[Regular Paper]

Effect of Support Species on Performance of Transition Metal-based Catalysts for Propane Dehydrogenation with Co-feeding of H$_2$S

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(Received March 10, 2020)

This study investigated the effect of catalyst supports (SiO$_2$, γ-Al$_2$O$_3$, ZrO$_2$, CeO$_2$, MgO) on the performance of transition metal (Fe, Co, Ni) catalysts for propane dehydrogenation (PDH) with co-feeding of hydrogen sulfide (H$_2$S). Evaluation of the catalyst activity indicated that inert SiO$_2$ is a suitable support for the PDH catalysts. The SiO$_2$-supported Fe catalysts showed the highest activity and selectivity among the investigated catalysts. In order to clarify the effect of the support species on the structure and electronic state of the catalyst components, X-ray diffraction (XRD), X-ray absorption fine structure (XAFS), and X-ray photoelectron spectroscopy (XPS) were used to characterize the various Fe-loaded catalysts. From Fe K-edge X-ray absorption near edge structure (XANES) analysis, it is deduced that the catalysts in which Fe was in a higher oxidation state showed better performance for PDH with co-feeding of H$_2$S. When SiO$_2$ and Al$_2$O$_3$ were used as the supports, divalent and trivalent Fe cations were detected by XPS analysis. Such high-valence Fe species can accept an electron from an intermediate species, thereby enhancing the dehydrogenation performance.

Keywords
Propane dehydrogenation, Hydrogen sulfide, Metal sulfide

1. Introduction

Propane dehydrogenation (PDH, C$_3$H$_8$ → C$_3$H$_6$ + H$_2$) has gained much attention in recent years as it enables the direct conversion of low-value propane to high-value propylene$^{13}$. Cr-based catalysts having high activity for PDH and excellent selectivity for the production of propylene have been reported in a number of studies$^{2,4}$. Catalyst deactivation by coke deposition is a significant issue for these proposed catalysts, leading to considerable deterioration of the dehydrogenation performance. Thus, a regeneration process is required to eliminate coke on the catalyst by oxidation using diluted air$^5$. To overcome the catalyst deactivation problem, many promising catalytic systems have been proposed thus far, based on vanadium$^{6,7}$, gallium$^{8,9}$, iron$^{10}$, tungsten$^{11}$, and indium oxides$^{12}$. We also developed a selective catalyst for PDH, comprising a transition metal (Fe, Co, Ni) supported on aluminum oxide (γ-Al$_2$O$_3$) with a sulfate ion (SO$_4^{2-}$). In the reaction atmosphere, the loaded SO$_4^{2-}$ was reduced to the sulfide ions (S$^{2-}$) which functioned as the active species in PDH$^{13}$. The effectiveness of metal sulfide catalysts for the dehydrogenation of alkanes was also reported by some researchers$^{14-16}$. Metal sulfide catalysts suffer from the crucial problem of S$^{2-}$ loss due to H$_2$ reduction of the metal sulfide$^{17}$. Suppression of the release of S$^{2-}$ in the metal sulfide is an important undertaking for achieving stable dehydrogenation performance.

Recently, we investigated the effect of the co-supply of H$_2$S with propane on the dehydrogenation performance of transition metal catalysts (Fe, Co, Ni, Cu, Mn), where an improvement in the catalytic performance via the continuous regeneration of S$^{2-}$ during the reaction was anticipated$^{18}$. Among the transition metal catalysts, the Fe-, Co-, and Ni-based catalysts showed relatively stable performance and were highly-active and selective for PDH with co-feeding of H$_2$S. However, the effect of the catalyst support on the dehydrogenation performance of transition metal catalyst has not been clarified thus far.

