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Citation	Catalysis science and technology, 14(20), 5909-5917 https://doi.org/10.1039/d4cy00894d
Issue Date	2024-10-21
Doc URL	https://hdl.handle.net/2115/95829
Type	journal article
File Information	manuscript-Revision-.pdf



ARTICLE

High-Pressure *in situ* X-ray Absorption Fine Structure Measurements for Hydrogenation of CO₂ to Methanol over Zn-Doped ZrO₂

Received 00th January 20xx,
Accepted 00th January 20xx

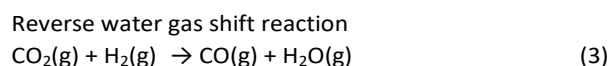
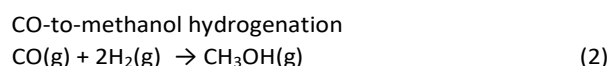
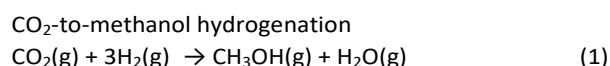
DOI: 10.1039/x0xx00000x

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Obtaining insights into the active-site structure of a catalyst during high-pressure and high-temperature catalytic reactions is extremely challenging. In this study, changes in the coordination structure of Zn species in Zn-doped ZrO₂ catalysts (Zn/(Zn+Zr) atomic ratio = 9%) during CO₂-to-methanol hydrogenation (cell temperature = 400 °C, pressure = 9 bars) was investigated using high-pressure *in situ* X-ray absorption fine structure measurements and density functional theory calculations. The formation of Zn-H species, which are considered the active sites for the reaction, was very limited, with most Zn species existing as [ZnO₄] isolated clusters. Additionally, the adsorption of CO₂ at the Zr⁴⁺ sites near the Zn species induced significant distortions in the coordination structure of the Zn species. This study provides new insights into the catalytic active-site structure.

Introduction

The development of new solid catalysts specific to high-temperature (higher than 200 °C) and high-pressure (higher than 10 bars) reactions, including CO₂ hydrogenation reactions^{1–3} and ammonia synthesis,⁴ is crucial. This study specifically focuses on the hydrogenation of CO₂ to methanol using Zn-doped ZrO₂, a type of metal oxide solid solution.⁵ Methanol synthesis via CO₂ hydrogenation is related to the following reactions:



In general, Cu- and Pd-based catalysts have been used for methanol synthesis at mild temperatures (200–250 °C).^{2, 3} Owing to the well-established effectiveness of these catalysts, other potential catalysts have received little attention. Pérez-Ramírez et al. reported an In₂O₃/m-ZrO₂ (m-: monoclinic) catalyst for CO₂-to-methanol hydrogenation.⁶ Since then, research on metal oxide solid-solution catalysts for this reaction has become increasingly active.^{7–11} For example, Li et al. reported Zn-doped ZrO₂ in 2017¹⁰ and Ga- and Cd-doped ZrO₂ in 2019.⁹ Compared to Cu- and Pd-based catalysts, these metal oxide solid solution catalysts operate at higher reaction temperatures of 300–350 °C. Consequently, they have attracted a significant attention for new and unprecedented applications. The research group of Fukuoka and Shrotri has successfully enhanced the H₂ dissociation ability by co-doping Co species into Zn-, In-, and Ga-doped ZrO₂, achieving a high methanol selectivity of 86%.⁸ Recently, the co-doping of Zn and Cu into ZrO₂ was reported to facilitate H₂ dissociation during CO₂-to-methanol hydrogenation.¹²

We have also reported the catalytic performances of Zn-^{13–15} and In-doped ZrO₂¹⁵ in CO₂-to-methanol hydrogenation. Experimental and computational analyses in our previous studies revealed that Zn species in the as-prepared Zn-doped ZrO₂ are [ZnO₄] isolated clusters. During the CO₂ hydrogenation, these clusters are expected to transform into Zn-H species.¹³ Regardless of whether they form [ZnO₄] clusters or Zn-H species, the Zn species are considered divalent cations. Simultaneously, CO₂ adsorbs onto the Zr⁴⁺ sites in the proximity of Zn-H species, and the reaction between these sites produce of methanol. The formation of Zn-H species has also been reported by several studies.^{9, 10, 12} Redekop et al. used the Auger parameter to show that subjecting Zn-doped ZrO₂ to H₂ flow partially reduced the Zn species in the catalyst.¹⁶ Li et al. showed that in Zn-doped

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Supplementary Information available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

ZrO₂, electron transfer occurs from Zr to Zn, leading to electronic interactions between Zr and Zn.⁷ This promotes the dissociation of H₂ to form more Zn-H species.

In high-pressure reactions, such as CO₂-to-methanol hydrogenation, the reactor is generally made of stainless steel; hence, the state of the catalyst during the reaction can only be speculated. For example, in high-temperature reactions at 300–400 °C, it is challenging to confirm whether H₂ molecules are adsorbed via heterolytic cleavage near the Zn species, resulting in the formation of Zn-H species.

In this study, we aimed to elucidate subtle variations in the Zn coordination structure during CO₂-to-methanol hydrogenation. This was achieved through high-pressure *in situ* X-ray absorption fine structure (XAFS) measurements and density functional theory (DFT) calculations for a metal oxide solid solution of Zn-doped ZrO₂. Although Cu-added ZnZrO_x catalysts have been evaluated using high-pressure *in situ* XAFS, little structural changes have been observed in the Zn species.¹² Hence, capturing structural changes in the stable divalent cation Zn²⁺ species is inherently challenging. Our current research demonstrates that the fine structure of Zn species undergoes modification upon CO₂ adsorption onto the Zn-O-Zr sites.

Experimental

Catalyst preparation

Zn-doped ZrO₂ was prepared using the incipient wetness impregnation method. Amorphous ZrO₂ (NND provided by Daiichi Kigenso Kagaku Kogyo) was impregnated with an aqueous solution of Zn nitrate hydrate (Fujifilm Wako). The obtained powder was dried at 110 °C for 12 h, followed by calcination at 500 °C for 3 h.

