1. Introduction

Propylene is an important building block for the production of polypropylene, propylene oxide, and acrylonitrile. The main processes for propylene production are steam cracking (SC) of naphtha and fluid catalytic cracking (FCC). The processes of SC and FCC produce ethylene and gasoline as the main products, respectively, and propylene as a by-product\(^1\),\(^2\). Although the global demand for propylene increases by approximately 4-5 % per year, there is a risk of shortage of propylene supply\(^3\). Therefore, to fulfill the global demand for propylene, the operations of the SC and FCC processes are optimized for lesser production of ethylene and gasoline, respectively, and greater production of propylene\(^4\),\(^6\).

Recently, the dehydrogenation reaction of propane \((\text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2)\) has received significant attention because dehydrogenation can convert the economic feedstock of propane to valuable propylene\(^7\). Because the reaction is reversible, prone to volume expansion, and highly endothermic, higher temperatures and lower pressures are preferred for this reaction. The most important aspect of propane dehydrogenation is the energy required for the endothermic reaction\(^9\),\(^10\). However, high reaction temperature used for the replenishment of the heat absorbed during the endothermic reaction results in the occurrence of side reactions and formation of coke, and deactivates the catalyst\(^9\),\(^10\).

Current state-of-the-art research focuses on investigating the synergistic effects of gas-phase oxidants and alkanes to overcome the obstacles to industrial dehydrogenation reactions\(^11\). It has been established that catalytic oxidative dehydrogenation (ODH) reactions are sensitive to certain oxidizing agents. A number of oxidants such as oxygen, nitrous oxide, and carbon dioxide have been investigated for the propane dehydrogenation reaction\(^12\)\(^-\)\(^16\). ODH can proceed at low temperatures because of the exothermic nature of the reaction without thermodynamic constraints. A vanadium-based material was found to be a selective catalyst for ODH with oxygen, because of its favorable redox properties. Carrero et al. reported that \((\text{VO}_x)_{(\text{TiO}_x)}\)-supported on SBA-15 catalyst showed a propane conversion of 10 % with a 60 % selectivity for the production of propylene; these values are superior to those of all other V-based catalysts reported to date\(^17\). High \(\text{VO}_x\) dispersion is required to achieve high propylene selectivity, and the formation of a linked \(\text{V}-\text{Ti}\) oxide monolayer is crucial to obtain high reaction rates with relatively high propylene selectivity. Boron nitride (BN) was also reported to display high activity and selectivity; the resultant conversion was 14 % with a 79 % selectivity for the propylene\(^18\),\(^19\). Lots of studies are focused on enhancing propylene selectivity, however it
remains insufficient for a commercially viable ODH process. Thus, suppression of the sequential reactions of propylene remains a challenge for future research.

From a practical perspective, simple dehydrogenation (SDH) of propane is a desirable process because a high propylene selectivity can be achieved using industrial catalysts such as Cr- and Pt-based catalysts\(^{20,21}\). Severe coke deposition on these catalysts during the dehydrogenation of propane deactivates their performance within a short reaction period\(^{22,25}\). Regeneration of the coked catalyst by coke combustion using diluted air is required after such short reaction periods\(^{26}\). Such a regeneration process for coke removal causes irreversible deactivation of the catalyst by phase transformation and sintering. Therefore, the development of a novel catalyst with stable performance is strongly required.

In recent years, there have been some reports on the development of Pt-based catalysts with excellent stability for SDH\(^{27,28}\). On the other hand, there are few reports on the catalysts with high stability using inexpensive transition metal-based catalysts. Therefore, the objective of this paper is to review our recent work on transition metal-based catalysts for catalyzing the SDH of propane, and explore a novel dehydrogenation process using hydrogen sulfide (H\(_2\)S) in order to provide useful information regarding novel catalytic processes.