Therefore, this study focuses on investigating the effect of supports (γ-Al$_2$O$_3$, SiO$_2$, ZrO$_2$, MgO, CeO$_2$) on the performance of transition metal (Fe, Co, Ni) catalysts for PDH with co-feeding of H$_2$S. Evaluation of the catalyst activity shows that SiO$_2$ is a suitable support for PDH with co-feeding of H$_2$S. The origin of the high performance of the SiO$_2$-supported catalyst is investigated by analysis of the structure and electronic state via X-ray diffraction (XRD), X-ray absorption fine
structure (XAFS), and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Catalyst Preparation

Various types of supports, including γ-Al2O3 (JRC-ALO-8), SiO2 (JRC-SIO-4), ZrO2 (JRC-ZRO-3), MgO (JRC-MGO-4), and CeO2 (JRC-CEO-2), were supplied by the Catalysis Society of Japan. The transition metal oxide (Fe, Co, Ni) and sulfate ions (SO₄²⁻) were loaded on the support by an impregnation method. Firstly, 2.0 g of the support was degassed at room temperature for 6 h, in order to remove air and impurities in the pore. Then, the various supports were impregnated with the corresponding metal nitrate (Fe(NO₃)₃, Co(NO₃)₂·6H₂O, or Ni(NO₃)₂·6H₂O) and ammonium sulfate (0.146 g of [(NH₄)₂SO₄]) solution, and the solution was evaporated to dryness at 80 °C. After calcination of the catalyst at 700 °C for 1 h, we obtained the sulfated catalyst. The loading of SO₄²⁻ and the transition metal were respectively 5 wt% and 20 wt%, which were the same amount of previous our reports¹³,¹⁸).

2.2. Activity Tests

The PDH performance of the prepared catalysts, including the catalytic activity, selectivity for the product, and stability, were examined using a conventional fixed-bed reactor. Before the reaction, a pre-treatment was performed by feeding 2.5 mL min⁻¹ of H₂ and 47.5 mL min⁻¹ of H₂S at 600 °C for 1 h, in order to reduce sulfate ion to sulfide ion on the catalyst. Then, the reaction was performed at 600 °C under atmospheric pressure. The propane feed rate was 2.5 mL min⁻¹ (SATP), and the catalyst weight was 0.25 g. The flow rate of the co-feeding H₂S was 3.5 mL min⁻¹, balanced by He (20.0 mL min⁻¹). The molar ratio of H₂S to propane was 1.4 mol mol⁻¹. The gaseous reactants and products (i.e., C₃H₈, C₂H₄, C₂H₂, and C₃H₆) were collected with a micro-syringe and subsequently injected into the off-line gas chromatograph with a thermal conductivity detector and gas chromatograph with a flame ionization detector (GC-8A; Shimadzu Corp., Japan). The Propane conversion (X₀) and the selectivity for the products (Sᵢ) were calculated by the following equations:

\[ X_{C₃H₈} = \frac{F_{CH₃} + 2 \times F_{C₂H₂} + 3 \times F_{C₃H₆}}{3 \times F_{C₃H₈}} \times 100 \] (1)

\[ Sᵢ = \frac{N \times Fᵢ}{F_{CH₃} + 2 \times F_{C₂H₂} + 3 \times F_{C₃H₆}} \times 100 \] (i: CH₄, C₂H₄, C₂H₂)

where \( Fᵢ \) denotes the flow rate of the products, and \( N \) indicates the number of carbon atoms in the product.

2.3. Characterization of Catalysts

The amount of coke deposited on the catalyst was measured using a Flash EA 1112 element analyzer (Thermo Fisher Electron Inc., USA). The crystalline structure of the prepared catalyst was determined by XRD analysis using Cu-Kα radiation (\( \lambda = 1.54 \, Å \), Ultima IV; Rigaku Corp., Japan). The Fe K-edge XAFS measurement was performed at the hard X-ray XAFS beamlines of BL5S1 in the Aichi Synchrotron Radiation Center (Aichi SR, Japan). The X-ray absorption near edge structure (XANES) spectra were normalized relative to the edge height. The extended X-ray absorption fine structure (EXAFS) oscillation \( \chi(k) \) was weighted by \( k^2 \) in order to compensate for the diminishing amplitude in the high-\( k \) range due to decay of the photoelectron wave. The filtered \( k^2 \)-weighted \( \chi(k) \) was then Fourier-transformed into R space (\( k \) range: 2.0-14.0 Å⁻¹) with a Hanning function window. In the curve-fitting step, the possible backscattering amplitude \( \chi(k) \) and phase shift were calculated by using the FEFF6 code. X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD; Shimadzu Corp., Japan) was used for analysis of the oxidation state of the catalyst components using monochromatic Al-Kα radiation. The charging effect on the catalyst surface was eliminated with a neutralization gun under following conditions: filament current was 1.6 A; charge balance was 2.6 V; filament bias was 0.9 V. The binding energy was referred to the carbon C₁s peak at 284.7 eV for convenience.

