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Active Species of Sulfated Metal Oxide Catalyst for Propane Dehydrogenation

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This study focuses on clarifying the active species over a sulfated transition metal oxide (Cr, Mn, Fe, Co, Ni, Cu) catalyst for propane dehydrogenation. The unsulfated catalyst showed a high conversion for the dehydrogenation of propane, with significantly low selectivity to the desired product of propylene. On the other hand, the sulfated catalyst displayed a high selectivity to propylene, though the conversion was slightly decreased. The sulfation treatment was especially effective for the Co and Fe catalysts. The sulfate species (SO_4^{2-}) were reduced to the active species of the sulfide ion (S^{2-}) in the reaction atmosphere, which increased a selectivity to propylene.

Keywords

Propane dehydrogenation, Transition metal oxide, Sulfation treatment, Sulfide ion

1. Introduction

Propylene is utilized in petrochemical industry as an important intermediate for the production of polypropylene, propylene oxide, and acrylonitrile^{1),2)}. The main routes for the production of propylene are the thermal cracking of naphtha and the fluid catalytic cracking (FCC)^{3)~5)}. The naphtha steam cracker and FCC units, respectively, produce ethylene and gasoline as the main products. The propylene is produced as a by-product. The growth rate of the propylene demand is estimated at 4–5 % per year⁶⁾. The market demand of propylene will not be easily satisfied, because the operations of the steam cracker and FCC units are mainly optimized for the production of ethylene and gasoline. Thus, the risk of a propylene supply shortage is expected in the near future. Recently, a great deal of attention has been devoted to the on-purpose technologies for the propylene production, such as the dehydrogenation of propane, olefin metathesis, and the catalytic cracking of C4/C5^{2),7),8)}.

Among these processes, the dehydrogenation of propane (Eq. (1)) is attractive in terms of the direct conversion of an economical feedstock to the valuable olefin,

which could contribute to the chemical industry.

The $\text{CrOx}/\text{Al}_2\text{O}_3$ catalyst shows a high activity and excellent selectivity to propylene for the dehydrogenation of propane. However, on the $\text{CrOx}/\text{Al}_2\text{O}_3$ catalyst, severe coke deposition during dehydrogenation of propane deactivates the performance in short reaction periods^{9)~13)}. The steam is normally used for suppressing the coke deposition, but deactivates the activity of the $\text{CrOx}/\text{Al}_2\text{O}_3$ catalyst by adsorbing the active site of Cr. Thus, a regeneration process by the coke combustion using diluted air is required after short reaction periods¹⁴⁾. Such a cyclic regeneration process for removing the deposited coke causes the irreversible deactivation of the catalyst by a phase transformation and sintering. Hence, the development of a novel catalyst with a stable performance is strongly required.

Recently, the iron-based catalyst supported on a sulfated alumina was reported to be highly active and selective in catalytic dehydrogenation of propane^{15),16)}. The sulfate addition to the Co based catalyst also promoted the propane dehydrogenation¹⁷⁾. Although the sulfation treatment was effective for the catalytic performance, the reason for a promoting effect has not been clarified so far. Therefore, in this study, the effect of the sulfation treatment was investigated to improve the catalytic performance of transition metal oxide, and to clarify the reason for a high dehydrogenation performance by characterizing the unsulfated and sulfated catalysts using X-ray diffraction (XRD), Raman, X-ray

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photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) analysis.

2. Experimental

2.1. Catalyst Preparation

The catalyst support of γ -Al₂O₃ was prepared by a sol-gel method (Al[OCH(CH₃)₂]₃: 12 g, HNO₃ aq.: 6 mL, HCHO: 4 mL, H₂O: 80 mL). Then, ammonium sulfate was added to the γ -Al₂O₃ sol. In case of the preparation of the unsulfated catalyst, the addition of the ammonium sulfate was skipped. After a dry and calcination processes at 700 °C for 2 h, a sulfated γ -Al₂O₃ support was obtained (abbreviated as Al₂O₃ or SO₄²⁻/Al₂O₃). The transition metal oxide (Cr, Mn, Fe, Co, Ni, Cu) was supported by an evaporation to dryness as follows; each metal nitrate was impregnated on SO₄²⁻/Al₂O₃. After a calcination of the catalyst at 700 °C for 2 h, the sulfated catalyst was obtained (abbreviated as M/Al₂O₃ or M/SO₄²⁻/Al₂O₃, M: Cr, Mn, Fe, Co, Ni, Cu). The loading of SO₄²⁻ and metal was 5 wt% and 20 wt%, respectively.