2. Transition Metal Catalysts for SDH

2.1. Modification Effect of Sulfate Ion\(^{30}\)

Transition metals (Fe, Co) supported on sulfated alumina have been reported to be highly active and selective for the catalytic dehydrogenation of propane\(^{27,29}\). However, the reason for this promotional effect has not yet been determined. Hence, the effect of sulfation treatment was investigated to elucidate the reason for the superior dehydrogenation performance. Coke deposition was performed on transition metal oxide catalysts modified with sulfate ions (SO\(_4^{2-}\)) using ammonium sulfate as the sulfating agent\(^{30}\). The catalysts of transition metals (Fe, Co, Cr, Ni, Cu and Mn) were impregnated with 20 wt% of the catalyst components (abbreviated henceforth as M/\(\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\)). The catalyst without sulfation treatment was used as the reference (abbreviated henceforth as M/\(\text{Al}_2\text{O}_3\)). Figure 1 shows the product yields of the M/\(\text{Al}_2\text{O}_3\) and M/\(\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\) catalysts. The Fe/\(\text{Al}_2\text{O}_3\) and Co/\(\text{Al}_2\text{O}_3\) catalysts were found to be highly reactive; however, only a small amount of propylene was produced. With the remaining transition metal catalysts (except for Fe- and Co-based), propylene was produced even though they were less reactive. In the case of the M/\(\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\) catalysts, substantial amounts of propylene were produced with higher selectivity than those in the case of the M/\(\text{Al}_2\text{O}_3\) catalysts. In particular, the Fe/\(\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\) and Co/\(\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\) catalysts showed higher propylene yields (> 10 %) than the other catalysts. Table 1 shows deposited coke amount on the unsulfated and sulfated catalysts. The amount of coke deposition was significantly decreased by the sulfation treatment. This decrease may contribute toward the improvement of the catalytic performance. Although transition metal catalysts (except Cr-based) are generally considered to be ineffective for dehydrogenation, activation of the inactive catalysts by a simple method of sulfate modification is an important finding that can lead to new directions in catalyst development.

2.2. State of S Species\(^{30}\)

To elucidate the reason for the enhancement of the catalytic performance by sulfate modification, X-ray photoelectron spectroscopy (XPS) analysis was performed to investigate the state of the S species on the Co/\(\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\) catalyst before and after the dehydrogenation of propane. Figure 2 shows the XPS profiles of the S\(_{2p}\) core-level electrons of the catalyst before and after the reaction. The peak at 169.7 eV can be attributed to the SO\(_4^{2-}\) ion of the catalyst before the reaction, whereas the peaks at 169.7 eV and 162.4 eV can be assigned to the SO\(_4^{2-}\) and sulfide (S\(_2^-\)) ions, respectively\(^{31}\), after the reaction. The reductive atmosphere causes the reduction of S from the +6 oxidation state in the SO\(_4^{2-}\) ion to the −2 oxidation state in the S\(_2^-\) ion.

![Fig. 1 Product Yields at the End of Reaction Period over (a) M/\(\text{Al}_2\text{O}_3\) and (b) M/\(\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\) Catalysts](image)

| Catalyst                        | Amount of deposited coke [wt%] |
|---------------------------------|--------------------------------|
| Fe/\(\text{Al}_2\text{O}_3\)     | 31.7                           |
| Fe/\(\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\) | 3.7                           |
| Co/\(\text{Al}_2\text{O}_3\)     | 16.3                           |
| Ni/\(\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\) | 6.4                           |
| Ni/\(\text{Al}_2\text{O}_3\)     | 38.2                           |
| Cr/\(\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\) | 21.2                           |
| Cr/\(\text{Al}_2\text{O}_3\)     | 6.0                            |
| Mn/\(\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\) | 4.5                            |
| Mn/\(\text{Al}_2\text{O}_3\)     | 0.1                            |
| Cu/\(\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\) | 1.0                            |
| Cu/\(\text{Al}_2\text{O}_3\)     | 1.9                            |

