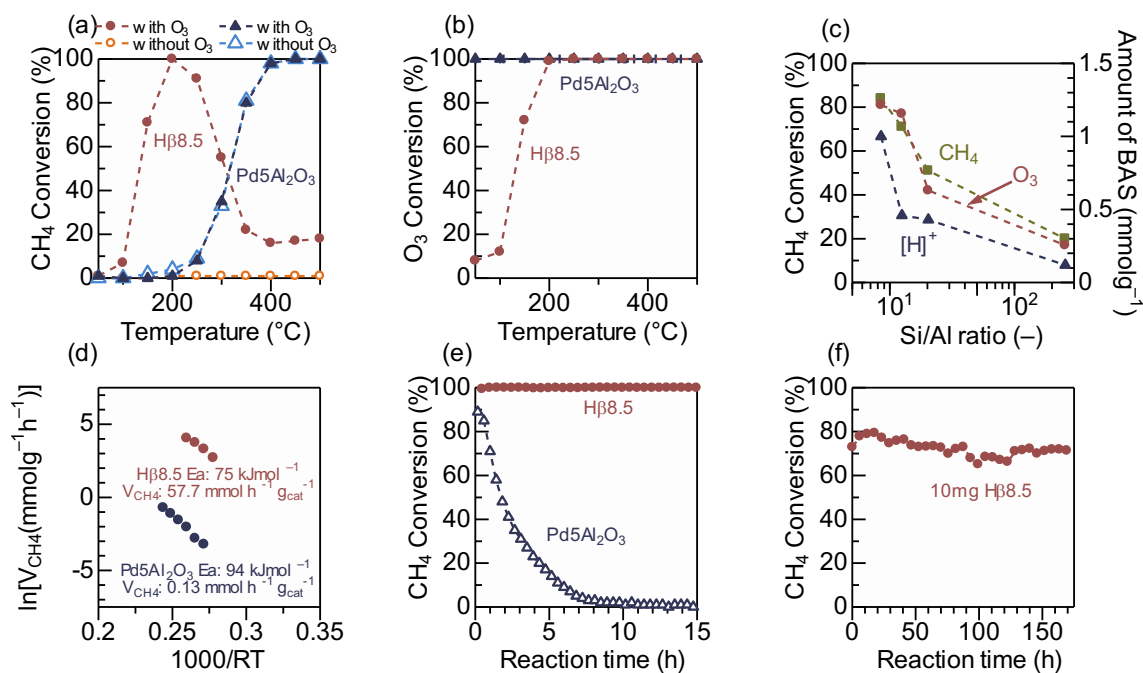


Figure 5 (a) CH₄ and (b) O₃ conversions over 40 mg of the Hβ zeolite with an Si/Al ratio of 8.5 (Hβ8.5) and 40 mg of 5 wt% Pd-loaded Al₂O₃ (Pd5Al₂O₃) in 0.1% CH₄ + 5.95% O₂ + 0.7% O₃ and 0.1% CH₄ + 10% O₂ flows as functions of the reaction temperature. (c) Conversions of CH₄ and O₃ over 40 mg of the Hβ zeolite with different Si/Al ratios (8.5, 12.5, 20, and 255) in a 0.1% CH₄ + 5.95% O₂ + 0.7% O₃ flow at 150 °C, together with the amount of BAS in the β zeolite, as evaluated via NH₃-adsorption measurements. (d) Arrhenius plots for the combustions of CH₄ over Hβ8.5 in 0.1% CH₄ + 5.95% O₂ + 0.7% O₃ at 160–190 °C, as well as over Pd5Al₂O₃ in 0.1% CH₄ + 10% O₂ at 170–220 °C. The reaction rates (V_{CH4}) at 190 °C over Hβ8.5 and Pd5Al₂O₃ are shown together ($R^2 = 0.99$ for both catalyst). (e) Time course of CH₄ conversion over 40 mg of Pd5Al₂O₃ (at 400 °C) and Hβ8.5 (at 200 °C) in 0.1% CH₄ + 3% H₂O + 40 ppm SO₂ + 10% O₂ or 5.95% O₂ + 0.7% O₃ for Pd5Al₂O₃ and Hβ8.5, respectively, with He balance (total flow: 100 ml/min). (f) Long-term reaction test for 10 mg of Hβ8.5 in 0.1% CH₄ + 5.95% O₂ + 0.7% O₃ + 3% H₂O + 40 ppm SO₂ at 200 °C