3. Results and Discussion

3.1. Effect of Support on PDH with Co-feeding of H₂S

First, we investigated the effect of the type of support (γ-Al₂O₃, SiO₂, ZrO₂, MgO, and CeO₂) on the performance of the transition metal catalysts (Fe, Co, Ni) for PDH with co-feeding of H₂S. Figure 1(a) shows the propane conversion over the Fe-based catalysts with various supports. Hereinafter, the supported catalyst is denoted in the metal/support format. High propane conversion was achieved with the Fe/γ-Al₂O₃ and Fe/SiO₂ catalysts at the reaction time of 35 min. The Fe/SiO₂ catalyst displayed better stability for PDH with co-feeding of H₂S than the Fe/γ-Al₂O₃ catalyst. The Fe/ZrO₂ and Fe/CeO₂ catalysts showed some activity; however, these catalysts underwent significant deactivation. In contrast, the Fe/MgO catalyst exhibited no activity for PDH with co-feeding of H₂S: the conversion was almost identical to the thermal decomposition profile of propane at 600 °C. The stability of these catalysts was largely dependent on the type of support. Figure 1(b) shows the product selectivity at the reaction time of 200 min. Methane (CH₄) and ethylene (C₂H₄) were confirmed as the products. Since the selectivity ratio of C₃H₈ and C₂H₄ is approximately 2 : 1, CH₄ and C₂H₂ were produced by propane cracking (C₃H₈ → CH₄ + C₂H₂) and/or propylene hydrogenolysis.
(C₃H₆ + H₂ → CH₄ + C₂H₄) on the catalyst. The highest C₃H₆ selectivity of 92.8% was achieved with the Fe/γ-Al₂O₃ catalyst. The C₃H₆ selectivity of the Fe/γ-Al₂O₃, Fe/ZrO₂, Fe/MgO, and Fe/CeO₂ catalysts was 82.7, 74.5, 73.0, and 67.3%, respectively. The difference in the selectivity might originate from the effect of the support on the dehydrogenation. The γ-Al₂O₃, ZrO₂, and CeO₂ supports all contain electron-deficient cations that act as Lewis acid sites. The propylene molecule possesses a π-bond, which makes it more basic than propane. Accordingly, propylene undergoes stronger interactions with the electron-deficient Lewis centers on the oxide surfaces than the propane molecules. This basicity leads to cleavage of the allylic C-C bonds in propylene, which might decrease the propylene selectivity. In the Fe/MgO catalyst, the Fe atoms interact strongly with MgO, resulting in the formation of a solid solution, which might decrease the selectivity for the propylene product. Because the SiO₂ support is inert, the support did not affect the dehydrogenation. Therefore, the Fe/SiO₂ catalyst might show excellent selectivity for propylene.

Table 1 shows the amount of coke deposited after PDH with co-feeding of H₂S. The relatively inactive catalysts, such as Fe/ZrO₂, Fe/MgO, and Fe/CeO₂, had very little or no coke deposition, whereas the more active Fe/γ-Al₂O₃ catalyst had significantly more deposited coke. The lack of coke on the Fe/MgO catalyst is plausibly attributed to its lack of activity for PDH. Interestingly, the highly active Fe/SiO₂ catalyst also had very little deposited coke. These results might be related to the difference in the selectivity for propylene. The side-reactions involving cleavage of the C-C bond in propylene and propane cracking generate hydrocarbon fragments (i.e., CHₓ and carbon atoms) that accumulate on the catalyst. The relatively low amount of deposited coke on the Fe/SiO₂ catalyst might be due to suppression of these side-reactions.