![Table 1 Amounts of Coke Deposited on Unsulfated and Sulfated Catalysts](image)
To evaluate the relationship between the catalytic performance and S\(^2–\) species on the surface of the catalyst, XPS analyses were performed on the Co/SO\(_4^{2–}/\)Al\(_2\)O\(_3\) catalyst after 20, 50, and 200 min of reaction. The ratios of the areas of S\(^2–\) and SO\(_4^{2–}\) species to that of Al\(^{3+}\) were calculated and are summarized in Table 2. The SO\(_4^{2–}/\)Al\(^{3+}\) ratio had no effect on the propylene yield. The SO\(_4^{2–}/\)Al\(^{3+}\) ratio significantly decreased after 20 min of the reaction compared to that before the dehydrogenation. During the reaction, the SO\(_4^{2–}\) species were reduced and/or desorbed from the catalyst surface. This phenomenon could be causing a large decrease in the SO\(_4^{2–}/\)Al\(^{3+}\) ratio. In addition, the SO\(_4^{2–}/\)Al\(^{3+}\) ratio did not attain a constant value even as the reaction progressed. In contrast, the S\(^2–/\)Al\(^{3+}\) ratio marginally increased with time-on-stream. Because the catalytic activity increased with the time-on-stream, the activity could be related to the S\(^2–\) ion rather than the SO\(_4^{2–}\) ion.

### 2.3. Performance of Metal Sulfide Catalysts

Because a metal sulfide, consisting of a metal component and a lattice S\(^2–\), was effective for the dehydrogenation of propane, cobalt sulfide catalysts were prepared and their catalytic performance was evaluated. Sulfide-loaded Al\(_2\)O\(_3\) (JRC-ALO-8) was prepared by a conventional hydrothermal synthesis method using thiocetamide as the sulfurizing agent. The synthesis was carried out at 180 °C. Figure 3 shows the time course of propane conversion and propylene selectivity. The cobalt sulfide catalyst showed high conversion and selectivity. However, the lattice S\(^2–\) ions were considered to play an important role in dehydrogenation. However, a decrease in the conversion and selectivity was observed with time owing to the loss of lattice S\(^2–\) from the metal sulfide. H\(_2\)S was supplied to the catalyst to regenerate the lattice S\(^2–\) and improve the dehydrogenation performance. The reaction was carried out again; these operations were repeated four times. The results of propane conversion and propylene selectivity as a function of time-on-stream are shown in Fig. 3. After H\(_2\)S was supplied to the deactivated catalyst, the conversion and selectivity were found to have recovered. When the operation was repeated after H\(_2\)S supply, high propane conversion and selectivity were achieved. This phenomenon can be explained as follows: the dehydrogenation reaction proceeds on the surface of the sulfide catalyst with the loss of lattice S\(^2–\) via H\(_2\) reduction (H\(_2\) + S\(^2–\) → H\(_2\)S) and/or oxidative dehydrogenation (C\(_3\)H\(_8\) + S\(^2–\) → C\(_3\)H\(_6\) + H\(_2\)S). The regeneration of S\(^2–\) progresses on the surface of the catalyst with the supply of H\(_2\)S, which enhances the dehydrogenation performance.

### 3. Propane Dehydrogenation with Co-feeding of H\(_2\)S

#### 3.1. Effect of Transition Metal Species

The loss of lattice S\(^2–\) from the metal sulfide via reaction with H\(_2\) and/or propane leading to decreased dehydrogenation activity is a critical issue. Suppression of the loss of S\(^2–\) from the metal sulfide could lead to a high dehydrogenation performance. Therefore, the dehydrogenation of propane in the presence of H\(_2\)S was investigated.

The catalytic performance was investigated for propane dehydrogenation with co-feeding H\(_2\)S over SiO\(_2\)-supported transition metal (Fe, Co, Ni, Mn, Cu) catalysts (described henceforth as Metal/SiO\(_2\)). Figure 4(a) shows the conversion of propane over the Metal/SiO\(_2\)
The Fe/SiO₂, Co/SiO₂, and Ni/SiO₂ catalysts showed high propane conversion at the initial stage of the reaction. In addition, the Fe/SiO₂ catalyst displayed better stability during propane dehydrogenation with co-feeding H₂S than the other transition metal catalysts. The Mn/SiO₂ and Cu/SiO₂ catalysts showed low propane conversions. The product selectivity at 200 min is shown in Fig. 4(b). From the figure, propylene, methane and ethylene were confirmed as the products formed over all the catalysts. CH₄ and C₂H₄ by-products were produced by decomposition of propane (C₃H₈ → CH₄ + C₂H₄) and/or hydrogenolysis of propylene (C₃H₆ + H₂ → CH₄ + C₂H₄). A comparison of the propylene selectivity over each catalyst revealed that the Fe/SiO₂ catalyst displayed the highest selectivity of 93%; this high selectivity almost remained constant throughout the dehydrogenation.