2.2. Catalytic Activity Test

The catalytic activity was evaluated using a fixed-bed reactor. The reactant of C₃H₈ and diluent He were supplied to the reactor by 5.0 mL min⁻¹ and 45.0 mL min⁻¹, respectively. Reaction temperature and catalyst weight were 600 °C and 500 mg. Outlet gases were analyzed using hydrogen-flame ionization detector (FID) and thermal conductivity detector (TCD) gas chromatographs.

2.3. Characterization

The crystalline structure of the prepared catalyst was ascertained by X-ray powder diffraction with CuK α radiation ($\lambda = 1.54$ Å, Ultima IV; Rigaku Corp.). Raman spectroscopy was performed using a Renishaw spectrometer. The spectra were collected between 100 cm⁻¹ and 1000 cm⁻¹ under the sample exposed to air at ambient temperature. The quantifications of the S species and carbon deposited on the catalysts were accomplished using an elemental analyzer of a FlashEA 1112 (Thermo Electron Corp.). For analysis of the catalyst surface, an XPS (Axis Ultra DLD; Shimadzu Corp.) measurement was performed using monochromatic AlK α radiation. The binding energy was referred to the carbon of C_{1s} = 284.7 eV for convenience. The S K-edge XANES measurements were performed by fluorescence X-ray yield method at the soft X-ray absorption fine structure (XAFS) beamline BL6N1 of the Aichi Synchrotron Radiation Center (Aichi SR), which has an electron storage ring with a circumference of 72 m and is operated at an electron energy of 1.2 GeV with a current of 300 mA.

Fig. 1 Propane Conversion over (a) M/Al₂O₃ and (b) M/SO₄²⁻/Al₂O₃ Catalysts with Time on Stream

3. Results and Discussion

3.1. Catalytic Performance

In order to investigate the effect of sulfation treatment on a catalytic performance, the activity test was performed over the M/Al₂O₃ and M/SO₄²⁻/Al₂O₃ (M: Cr, Mn, Fe, Co, Ni, Cu) catalysts. Figures 1(a) and 1(b) showed propane conversion with time on stream. The Cr/Al₂O₃ catalyst displayed a high initial conversion, but showed a gradual deactivation behavior. The Ni/Al₂O₃ catalyst denoted a similar catalytic behavior to the Cr/Al₂O₃ catalyst. The Co/Al₂O₃ and Fe/Al₂O₃ catalysts also revealed a high propane conversion, however the activity tests could not be performed due to a considerable coke deposition on these catalysts, leading to a blockage of the reactor. The Mn/Al₂O₃ and Cu/Al₂O₃ catalysts showed a considerably low conversion.

Table 1 The Amount of Coke Deposited on the Unsulfated and Sulfated Catalysts

Catalyst	The amount of deposited coke [wt%]
Fe/Al ₂ O ₃	31.7
Fe/SO ₄ ²⁻ /Al ₂ O ₃	3.7
Co/Al ₂ O ₃	16.3
Co/SO ₄ ²⁻ /Al ₂ O ₃	6.4
Ni/Al ₂ O ₃	38.2
Ni/SO ₄ ²⁻ /Al ₂ O ₃	21.2
Cr/Al ₂ O ₃	6.0
Cr/SO ₄ ²⁻ /Al ₂ O ₃	4.5
Mn/Al ₂ O ₃	0.1
Mn/SO ₄ ²⁻ /Al ₂ O ₃	0.4
Cu/Al ₂ O ₃	1.0
Cu/SO ₄ ²⁻ /Al ₂ O ₃	1.9

In case of the sulfated catalyst (**Fig. 1(b)**), the M/SO₄²⁻/Al₂O₃ catalysts (M: Co, Fe, Ni, Cr) showed a lower propane conversion, compared to the unsulfated bare catalysts. However, the important finding in the sulfation treatment is the improvement of the catalytic stability of the Co/SO₄²⁻/Al₂O₃ and Fe/SO₄²⁻/Al₂O₃ catalysts. Especially, the Co/SO₄²⁻/Al₂O₃ catalyst has no deactivation during the dehydrogenation reaction for 200 min. **Table 1** showed the amount of coke deposited on the unsulfated and sulfated catalysts. The amount of coke deposition was significantly decreased by the sulfation treatment. Such a decrease of the coke amount might contribute to the improvement of the catalytic stability.

