



Title	The Effect of Structural Change during the Activation Process on the Catalysis of In/SiO ₂ Nonoxidative Coupling of Methane : An Operando XAFS Study
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The Effect of Structural Change during the Activation Process on the Catalysis of In/SiO₂ Non-Oxidative Coupling of Methane: An *Operando* XAFS Study

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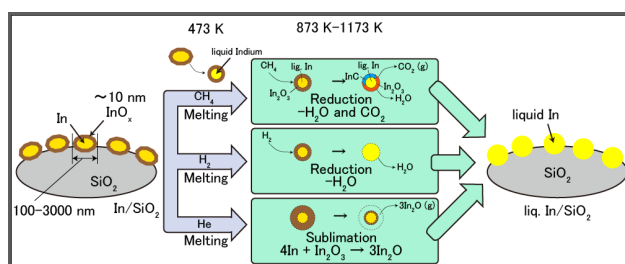
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TOC Graphic

The Effect of Structural Change during the Activation Process on the Catalysis of In/SiO₂ Non-Oxidative Coupling of Methane: An *Operando* XAFS Study

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Abstract: A SiO₂-supported indium catalyst (In/SiO₂) has shown high performance for the non-oxidative coupling of CH₄ (NOCM). Previous *operando* X-ray absorption fine structure (XAFS) studies revealed that the In/SiO₂ catalyst undergoes dynamic structural changes during the activation process under flowing CH₄, such as melting, new bond formation, and regeneration of the metallic form. To understand the effect of these dynamic changes, especially the formation of new bonds, on the catalytic properties, we examined the structures of an In/SiO₂ catalyst during the activation process under various gas flows (CH₄, H₂, and He) using *operando* XAFS. Fresh In/SiO₂ catalysts are composed of metallic In particles covered with InO_x. All of the samples melted at 430 K. In the XAFS spectrum of the sample under the He flow, peaks associated with the In–O bonds on the surface became visible at ~800 K. In was partially evaporated at 1100 K because of the formation of volatile In₂O. When the gas was switched from He to CH₄, the In/SiO₂ was reduced to liquid-metal In. By contrast, in the In/SiO₂ under the H₂ flow, the In–O bonds were removed at ~600 K. In the spectra of In/SiO₂ under the CH₄ flow, an In–X peak appeared at 800 K and then increased in intensity as the temperature was increased to 1100 K; this latter peak-increasing process was not observed under the He flow. The

In- X peak was assigned to either In-CH₃ formed via the reaction with CH₄ or to In-O of surviving InO _{x} species. The In- X peaks completely disappeared at 1100 K, and the catalyst became active toward the NOCM. Under all three gas-flow conditions, the liquid-metal In served as the active site during the reaction. The remarkable activity and long lifetime of the active site stem from the exceptional mobility and flexibility of the In atoms within the liquid metal.

Keywords: Nonoxidative Coupling of Methane; In/SiO₂ catalysts; *operando* XAFS

1 Introduction

Methane (CH_4) is the simplest and the most stable hydrocarbon. CH_4 is the primary component of both natural gas (~95%) and shale gas (>70%). Although CH_4 as a raw material can potentially replace petroleum, it is now mainly used as an energy source. The synthesis of higher hydrocarbons from CH_4 gas with high selectivity is an interesting challenge.¹ The problem stems from the high stability of CH_4 , which necessitates severe reaction conditions. Various methods have been proposed for CH_4 activation, including the oxidative coupling of methane (OCM).²⁻⁵ Compared with the selectivity toward the synthesis of hydrocarbons via the OCM, that toward the synthesis of hydrocarbons via the direct non-oxidative coupling of methane (NOCM) at high temperatures has been improved even though the NOCM is thermodynamically unfavourable.⁶⁻⁹

Recently, Nishikawa *et al.* found that, as an alternative to transition-metal catalysts, 10 wt% In/ SiO_2 showed high activity for the NOCM reaction at 1173 K.¹⁰⁻¹¹ The 10 wt% In/ SiO_2 catalyst activated under the CH_4 flow up to 1173 K showed 3–4% CH_4 conversion with 63% selectivity to higher hydrocarbons at 1173 K. On the other hand, when activated under the He flow, the In/ SiO_2 catalyst showed a decrease in activity and the In sublimated which was visible at the cool downstream part of the reactor.

The characterizations of In under high temperature and CH_4 flow conditions are not easy.¹⁰⁻¹¹ X-ray absorption fine structure (XAFS) is a unique characterization method applicable to such reaction conditions. In our previous study, we followed the activation process of a 10 wt% In/ SiO_2 catalyst under a CH_4 flow using an *operando* quick X-ray absorption fine structure (XAFS) technique.¹² *Operando* XAFS provides information about the local structure around the X-ray-absorbing atom even under a reaction temperature exceeding 1000 K and under the pure CH_4 flow. This feature is unique to *operando* XAFS. During the activation process under the CH_4 flow, we observed dynamic metamorphosis-like transformations in the structure of the In species on SiO_2 . These transformations included melting at 430 K, the formation of a new In–*X* bond at 873 K, and the regeneration of liquid-metal In at the reaction temperature (1173 K). We tentatively assigned species *X* as C. The sublimation of In might be prevented by the formation of In–C under the CH_4 flow. The other merit of *operando* XAFS is the ability

to simultaneously characterize the effluent gases, thereby providing additional information about the chemical reactions. The difficulty of *operando* XAFS at higher temperatures, on the other hand, is that the curve fitting analysis of the high-temperature XAFS may not evaluate the correct structure parameters because there is a large asymmetric radial distribution. In the present study, we focused on the change of structure derived from the *operando* XAFS. We carried out the *operando* XAFS analysis together with analysis of the gas products during the activation processes under different gas flows (i.e., CH₄, H₂, and He flows) to clarify the structure change of In species and the origin and role of the In–X bond. The active phase structure is discussed.

2 Experimental Section

In/SiO₂ samples were prepared using an impregnation method previously reported by Nishikawa *et al.*^{10, 11} The In particles size was 100–3000 nm as a result of SEM.¹⁰ The *operando* In *K*-edge XAFS measurements of the In/SiO₂ catalyst were carried out at the NW-10A beamline of the Photon Factory Advanced Ring (PF-AR, 6.5 GeV, 100 mA) at KEK-IMSS-PF (Tsukuba, Japan) using a Si (311) double-crystal monochromator in a quick XAFS mode to acquire the whole spectrum every 40 sec.^{13–15} *Operando* XAFS experiments were carried out in a specially designed quartz cell and gas-flow system (**Figure S1**). Although the quartz cell was fragile, we used it instead of a robust stainless-steel cell because the stainless-steel cell would be active at high temperatures, precluding monitoring of the product distribution during the reaction. Two X-ray windows were made of Vespel SP-21 (polyimide) with a thickness of 1 mm and were cooled with circulating water. The In/SiO₂ catalyst (100 mg) was compacted into a disk to adjust the edge jump to be nearly unity. The sample disk was placed in the middle of the quartz cell, and the cell was placed in the center of an electric heater. Quadrupole mass spectrometry (QMS, Omni Star GSD320; Pfeiffer Vacuum, Asslar, Germany) was used to monitor the outlet gases. The catalyst temperature was monitored by a thermocouple. The temperature was ramped linearly from 300 to 1173 K at 10 K/min under a 10 mL/min flow of CH₄, H₂, or He gas. Under the H₂ or He gas flow, the catalysts were activated at 1173 K and then the gases were switched to CH₄ for the NOCM reaction. The change in the amount of In was monitored from the edge jump determined by the difference between the pre-

edge and the post-edge smooth curves. The EXAFS data were analyzed using the REX 2000 software program (Rigaku, Tokyo, Japan).¹⁶⁻¹⁷ The photoelectron kinetic energy was converted to wavenumber, k , using equation (1):

$$k = \sqrt{\frac{2m}{\hbar^2} (E - E_0)} \quad (1)$$

where E and E_0 are the incident X-ray energy and the absorption edge energy, respectively. We carried out background removal and normalization, followed by Fourier transformation. The Fourier transformed peaks were filtered and inversely Fourier transformed to the k -space. The XAFS oscillation, $\chi(k)$, was fitted with N_i , r_i , ΔE_{0i} , and σ_i^2 , which are the coordination number, the bond distance, the correction of the absorption edge energy, and the Debye–Waller factor for the i -th shell, respectively, using the following equations:¹⁸

$$k^3 \chi(k) = \sum \frac{k_i^2 N_i F_i(k_i) e^{-2\sigma_i^2 k_i^2}}{r_i^2} \sin(2k_i r_i + \phi_{i(k)})$$

$$k_i = \sqrt{k^2 - \frac{2m}{\hbar^2} \Delta E_{0i}} \quad (2)$$

where $F_i(k)$ and $\phi_i(k)$ are the backscattering amplitude and phase-shift functions for the i -th coordination shells, as determined by calculations using the FEFF software, respectively;¹⁹⁻²¹ $\hbar = \frac{h}{2\pi}$ and m is the mass of an electron. Note that the curve fitting analysis of the In/SiO₂ at higher temperature is limited¹⁷ because of its asymmetric radial distribution of In-In bond. We must be careful about the obtained curve fitting results. The relative values have some meaning because all data were measured in a series of one sample with different temperatures and different gas flows.

The X-ray photoelectron spectroscopy (XPS) experiments were conducted using a JPS-9010MC (JEOL, Japan) operated at 12 kV and 10 mA with Mg K α radiation under the charge-neutralization system. The vacuum in the analysis chamber was 10⁻⁶ Pa under the operating conditions. The binding energies were calibrated using C 1s.

3 Results

3.1 XANES Analysis

Figure 1 shows the In K-edge X-ray absorption near edge structure (XANES) spectra¹² of the In/SiO₂ catalyst subjected to three different activation processes (CH₄, H₂, and He) at 300, 473, 873, and 1173 K, as well as the spectra of In foil and bulk In₂O₃. The data acquired at 300 K were normalized to the edge jump equal to unity. Because the data at different temperatures were acquired under the same conditions, we used the same normalization factor; thus, a decrease in the edge jump indicated a decrease in the amount of In in the X-ray optical path during the activation processes. The K-edge spectra of the In in the In/SiO₂ at room temperature had a smaller edge peak (denoted as “F”) at 27,950 eV and the edge appeared at the lower-energy side compared with the peak in the spectrum of In₂O₃. The edge peak “F” intensity and edge position in the spectra of the In/SiO₂ samples are similar to those in the spectrum of the In foil, indicating that the In in the In/SiO₂ at 300 K had a valence state of ~0 even though the edge peak intensity was slightly greater than that of the pure In metal. Thus, a small amount of In–O was present on the surface region, likely formed during the storage process. **Figure S3(a)** shows the peak deconvolution of the peak “F” of In/SiO₂ at room temperature by those of In foil and In₂O₃. The amount of InO_x was estimated to be 3 ± 1 %.

The XPS analysis also showed that the surface In was present in the oxidized state (denoted as InO_x); no In metal was detected (**Figure S2**). The thickness of surface InO_x should be greater than several nanometers, considering the escape depth of the Indium 4d photoelectrons.

In the spectra acquired under all the investigated gas flows, the second and third peak positions (denoted as “S” and “T” in the Fig.1) showed slight shifts to the higher-energy side at 473 K. These shifts were corresponding to the melting of In, which occurs at 429.5 K for bulk In.²²

When the sample was heated to the reaction temperature of 1173 K, the XANES edge positions did not substantially change during the heating process irrespective of the gas atmosphere, indicating that the valence state of In was maintained. However, the peak intensities changed depending on the flow gas conditions. In the spectrum acquired under the H₂ flow, the peak intensity decreased at 873 K; under the He flow, the decrease in

peak intensity at 873 K was smaller. When the sample was treated under the CH₄ flow, the change was slightly larger than that under the He flow but smaller than that under the H₂ flow, indicating the partial removal of InO_x or the formation of other species.