Characterisation

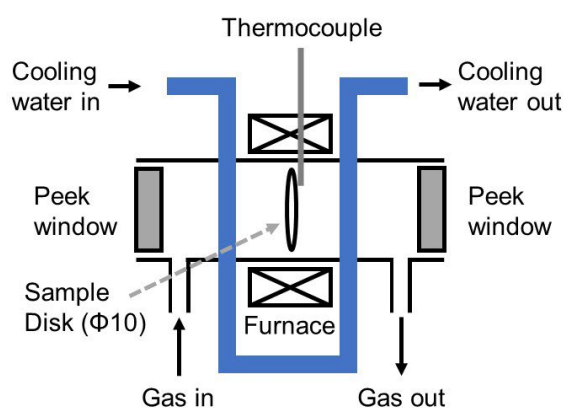
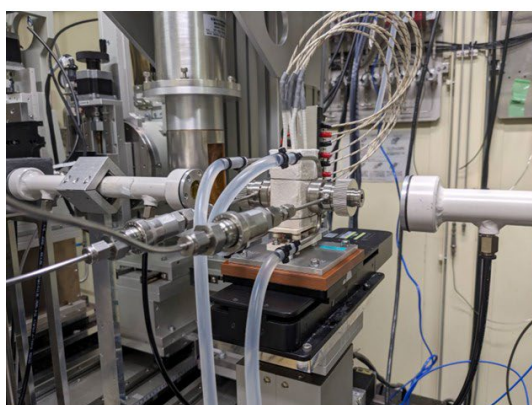


Figure 1 Photograph and schematic of a high-pressure *in situ* XAFS cell.

Calculation

We conducted DFT calculations using the Perdew–Burke–Ernzerhof (PBE)¹⁸ exchange and correlation functional, along with a D3 dispersion correction.¹⁹ The cp2k program package was used for the calculations.²⁰ The Goedecker–Teter–Hutter pseudopotentials^{21, 22} and a double- ζ valence Gaussian basis

We conducted X-ray diffraction (XRD) measurements using a Rigaku Ultima IV diffractometer with Cu-K α radiation, operating at 40 kV and 20 mA. The catalyst composition was measured using X-ray fluorescence (Malvern Panalytical, Epsilon 1, Ag radiation). Omnia software (Malvern Panalytical) was used to analyse the raw data.

Scanning transmission electron microscopy (STEM) was used to observe the catalyst powder directly (JEOL, JEM-ARM200F). The samples were dispersed in ethanol, dropped onto Cu microgrids (Ohkushoji, NP-C15), and dried. Elemental maps of Zr, Zn and O were obtained using energy-dispersive X-ray spectroscopy.

We also performed high-pressure *in situ* XAFS measurements at the Zn K-edge (9.6 keV) on the Zn-doped ZrO₂ catalyst (**Figure 1**). The resulting catalyst powder was packed into a stainless-steel tube, which was then placed in a high-pressure in-situ cell. The cell window was composed of polyether ether ketone with a thickness of 0.5 mm. The temperature of the cell was increased to 400 °C (measured by an electric furnace) at a rate of 10 °C min⁻¹ under a N₂ flow (30 sccm). The sample temperature was measured to be approximately 50 °C lower than the temperature of the electric furnace. Subsequently, the gas was switched to H₂ (30 sccm), and the pressure was increased from 1 to 9 bar. This experiment is referred to as **Test-1**. Additionally, a similar test was conducted using a reaction gas mixture (CO₂/H₂/N₂ = 1/3/1, 30 sccm) instead of H₂ to observe the structural changes in the Zn species under different reaction conditions. This experiment is referred to as **Test-2**. Measurements were performed using a Si (111) double-crystal monochromator at BL14B2 with a quick scan measurement time of approximately 180 s per spectrum. XAFS data analysis was performed using the Athena and Artemis software.¹⁷ The composition of the outlet gas was analysed using a mass spectrometer (Pfeiffer Vacuum, OmniStar GSD301 O1).

set²³ for the orbitals were used. The cutoff associated with mapping Gaussians onto a multi-grid was set to 60 Ry, and the plane-wave cutoff for the finest level of the multi-grid was 400 Ry. A 3 $\times$ 3 $\times$ 1 Monkhorst-Pack²⁴ *k*-point mesh was used. The (101) surface of tetragonal Zn_xZr_{1-x}O_{2-x}, with *x* = 0.125 (ZnZr₁₉O₃₉), and the adsorption structure of H₂ were obtained from our previous work.¹³ Additionally, CO₂ + H₂, formate

(HCOO) + 3H, and methoxy (CH₃O) + 3H, which are possible intermediates in the formate pathway for CO₂ hydrogenation to methanol,¹⁰ were also introduced to the Zn_xZr_{1-x}O_{2-x} surface and their geometry was optimised. On this surface, Zr and O atoms were replaced by Zn atoms and oxygen vacancies, respectively, to maintain the neutrality of the system. The surface consisted of five ZrO₂ layers, and the dimensions of the simulation cell were $L_x \times L_y \times L_z = 6.361 \times 7.227 \times 35.000$ Å³. Hirshfeld analysis²⁵ was performed to examine the partial atomic charges.