3.2. Effect of Type of Support

Effect of the type of support (γ-Al₂O₃, SiO₂, ZrO₂, MgO and CeO₂) on the performance of the Fe-based catalyst for propane dehydrogenation with co-feeding of H₂S was investigated. Figure 5(a) shows the conversion of propane over the Fe-based catalysts with various supports. The value in parenthesis in Fig. 5(a) shows the amount of coke deposited after propane dehydrogenation with co-feeding H₂S. The supported catalyst is described as Fe/support henceforth. From Fig. 5(a), it is clear that the Fe/γ-Al₂O₃ and Fe/SiO₂ catalysts showed high propane conversion after 35 min of reaction. In addition, the Fe/SiO₂ catalyst displayed better stability for propane dehydrogenation with co-feeding H₂S than the Fe/γ-Al₂O₃ catalyst. The Fe/ZrO₂ and Fe/CeO₂ catalysts showed catalytic activity to a certain degree; however, these catalysts were deacti-
Catalytic performances were evaluated for propane dehydrogenation with H$_2$S. Reaction conditions were as follows: reaction temperature was 600 °C, catalyst weight was 250 mg, and ratio of H$_2$S/C$_3$H$_8$/He flow rates were 3.5 : 2.5 : 20 mL min$^{-1}$.

Fig. 6 Effect of H$_2$S Addition on C$_3$H$_6$ Yield of Fe/SiO$_2$ and Cr/γ-Al$_2$O$_3$ Catalysts

In contrast, the Fe/MgO catalyst exhibited no catalytic activity for propane dehydrogenation with co-feeding H$_2$S. Therefore, the stability of these catalysts was largely dependent on the type of support used. Figure 5(b) shows the product selectivity after 200 min of reaction. The Fe/SiO$_2$ catalyst showed the highest propylene selectivity. The propylene selectivities of the Fe/γ-Al$_2$O$_3$, Fe/ZrO$_2$, Fe/MgO and Fe/CeO$_2$ catalysts were respectively 83, 75, 73, and 67 %. The difference in selectivity could be attributed to the effect of the properties of the support on the dehydrogenation reaction. The γ-Al$_2$O$_3$, ZrO$_2$ and CeO$_2$ catalyst supports contain electron-deficient cations that act as Lewis acid sites$^{34}$. The propylene molecule contains a π-bond which makes it more basic than propane. Therefore, propylene exhibits stronger interactions with the electron-deficient Lewis centers on the oxide surfaces than with propane molecules. This basicity leads to the cleavage of the allylic C=C bonds in propylene, which may decrease the propylene selectivity. In the Fe/MgO catalyst, the Fe atoms strongly interact with MgO resulting in the formation of a solid solution, as confirmed by X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) analyses. Such an effect may decrease the selectivity toward the formation of propylene as the product. Because the SiO$_2$ support is inert, it did not affect the dehydrogenation reaction. Therefore, the Fe/SiO$_2$ catalyst exhibited excellent propylene selectivity. As for the amount of coke deposited after propane dehydrogenation with co-feeding H$_2$S, relatively inactive catalysts such as Fe/ZrO$_2$, Fe/MgO and Fe/CeO$_2$ exhibited negligible or no coke deposition, whereas the more active Fe/γ-Al$_2$O$_3$ catalyst exhibited significant amount of coke deposition. The lack of coke deposition on the Fe/MgO catalyst is probably because it exhibited no activity toward propane dehydrogenation. Interestingly, the highly active Fe/SiO$_2$ catalyst also showed negligible coke deposition. These results might be related to the differences in the propylene selectivity. The side-reactions of cleavage of the C-C bond in propylene and propane cracking generate hydrocarbon fragments (i.e., CH$_x$ and carbon atoms) which accumulate on the catalyst surface$^{35,36}$. The relatively low amount of coke deposition on the Fe/SiO$_2$ catalyst may be due to the suppression of the above-mentioned side reactions.