At 1173 K the peak intensity in the In/SiO₂ under the CH₄ flow decreased to the same extent as under the H₂ flow, indicating full reduction to the metallic state under the CH₄ flow. Under the He flow, the total absorption decreased, indicating the loss of In at 1173 K.

Figure 2 shows the temperature dependence of the edge jump variation normalized by the edge jump measured at 300 K, which corresponded to the amount of In in the X-ray optical path. The edge jump remarkably decreased for the sample under the He flow at 1100 K, whereas the edge jumps for the sample under the H₂ and CH₄ flows little decreased with temperature. The decrease in the edge jump for the sample under the He flow indicated partial sublimation of In from the catalyst. The change in edge jump under the O₂ flow was constant, which will be discussed later.

Figure 3 shows the changes in the edge peak intensity as a function of temperature ($I(T)$), normalized by the peak intensity at room temperature ($I(RT)$). Under all of the investigated gas-flow conditions, the edge peak decreased abruptly at 430 K, corresponding to the melting of In. When the sample was under the H₂ flow, the edge peak intensity decreased steeply at 600 K, indicating the reduction of the surface InO_x layer, and then gradually decreased as the temperature was increased to the reaction temperature. Under the CH₄ atmosphere, the peak intensity decreased as the temperature was increased to 800 K and then increased slightly as the temperature was increased to 1000 K. The peak intensity then suddenly decreased in the range 1000–1100 K to the level observed under the H₂ flow. Under the He flow, little change was observed as the temperature was increased to 1100 K after the melting at 430 K; the peak intensity then rapidly decreased at temperatures beyond 1100 K, mainly because of the loss of In. However, when the He flow was changed to CH₄ flow at 1173 K to start the reaction, the edge peak intensity decreased dramatically. **Figure S3b** shows the XANES spectra of the sample before and after the CH₄ flow, where the edge peak intensity corresponds to those of the sample activated under the H₂ or CH₄ flow. The InO_x was fully removed by the reaction with CH₄ at 1173 K.

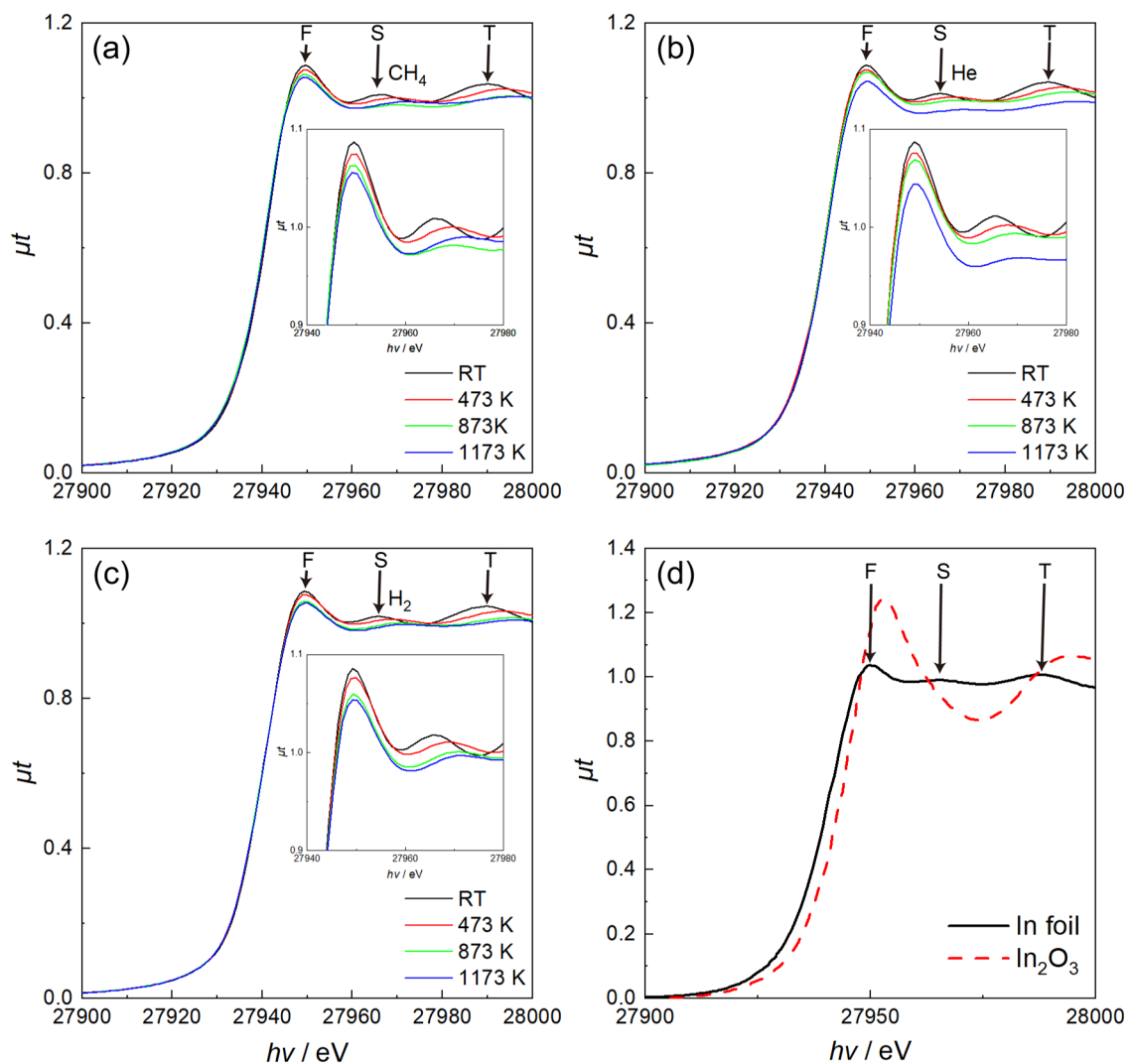


Figure 1 XANES spectra of In/SiO₂ under different heating processes: (a) under CH₄ flow, (b) under He flow, and (c) under H₂ flow. Black RT, Red 473 K, Green 873 K and Blue 1173 K. (d) XANES spectra of In foil (black) and In₂O₃ (red dashed curve).

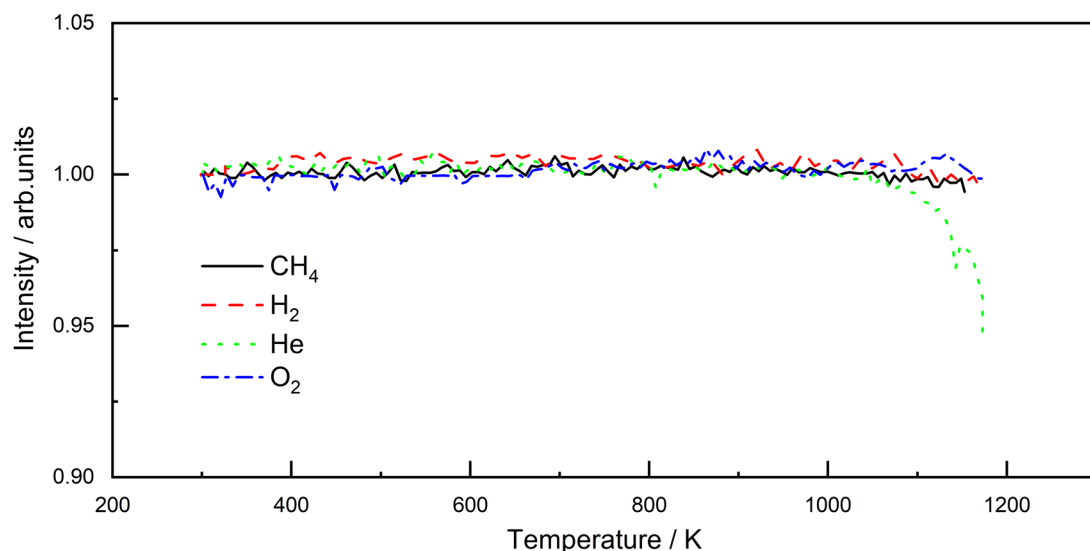


Figure 2 Edge jump of the In K-edge in the spectra of In/SiO₂ under CH₄ (black solid), H₂ (red broken), He (Green dotted), and O₂ (blue dashed dotted) flows.

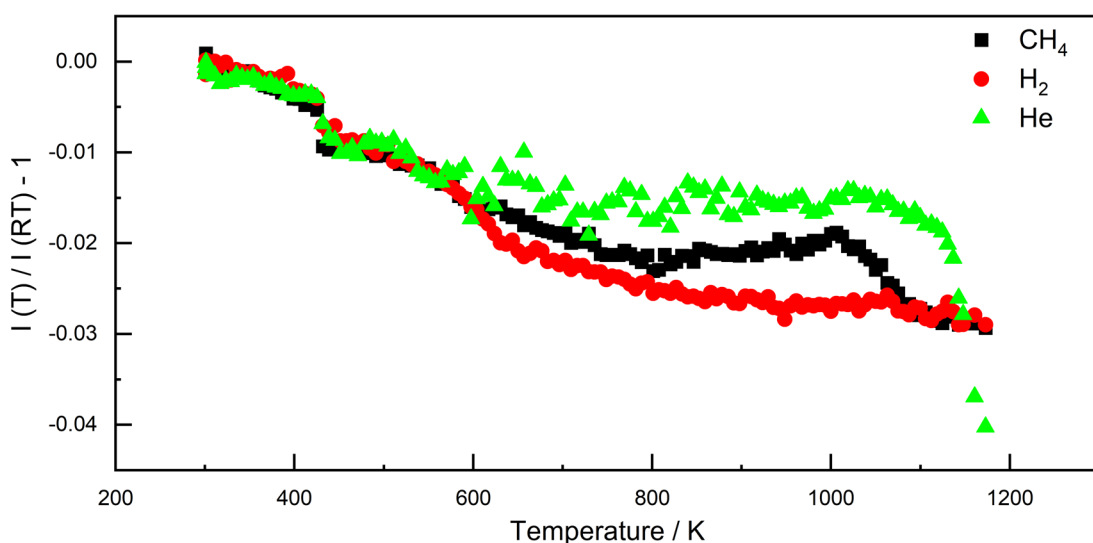


Figure 3 The edge peak intensity dependence on temperature for In/SiO₂ under CH₄ (black filled squares), H₂ (red filled circles), and He (green filled triangles) flows.

3.2 EXAFS Analysis

Figure 4 shows the k^3 -weighted EXAFS ($\chi(k)$) oscillations and their Fourier transforms (FTs) at different temperatures. In the spectra acquired at room temperature, one peak corresponding to the In–In bond distance in the In/SiO₂ samples appeared. The peak position corresponded well with that of In metal. The coordination numbers of the In/SiO₂

also agreed with that of the In metal as shown in Table S1, indicating that the In/SiO₂ was composed of large particles.¹² The coordination numbers of both In metal and In / SiO₂ (3.4) determined by the conventional EXAFS analysis were quite smaller than that expected from crystallographic data(12). This was because In-In bond in In metal had the large thermal and static disorders as discussed later. Since we used the same sample with different treatments (different gas flows and temperatures) in the operando XAFS measurements, the structure parameters given in Table S1 had meaning when they were compared with each other at the same temperatures or under the same gas flow conditions.

The EXAFS oscillations for all the activation processes at 473 K differed from those at room temperature irrespective of the gas flows. This change was related to the melting of In. The FT peak shifted to the shorter side.