Figures 2 and 3 show the dehydrogenation properties of the Co and Ni catalysts on various supports (i.e., SiO₂, γ-Al₂O₃, ZrO₂, MgO, and CeO₂). As shown in Fig. 2(a), the Co/γ-Al₂O₃, Co/SiO₂, and Co/ZrO₂ catalysts showed high initial activity; this behavior is similar to that of the Fe-based catalysts. These three Co catalysts also showed relatively high propylene selectivity, as illustrated in Fig. 2(b). In contrast, the Co/MgO and Co/CeO₂ catalysts showed significantly lower activity and only mild selectivity for propylene. The support-dependent selectivity of the Co-based catalysts followed trends similar to that of the Fe catalysts: the Co catalyst on the inert SiO₂ support exhibited high selectivity, whilst the Co catalysts on the supports containing acid sites showed low selectivity. The reactivity trends of the Ni catalysts on the various supports (i.e., γ-Al₂O₃, SiO₂, ZrO₂, MgO, and CeO₂) were also similar.

**Table 1** Amount of Coke on Various Catalysts after PDH with Co-feeding of H₂S

| Catalyst | Support  | Amount of coke [wt%] |
|----------|----------|----------------------|
| Fe       | γ-Al₂O₃  | 5.8                  |
|          | SiO₂     | 1.3                  |
|          | ZrO₂     | 1.5                  |
|          | MgO      | 0.0                  |
|          | CeO₂     | 0.1                  |
| Co       | γ-Al₂O₃  | 7.1                  |
|          | SiO₂     | 0.4                  |
|          | ZrO₂     | 2.4                  |
|          | MgO      | 0.5                  |
|          | CeO₂     | 0.4                  |
| Ni       | γ-Al₂O₃  | 8.1                  |
|          | SiO₂     | 0.7                  |
|          | ZrO₂     | 2.9                  |
|          | MgO      | 0.3                  |
|          | CeO₂     | 0.1                  |

Fig. 1 (a) Propane Conversion and (b) Product Selectivity over Fe Catalysts on Various Supports (i.e., SiO₂, γ-Al₂O₃, ZrO₂, MgO, and CeO₂) for PDH with Co-feeding of H₂S.
to those of the Fe and Co catalysts: the Ni catalyst on SiO₂ displayed relatively high activity, compared to the other Ni catalysts. However, the catalyst deactivation rapidly progressed in a short reaction period, which might cause a low propylene selectivity. Elemental analyses showed that only small amounts of coke were deposited on the Co/SiO₂ and Ni/SiO₂ catalysts, similar to the case for the Fe/SiO₂ catalyst (Table 1). In terms of the catalytic performance and coke deposition, the Fe/SiO₂ catalyst is a suitable material for PDH with co-feeding of H₂S.

We compared the performance of the Fe/SiO₂ catalyst to that of the catalysts developed in previous studies (Co/SO₄²⁻/Al₂O₃, Nd₀.₉₅CrO₃⁻, LaCo₀.₂Mn₀.₈O₃) [13,22,23]. Figure 4 shows the space time yield (STY) and selectivity to C₃H₆ over the Fe/SiO₂, Co/SO₄²⁻/Al₂O₃, Nd₀.₉₅CrO₃⁻, LaCo₀.₂Mn₀.₈O₃ catalysts. Here, the performances of the Nd₀.₉₅CrO₃⁻ and LaCo₀.₂Mn₀.₈O₃ catalysts were the evaluated-values of 625 °C and 650 °C. Apparently, the Fe/SiO₂ was highly-active and selective catalyst for PDH.