Figures 2(a) and **2(b)** showed a product selectivity at the end of the reaction period over the M/Al₂O₃ and M/SO₄²⁻/Al₂O₃ (M: Cr, Mn, Fe, Co, Ni, Cu) catalysts. The selectivity to propylene was clearly improved by the sulfation treatment. Namely, the improvement from 63.1 to 88.7 % was observed over the Fe/Al₂O₃ catalyst; that from 0 to 87.2 % over the Co/Al₂O₃ catalyst; that from 85.6 to 92.2 % over the Cr/Al₂O₃ catalyst; that from 36.5 to 79.9 % over the Ni/Al₂O₃ catalyst.

In order to compare the selectivity at the almost same conversion over the Co/Al₂O₃ and Co/SO₄²⁻/Al₂O₃ catalysts, we investigated the products selectivity at different propane conversion under various *W/F*s, which is the ratio of a catalyst weight to the flow rate of propane. **Figures 3(a)** and **3(b)** showed products selectivity at various propane conversion over the Co/Al₂O₃ and Co/SO₄²⁻/Al₂O₃ catalysts, respectively. Over the Co/Al₂O₃ catalyst, propylene selectivity was 69.7 % at 3.7 % conversion. Methane, ethylene and carbon monoxide were obtained as by-products. By-products of methane and ethylene probably produced *via* propane decomposition on the catalyst as the following Eq. (2).

Slight by-product of carbon monoxide was probably produced *via* the propane and/or propylene oxidation

Fig. 2 Product Selectivity at the End of the Reaction Period over (a) M/Al₂O₃ and (b) M/SO₄²⁻/Al₂O₃ Catalysts

using a lattice oxygen in the Co oxide species. By increasing propane conversion from 3.7 to 16.3 %, the propylene selectivity was decreased from 69.7 to 50.4 %. The selectivity to methane and carbon monoxide was increased. The propylene sequentially reacted on the catalyst *via* the hydrogenolysis of propylene (Eq. (3)) and oxidation of the produced ethylene by lattice oxygen (Eq. (4)) proceeded on the catalyst.

Here, $\text{O}_{\text{lat}}^{2-}$ means lattice oxygen in Co oxide species. As for the Co/SO₄²⁻/Al₂O₃ catalyst, the propylene selectivity was 91.4 % at 11.0 % conversion. Although the selectivity was decreased by increasing a propane con-

Fig. 3 Selectivity to Products over (a) Co/Al₂O₃ and (b) Co/SO₄²⁻/Al₂O₃ Catalysts at Various Propane Conversions

version, the Co/SO₄²⁻/Al₂O₃ catalyst displayed a high propylene selectivity: 84.6 % at 18.3 % conversion; 80.0 % at 26.1 % conversion; and 72.6 % at 29.6 % conversion. Compared to the propylene selectivity at the almost same conversion over the unsulfated and sulfated catalysts, the dehydrogenation was found to selectively proceed on the sulfated catalyst. In other words, there was an interaction between the sulfate ion and Co element, which produced a higher propylene selectivity over the Co/SO₄²⁻/Al₂O₃ catalyst than that over the Co/Al₂O₃ catalyst.

3.2. Catalyst Structure

Table 2 indicated the amount of S species on the SO₄²⁻/Al₂O₃ before and after calcination process. The

Table 2 The Amount of S Species on Various Samples

Catalyst	The amount of S [wt%]	
	Fresh	Used
SO ₄ ²⁻ /Al ₂ O ₃ before calcination	1.74	-
SO ₄ ²⁻ /Al ₂ O ₃ after calcination	0.98	-
Co/SO ₄ ²⁻ /Al ₂ O ₃	0.63	0.59

amount of S species on the Co/SO₄²⁻/Al₂O₃ catalysts before and after reaction was also shown in Table 2. The SO₄²⁻/Al₂O₃ before calcination had 1.74 wt%, which was corresponded to 5.22 wt% of the sulfated ion (SO₄²⁻). By calcining the SO₄²⁻/Al₂O₃ sample, the amount of S species was decreased by 43.7 %. Further calcination process and the dehydrogenation reaction caused a decrease of the S species on the catalyst. The portion of the sulfated ion (SO₄²⁻) was disappeared from the catalyst by the calcination process and the reaction. However, the S species was remained on the catalyst, even if the catalyst was exposed to the reaction atmosphere.