Results and Discussion

As-prepared catalyst

Figure 2 shows the XRD patterns of as-prepared Zn-doped ZrO₂. No peaks corresponding to Zn species were observed, indicating that the Zn species were either amorphous, smaller than the XRD detection limit (< 5 nm), or dissolved in the ZrO₂ lattice. The peaks indicated by the filled circles are assigned to tetragonal (t-) ZrO₂, whereas those indicated by the cross marks are assigned to m-ZrO₂. As described in the experimental part, the catalyst was pre-calcined at 500 °C. Considering the thermal stability of pure ZrO₂, m-ZrO₂ is expected to appear at this temperature.²⁶ However, the predominant presence of t-ZrO₂ suggests that guest cations (such as Zn²⁺) were doped into the ZrO₂ lattice, thereby stabilising the t-ZrO₂ phase. This stabilisation effect has been clearly demonstrated in our previous study.^{13, 27} On the other hand, the presence of monoclinic ZrO₂ indicates that a small portion of the prepared catalyst was pure ZrO₂, which existed in the monoclinic phase. The Zn/(Zn+Zr) atomic ratio was 9%, as measured by X-ray fluorescence. In our previous studies, we showed that Zn-doped ZrO₂ with a ratio of less than 20% exhibited a high methanol production rate per unit Zn content.¹³

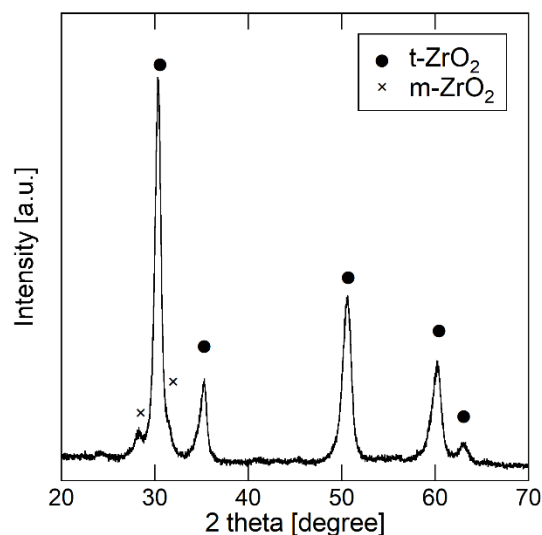


Figure 2 XRD patterns of as-prepared Zn-doped ZrO₂.

Figure 3a shows the Zn K-edge XANES spectra of the Zn-doped ZrO₂, ZnO, and Zn foil. The shape of the spectrum of Zn-doped ZrO₂ was similar to that of ZnO, indicating that the Zn species in Zn-doped ZrO₂ were similar to the Zn²⁺ species in ZnO. **Figure 3b** shows the Zn K-edge radial structure functions (RSFs) of Zn-doped ZrO₂ and ZnO. In ZnO, the RSF plot displays peaks corresponding to Zn-O bonds at 1.5 Å and Zn-Zn interactions at 3 Å. On the other hand, the RSF plot for Zn-doped ZrO₂ only shows a peak corresponding to Zn-O bonds. According to the EXAFS fitting (**Table 1**), the Zn species in Zn-doped ZrO₂ prepared in this study formed isolated [ZnO₄] clusters, as previously reported.¹³