A substantial change was observed in the EXAFS spectrum of the sample under the CH₄ flow at 873 K. A new peak appeared at 1.7 Å (**Figure 4(c)**, black curve). This peak might have originated from light elements such as C or O. We considered two possibilities: C originating from CH₄ decomposition and O originating from the surface InO_x. Determining whether the lighter element *X* was C or O based on EXAFS analysis alone was difficult.

Under the He flow, the peak appeared at 1.7 Å (**Figure 4(c)**, green curve). In this case, the peak at 1.7 Å was uniquely assigned to In–O because no CH₄ was present. The origin of In–O observed under the He flow was the surface oxygen that covered the In particles, as described in the discussion of the XAFS results, where we discussed why the peak appeared at high temperatures. In contrast, no extra peak was observed under the H₂ flow. The reaction of H₂ with surface O removed the In–O bond. We carried out the curve-fitting analysis in the In–*X* region under the assumption that *X* was O and derived the coordination numbers at each temperature (**Figure 5**). Because the peak was not visible at room temperature, we assumed that an In–O bond formed with the same bond distance observed under the He flow at higher temperatures. We used the $\Delta E = 11$ eV and the Debye Waller factor $\sigma^2=0.011$ Å² (873 K) with temperature dependence estimated by In–O vibrational frequency and equation (3) given below. The error bar in **Figure 5** was smaller than that given in Table S1 because of the smaller number of adjustable parameters in the fitting processes. In this analysis we found that the finite apparent

coordination number at room temperature was ~ 0.18 . Notably, the coordination number of 0.18 has only a relative meaning. At ~ 435 K, sudden changes in the coordination numbers for In–X were observed, which were related to melting of In metal. At 600 K, the coordination number decreased in the H₂ flow but was maintained under the He and CH₄ flows. The decrease in the coordination number under the H₂ flow corresponded well to the decrease in the edge peak intensity in **Figure 3**. Under the He flow, the apparent coordination number of In–X remained almost constant as the temperature was increased to the reaction temperature; by contrast, under the CH₄ flow, it gradually increased at 800 K, reached its maximum value at ~ 1000 K, and then decreased at higher temperatures. This behavior corresponds well with that observed for the change in edge peak intensity in the XANES spectra under the CH₄ flow (**Figure 3**). **Figure S4** shows the FTs of the spectra under flowing CH₄ at different temperatures of 600, 873, 1000, and 1117 K. The peak at ~ 1.7 Å in the FTs gradually increased as the temperature was increased to 1000 K. The In–X might be originally assigned to surface In–O species. The In–X peak increased in intensity because of the formation of an additional In–C bond alongside the In–O bond. However, the EXAFS technique could not distinguish between In–C and In–O bonds because of their similar backscattering amplitude and phase shift.

At 1173 K, the In–X peak under the CH₄ flow disappeared (**Figure 4(d)**). The peak corresponding to In–In was present under both the CH₄ and H₂ flows, whereas the In–O peak remained under the He flow at 1173 K. When the He flow was switched to CH₄ flow, the In–O peak disappeared (**Figure S5**) and the In–O species was converted to metallic In species, consistent with the XANES (**Figure S3(b)**). Under all three investigated activation atmospheres, the metallic In structure was observed under the reaction conditions (**Figure S6**) where FT peaks with a similar height were observed at the position corresponding to the In–In distance.

Figure 6 shows the FTs corresponding to the cooling process of the In/SiO₂ under the CH₄ flow. During the cooling process, the main peak gradually increased in intensity. **Figure 6(b)** shows the FT peaks acquired in the temperature range from 1173 K (reaction temperature) to 583 K. Although the peaks increased in intensity, no new peak appeared at 1–2 Å, indicating that In–C was not formed during the cooling process. **Figure 6(c)** shows the FTs corresponding to the region 450–387 K. The FT peaks shifted to larger r values and were broadened at 411–406 K, indicating that the In had solidified. At 406 K,

where both the liquid and solid phases were present, the peak width was the largest. The freezing point and melting point differed by 20 K because of overcooling, as previously reported.²³ We concluded that the active structure was liquid-metal In.

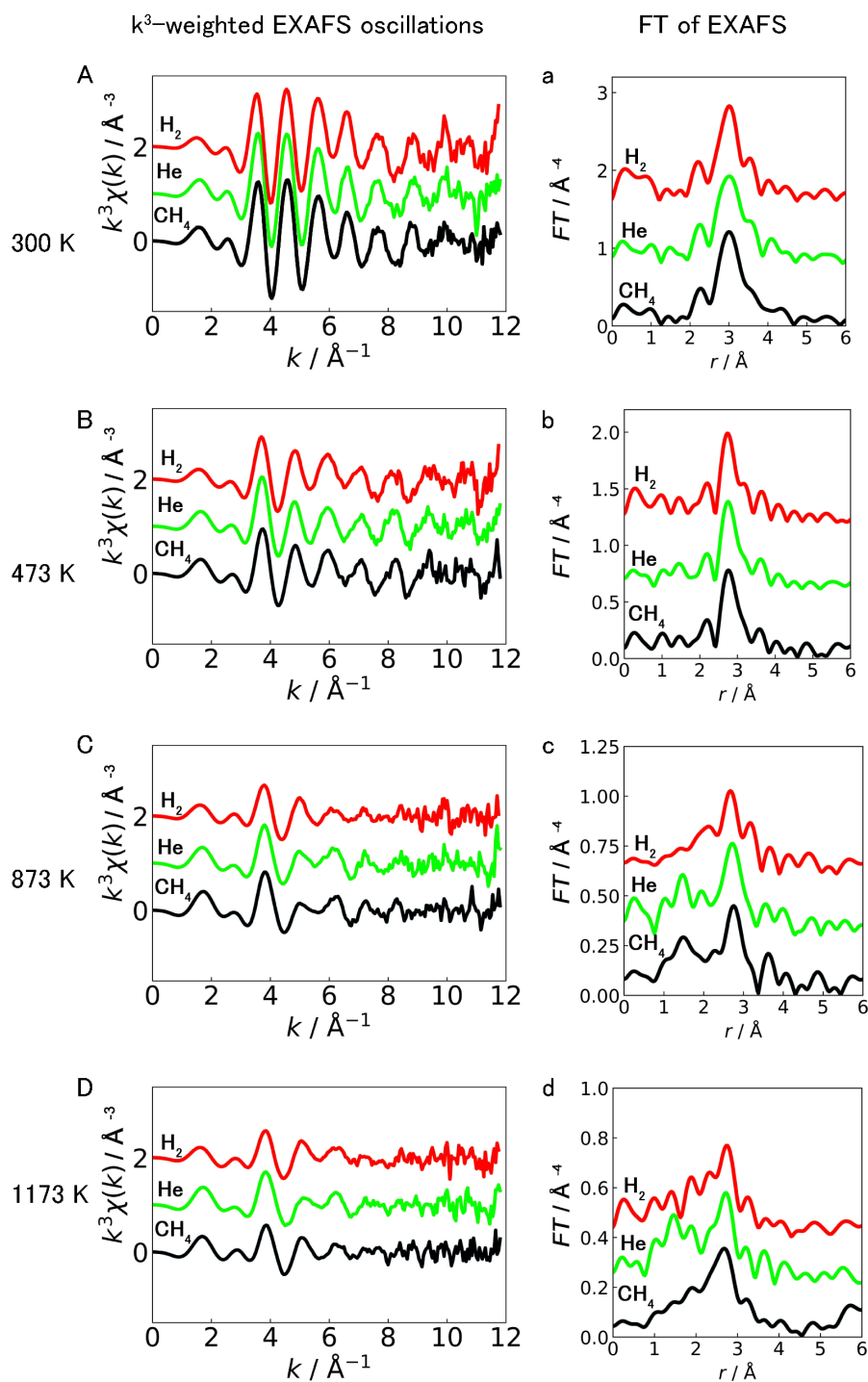


Figure 4 The k^3 -weighted EXAFS oscillations (A, B, C, D) and FTs (a, b, c, d) of EXAFS spectra acquired during different activation processes: (A, a) 300 K, (B, b) 473 K, (C, c) 873 K, and (D, d) 1173 K under the H₂ (red), He (green), and CH₄ (black) flows.

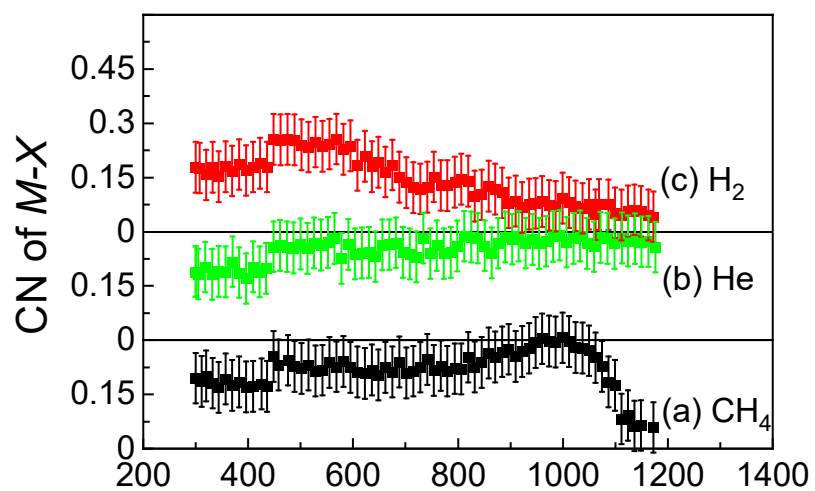


Figure 5 Temperature dependence of the coordination number of In-X in the flows of (a) CH_4 , (b) He , and (c) H_2 .

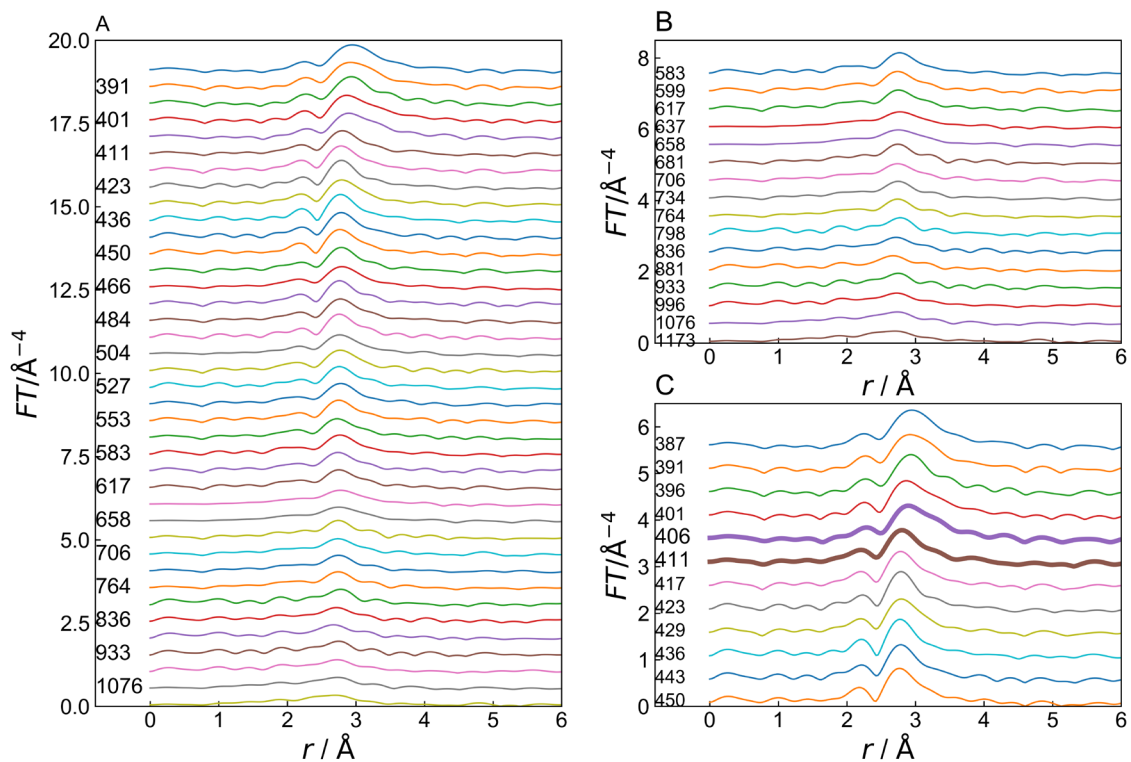


Figure 6 The FTs of In/SiO₂ under the CH₄ flow during the natural cooling process: (a) 1173–387 K, (b) 1173–583 K, and (c) 450–387K.