6.4 Conclusion

In this study, we rationally designed a catalyst for low-temperature O₃-driven catalytic combustion of CH₄ based on the elucidation of an unexplored reaction network. The CH₄ + O₃ reaction toward generating CO₂ was explored via SC-AFIR, and the formation of CH₃OH via CH₄ + O₃ (CH₄ + O₃ → CH₃OH + O₂) was determined as RDS of CH₄ combustion ($E_a = 142.7$ kJ/mol). To assess the various types of active sites (acid, base, redox, and radical sites), model molecules (H₂SO₄, C₅H₅N, a Cu atom, and HNO₃) were introduced into the system, and reaction route was calculated. Among the examined active sites, H₂SO₄ effectively decreased the reaction ($E_a = 126.2$ kJ/mol); thus, different Brønsted acid catalysts with different acid strengths were examined for the TS calculation. The relationship between the acidity and calculated E_a of the CH₄ + O₃ reaction (CH₃OH formation) availed a facile catalyst design concept; the stronger the BASs afford the higher the catalytic activity. Thereafter, the theory-driven concept was experimentally verified by CH₄ combustion with O₃ at 200 °C. An Hβ zeolite, which was the most effective candidate, as predicted by this concept, was experimentally tested for the CH₄ + O₃ reaction. The apparent activation energy (75 kJ/mol), which was estimated by the kinetic experiment, was consistent with the computed value (71.2 kJ/mol). Hβ exhibited a very high reaction rate, which was 442 times higher than that of the benchmark catalyst, Pd5Al₂O₃, at 190 °C. During the catalytic tests in the presence of SO₂ and H₂O, Hβ achieved the full conversion of CH₄ at 190 °C, whereas Pd5Al₂O₃ was completely deactivated even at a higher temperature (400 °C) owing to the poisoning of its active sites by water and SO₂. Finally, the developed catalyst (Hβ zeolite) was tested in a 170-h long-term reaction in which it exhibited very high resistance against water and SO₂. These

results demonstrated that a computationally designed catalyst based on earth-abundant metal elements (Si and Al) could achieve higher activities and durabilities compared with their PGM-based counterparts for the unprecedented low-temperature CH₄ combustion.

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Table S1 Summarized data of acids for stabilization energy of pyridine on the BASs (E_{pyr}) and reported experimental value of deprotonation enthalpy (ΔH_{DP}).

Acids	E_{pyr} (kJ/mol)	ΔH_{DP} (kJ/mol)
H_3PO_4	-76.2	1383 ± 21^{70}
HNO_3	-70.9	1358 ± 0.84^{71}
H_2SO_4	-91.1	1295 ± 11^{72}
HClO_4	-94.3	1255 ± 24^{73}