To investigate the origin of the high propylene selectivity of the Fe/SiO₂ catalysts, the apparent activation energies for PDH and the propylene hydrogenolysis (HG, C₃H₆ → CH₄ + C₂H₄) side reaction were evaluated. For the apparent activation energy calculation, the PDH and HG reactions were carried out at conversion levels below 10 %. Figure 5(a) shows the STY of C₃H₆ as the product of PDH, and that of CH₄ as the product of HG. Both reactions were accelerated by increasing the reaction temperature. The rate constant was calculated based on the STY of each reaction. Figure 5(b) shows the Arrhenius plot for PDH and
The apparent activation energy for PDH, determined from the slope of the plot, was 109 kJ mol\(^{-1}\), while that for HG was 163 kJ mol\(^{-1}\). The structural evaluation presented below in Section 3.2 shows that after PDH with co-feeding of H\(_2\)S, the catalyst structure comprised the metal sulfide. According to Wang et al.\(^{17}\), sulfide catalysts have been reported as being selective for dehydrogenation of isobutane through suppression of subsequent reactions due to the decreased adsorption of isobutene. Bonding sulfur to the metal component increases the electron density of the surface metal atom and facilitates repulsive interaction between isobutene and the catalyst surface, which promotes the desorption of propylene. Sun et al. stated that the facile desorption of propylene from the surface of the catalyst inhibited further reaction of propylene\(^{24}\). The repulsive interaction enhances desorption of propylene from the metal sulfide catalyst, which may suppress the subsequent HG reaction, leading to high propylene selectivity of the Fe/SiO\(_2\) catalyst.

### 3.2. Surface Area and Bulk Structure of Various Fe-based Catalysts

The specific surface area (S.S.A.) of the catalyst before the reaction was measured for investigating the relation between the dehydrogenation activity and surface area. Table 2 shows the S.S.A. of the Fe-based catalysts. The S.S.A. was varied from 19.0 m\(^2\) g\(^{-1}\) (Fe/CeO\(_2\)) to 208.6 m\(^2\) g\(^{-1}\) (Fe/SiO\(_2\)). There was no relationship between activity order and surface area, thereby the catalytic activity is considered not to be related to the specific surface area of the Fe-based catalyst.

The structure of the catalyst after PDH with co-feeding of H\(_2\)S was analyzed by XRD analysis, in order to investigate the origin of the high performance of the Fe/SiO\(_2\) catalyst. Figure 6 shows the XRD pattern of the Fe catalysts on various supports (\(\gamma\)-Al\(_2\)O\(_3\), SiO\(_2\), ZrO\(_2\), MgO, and CeO\(_2\)) before and after the reaction with co-feeding of H\(_2\)S. Before the reaction, the Fe species in the Fe/\(\gamma\)-Al\(_2\)O\(_3\), Fe/SiO\(_2\), Fe/ZrO\(_2\), and Fe/CeO\(_2\) catalysts had the hematite (\(\alpha\)-Fe\(_2\)O\(_3\)) structure. The XRD pattern of the Fe/MgO catalyst was almost identical to that of the spinel phase of FeO\(_4\). According to Asakura and Iwasawa\(^{25}\), the MgFe\(_2\)O\(_4\) spinel phase is formed in the Fe/MgO catalyst due to the dispersion of Fe\(^{3+}\) on the MgO matrix during the impregnation process.
First, Fe\(^{3+}\) is anchored to the OH group on the MgO surface, and MgFe\(_2\)O\(_4\) is generated after calcination. For all the investigated catalysts, after PDH with co-feeding of H\(_2\)S, the initially present \(\alpha\)-Fe\(_2\)O\(_3\) structure was converted to the pyrrhotite (Fe\(_{1-x}\)S) structure due to the sulfidation of \(\alpha\)-Fe\(_2\)O\(_3\). A schematic representation of the sulfidation of \(\alpha\)-Fe\(_2\)O\(_3\) is presented in Fig. 7. First, H\(_2\)S dissociates into H\(_2\) and S\(^{2-}\) species on the catalyst. Thereafter, the iron cation (Fe\(^{3+}\)) and lattice oxygen (O\(^{2-}\)) in \(\alpha\)-Fe\(_2\)O\(_3\) diffuse from the bulk toward the surface; the H\(_2\) and O\(^{2-}\) react to produce H\(_2\)O, accompanied by the reduction of Fe\(^{3+}\) to Fe\(^{2+}\). The produced Fe\(^{2+}\) reacts with the S\(^{2-}\) species to form iron sulfide (Fe\(_{1-x}\)S) on the surface of the catalyst. Finally, sulfidation proceeds to the center of \(\alpha\)-Fe\(_2\)O\(_3\). During PDH with co-feeding of H\(_2\)S, the conversion increased over the Fe-based catalysts, as shown in Fig. 1. Such induction period might involve the reduction of the Fe cation and subsequent sulfidation. The MgO and CeO\(_2\) supports were also converted to metal sulfide species such as MgS, Ce\(_2\)S\(_3\), Ce\(_{10}\)S\(_{14}\)O, and Ce\(_2\)(SO\(_4\))\(_3\), where these species might be formed during the reduction and subsequent sulfidation of oxide species during PDH with co-feeding of H\(_2\)S. The drastic change in the support structure may contribute to the low dehydrogenation performance over the Fe/MgO and Fe/CeO\(_2\) catalysts.