3.3. Practicability of Fe-based Catalyst$^{32}$

The dehydrogenation performance of the Fe/SiO$_2$ catalyst was compared to that of the CrO$_x$/γ-Al$_2$O$_3$ catalyst, which is known to be a highly active catalyst for propane dehydrogenation. Figure 6 shows the propylene yields as a function of the reaction time. The CrO$_x$ loadings of 10, 15 and 20 wt% were investigated. At the beginning of the reaction, the Fe/SiO$_2$ catalyst exhibited less activity than the CrO$_x$/γ-Al$_2$O$_3$ catalyst. However, the stability of the Fe/SiO$_2$ catalyst was superior to that of the CrO$_x$/γ-Al$_2$O$_3$ catalyst.

Figure 7 shows the durability of the Fe/SiO$_2$ catalyst during a reaction period of 50 h using H$_2$S/C$_3$ values of 0.2, 0.4 and 1.4. The initial propylene yield was high at a H$_2$S/C$_3$ ratio of 1.4. However, the catalyst underwent deactivation as the reaction proceeded. After 0.6 h, the conversion was 49 % with 94 % propylene selectivity; the activity decreased, exhibiting a conversion of 15 % with 78 % propylene selectivity after 50 h. This result indicates that the catalyst degraded significantly during the reaction. At H$_2$S/C$_3$ values of 0.2 and 0.4, the initial conversion was lower than that at the H$_2$S/C$_3$ value of 1.4. However, only a slight decrease in the conversion and selectivity was observed. Additionally, the catalyst underwent marginal deactivation over the 50-h reaction period at H$_2$S/C$_3$ values of 0.2 and 0.4, that is, a relatively high conversion and up to 90 % selectivity were observed at a H$_2$S/C$_3$ ratio of 0.4.
3.4. Catalyst Structure

To elucidate the reason for the high performance of the Fe/SiO2 catalyst in the propane dehydrogenation reaction with co-feeding H2S, the active species were investigated by X-ray absorption near-edge structure (XANES) analysis. Figure 8(a) shows the Fe K-edge XANES spectra of the Fe/SiO2 catalysts before and after dehydrogenation with co-feeding of H2S. The XANES spectra of the reference Fe species, that is, hematite (α-Fe2O3), magnetite (Fe3O4), Wüstite (FeO) and cation-deficient iron sulfide (Fe1–xS), are also shown in Fig. 8. Fe1–xS was prepared by supplying H2 and H2S to α-Fe2O3 at 700 °C for 2 h. The XANES spectrum of Fe1–xS corresponds to the reported pyrrhotite phase37). As shown in Fig. 8(a), the XANES spectrum of the Fe/SiO2 catalyst before the reaction corresponds to that of α-Fe2O3. The XANES spectrum of the Fe/SiO2 catalyst was different after the reaction and was identical to that of Fe1–xS. The Fe phase on the SiO2 support transformed into the Fe1–xS species during the reduction and subsequent sulfidation occurring during the reaction. Figure 8(b) shows the Fourier transforms of the filtered EXAFS oscillations k^2χ(k) into R space.