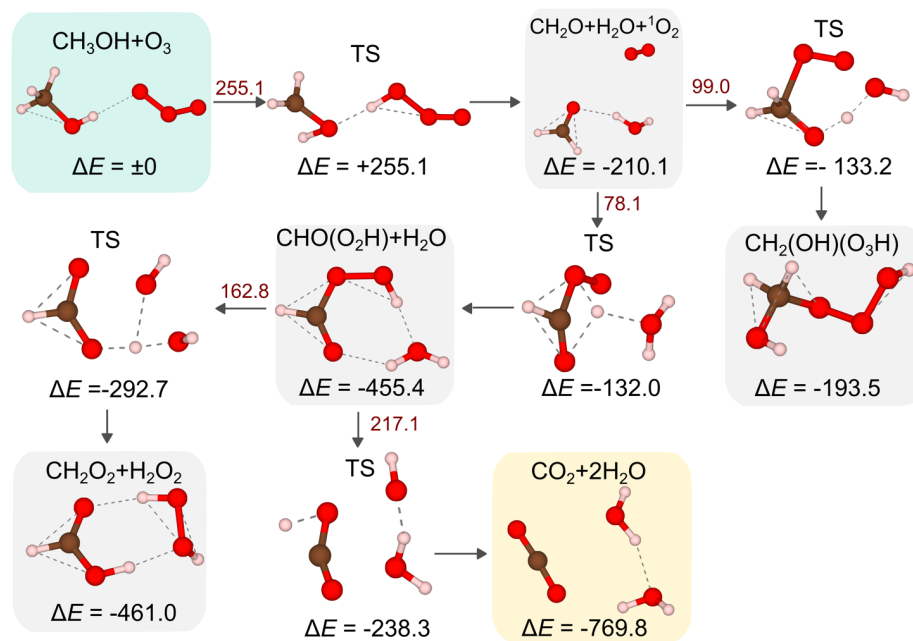


Figure S1 Calculated reaction pathway of $\text{CH}_3\text{OH} + \text{O}_3$ together with the values of relative energy (ΔE). Values written in dark red shows the activation barrier. (Unit: kJ/mol)

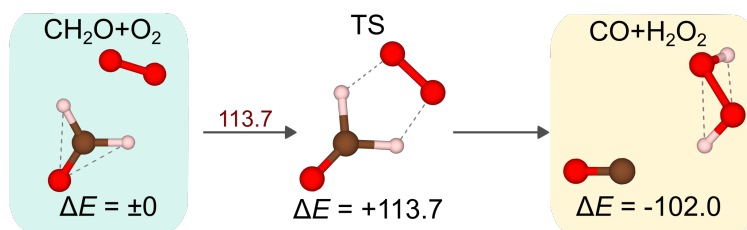


Figure S2 Calculated reaction pathway of CH₂O + O₂ together with the values of relative energy (ΔE). Values written in dark red shows the activation barrier. (Unit: kJ/mol)

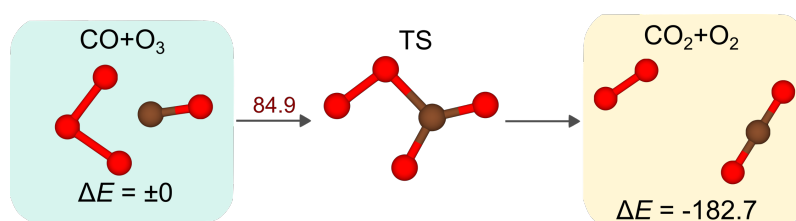


Figure S3 Calculated reaction pathway of CO + O₃ together with the values of relative energy (ΔE). Values written in dark red shows the activation barrier. (Unit: kJ/mol)

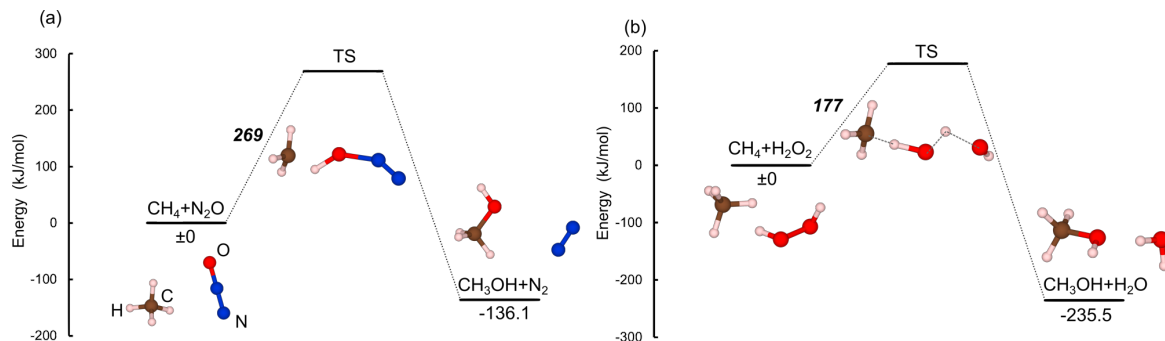


Figure S4 Energy profiles of CH₃OH formation from (a) CH₄ + N₂O or (b) CH₄ + H₂O₂ reactions. Relative energies are provided under each bar and the activation barriers are described by bold italic style. (Unit: kJ/mol)