In order to clarify the relationship between the dehydrogenation performance of the Fe-based catalyst and its local structure, the Fe/support (\(\gamma\)-Al\(_2\)O\(_3\), SiO\(_2\), ZrO\(_2\), MgO, and CeO\(_2\)) catalysts were subjected to EXAFS analyses. Figure 8 shows the Fourier-transform of the filtered EXAFS oscillations, \(k^2\chi(k)\), of the Fe K-edge, i.e., the so-called radial structure function (RSF), for the Fe/support (support: \(\gamma\)-Al\(_2\)O\(_3\), SiO\(_2\), ZrO\(_2\), MgO, and CeO\(_2\)) catalysts before and after the re-

![Fig. 6 XRD Pattern of the Fe Catalysts on Various Supports (i.e., SiO\(_2\), \(\gamma\)-Al\(_2\)O\(_3\), ZrO\(_2\), MgO, and CeO\(_2\)) (a) before and (b) after PDH with Co-feeding of H\(_2\)S](image)

![Fig. 7 Schematic Image of Sulfidation Mechanism of \(\alpha\)-Fe\(_2\)O\(_3\)](image)
actions, into R space in the k range of 2-14 Å−1. The RSF was determined for hematite (α-Fe2O3), magnetite (Fe3O4), wüstite (FeO), iron sulfate heptahydrate (FeSO4·7H2O), and cation-deficient iron sulfide (Fe1–xS) as reference samples. Note that α-Fe2O3, Fe3O4, and FeO were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Fe1–xS was prepared by supplying H2 and H2S to α-Fe2O3 at 700 °C for 2 h. The RSF of Fe1–xS corresponded to the reported pyrrhotite phase. The RSF of the Fe/support (support: γ-Al2O3, SiO2, ZrO2, and CeO2) catalysts before the reaction was in accordance with the α-Fe2O3 phase. The RSF of Fe/MgO corresponded to Fe3O4, consistent with the XRD pattern in Fig. 6(a). The RSF after PDH with co-feeding of H2S depended on the type of support. A large peak was observed for the Fe/support (support: γ-Al2O3, SiO2, ZrO2, and CeO2) catalysts. The bond length determined from this peak was around 2.40 Å, suggesting that the pyrrhotite phase was formed in these catalysts. The iron oxide phase appeared to be present in the Fe/MgO and Fe/ZrO2 catalysts, which may account for the low dehydrogenation activity. Thus, the origin of the excellent dehydrogenation performance of the Fe/SiO2 catalyst was not clarified by the EXAFS analysis, as it was confirmed that the iron phase was roughly the same in the Fe/support (support: γ-Al2O3, SiO2, and CeO2) catalysts. Consequently, XANES analysis of these catalysts was performed to investigate the difference in the electronic state of the Fe cation.