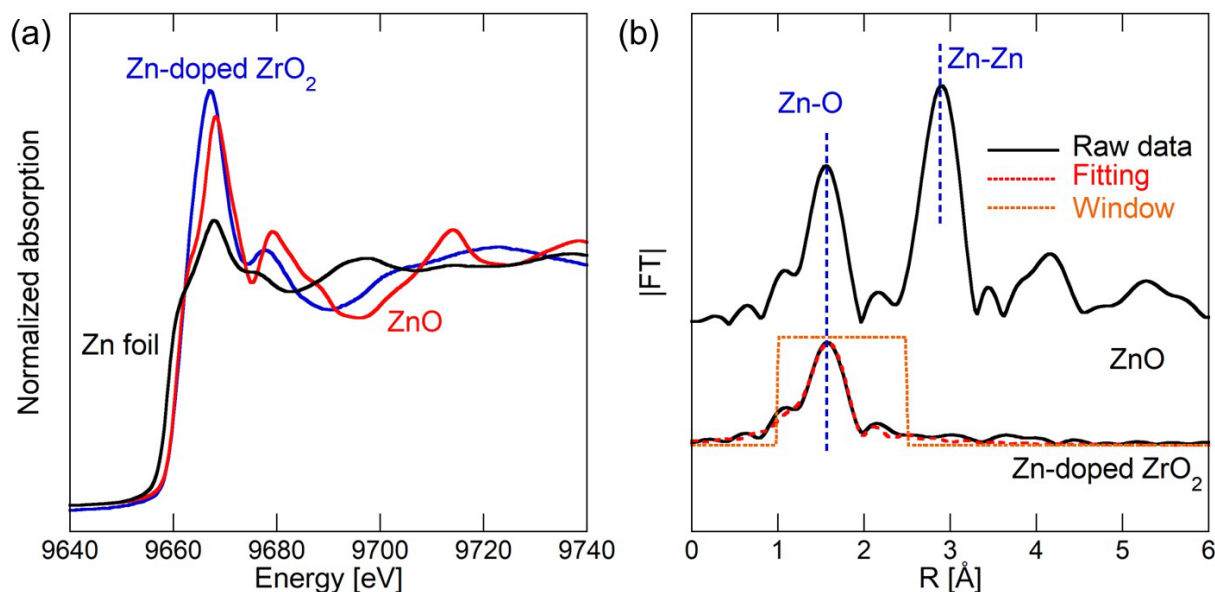


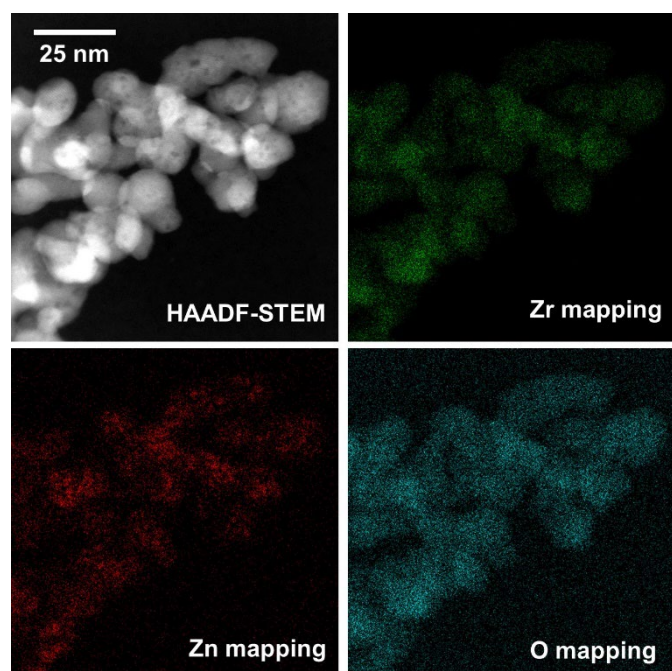
Figure 3 (a) Zn K-edge XANES spectra of Zn-doped ZrO₂, ZnO, and Zn foil. (b) Fourier transforms of k^3 -weighted extended X-ray absorption fine structure (EXAFS) oscillations measured at room temperature near the Zn K-edge of Zn-doped ZrO₂ and ZnO. k range: 3–12 Å⁻¹. R range: 1–2.5 Å. Solid line: experimental; red dashed line: EXAFS model; orange dotted line: window.

Table 1 Parameters calculated by fitting the EXAFS signals of Zn-doped ZrO_2 shown in Fig. 3b

Path	CN	σ^2 [$\text{\AA}^2$]	ΔE_0 [eV]	R [$\text{\AA}$]	R factor
Zn-O	3.1 $\pm$ 0.3	0.007 $\pm$ 0.001	3.7 $\pm$ 1.3	2.00 $\pm$ 0.01	0.01

Notation: CN, coordination number; σ , Debye–Waller factor; ΔE_0 , increase in the threshold energy; R , distance. Confidence interval = 68%.

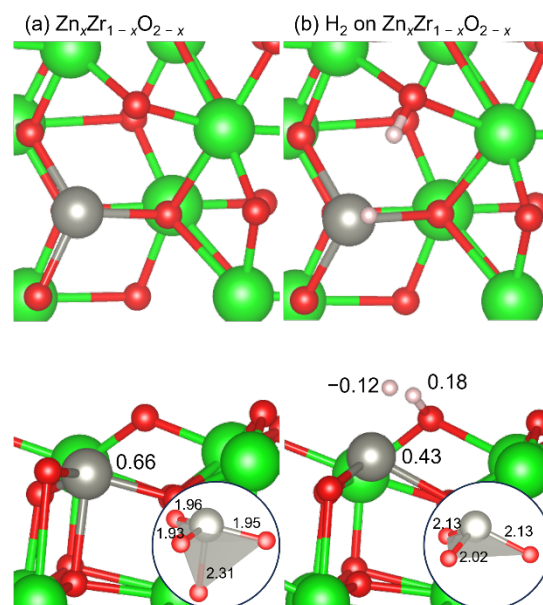
Figure 4 shows a high-angle annular dark field STEM (HAADF-STEM) image of Zn-doped ZrO_2 . Particles with sizes ranging from 10 to 20 nm were observed. The elemental maps for each element overlapped with each other. This image also supports that a portion of the Zn species was dissolved in the ZrO_2 . A closer examination of the HAADF-STEM image reveals areas with varying contrast. Additionally, the Zn map shows that the locations of the Zn species do not completely coincide with the particles observed in the HAADF-STEM image. Therefore, it is concluded that the doped Zn species were unevenly distributed on the ZrO_2 .¹³

**Figure 4** HAADF-STEM image and elemental maps of Zn-doped ZrO_2 .

High-temperature and high-pressure H_2 treatment

Figure 5 shows the DFT-calculated structures of the $\text{Zn}_x\text{Zr}_{1-x}\text{O}_{2-x}$ surface ($x = 0.125$) and the adsorption structure of H_2 . The Hirshfeld charges in **Figure 5** show that a H_2 molecule dissociates into a hydride (H^-) on the Zn atom and a proton (H^+) on the O atom when adsorbed on the $\text{Zn}_x\text{Zr}_{1-x}\text{O}_{2-x}$ surface. The partial charge of the Zn atom in the catalyst surface decreases from 0.66 to 0.43 after H_2 adsorption, indicating the reduction of Zn atom. In other words, by discussing the valence state of the Zn species during the high-temperature and high-pressure H_2 treatments, it is possible to consider the formation of Zn-H species. The DFT calculations reported by Wang *et al.*¹⁰ have

suggested that CO_2 hydrogenation over Zn-doped ZrO_2 involves the dissociative adsorption of H_2 ; therefore, they revealed that Zn atoms are reduced during CO_2 hydrogenation. They were in line with the experimental findings that the Zn species are slightly reduced during heat treatment under H_2 flow. However, in their study, the experimental evaluation of H_2 adsorption was limited to ambient pressure.

**Figure 5** Top and side views of the (a) $\text{Zn}_x\text{Zr}_{1-x}\text{O}_{2-x}$ ($x = 0.125$) surface and (b) H_2 on the $\text{Zn}_x\text{Zr}_{1-x}\text{O}_{2-x}$ surface, visualised using VESTA.²⁸ The numbers in the figure indicate the computed Hirshfeld charges. The insets provide the close-ups of the ZnO clusters with the bond lengths indicated in $\text{\AA}$. Only the top two ZrO_2 layers are shown for clarity.