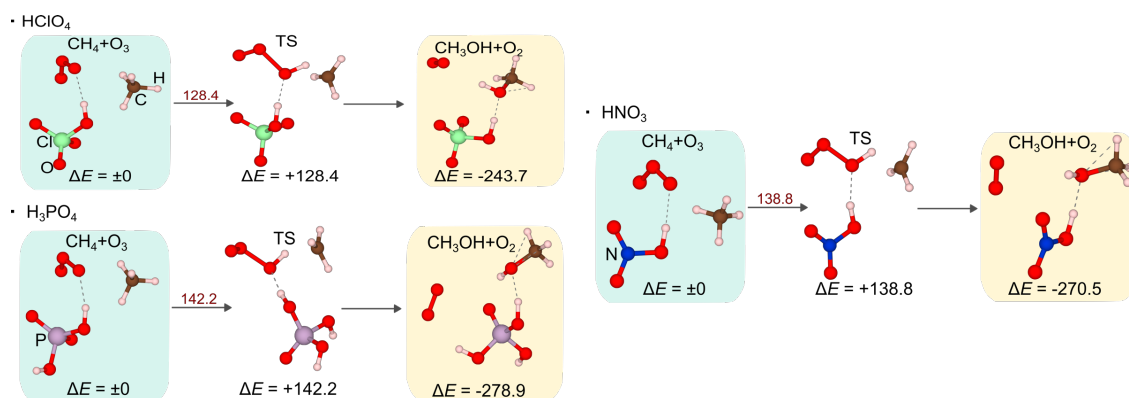


Figure S5 Calculated reaction pathway of $\text{CH}_4 + \text{O}_3$ on HClO_4 , H_3PO_4 , and HNO_3 . Relative energy (ΔE) is provided in the unit of kJ/mol. Activation barriers (E_a) are shown with dark red color.

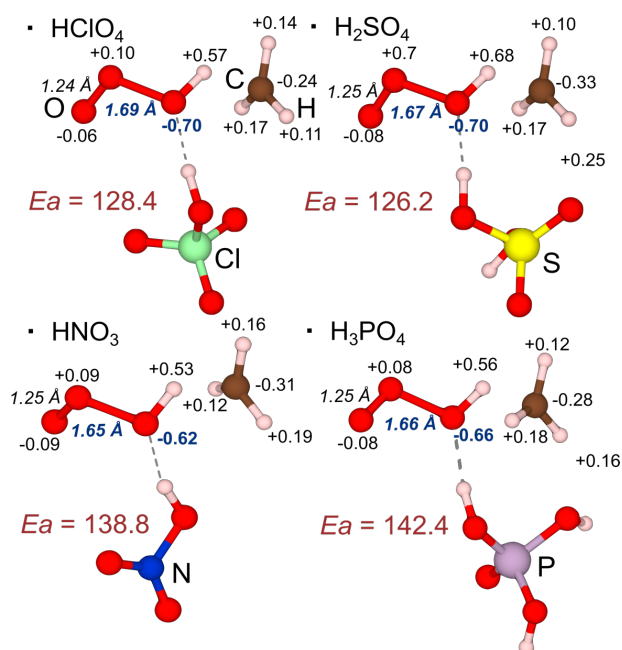


Figure S6 Bader charge analysis of the structure of the transition state of $\text{CH}_4 + \text{O}_3$ reaction on acids.

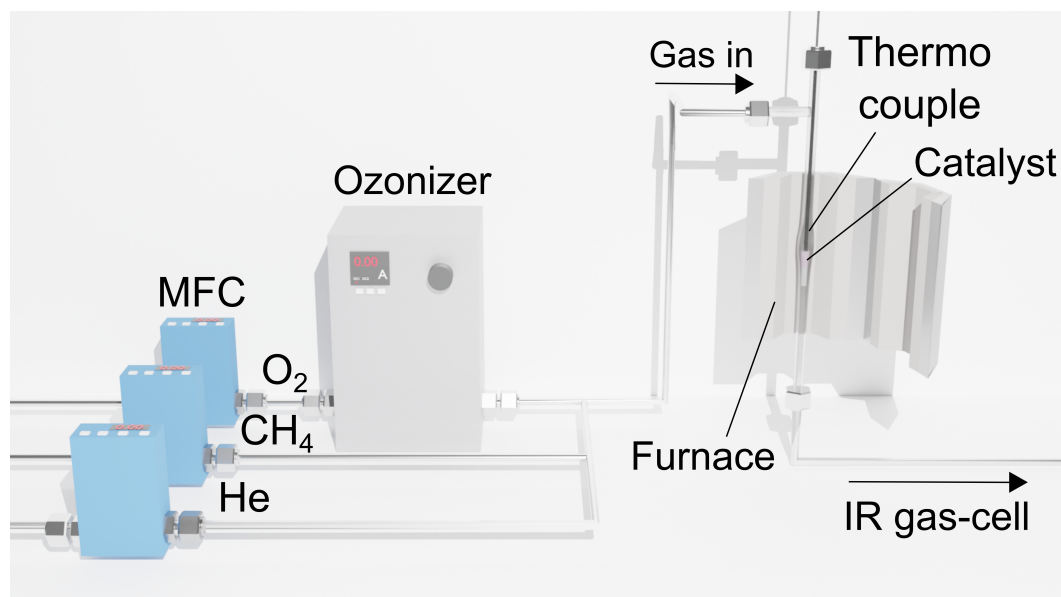
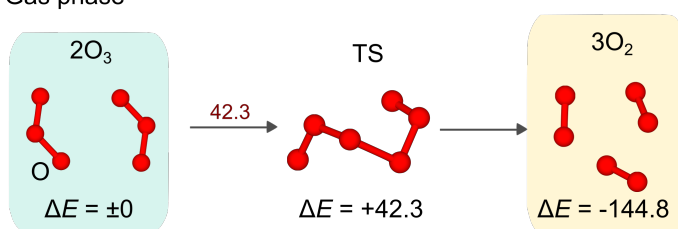