3.3. Oxidation State of Fe in Various Catalysts

Figure 9 shows the Fe K-edge XANES spectra of the catalysts on the various supports (i.e., γ-Al2O3, SiO2, ZrO2, CeO2, and MgO) before and after the reactions with co-feeding of H2S. XANES spectra of the reference Fe species, i.e., α-Fe2O3, Fe3O4, FeO, FeSO4·7H2O, and Fe1–xS, are also shown in Fig. 9. As shown in Fig. 9(a), the XANES spectra of the Fe/γ-Al2O3, Fe/SiO2, Fe/ZrO2, and Fe/CeO2 catalysts corresponded to α-Fe2O3. The XANES spectrum of the Fe/MgO catalyst was almost identical to that of the spinel phase of Fe3O4. These data are consistent with the XRD and EXAFS analyses. As shown in Fig. 9(b), the XANES spectra after the reaction were different for each catalyst. When the XANES spectra of the Fe-supported catalysts were compared to those of the standard samples, the spectra of the Fe/support (support: SiO2, γ-Al2O3, and CeO2) catalysts were found to be identical to that of Fe1–xS. However, the profile of the XANES spectrum of Fe/ZrO2 after the reaction was not the same as that of Fe1–xS, but was the same as that of Fe3O4, which agreed well with the RSF of Fe/ZrO2 presented in Fig. 8(a). Based on the reported H2 reduction behavior of α-Fe2O3 on ZrO2, α-Fe2O3 is reduced to Fe3O4 by H2 on the ZrO2 support. The Fe3O4 subsequently reacts with ZrO2 to produce (ZrFe1−x)O4, which indicates a strong interaction between the iron component and zirconia. Such strong interaction might suppress the sulfidation to Fe1–xS in the reaction atmosphere. In the case of the Fe/MgO catalyst, the XANES spectra before and after the reactions were
similar. The MgFe$_2$O$_4$ phase in the Fe/MgO catalyst might not be affected by H$_2$S due to the strong interaction between the iron and magnesium components, causing no change in the catalyst structure. Although the Fe/support (support: CeO$_2$, γ-Al$_2$O$_3$, and SiO$_2$) catalysts comprised single-phase Fe$_{1-x}$S, the dehydrogenation performance differed for these catalysts, as shown in Fig. 1. The Fe/SiO$_2$ and Fe/γ-Al$_2$O$_3$ catalysts showed high performance, whereas the Fe/CeO$_2$ catalyst exhibited low performance. To evaluate the difference in the catalyst performance, the XANES spectra of these catalysts were considered in detail. Figure 9(c) shows an extended region of the XANES spectra of the Fe/support (support: CeO$_2$, γ-Al$_2$O$_3$, and SiO$_2$) catalysts after PDH with co-feeding of H$_2$S (the XANES spectra of the Fe/MgO and Fe/ZrO$_2$ catalysts are not shown in Fig. 9(c) because these catalysts partially comprised the iron oxide phase.). The edge jump energy of the low-active Fe/CeO$_2$ catalyst was low compared to that of the high-active Fe/SiO$_2$ and Fe/γ-Al$_2$O$_3$ catalysts, indicating higher valency of the Fe species in the high-active catalysts.

In order to further identify the presence of high-valence iron species in the highly active Fe/SiO$_2$ and Fe/γ-Al$_2$O$_3$ catalysts, Fe 2p XPS measurement was carried out. Figure 10 shows the XPS spectra of the core electron for the Fe 2p state of the Fe/SiO$_2$ and Fe/γ-Al$_2$O$_3$ catalysts after PDH with co-feeding of H$_2$S. The XPS spectra of α-Fe$_2$O$_3$ (Kanto Kagaku Co., Ltd.) and FeS$_2$ (Mitsuwa Chemicals Co., Ltd.) as the standard samples are also included in Fig. 10, to identify S atom bonded to an Fe(II) atom, i.e., Fe$^{2+}$–S. The XPS spectra were curve-fitted, and each curve assigned to the corresponding species is also presented in Fig. 10. For the Fe/SiO$_2$ and Fe/γ-Al$_2$O$_3$ catalysts, three peaks were observed at 707.5, 710.5, and 713.7 eV in the Fe 2p$_{3/2}$ region, corresponding to a S atom bonded to an Fe(II) atom, i.e., Fe$^{2+}$–S, S atom bonded to an Fe(III) atom, i.e., Fe$^{3+}$–S, and a satellite peak, respectively$^{28,29}$. The Fe$^{3+}$–S species are generated by the formation of nonstoichiometric pyrrhotite on the catalyst$^{30}$. Most of the iron species in pyrrhotite are in the divalent state,