3.3 Heating process of the In/SiO₂ under the O₂ flow

The edge jump analysis in **Figure 2** shows the loss of In under the He flow during the heating process, where the surface In-oxide (InO_x) was present. Thus, the surface InO_x might be the origin of the loss of the In by sublimation. To confirm this point, we heated the In/SiO₂ under the O₂ flow. **Figure S7** shows the XANES spectra of the In K-edge under the O₂ flow, where the spectra were normalized by the edge jump of the In spectrum acquired at room temperature. The edge peak increased in intensity with increasing temperature, indicating bulk oxidation of In to In₂O₃. In addition, we observed the isosbestic point, indicating little loss of In. **Figure 2** shows the change in the edge jump during the heating process under the O₂ flow. The edge jump did not decrease even at 1173 K. The sublimation of the surface InO_x was less likely.

3.4 Quadrupole mass analysis

Figure 7 shows the QMS results for the effluent gases during the activation process. Higher hydrocarbons were observed in the CH₄ flow. However, they were mainly observed immediately after the In–X bond disappeared in the FT resulting in the In reduction at temperatures greater than 1100 K, as indicated by the XAFS results. The CO₂ evolution and H₂O formation were observed at temperatures greater than 1000 K. H₂ was observed at temperatures greater than 1100 K. **Figure 8** shows the H₂O evolution under the H₂ flow. We observed a peak at 600 K, which corresponds well to the temperature associated with the reduction of the edge peak intensity in the XANES spectrum and the disappearance of In–O in the FT. **Figure 9** shows the results of the gas-product analysis during the reaction. Under the He flow, the activity per amount of In after its sublimation was corrected by the edge jump shown in **Figure 2**. The steady-state activity and selectivity were approximately the same among the three gas flows, indicating that the active structures were similar.

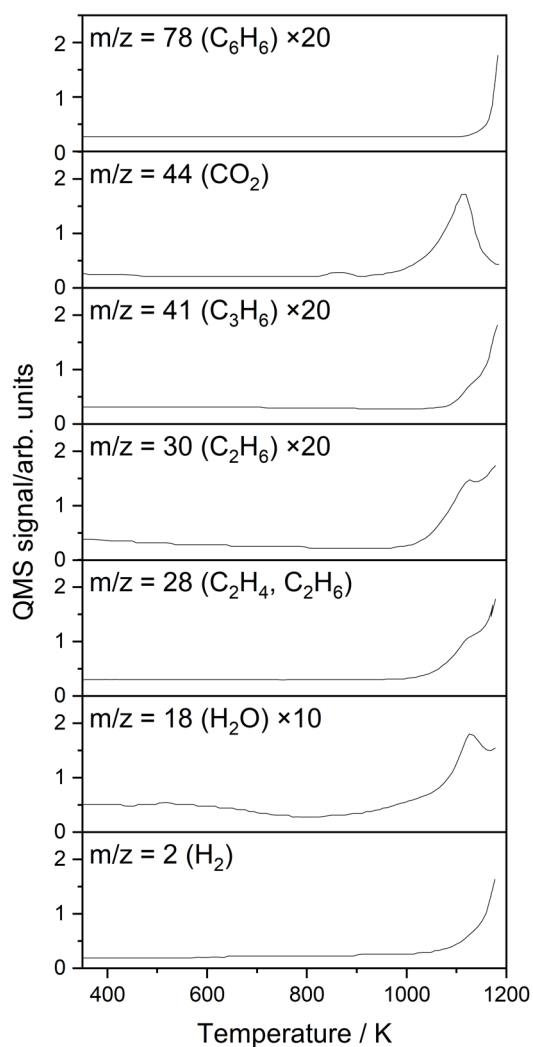


Figure 7 QMS analysis of the effluent gases under the CH_4 flow.

$m/z = 2$, corresponding to H_2 ; $m/z = 18$, corresponding to H_2O and multiplied by 10; $m/z = 28$, corresponding mainly to C_2H_4 ; $m/z = 30$, corresponding mainly to C_2H_6 and multiplied by 20; $m/z = 41$, corresponding mainly to C_3H_6 and multiplied by 20; $m/z = 44$, corresponding mainly to CO_2 ; $m/z = 78$, corresponding mainly to C_6H_6 and multiplied by 20.

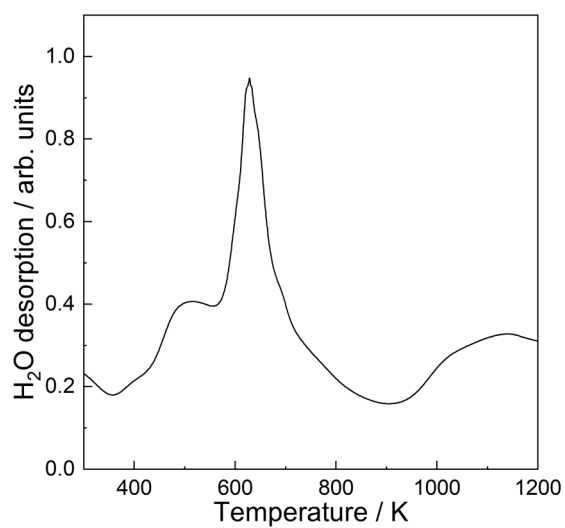


Figure 8 H₂O formation during the activation process under the H₂ flow.

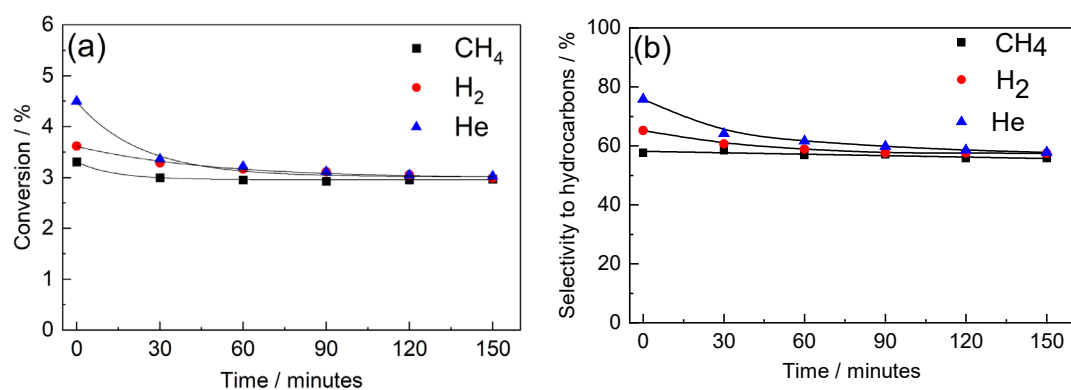


Figure 9 The (a) CH₄ conversion and (b) the selectivity to hydrocarbons under different activation processes. Black squares: under the CH₄ flow; red circles: under the H₂ flow; blue triangles: under the He flow. Under the He flow, In sublimed. The amount of In was calibrated by the edge jump reduction in the XAFS analysis.

4 Discussion

We followed the activation processes of the In/SiO₂ under several different gas-flow conditions. The structure changes during activation processes depended on the activation conditions. We here summarize and discuss the structural changes during each activation process and the active structures under the reaction conditions.

4.1 Summary of the structure change during the activation processes

Table 1 summarizes the structural changes during the activation processes under the different gas-flow conditions. Before and immediately after the melting, the structural changes were not dependent on the gas-flow conditions. However, at temperatures greater than 600 K, the behavior differed among the different gas-flow conditions. The differences are discussed in detail in the following subsections.

Table 1 Summary of the structural changes during the pretreatment process

Gas	373 K	430 K	873 K	1173 K	Reaction
CH ₄	In metal	Melting	In–X	In metal	In metal
He	In metal	Melting	In–X	In–X	In metal
H ₂	In metal	Melting	In metal	In metal	In metal

4.2 Temperature dependence of structural changes

The spectra acquired at room temperature indicated an In–In bond, showing that the catalyst was In solid metal. In metal has a body-centered tetragonal (bct) structure with 4 and 8 In–In bonds with bond lengths of 3.25 Å and 3.38 Å, respectively.²⁴ The coordination numbers determined by EXAFS analysis at room temperature were much smaller than those expected on the basis of the crystallographic data (**Table S1**). This difference was due to the large static and thermal disorder effects that could not be expressed by the Debye–Waller factor. The structural parameters obtained from the In EXAFS were in good agreement with the crystallographic data when In foil and In/SiO₂ were measured at 30 K (**Figure S8**, **Figure S10** and **Table S2**). At 30 K, the EXAFS oscillation in In foil was much greater than that at room temperature. We carried out two-

shell curve-fitting analysis (**Figure S 10**, **Table S2**). The Einstein temperature (or Debye temperature) derived from EXAFS data was ~ 100 K (or ~ 130 K). The Debye temperature was lower than those of normal transition metals such as Cu (315 K),²⁵ Ag (232 K),²⁶ Pt (240 K),²⁷ Pd (281 K),²⁶ and Rh (362 K).²⁸ The EXAFS oscillations at room temperature were substantially reduced because of the Debye–Waller factors. Consequently, the curve-fitting analysis of the EXAFS spectra collected at room and high temperatures was less accurate though the degree of fitting was not bad shown in Figure S11. As mentioned, the EXAFS analysis for the In–In bond enabled a relative comparison of data corresponding to different temperatures or different flow conditions.

4.3 In–X

The In–X (X is a light element) peak was observed at 1.8–2.0 Å in the spectra collected at 873 K under CH₄ activation and He activation. In a previous paper, we assigned the In–X peak to In–C formed in the reaction with CH₄.¹² If no such peak were observed under the H₂ or He flow, then In–X could be assigned to In–C with certainty. However, the In–X peak was observed in spectra collected under the He flow. The In–X peak in the spectrum collected under the CH₄ flow first increased in intensity and then disappeared at 1100 K. However, the In–X peak remained under the He flow when the sample was heated to 1173 K (reaction temperature) and disappeared after the He was switched to CH₄ gas. The In–X peak did not appear under the H₂ flow. We assigned In–X to In–O in the spectra corresponding to the He flow conditions. (1) The In–O was present on the surface of In particles at room temperature, as indicated by the results of the XPS, XANES, and EXAFS analyses. (2) The In–O coordination number appeared to be constant under the He flow (**Figure 5(b)**). (3) The In–O species was removed under the H₂ flow. The formation of H₂O was observed around 600 K (**Figure 8**), coinciding with the disappearance of the In–O peak and the decrease in the In peak intensity in the XANES spectrum.