We carried out *in situ* XAFS measurements to understand H_2 adsorption on Zn species under high-pressure conditions. The coordination structure change of the Zn species in Zn-doped ZrO_2 under a N_2 or H_2 flow was examined in **Test-1**. The experimental procedure is summarised in **Figure 6a**. **Figure 6b** shows the Zn K-edge XANES spectra of Zn-doped ZrO_2 during heat treatment from room temperature to 400 $^\circ\text{C}$ under a N_2 flow. With the increase in the time on the stream from 0 to 69 min, the peak intensity at 9667 eV gradually decreased, and the slope near 9662 eV shifted slightly to a lower energy region. This could be attributed to the Debye–Waller factor caused by the sample temperature change. The XANES spectra remained stable between 69 and 82 min, indicating that the sample temperature was stable and unaffected by the Debye–Waller factor. After 82 min, the gas stream was switched from N_2 to H_2 . **Figure 6c** shows the Zn K-edge XANES spectra during heat treatment at 400 $^\circ\text{C}$ under a H_2 flow. Following the gas exchange,

no significant differences were observed in the XANES spectra between 82 and 142 min. After 150 min, the pressure of the H₂ gas increased from 1 bar to 9 bar, but little change was observed in the XANES spectrum. Therefore, even after the high-temperature and high-pressure H₂ treatment, most of the Zn species remained as [ZnO_o] isolated clusters, and the formation of Zn-H, if present at all, was very limited.

As shown in **Figure 6a**, at 195 min, both the cell temperature and H₂ gas pressure started to decrease. After 270 min, the temperature was returned to room temperature, and the pressure was decreased to 1 bar. **Figure 6d** compares the XANES spectra at the start (0 min) and end (270 min) of **Test-1**. After 270 min, the slope at 9662 eV shifted to lower energies, indicating that the Zn species in Zn-doped ZrO₂ were slightly reduced by the high-pressure H₂ treatment. Additionally, Zn-H

species were formed. Considering that there was almost no change in the XANES spectrum after the high-temperature and high-pressure H₂ treatment, the formation of Zn-H species likely resulted from H₂ chemisorption at the Zn-O binding sites near room temperature. This phenomenon has been well-documented.²⁹

Figure 6e shows the results of Q-mass analysis of the outlet gas during this experiment. At 82 min, the gas was switched from N₂ to H₂, slightly increasing the mass intensity to 31. This increase was not due to the production of methanol ($m/z = 31$), but was likely caused by a baseline shift due to the change in the gas type. This result is important for the subsequent **Test-2** experiment.

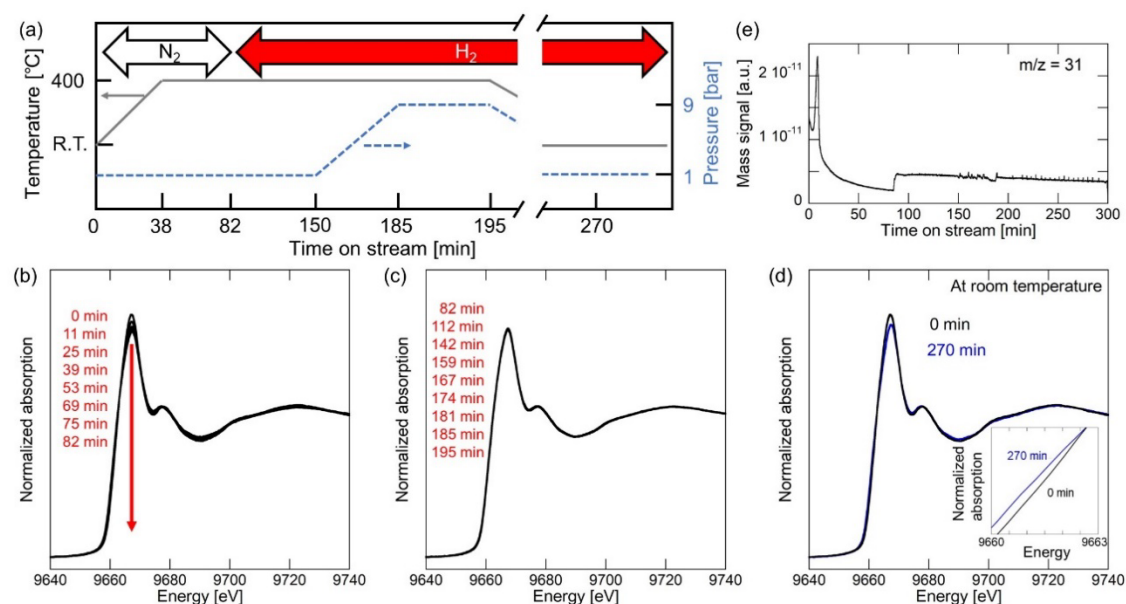


Figure 6 (a) Schematic of cell temperature and gas pressure profiles in **Test-1**. (b-d) Zn K-edge XANES spectra of Zn-doped ZrO₂ during **Test-1**: (b) 0-82 min, (c) 82-195 min, and (d) 0 and 270 min. (e) Mass spectrometer signal of mass 31 for the outlet gas stream from the in situ XAFS cell during **Test-1**.

High-temperature and high-pressure CO₂ hydrogenation condition

Before presenting the XAFS measurement results under reaction conditions, we summarize our results on the reaction performance of ZrO₂, ZnO, and Zn-doped ZrO₂ at 1.0 MPa using a CO₂ hydrogenation model gas (CO₂/H₂/N₂ = 1/3/1, 1.0 MPa). All experiments were carried out using a stainless-steel fixed-bed tubular reactor. When using commercial ZrO₂ (NND) in the temperature range between 190 and 250 °C, no changes were observed (not shown, W/F = 17 g min⁻¹ L⁻¹). Additionally, when using commercial ZnO (Fujifilm Wako), CO₂ was converted, but

most of it became CO (for the catalytic reaction (325°C, W/F = 7 g min⁻¹ L⁻¹).¹⁵ In other words, methanol production was very low. We have evaluated the performance of Zn-doped ZrO₂ by varying the amount of Zn doping (300°C, W/F = 17 g min⁻¹ L⁻¹).¹³ As the Zn/(Zn+Zr) atomic ratio was increased from 7% to 25%, the space-time yield of methanol slightly increased from 1.5 to 1.9 mmol g_{cat}⁻¹. Conversely, within this ratio range, it was found that the space-time yield remained stable between 1.5 and 1.9 mmol g_{cat}⁻¹. Even from the reaction tests alone, it is evident that the Zn species in Zn-doped ZrO₂ play a crucial role in the methanol synthesis from CO₂ hydrogenation.