Figure S7 Illustration of experimental setup for CH₄ combustion test with ozonizer.

- Gas phase



- On BAS

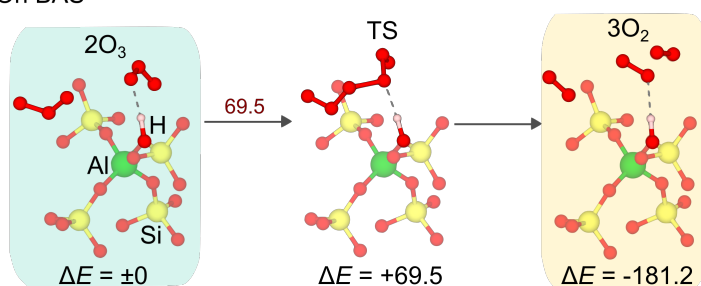


Figure S8 Transition state calculations for self-decomposition reaction of ozone in gas-phase and on Brønsted acid site (BAS) of BEA zeolite. Relative energy (ΔE) is provided in the unit of kJ/mol. Activation barriers (E_a) are shown with dark red color. Only atoms around BAS are shown for

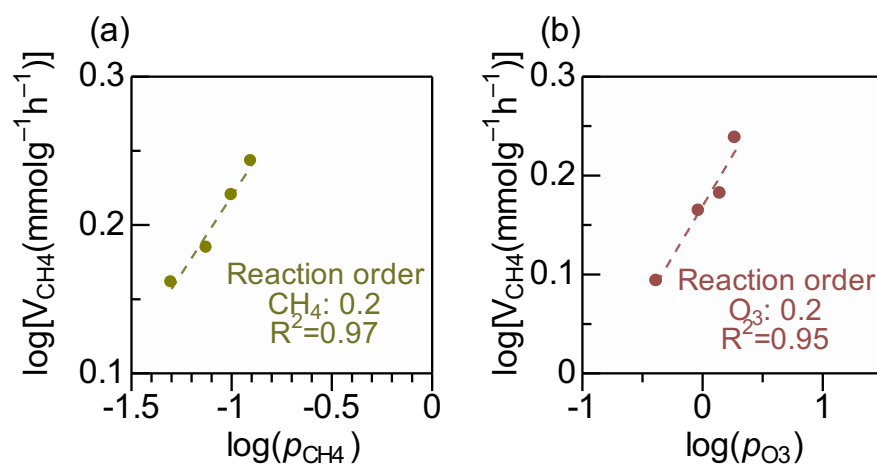


Figure S9 Log–log plot of the reaction rate of CH₄ consumption at 130 °C vs (a) CH₄ pressure (at 0.7% O₂) and (b) O₃ pressure (at 0.1% CH₄)

Chapter 7

General conclusions

In this thesis, the author described the studies on the structure–function relationship of active species in zeolite framework. General conclusions are summarized as follows.

In **Chapter 1**, a brief introduction to the structure–function relationship of active species was discussed.