![Fig. 9](image1.png)

**Fig. 9** Fe K-edge XANES Spectra of the Fe Catalysts on Various Supports (i.e., γ-Al$_2$O$_3$, SiO$_2$, ZrO$_2$, MgO, and CeO$_2$) (a) before, (b) after PDH with Co-feeding of H$_2$S, and (c) Extended Part of XANES Spectra of Fe/γ-Al$_2$O$_3$, Fe/SiO$_2$, and Fe/CeO$_2$

![Fig. 10](image2.png)

**Fig. 10** XPS Spectra of Core Electron for Fe 2p of the Fe/SiO$_2$ and Fe/γ-Al$_2$O$_3$ Catalysts after PDH with Co-feeding of H$_2$S
while a portion of the iron species is in the trivalent state to satisfy the electroneutrality of the non-stoichiometric Fe₁₋ₓS₁₋ₓ. In a previous study, we proposed a reaction mechanism for PDH on iron sulfide. Based on density functional theory (DFT) calculations, we propose that the reduction-oxidation property of Fe in Fe₁₋ₓS₁₋ₓ is involved in the reaction mechanism. The Feⁿ⁺ (n: 2, 3) component of the iron species was reduced to Feⁿ⁻ through the transfer of an electron from the reaction intermediate. The Feⁿ⁻⁻ was oxidized to Feⁿ⁺⁺ by electron transfer, accompanied by the desorption of propylene. The high-valence Fe cation may promote the acceptance of an electron from reaction intermediate species, leading to high dehydrogenation performance for PDH with co-feeding of H₂S over the Fe/support (support: γ-Al₂O₃ and SiO₂ catalyst).

Although future work is required to clearly verify the role of the Fe cation in iron sulfide, the present study introduces the concept that high valency of the Fe species leads to high activity for PDH with co-feeding of H₂S.

4. Conclusion

We evaluated the catalytic properties of transition metal (Fe, Co, and Ni) catalysts on various supports (SiO₂, γ-Al₂O₃, ZrO₂, CeO₂, MgO) for PDH with co-feeding of H₂S. Among investigated catalysts, the SiO₂-supported Fe catalyst displayed high activity and selectivity for the production of C₃H₆. Structural characterization via XRD and XAFS analyses showed the formation of iron sulfide on the SiO₂-supported Fe catalyst. Fe K-edge XANES and XPS analyses demonstrate that catalysts with higher valence Fe species exhibit better performance for PDH with co-feeding of H₂S. High-valence Fe cations can accept an electron from intermediate species, which might enhance the dehydrogenation performance.

Acknowledgment

This study was financially supported by a Grant-in-Aid for Scientific Research (grant number: 18H01775).

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要  旨

H₂S 共存のプロパン脱水素に対する遷移金属系触媒の反応特性に及ぼす担体種の影響

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硫化水素共存下におけるプロパン脱水素反応に対する遷移金属系触媒の反応特性について検討した。SiO₂，γ-Al₂O₃，ZrO₂，CeO₂，MgO に担持した Fe や Co，Ni 系触媒の中で，SiO₂ に担持した Fe 系触媒が高選択的にプロピレンを生成することを見出した。また，触媒上への炭素析出量はわずかであった。各触媒について XRD や EXAFS 測定によりパルク構造や表面局所構造を，XANES や XPS 測定により電子状態などの物理化学的特性を評価した。その結果，優れた脱水素能を発現する触媒上には硫化物が形成され，酸化数の高い Fe 種が確認された。高い酸化数の Fe が反応中間体からの電子の授受を促進し，優れた脱水素特性を示したものと推測された。

J. Jpn. Petrol. Inst., Vol. 63, No. 4, 2020