In addition, to understand CO₂ adsorption property, we introduce our previously reported CO₂-TPD (temperature programmed desorption of CO₂) data for ZrO₂ (NND) and Zn-doped ZrO₂ (**Figure 7**).²⁷ To briefly explain the procedure, 200 mg of the sample was preheated at 300 °C for 3 h in a N₂ flow. After that, CO₂ was adsorbed at 50 °C, followed by a switch to N₂ gas and heating up to 800 °C. Comparing the CO₂ desorption profiles per unit surface area, both catalysts exhibited similar shapes. There was a peak top at 130 °C, which gradually weakened up to about 400 °C. From these results, it can be conclusively stated that CO₂ adsorbs near Zr⁴⁺ sites.

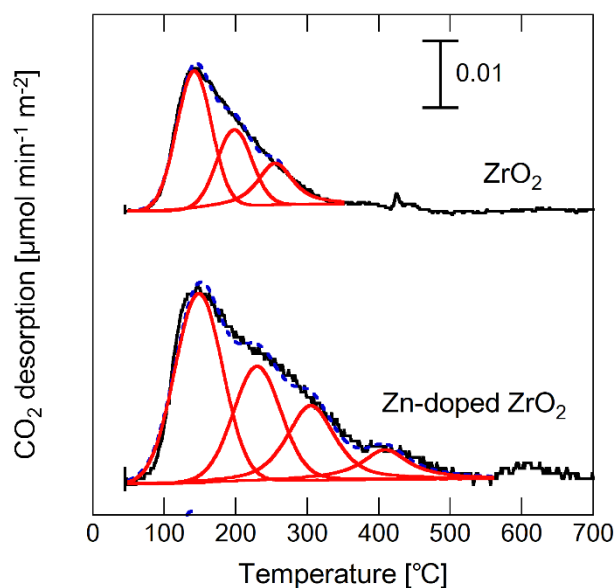
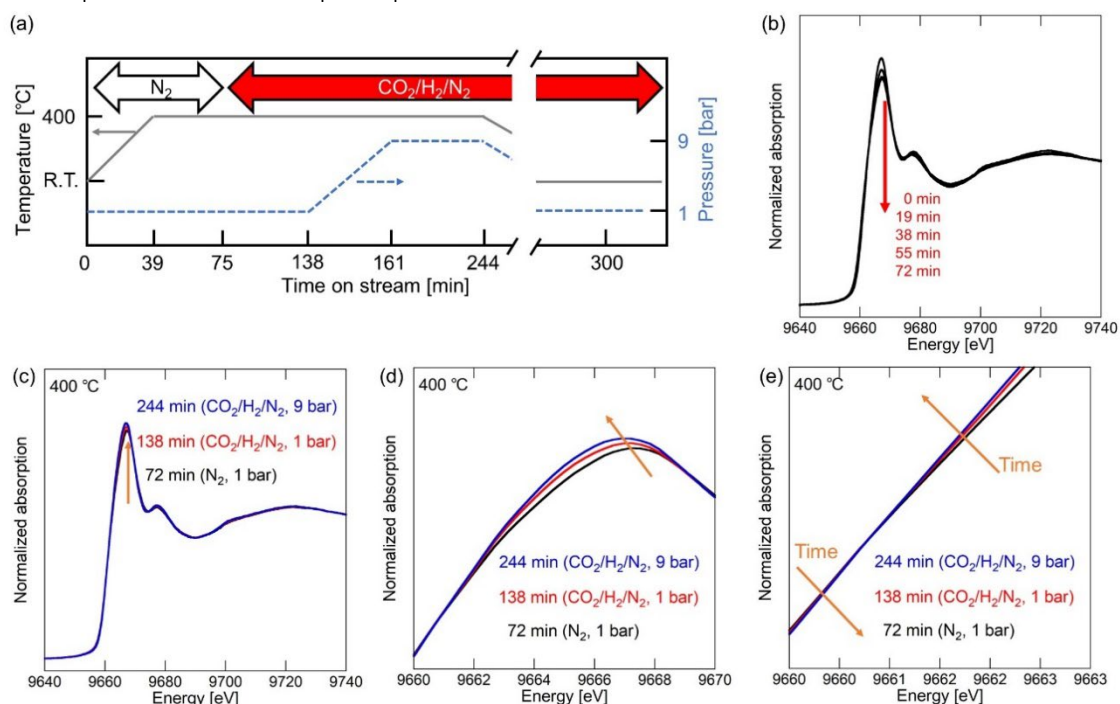


Figure 7 CO₂-TPD profiles of ZrO₂ and Zn-doped ZrO₂. Black solid line: raw data. Blue dotted line: peak sum. Red solid line: separated peak.



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Under the CO₂ hydrogenation reaction conditions, the Zn species in the Zn-doped ZrO₂ catalyst were observed using *in situ* XAFS measurements (**Test-2**). A simplified procedure for this experiment is shown in **Figure 8a**. **Figure 8b** shows the changes in the XANES spectra when heated under a N₂ flow. The results are similar to those of **Test-1** (**Figure 6b**), with the spectra at 55 and 72 min being almost identical. This was likely due to the stabilisation of cell heating after 55 min, resulting in no further temperature changes in the cell. **Figure 8c** shows the XANES spectra obtained when a CO₂/H₂/N₂ mixed gas was introduced. For CO₂/H₂/N₂ supplied at 1 bar, the peak at 9667 eV increased. To examine this change in detail, the region of peak rise between 9660 and 9663 eV was enlarged, as shown in **Figure 8d**. In the 9661–9663 eV range, the spectrum shifted to the lower energy side, whereas it shifted to higher energy in the 9660–9661 eV range. Next, the CO₂/H₂/N₂ gas was pressurised from 1 bar to 9 bar. The intensity of the peak at 9667 eV further increased (**Figure 8c**). In **Figure 8d**, the peak increased slightly and its position shifted to a lower energy region. As shown in **Figure 8e**, in the 9661–9663 eV range, the spectrum shifted further to the lower energy side, whereas in the 9660–9661 eV range, it was shifted further to the higher energy side. Hence, the spectral changes observed after the introduction of CO₂/H₂/N₂ gas suggest a change in the coordination structure of Zn. Furthermore, upon increasing the pressure, the structural changes became even more pronounced.