In **Chapter 2**, we demonstrated that CH₄ oxidation at room temperatures is promoted by O₂-activated In, Ga-exchanged CHA zeolite. The results of in situ XAFS and H₂-TPR studies suggest that multinuclear In, Ga-oxo clusters are produced by sequential RSSIE (H₂, 973 K) and oxidation (O₂, 773 K). Possible structures of In, Ga-oxo clusters responsible for this process were explored by using ab initio thermodynamic analysis. The results suggest that the plausible active species are [In₂O₂]²⁺ and [Ga₂(O)(OH)₂]²⁺ under $p_{\text{O}_2} = 0.1$ atm, dry conditions ($p_{\text{H}_2\text{O}} = 0.001$ atm), and room temperature (300 K). The generation of adsorbed formic acid and formaldehyde in this process was demonstrated by using in situ IR spectroscopic monitoring of the reaction of a CH₄ flow over Ga-oxo clusters in CHA zeolite at room temperature. The energy barriers for C–H bond cleavage over possible Ga-oxo species were calculated using DFT calculations. The results show that the process promoted by [In₂O₂]²⁺ and [Ga₂(O)(OH)₂]²⁺ ion has the lowest activation barrier. Finally, the results suggest that the C–H bond cleavage reaction promoted by In, Ga-oxo species proceeds through a

heterolytic pathway rather than a homolytic pathway. Overall, this effort demonstrates the potential of using zeolite-supported main-group metal-oxo clusters as catalysts for CH₄ oxidation under mild conditions.

In **Chapter 3**, Herein, the first report of surface isolated In-hydrides in zeolites including formation, characterization, and catalysis is described. The isolated In-hydrides were formed in CHA zeolites by H₂ treatment of In-CHA at high reaction temperatures. Characterization by in situ FTIR measurement including isotopic experiments with D₂ and vibration calculations revealed that the [InH₂]⁺ ions are plausible structures. The necessity of high temperature for the formation of [InH₂]⁺ ions and their kinetic stability were also discussed in the context of TS calculations. The results of in situ XAFS measurement are compatible with the formation of In-hydrides. Regarding the catalysis, In-CHA exhibited high selectivity and durability for the non-oxidative ethane dehydrogenation without co-feeding H₂. The activity and selectivity of In-CHA were maintained for at least 90 h and the catalyst was reusable without loss of its efficiency. Rational studies for the formation and characterization of In-hydrides in various types of zeolites and their dehydrogenation catalysis activity remain under investigation.

In **Chapter 4**, I have shown that bulk Pd can be atomically dispersed into small pores of CHA zeolite with 4% NO flow at 600°C. The microscopic (SEM, STEM, EDX) and spectroscopic (XRD, FTIR, XAS) characterizations showed that Pd²⁺ cations on zeolite anionic sites were mainly formed. The amount of Pd²⁺ cations reached 4.1 wt%, which is higher than the highest value reported previously. From in situ XAS and DRIFTS, combined with online gas monitoring, atomic dispersion occurs through oxidation of Pd metal by NO, yielding Pd cations on Al sites with concomitant formation of N₂O and H₂O (as HNO₃). The phase diagram, determined by ab initio thermodynamics analysis, showed

that divalent Pd cations on paired Al sites are thermodynamically favored under the experimental conditions (4% NO and 600 °C), consistent with the occurrence of atomic dispersion of bulk Pd. Additionally, we revealed the relationship between the atomic-scale structure of the Pd²⁺ cations in CHA zeolite and the NO adsorption/desorption property by a combined approach of DFT calculations, *in-situ* IR spectroscopy, and NO-TPD measurement. It was also observed that the amount of NO adsorbed in the high-temperature region increased upon decreasing the proportion of paired Al sites in 6MR in the CHA zeolite support, despite using the same Pd loading, indicating that weak NO adsorption is likely to occur on Pd cations at 6MR(3NN). For strong NO adsorption, the experimental adsorption energies of the NO desorption at low (350–450 °C) and high (> 450 °C) temperatures agree reasonably with the theoretically estimated values of the moderately stable Pd cations at 8MR(2NN) and the relatively unstable ones at 8MR(3NN), 8MR(4NN), and 5NN.