We questioned why In–O was not visible in the FT corresponding to room temperature but became visible in the FTs corresponding to high temperatures. This observation can be explained as follows. The In–O bond is hindered by the still larger In–In FT peak. The Debye–Waller factor for the In–In bond is much larger than that for the In–O bond. As previously mentioned, solid In metal has a small Debye temperature and a large Debye–

Waller factor. Moreover, the Debye–Waller factor of In–In in liquid-metal In is greater than that of In–O. If the Debye–Waller factors of the liquid-metal In and In–O could be calculated from the vibration frequency, ω , of the In–In and In–O bonds, as shown in equation (3):

$$\sigma^2 = \frac{\hbar}{2\mu\omega} \coth\left(\frac{\hbar\omega}{2k_B T}\right), \quad (3)$$

where μ and k_B are the reduced mass and the Boltzmann constant, respectively, we could roughly estimate them though the equation (3) is based on a harmonic approximation and less valid to apply such anharmonic systems. The ω for In–In in the liquid-metal phase has been reported to be 1.2×10^{13} Hz.²⁹ On the other hand, the ω for In–O has been reported to be 9.4×10^{13} Hz,³⁰ which is eight times larger than that for In–In. The corresponding Debye–Waller factors (σ^2) at 1000 K calculated by equation (3) are $0.1 \text{ \AA}^2$ (for In–In) and $0.01 \text{ \AA}^2$ (for In–O). Consequently, the tremendous reduction in the In–In oscillation at high temperatures as a result of the large Debye–Waller factor made the In–O peak visible in the FT.

One may ask if the amount of InO_x on the surface layer was enough to explain the observed In–O bonding. We estimated the In ratio of the InO_x layer to the total number of In in the In particle (denoted as r_s) in the following two ways.

- 1) The peak deconvolution of the edge peak “F” in XANES indicated the presence of oxidized In species for 3 % as shown in Figure S3(a).
- 2) The surface InO_x layer was estimated to be more than several nanometers, judging from the XPS measurements. If the thickness of the surface InO_x layer (Δr) and In particle size ($2R$) were 10 nm and 1000 nm, respectively, the r_s could be estimated as follows.

$$r_s = \frac{N_{InO_x}}{N_{In+InO_x}} = \frac{(R + \Delta r)^3 - R^3}{R^3} \cong \frac{3\Delta r}{R} = 0.06(6 \%).$$

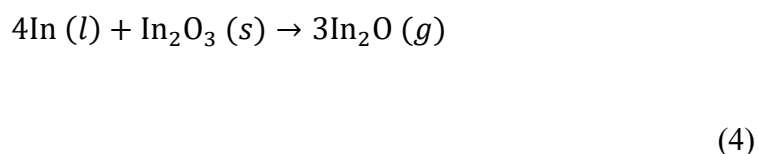
If the In was surrounded by 6 oxygen atoms, the estimated coordination numbers were 0.18 (from XANES) and 0.36 (from InO_x layer thickness) which had the same order as that found in EXAFS. Thus, we could observe the In–O by EXAFS.

By contrast, the In–X peak behavior under the CH₄ flow is complicated. The white line peak intensity and the FT peak intensity for the In–X peak increase at temperatures greater

than 800 K. We interpret that the number of In–C bonds may increase because of the reaction between In and CH₄. Because the amounts of H₂O and H₂ formed at 800 K are negligibly small, In–C bonds are formed after the dissociative adsorption of CH₄ to In–CH₃ + In–H. Some of the InO_x is removed at 800 K by the reaction between InO_x species and CH₄, as indicated by the decrease in the intensity of the edge peak in the XANES spectrum being slightly smaller than that under the He flow (**Figure 2**) and a small formation of CO₂. The In–O and In–C coexist at temperatures above 800 K under the CH₄ flow. In–C bond might be not atomic C but be In–CH₃ because negligible amount of H₂O at 800 K was observed. Ohtsuka *et al.* calculated the formation energies of an In–CH₃ complex. They found that the species In₂(CH₃)(H) was stable, with a negative formation enthalpy.³¹ Such small In–CH₃ complexes might be dissolved in the liquid-metal In. Because the formation of In–CH₃ species was not observed when the sample was cooled, the surface InO_x layer might be related to the formation of In–CH₃ species.

4.4 Loss of In under the He flow

The boiling point of liquid-metal In is 2300 K, and its vapor pressure at 1100 K is ~0.1 Pa.³² Thus, little In is evaporated during the activation process. We found little evaporation of metallic In under the reaction temperature (**Figure S9**). At 1100 K, In was lost only under the He flow (**Figure 2**). The surface of In was covered with InO_x, suggesting that the evaporation of InO_x was the likely cause of the loss of In. However, the direct evaporation of InO_x was not the case because no loss of In was observed under the O₂ flow (**Figure 2**). Valderrama *et al.* reported that volatile In₂O was produced by the following reaction:³³



Because under the He flow the surface was covered with InO_x and In metal was present at the core of the particle, reaction (4) occurred; thus, In was lost via the evaporation of In₂O.

4.5 Active phase structure

The In in In/SiO₂ in the active phase is a liquid metal, as demonstrated by the XAFS analysis. The difference in the activation process had little effect on the final active structure, although the loss of In was observed under the He flow conditions because of

the evaporation of In_2O_3 . **Figure 9** shows the activity and selectivity of the In/SiO_2 after the different activation processes. In/SiO_2 after the He treatment shows the highest conversion rate at the initial stage. A comparison of these results with the XAFS analysis results shows that $\text{In}-\text{O}$ is present as InO_x on the surface of In/SiO_2 after the He treatment, which might positively affect the conversion and selectivity of the hydrocarbons. However, the steady-state conversion and the selectivity to hydrocarbons are approximately the same, indicating that the active phase structure is the liquid-metal In and that the same structure is attained in the three activation processes.

The literature contains numerous examples of In catalysts (**Table 2**). In species are used in homogeneous catalysts.³⁴⁻³⁷ In -based heterogeneous catalysts are divided into four groups. One group is single-atom catalysts used for oxidation processes, where In is bound as cations to a metal–organic framework (MOF) or to the lattice oxygen (or nitrogen) of a support.³⁸⁻⁴⁵ The single-atom oxidized In species catalyzes oxidation and deNO_x reactions. The second group is oxide species, which are used to catalyze oxidation processes of hydrocarbons, similar to the single-atom case.⁴⁶⁻⁵⁵ The third group is supports or additives that promote the catalysis of main ingredients.⁵⁶⁻⁶² Bimetallic or alloy structures can be included in this category. Strong structural and electronic modifications in the bimetallic species introduce new catalytic activity and selectivity. The fourth group is liquid-metal In .⁶³ The In liquid metal can be used in two approaches. In the first approach, In liquid metal is used as a solvent for catalytically active elements, resulting in supported catalytically active liquid-metal solutions (SCALMS).⁶³⁻⁶⁶ The advantage of SCALMS is the ability to isolate the active species in the liquid-metal phase because of its high mobility. In the second approach, liquid metal In supported on oxides is used as a catalyst.^{10, 67-70} The resultant catalysts show dehydrogenation activity and catalyze graphene formation from CH_4 .² The advantage of liquid metals for catalyst applications is their long lifetime, which is attributable to their ability to avoid deactivation as a result of their high mobility.⁶³⁻⁶⁴ In addition, their flexible structure provides high activity, as demonstrated by Ohtsuka *et al.*, who found that coordinatively unsaturated In atoms present on the liquid-metal surface activated the C–H cleavage reaction.^{11, 31} The high catalytic performance and long lifetime of the liquid-metal In catalyst stem from its high mobility and high flexibility as a liquid.

Table 2. Examples of In catalysts in the literature

Catalyst	Structure	Reactions	Literature	
InX ₃	In Lewis acid	Rearrangement of epoxy	³⁴	H
In(III) triflate	In (OFT) ₃	Allylation microwave radiation	³⁵	H
InCl ₃	InCl ₃	Friedel–Crafts	³⁶	H
In/C(N)	In single-atom nitride	CO ₂ electrochemical reduction to CO	³⁸	S,EC
In-MOF	In single-atom oxide	CO ₂ fixation; carbonate	³⁹	S
In-MOF	In single-atom oxide	Acetalization of benzaldehyde	⁴⁰	S
In-MOF	In single-atom oxide	Strecker reaction	⁴¹	S
In-MOF	In single-atom oxide	Electrochemical conversion of CO ₂	⁴²	S,EC
In/ZSM-5	In single-atom oxide	CH ₄ + NO _x	⁴³	S
In/ZSM-5	In single-atom oxide	H–D exchange	⁴⁴	S
In/ZSM-5 + In ₂ O ₃	In ₂ O ₃	CH ₄ + NO _x	⁴⁶⁻⁴⁷	O
In ₂ O ₃ /SiO ₂	Nanoparticles	CH ₄ coupling	⁵⁰	O
In ₂ O ₃ /ZrO ₂	In ₂ O ₃	CO ₂ reduction by H ₂	^{48,49}	O
In _x Sn _{1-x} O _{2-x}	In ₈ Sn ₂ is the most active	CH ₄ combustion	⁵¹	O
In ₂ O ₃ /Al ₂ O ₃	In ₂ O ₃	NO _x reduction by hydrocarbons	⁵²	O
In ₂ O ₃ –Ga ₂ O ₃	In ₂ O ₃	Propane dehydrogenation	⁵³	O
In ₂ O ₃ –HZSM-5	Oxygen vacancy	CO ₂ hydrogenation to hydrocarbons	⁵⁴	O

In ₂ O _{3-x} (OH)	Porous In oxide nanorods	Photocatalyst	55	O
In–Cu	Promoter	Electrochemical CO ₂ reduction	56	P
MoP/In–C	Promoter	CO ₂ electroreduction	57	P
In on Cu	In-Promoted Cu	Electrochemical CO ₂ reduction	58	P
In	In mesoporous nanocrystalline	CO ₂ to formate by Electrochemistry	71	EC
In	In	CO ₂ to formate by electrochemistry	37	EC
In(OH) ₃ /C	In(OH) ₃	CO ₂ reduction by electrochemistry	72	EC
In–Cu	Cu ₂ In IMC,	Octanoic acid reduction	59	P
In–Ni	InNi	Acetic acid reduction	60	P
In–Ni/Al ₂ O ₃ , CeO ₂	In/ InO _x	Promoter for CH ₄ dry reform	61	P
Co/In ₂ O ₃	In ₂ O _x film on Co	CO ₂ to methanol	62	P
In	Molten In	Alcohol and amine dehydrogenation	67-69	LM
In/SiO ₂ , Al ₂ O ₃	Molten In	Methylcyclohexane dehydrogenation reactions	70	LM
In/SiO ₂	Molten In	CH ₄ non-oxidative coupling	10	LM
In–porous SiO ₂	Molten In on SiO ₂	NO + C ₂ H ₅ OH	73	LMS
Fe ₂ O ₃ in In	In acts as a solvent	H ₂ O splitting	74	LMS
Co–In	Co + liquid indium (SACLS)	CH ₄ to aromatics	66	LMS
H = Homogeneous, S = Single-atom catalyst, O = Oxide, P = Promoter, EC = Electrochemical catalyst, LM = Liquid metal, LMS = Supported catalytically active liquid-metal solutions				

5 Conclusions

We investigated the dynamic structural changes of In/SiO₂ in CH₄, H₂, and He gas flows from room temperature to 1173 K using *operando* XAFS spectroscopy. The In/SiO₂ catalyst was composed of In in its core and InO_x on its surface. The In particles were melted at 430 K. Under the He flow, we observed the In-O peak in the Fourier transforms at 873 K. When the gas was changed to CH₄ at the reaction temperature, the In was fully reduced. We also observed a decrease in the edge jump at temperatures above 1100 K, indicating the evaporation of In₂O as a result of the reaction of surface InO_x and the core In metal. On the other hand, the surface InO_x was reduced to In⁰ under the CH₄ and H₂ flows, although the reduction temperatures were different (~1000 K and ~600 K, respectively). Under the CH₄ flow, In-X, which was assigned to In-CH₃, was formed at ~800 K, in addition to In-O. The In-CH₃ was removed at 1000 K via the reaction with the surface InO_x, and the CH₄ coupling reaction was started. The active structure was liquid-metal In particles. The flexibility of liquid-metal In was the origin of the high activity.