Figure 8 (a) Schematic of cell temperature and gas pressure profiles in **Test-2**. (b-e) Zn K-edge XANES spectra of Zn-doped ZrO_2 during **Test-2**: (b) 0–72 min, and (c-e) 72–244 min.

Figure 9 shows the results of the Q-mass analysis of the outlet gas composition during the *in situ* XAFS measurements. At atmospheric pressure, when the gas was switched from N_2 to $\text{CO}_2/\text{H}_2/\text{N}_2$, the signal for mass intensity 28 decreased to one-third of its original value. This was consistent with the expected decrease in the concentration of N_2 (mass 28) in the outlet gas from 100% to 20%. Although the concentration of CO_2 (the mass 28 fragments) increased from 0% to 20%, its contribution to the mass signal at 28 was considered negligible. This is because the fragment signal of mass 28 from CO_2 is approximately 10% of the signal for mass 44 (around 3×10^{-9}), as explained in the reference.³⁰ When examining the signal for $m/z = 31$, a slight increase upon introduction of $\text{CO}_2/\text{H}_2/\text{N}_2$ was observed. As shown in **Figure 6e**, this was likely due to the baseline shift that

occurred when the gas type was changed. Notably, when pressurisation began (150 min), the signal for mass 31 increased significantly, and the signal for mass 18 became stronger. The former is attributed to the generation of methanol, whereas the latter is attributed to the generation of water. These results indicate that supplying $\text{CO}_2/\text{H}_2/\text{N}_2$ at 9 bar successfully promotes CO_2 -to-methanol hydrogenation. Integrating the results from the high-pressure *in situ* XAFS study, the $[\text{ZnO}_a]$ isolated clusters in the as-prepared Zn-doped ZrO_2 underwent a change in the coordination structure under the reaction conditions. The altered Zn species are important active sites for methanol synthesis.

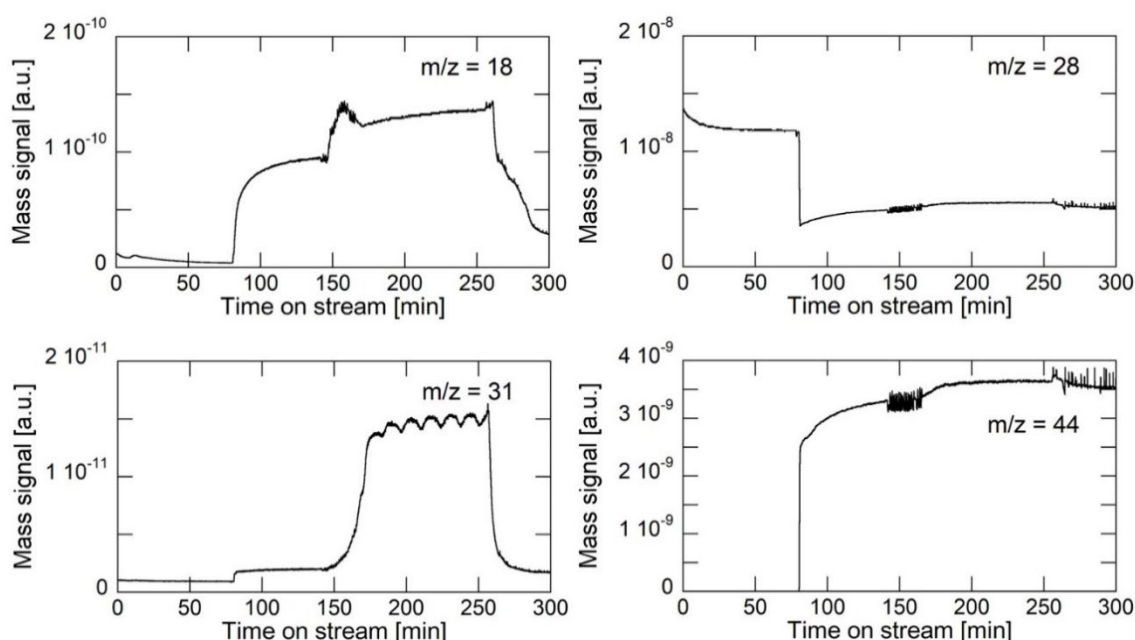


Figure 9 Mass spectrometry signal of mass 18, 28, 31, and 44 for the outlet gas stream from the *in situ* XAFS cell during **Test-2**.

At this stage, the nature and coordination structure of the distorted Zn species remain unclear. However, it is evident that the introduction of CO_2 induces this distortion, as demonstrated by a comparison with the results of the high-pressure *in situ* XAFS study. CO_2 selectively adsorbs onto the Zr sites of catalysts, as confirmed by adsorption experiments and DFT calculations.¹³ To investigate this, DFT simulations were conducted to model the structure of Zn-doped ZrO_2 with reaction intermediates such as CO_2 , formate (HCOO), and methoxy (CH_3O) on the Zr sites (**Figure 10**). The introduction of CO_2 transformed the tricoordinated Zn species (**Figure 10a**) into tetracoordinated clusters (**Figure 10b**). Additionally, when the adsorbed species were converted to formate (**Figure 10c**), the coordination structures of the Zn species differed from those of the Zn species in **Figure 10a**. For methoxy adsorption (**Figure 10d**), the coordination environment of the Zn species did not seem to

differ significantly from that of the initial H_2 adsorption state. The Zn-H distances in **Figures 10a-d** are 1.58, 1.91, 1.56, and 1.61 Å, respectively, indicating CO_2 species can strongly distort the $[\text{ZnO}_a]$ cluster. According to high-pressure *in situ* XAFS measurements and DFT calculations, we can conclude that the presence of CO_2 and CO_2 -derived intermediate species on the Zr sites induces distortions in the coordination structure of the Zn species. Because other possible structures beyond the calculated ones may exist, further investigation of this phenomenon will be pursued.