In **Chapter 5**, the dynamic structural evolution of Rh species in MOR zeolite was investigated by *in situ/operando* spectroscopy (IR and XAS) and DFT calculations, and the following conclusions were drawn. Under NO flow, metallic Rh species are oxidized and dispersed into [Rh(NO)₂]⁺ species at the Al sites in the zeolite, which thermodynamically stabilizes the isolated Rh⁺ species and thus prevents their overoxidation to Rh₂O₃. The isolated Rh complexes are reduced/aggregated to small Rh clusters under subsequent follow of H₂. This system is applicable to unsteady-state de-NO_x under periodic lean-rich cycles via an NH₃ intermediate. Under lean (NO + O₂) conditions, NO is captured as a [Rh(NO)₂]⁺ complex, which is reduced by H₂ to afford adsorbed NH₃ and Rh metal clusters under rich conditions. The [Rh(NO)₂]⁺ complexes are regenerated by the subsequent exposure of the reduced catalyst to NO + O₂,

accompanied by the selective reduction of NO by the adsorbed NH₃ to form N₂. Transition state calculation suggests that Rh metal clusters are preferable NH₃ formation sites. NH₃ formation from the surface N and H atoms has a lower barrier than the N₂O and N₂ formation pathways, which accounts for the negligible formation of N₂O and N₂ under NO. The reversible dynamic structural evolution of the Rh species, [Rh(NO)₂]⁺ ↔ Rh metal clusters, under lean and rich conditions, is a key mechanistic feature for unsteady-state deNO_x via NO capture by Rh⁺ sites, selective reduction of NO to afford adsorbed NH₃ on Rh metal clusters, and selective reduction of NO with adsorbed NH₃ on zeolite.

In **Chapter 6**, we rationally designed a catalyst for low-temperature O₃-driven catalytic combustion of CH₄ based on the elucidation of an unexplored reaction network. The CH₄ + O₃ reaction toward generating CO₂ was explored via SC-AFIR, and the formation of CH₃OH via CH₄ + O₃ (CH₄ + O₃ → CH₃OH + O₂) was determined as RDS of CH₄ combustion (*E_a* = 142.7 kJ/mol). Among the examined active sites, H₂SO₄ effectively decreased the reaction (*E_a* = 126.2 kJ/mol); thus, different Brønsted acid catalysts with different acid strengths were examined for the TS calculation. The result shows that the stronger the BASs afford the higher the catalytic activity. Thereafter, the theory-driven concept was experimentally verified by CH₄ combustion with O₃ at 200 °C. The experimental apparent activation energy (75 kJ/mol) of Hβ, which was estimated by the kinetic experiment, was consistent with the computed value (71.2 kJ/mol). Hβ exhibited a very high reaction rate, which was 442 times higher than that of the benchmark catalyst, Pd₅Al₂O₃, at 190 °C. Finally, the developed catalyst (Hβ zeolite) was tested in a 170-h long-term reaction in which it exhibited very high resistance against water and SO₂. These results demonstrated that a computationally designed catalyst based on earth-abundant metal elements (Si and Al) could achieve higher activities and

durabilities compared with their PGM-based counterparts for the unprecedented low-temperature CH₄ combustion.

Throughout all the studies, the author would like to emphasize the importance of atomic-scale understanding of the active site in zeolite toward the rational design of heterogeneous catalysis. By the combination of *in situ/operando* spectroscopy and DFT calculation, the unique active species formed in zeolite were determined under working conditions. For 13-group metals, multinuclear-oxo cluster/metal hydride species, which are formed under oxidative reductive conditions at high temperatures, work as catalytic active sites with superior properties (CH₄ activation at room temperature and very high C₂H₄ selectivity). As the utilization of the structural evolution under working conditions, High-loading Pd-exchange CHA zeolite is prepared via solid ion-exchange reaction under the oxidative condition (under NO flow). In addition, the reversible structural evolution of Rh species in zeolite was used to propose the new transient deNO_x system workable under periodic lean/rich conditions. Finally, based on the result of automated reaction route mapping, the low-temperature CH₄ combustion catalyst using O₃ was rationally designed.

Because of the ordered framework of zeolite, the structural evolution, adsorption/desorption properties, and catalytic activity, which change depending on the local structure, were comprehensively studied to gain an atomic-scale understanding.

This thesis proposed that zeolite-based material is not only an industrially useful catalyst but also the superior platform to understand the structure–property relationship in heterogeneous catalysis.

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