Supporting information: Operando XAFS experimental details, XPS data of In/SiO₂, In XANES with linear combination fitting and the change of XANES for In/SiO₂ under He activation after switching to CH₄ flow, Fourier transforms of EXAFS at different temperatures for In/SiO₂ during CH₄ activation, Fourier transforms of EXAFS for In/SiO₂ under He activation after switching to CH₄ flow, Comparison of Fourier transforms of EXAFS for In/SiO₂ with different activation conditions under reaction conditions, *Operando* XANES spectra of In K-edge under 10 % O₂, EXAFS of In foil and In/SiO₂ at 30 K, Edge jump of In K-edge at 1173 K, Curve fitting results at 30 K, Curve fitting results of In/SiO₂ at various temperatures, Curve fitting parameters of In/SiO₂ activated in different environments. Curve fitting results of In foil and In/SiO₂ at 30 K. Einstein temperature and frequency for In-In bond derived from Figure S8.

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Supporting Information for Publication
The Effect of Structural Change during the Activation Process on the
Catalysis of In/SiO₂ Non-Oxidative Coupling of Methane: An
***Operando* XAFS Study**

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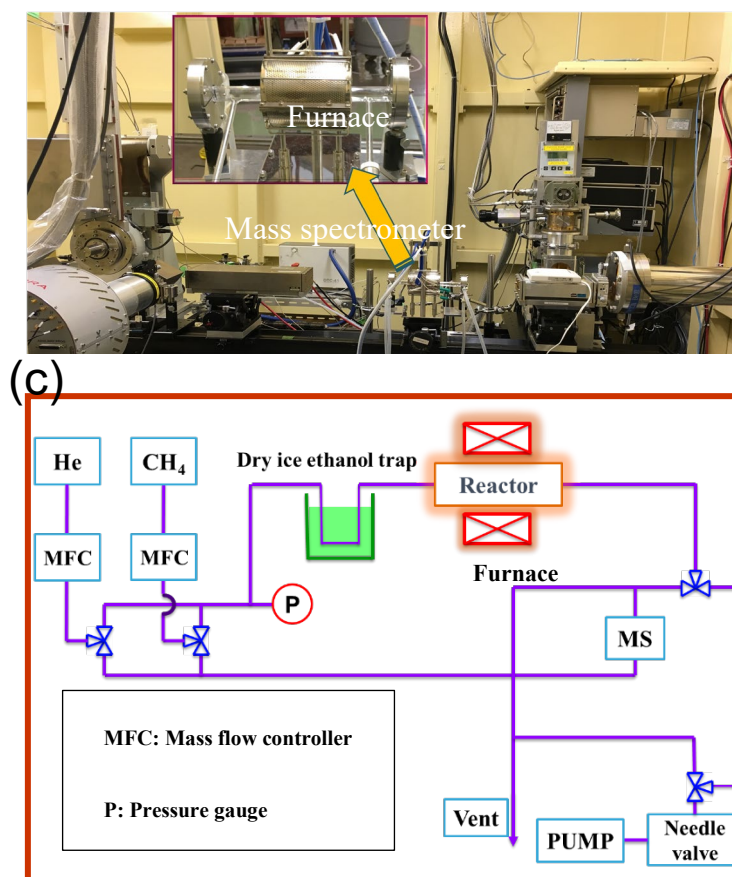
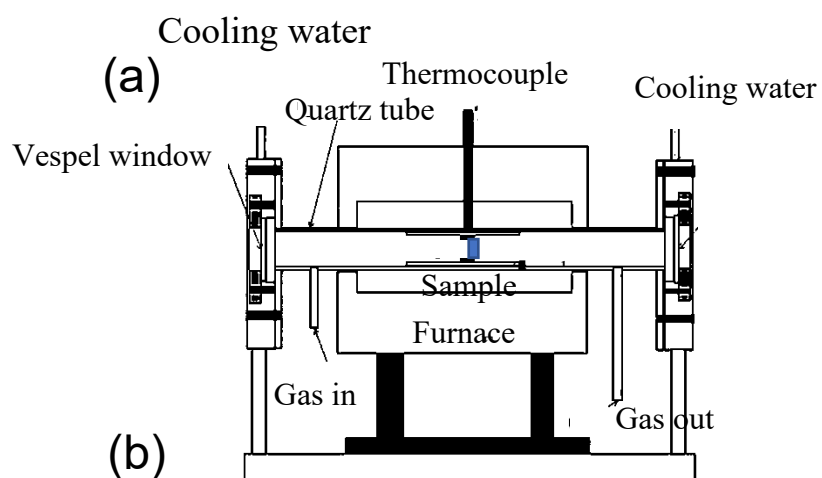


Figure S1 (a) XAFS cell. (b) Interior of the experimental hutch. (c) The gas lines.

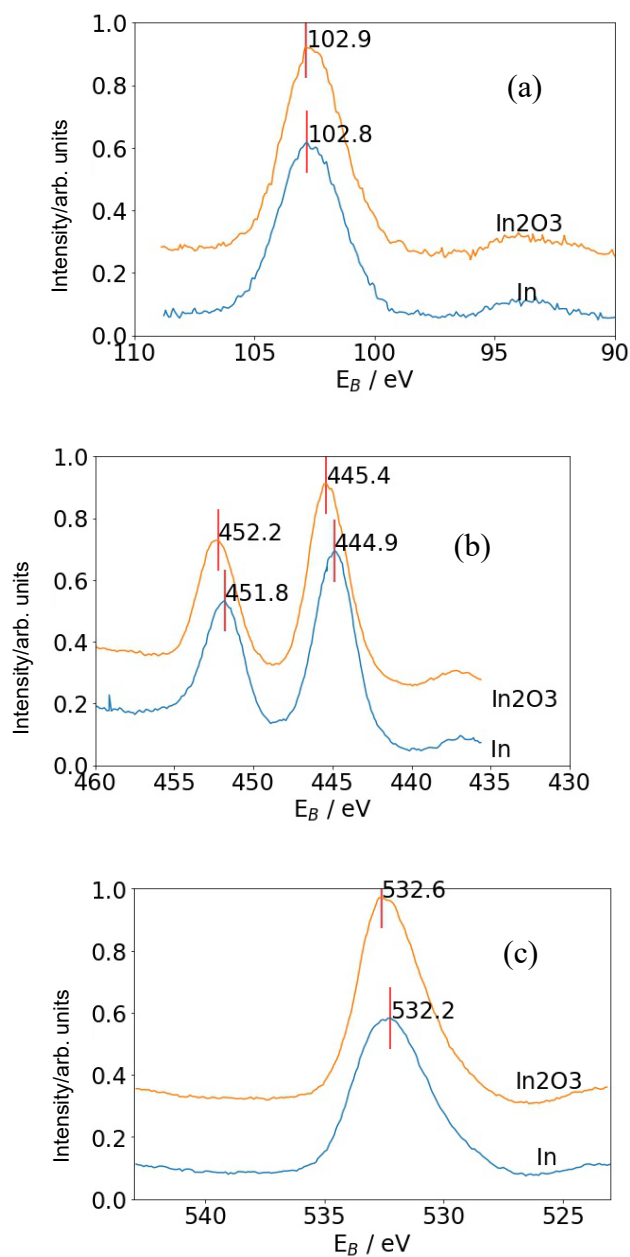


Figure S2 X-ray photoelectron spectra of $\text{In}_2\text{O}_3/\text{SiO}_2$ (red curve denoted as In_2O_3) and In/SiO_2 (blue denoted as In). In_2O_3 was prepared under flowing O_2 at 1023 K. In/SiO_2 was stored in the air and used before the reaction. (a) Si 2p, (b) In 4d, (c) O 1s. The binding energies were calibrated by the C 1s binding energy. The binding energies of In and In_2O_3 have been reported to be 443.6 and 444.9 eV, respectively [S1,S2]. The chemical shift of In is 1.3 eV. In this work, the difference was only 0.5 eV,

which was intermediate between those of In and In_2O_3 , indicating that the In was oxidized. The surface of the In particles was covered with an In-oxide layer denoted as InO_x . XAFS analysis indicated the presence of In metal. Thus, the large part of the core of the In particle was metal, whereas the surface region was In-oxide. Since no In metal was observed, the thickness of InO_x should be more than several nanometers.

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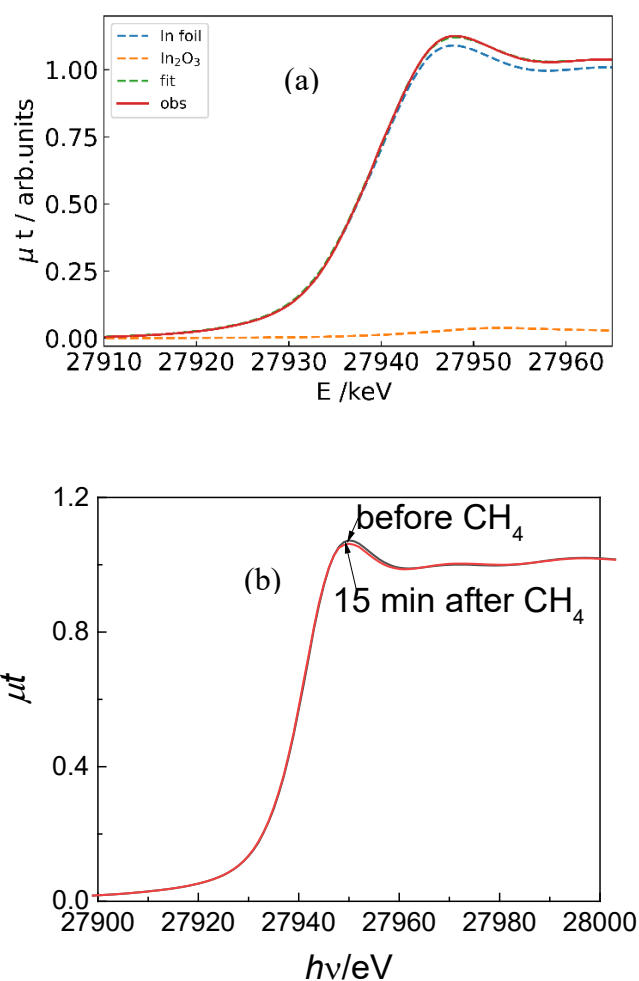


Figure S3 In *K*-edge XANES spectra of (a) In/SiO₂ at room temperature with a linear combination of the spectra of In foil and In₂O₃ and (b) In/SiO₂ under flowing He (black curve) and 15 min after the atmosphere was changed to flowing CH₄ at 1173 K (red curve). The XANES spectra were normalized by the edge jump.

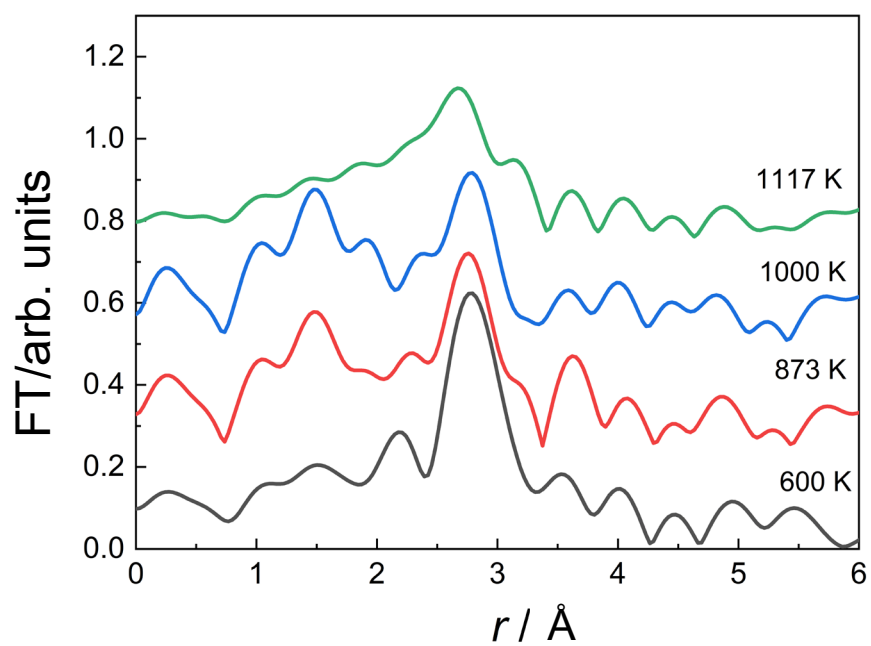


Figure S4 FTs of the spectra acquired under flowing CH_4 and at different temperatures of 600, 873, 1000, and 1117 K.