3.5. Role of H2S

To completely elucidate the influence of H2S on the catalyst, catalytic performance tests and XPS analysis were performed on the Fe/SiO2 catalyst. The catalytic performance test involved the following method: first, dehydrogenation with co-feeding H2S was conducted followed by purging of the surface adsorbate using He; second, dehydrogenation was carried out without co-feeding H2S followed by purging and desorption of the surface adsorbate (mainly physically adsorbed H2S on the catalyst); finally, dehydrogenation with co-feeding H2S was performed again. Figure 9 shows the propane conversion over the Fe/SiO2 catalyst as a function of the reaction time. The conversion reached as high as 50 % and decreased significantly when the supply of H2S co-feed was stopped. When H2S was supplied again for propane dehydrogenation, the catalytic activity recovered to 33 %. Under co-feeding H2S conditions, the catalyst surface could be covered by the surface lattice S2– ions, which possibly imparted the high activity. In contrast, during dehydrogenation without H2S, H2 reduction probably occurred at the expense of the surface lattice S2– ions. Therefore, a decrease in the dehydrogenation activity occurred as the S2– ions were consumed. However, by supplying H2S again, the surface lattice S2– ions were regenerated, resulting in the recovery of the dehydrogenation activity. This hypothesis is supported by the XPS analysis results. The surface atom concentrations of sulfur (S) and iron (Fe) atoms and the atomic ratio of S/Fe were obtained. Table 3 shows the atomic concentrations calculated from the areas of the Fe2p and S2p XPS profiles. The three catalyst samples, indicated by red circles in Fig. 9, were prepared by propane dehydroge-
nation with and without co-feeding H2S. Under co-feeding H2S conditions, the atomic ratio of S/Fe was 1.71. This non-stoichiometric composition indicates that the catalyst surface contained excess sulfur. In contrast, discontinuing the supply of H2S co-feed from the reaction decreased the S/Fe ratio to 1.05, which is very close to the stoichiometric value. This result implies that the catalyst surface contained the iron (II) cation, whereas the surface S2− ions were probably consumed by oxidative dehydrogenation as shown in Eq. (1).

\[
\text{C}_3\text{H}_6 + \text{S}^{2-} \rightarrow \text{C}_3\text{H}_5 + \text{H}_2\text{S} \quad (1)
\]

After resuming the supply of H2S co-feed, the S/Fe ratio recovered to a value of 1.58. The surface S2− ions were regenerated via the reaction shown in Eq. (2).

\[
\text{H}_2\text{S} \rightarrow \text{H}_2 + \text{S}^{2-} \quad (2)
\]

One possible reason why the S/Fe failed to attain its original value of 1.71 upon the re-supply of H2S could be because of the micro-structural changes occurring in iron sulfide due to redox cycling. Based on the atomic concentrations shown in Table 3, the high activity could be because of the presence of the iron sulfide phase. Therefore, one of the key roles of H2S is the formation of an iron sulfide phase. Propane dehydrogenation with co-feeding H2S on Fe-based catalysts proceeds via a redox mechanism consisting of oxidative dehydrogenation and regeneration of lattice S2− species. Such a smooth redox cycle may be responsible for the high durability performance.

4. Summary

Transition metal catalysts loaded with SO42− ions showed high selectivity for the dehydrogenation of propane. The high activity was attributed to the S2− ions formed by reduction during the reaction. Metal sulfides were effective catalysts for the dehydrogenation of propane; however, the loss of S2− ions from the catalyst surface under the reaction atmosphere employed degraded the catalytic performance. During the dehydrogenation reaction in the presence of H2S, the S2− ions were continuously restored on the catalyst surface, and high stability was achieved.

| Catalyst | Area ratio of S/Fe2p3/2 [−] | Atomic ratio of S/Fe [−] |
|----------|-------------------|-------------------|
| 50 min   | 0.462             | 1.71              |
| 125 min  | 0.285             | 1.05              |
| 200 min  | 0.426             | 1.58              |

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要 旨
硫化水素を活用する低級アルカンの脱水素反応
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プロパンの単純脱水素プロセスでは高いプロピレン選択性が得られるが、その工業触媒は脱水素反応に伴って生成するコーヌクにより失活する。そのため、安定した性能を有する触媒の開発が求められている。我々は、比較的安価な遷移金属系触媒を硫化イオンで修飾した触媒が、プロパン脱水素に優れた触媒特性を示し、高選択性に反応が進行することを見出した。また、担持した硫酸イオンが反応中に還元され、触媒表面に形成された格子硫黄（S²⁻）が脱水素の活性種として機能することを見出し、格子 S²⁻ の損失により触媒が失活することを明らかにした。そこで、硫化物触媒の格子 S²⁻ に着目し、脱水素反応場に高濃度の硫化水素（H₂S）を共存させ、連続的に格子 S²⁻ を復元する新規な脱水素プロセスを開発した。