The results of the high-pressure *in situ* XAFS measurements indicate that the amount of Zn-H formed during the reaction is very limited. Considering this, it seems quite natural that H atoms do not remain on Zn^{2+} at temperatures above 300 °C. We believe that this weak Zn-H bond enables mild reduction reactions such as CO_2 -to-methanol hydrogenation. However,

the scarcity of Zn-H bonds likely makes it challenging to improve CO₂ conversion rates. As a design principle for metal oxide catalysts like Zn-doped ZrO₂, the key will likely be how to

increase the adsorbed H species on the catalyst surface. Indeed, the development of catalysts that utilize spillover H species is crucial and cannot be overlooked.³¹

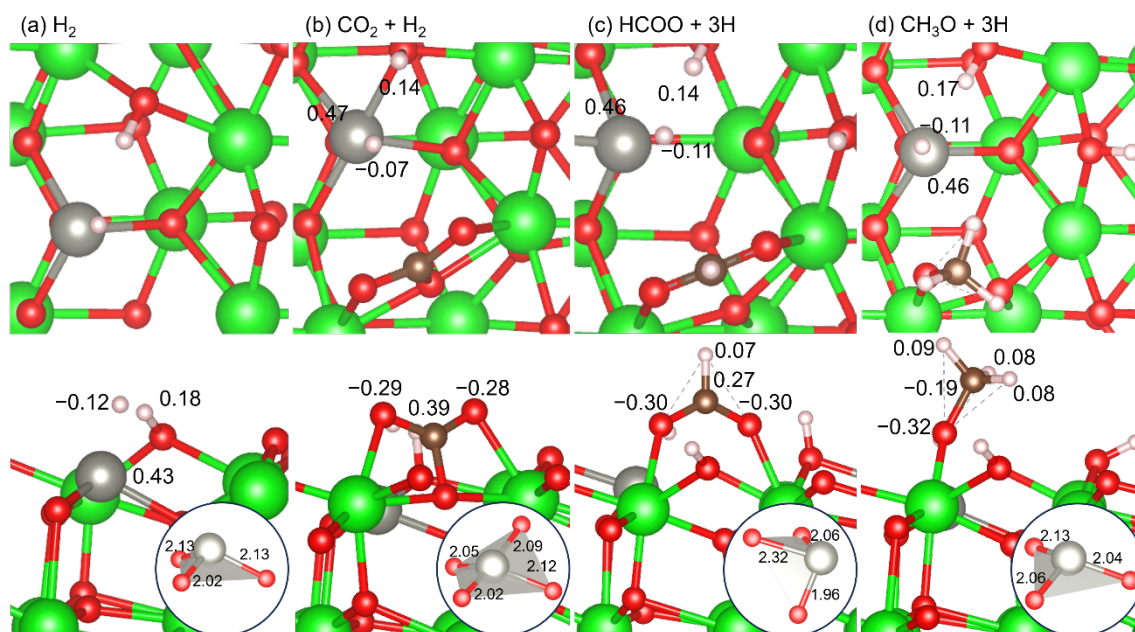


Figure 10 Top and side views of the $\text{Zn}_x\text{Zr}_{1-x}\text{O}_{2-x}$ ($x = 0.125$) surface adsorbed by (a) H_2 , (b) $\text{CO}_2 + \text{H}_2$, (c) $\text{HCOO} + 3\text{H}$, and (d) $\text{CH}_3\text{O} + 3\text{H}$, visualised using VESTA.²⁸ The numbers in the figure represent the computed Hirshfeld charges. The insets show the close-ups of the ZnO clusters with the bond lengths in Å. Only the top two ZrO_2 layers are shown for clarity.

Conclusion

The coordination structure changes of the Zn species in Zn-doped ZrO_2 , exhibiting remarkable performance in CO_2 -to-methanol hydrogenation, were investigated using high-pressure in situ XAFS measurements. During hydrogen reduction under pressurised conditions, structural changes in the Zn species were minimal. Even after the high-temperature and high-pressure H_2 treatment, the majority of the Zn species remained as isolated $[\text{ZnO}_4]$ clusters, and the formation of Zn-H bonds, if present at all, was very limited. In contrast, during the CO_2 hydrogenation reaction under pressurised conditions, slight distortions were observed in the structure of the Zn species. Our DFT calculations revealed that the adsorption of CO_2 at Zr^{4+} sites near Zn species can induce these structural distortions.

Acknowledgements

This study was financially supported by the Feasibility Study Program on Energy and New Environmental Technology (No. 22100386-0) of the New Energy and Industrial Technology

Development Organization of Japan, JSPS KAKENHI (Grant Number 24K01240) and the Environment Research and Technology Development Fund (JPMEERF20243RA3) of the Environmental Restoration and Conservation Agency provided by the Ministry of the Environment of Japan. The synchrotron radiation experiments were performed at BL14B2 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI, Proposal nos. 2023B1576 and 2024A1517). Calculations were performed using supercomputers at ACCMS, Kyoto University. We thank the Advanced Research Infrastructure for Materials and Nanotechnology of Japan (ARIM) program (Grant No. JPMXP1222OS0026) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan, at the Research Center for Ultra-HighVoltage Electron Microscopy (Nanotechnology Open Facilities), Osaka University.

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