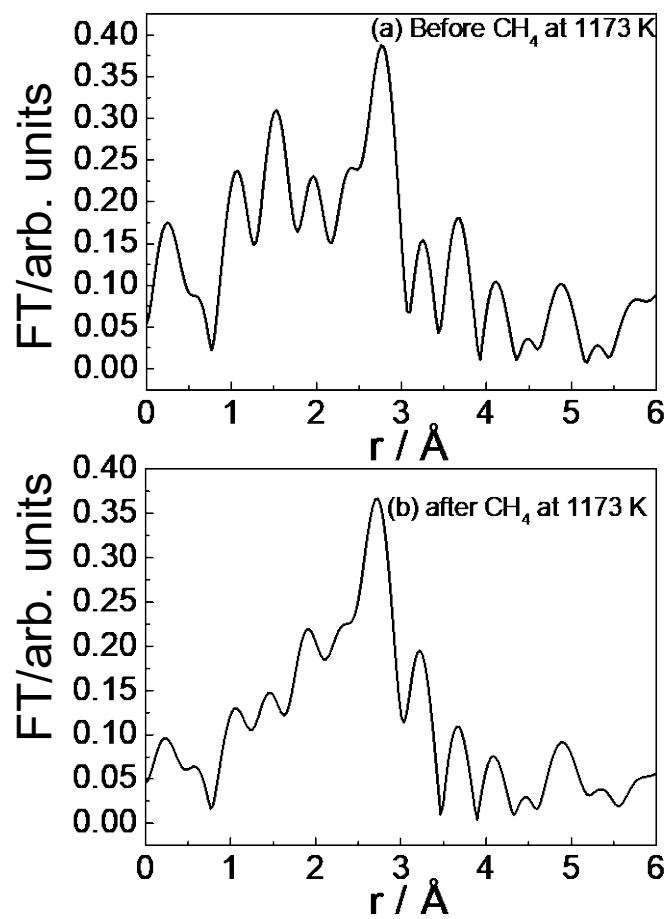


Figure S5 FTs of the EXAFS spectra of In/SiO₂ activated under He flow conditions at 1173 K: (a) before and (b) after CH₄ was introduced.

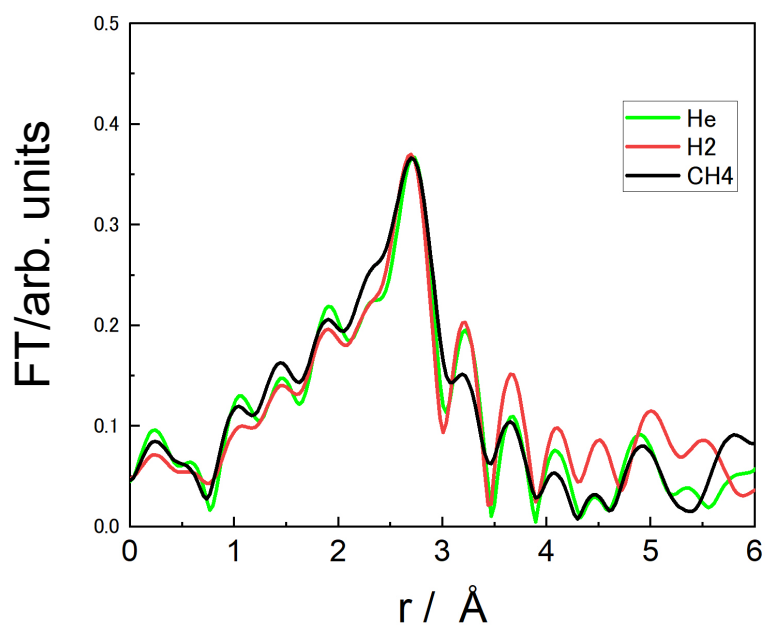


Figure S6 FTs of the spectra of In/SiO₂ under the reaction conditions (1173 K under flowing CH₄) after the sample was activated under various conditions (He: green line, H₂: red line, and CH₄: black line).

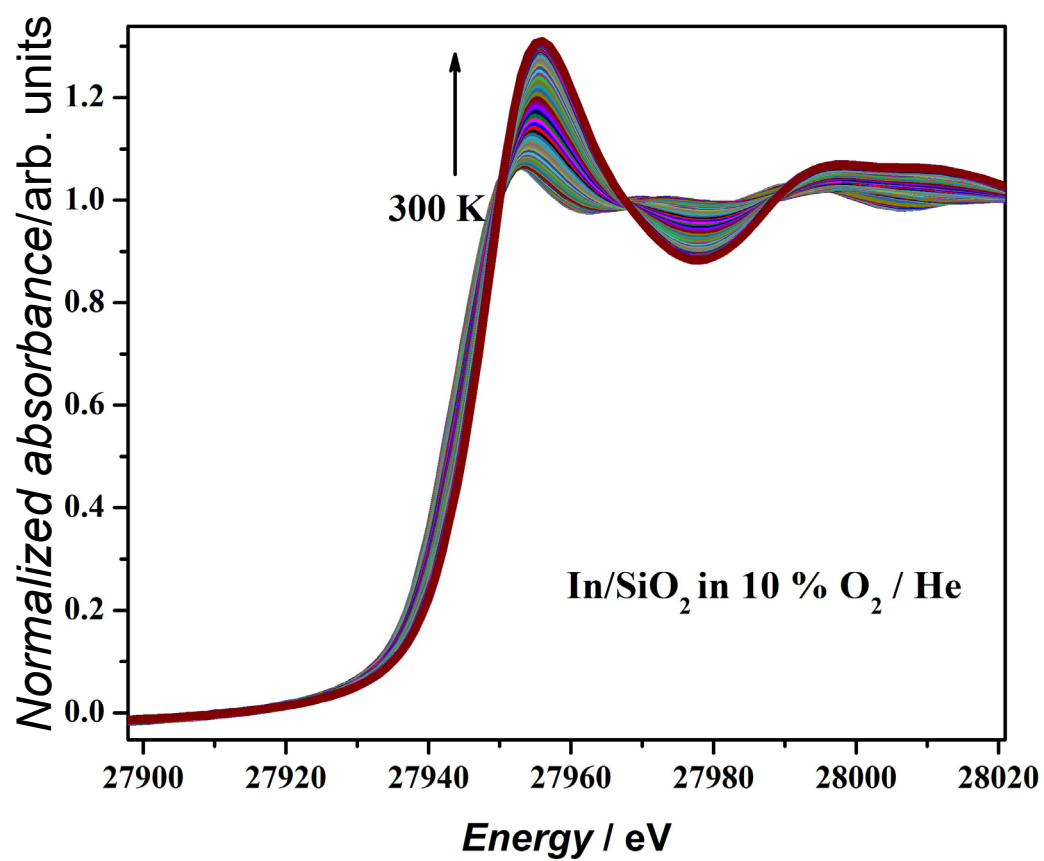


Figure S7 *Operando* XANES spectra of the In *K*-edge under 10% O₂ balanced with He.

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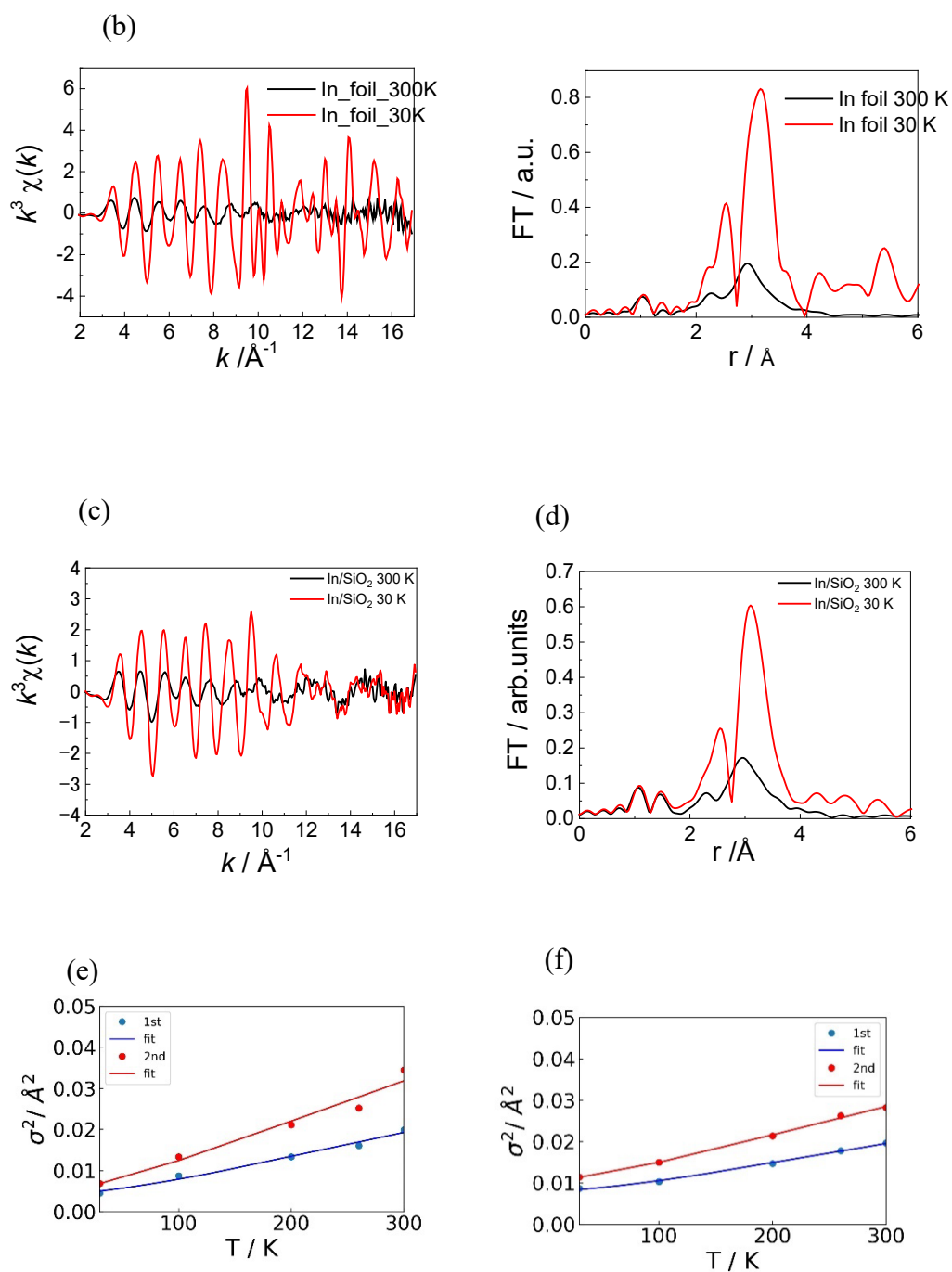


Figure S8 Comparison of (a,c) the EXAFS oscillations and (b,d) their FTs at 30 and 300 K for (a,b) In foil and (c,d) In/SiO₂. Temperature dependence of the Debye–Waller factor for (e) In metal and (f) In/SiO₂.

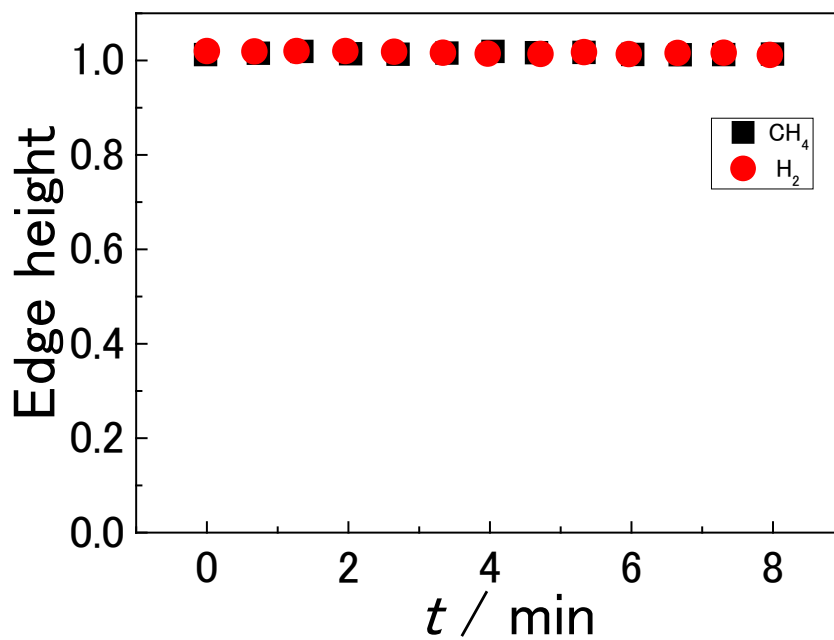


Figure S9 Edge jump of the In *K*-edge at 1173 K during the reaction under flowing CH_4 . The In/ SiO_2 was pretreated under He (red color) and CH_4 (black), where In metal was formed.

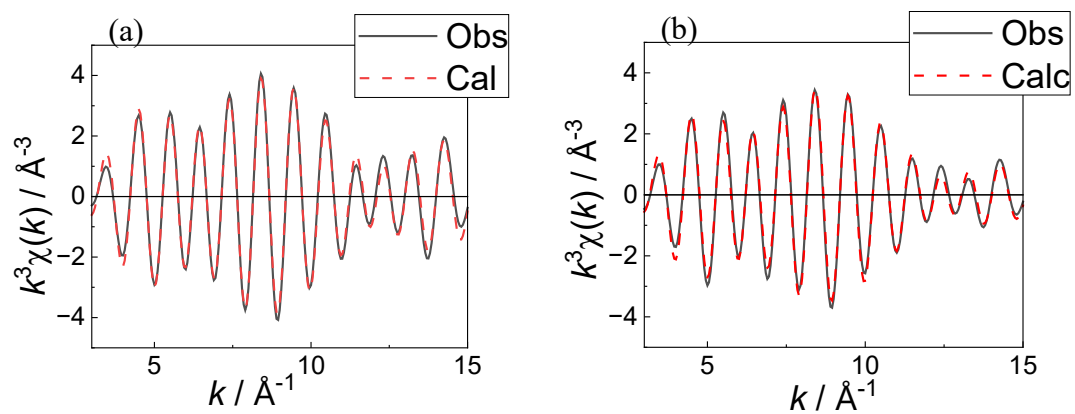


Figure S10 Curve fitting results of In foil(a) and In /SiO₂ (b) measured 30 K.

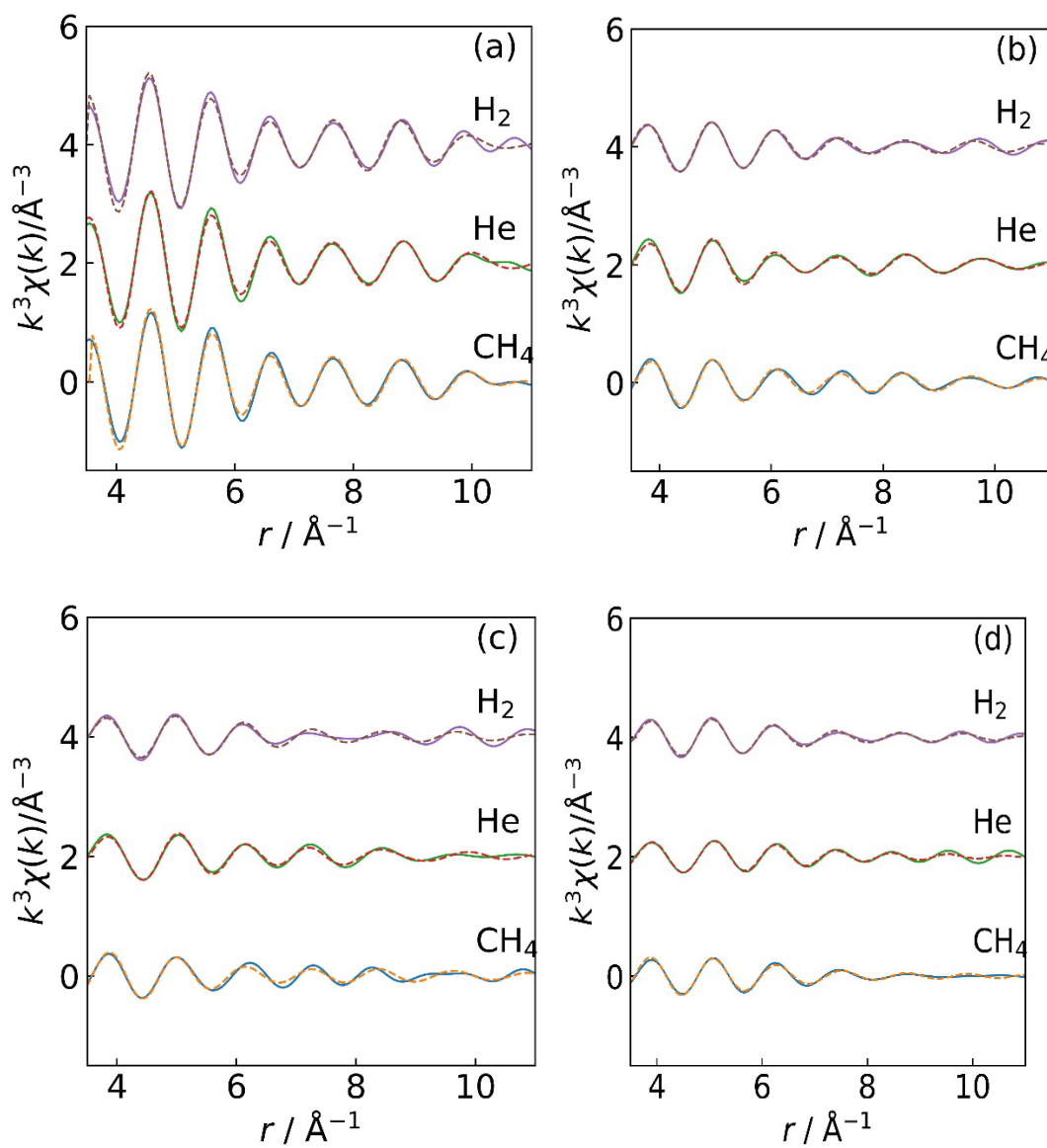


Figure S11 Curve fitting results of In/SiO₂ at room temperature (a) 300 K, (b) 473 K, (c) 874 K, (d) 1173 K under the H₂, He and CH₄ flows.

Table S1: Curve-fitting parameters of In/SiO ₂ activated in different environments						
	<i>T</i> (K)	CN	<i>R</i> (Å)	ΔE (eV)	σ^2 (Å ²)	<i>R</i> -factor (%)
CH ₄ flow						
In–In	300	3.4 ± 0.3	3.14 ± 0.03	24 ± 3	0.020 ± 0.007	2.0
In–In	473	1.4 ± 0.3	2.96 ± 0.03	25 ± 3	0.014 ± 0.007	3.8
In–In	873	1.4 ± 0.5	2.94 ± 0.05	28 ± 3	0.020 ± 0.007	6.4
In–C		0.3 ± 0.2	2.16 ± 0.05	11 ± 5	0.010 ± 0.007	
In–In	1173	1.3 ± 0.5	2.86 ± 0.04	24 ± 3	0.023 ± 0.003	2.7
H ₂ flow						
In–In	300	3.4 ± 0.8	3.14 ± 0.01	23 ± 3	0.020 ± 0.007	4.4
In–In	473	1.3 ± 0.5	2.96 ± 0.01	24 ± 3	0.013 ± 0.007	2.5
In–In	873	1.4 ± 0.5	2.92 ± 0.02	23 ± 3	0.023 ± 0.007	3.4
In–In	1173	1.4 ± 0.5	2.88 ± 0.02	26 ± 3	0.026± 0.007	4.0
He flow						
In–In	300	3.4 ± 0.8	3.14 ± 0.02	23 ± 3	0.022 ± 0.007	2.1
In–In	473	1.3 ± 0.5	2.96 ± 0.01	25 ± 3	0.013 ± 0.007	2.7
In–In	873	1.4 ± 0.5	2.89 ± 0.03	22 ± 3	0.022± 0.007	3.3
In–O		0.3 ± 0.2	2.16 ± 0.05	11 ± 5	0.011 ± 0.007	
In–In	1173	1.5 ± 0.5	2.88 ± 0.06	16 ± 3	0.028 ± 0.007	7.5
In–O		0.3 ± 0.2	2.14 ± 0.03	17 ± 4	0.012± 0.007	
In foil						
In–In	300	3.4 ± 0.3	3.14 ± 0.03	24± 3	0.020 ± 0.003	2.0

Special note: The coordination numbers and bond distances of In–In are not real ones due to the large asymmetric distribution effects. But they have meaning only when they are compared under the different gas conditions in the same temperature

Table S2 Curve-fitting results for In foil and In/SiO₂ at 30 K

The CN , R , ΔE and σ^2 were used as fitting parameters.

Sample	Path	CN	$r / \text{\AA}$	$\sigma^2 / \text{\AA}^2$	$\Delta E / \text{eV}$	$R\text{-factor}(\%)$
In foil	1st	3.9 ± 0.7	3.22 ± 0.02	0.005 ± 0.001	1 ± 3	0.8
	2nd	7.8 ± 1.2	3.36 ± 0.02	0.007 ± 0.001		
In/SiO ₂	1st	3.8 ± 0.8	3.24 ± 0.02	0.008 ± 0.001	1 ± 5	1.0
	2nd	7.7 ± 1.3	3.35 ± 0.02	0.011 ± 0.002		

Note ΔE 's for In foil are different in Tables S1 and S2 because in Table S2 two-shell fitting was carried out to give the real structure parameters while in Table S1 one-shell fitting was performed which was the approximation of the two-shell fitting and ΔE was used to compensate the phase difference.

Table S3 Einstein (Debye) temperature and vibrational frequency (ω) for the In–In bonds, as derived from Figure S8.

		Einstein (Debye) temperature /K	ω /THz
In metal	First shell	119 ± 5 (153 ± 5)	15.7 ± 0.6
	Second shell	92 ± 5 (119 ± 5)	12.1 ± 0.6
In/SiO ₂	First shell	133 ± 7 (147 ± 5)	17.5 ± 0.8
	Second shell	110 ± 7 (122 ± 5)	14.4 ± 0.8

The values in the parentheses show the Debye temperature.