The structure of the Co/Al₂O₃ and Co/SO₄²⁻/Al₂O₃ catalysts was investigated by an XRD measurement, to examine the effect of the sulfation treatment on the bulk structure. Figures 4(a) and 4(b) showed the catalyst structure before and after the dehydrogenation of the Co/Al₂O₃ and Co/SO₄²⁻/Al₂O₃ catalysts. Before the reaction, the peaks were identified with the γ -Al₂O₃, Co₃O₄ and CoAl₂O₄. As for the catalysts after the dehydrogenation, the peaks were fitted with the γ -Al₂O₃, Co₃O₄ and CoAl₂O₄ as well as Co metal. The reducing atmosphere caused the reduction of Co₃O₄ to Co metal. Compared to the XRD patterns between the unsulfated and sulfated catalyst, there were almost no differences in the catalyst structure. Figure 5 showed the Raman spectra of the Co/Al₂O₃ and Co/SO₄²⁻/Al₂O₃ catalysts before and after the reaction. The spectrum shows clearly the Raman peaks at 203, 485, 530, 624 and 692 cm⁻¹ in the range of 100-1000 cm⁻¹, which correspond respectively to the F_{12g}, E_g, F_{22g}, F_{32g} and A_{1g} modes of crystalline Co₃O₄ or CoAl₂O₄¹⁸⁾. There were almost no differences in all catalysts. These results obtained from XRD and Raman measurements indicated that the sulfation treatment did not affect the bulk structure of Co oxide.

3.3. Catalyst Surface

Figures 6(a) and 6(b) showed XPS spectra of core electron for Co_{2p} and S_{2p} of the Co/Al₂O₃ and Co/SO₄²⁻/Al₂O₃ catalysts before the dehydrogenation, respectively. From Fig. 6(a), the peaks for Co³⁺ were observed at around 779.4 eV and 795.2 eV¹⁹⁾. In the S_{2p} spectrum, the peak for sulfate ion of SO₄²⁻ was confirmed at 169.7 eV. Compared to the peak positions between the Co/Al₂O₃ and Co/SO₄²⁻/Al₂O₃ catalysts before the dehydrogenation, the peak of cobalt species was slightly

Fig. 4 XRD Patterns of Co/Al₂O₃ and Co/SO₄²⁻/Al₂O₃ Catalysts (a) before and (b) after Propane Dehydrogenation

shifted to higher binding energy and broadened by sulfation treatment: 779.5 eV and 795.2 eV over the Co/Al₂O₃ catalyst; and 780.6 eV and 796.3 eV over the Co/SO₄²⁻/Al₂O₃ catalyst. Because the XPS peak for Co²⁺ species appeared at higher binding energy than that for Co³⁺ species, the cobalt element in the Co/SO₄²⁻/Al₂O₃ catalyst had a lower oxidation state²⁰. This phenomenon might derive from the interaction between sulfated ion (SO₄²⁻) and cobalt element to form CoSO₄-like species. **Figures 7(a) and 7(b)** showed XPS spectra of core electron for Co_{2p} and S_{2p} of the Co/Al₂O₃ and Co/SO₄²⁻/Al₂O₃ catalysts after the dehydrogenation reaction, respectively. From **Fig. 7(a)**, a slight peak shift to higher binding energy was observed over both catalysts, compared to the catalysts before the reaction. This result meant that the Co₃O₄ might be reduced and

Fig. 5 Raman Spectra of Co/Al₂O₃ and Co/SO₄²⁻/Al₂O₃ Catalysts before and after the Dehydrogenation of Propane (DHP)

disappeared after reaction due to the reduction by produced H₂ in the propane dehydrogenation²¹. The peak for Co species over the sulfated catalyst was resulted in almost the same position, compared to that over the unsulfated catalyst. From **Fig. 7(b)**, the two peaks were observed in the S_{2p} spectra at 169.7 eV and 162.4 eV, which were corresponded to sulfated ion (SO₄²⁻) and sulfide ion (S²⁻)²². The reaction atmosphere was reductive, which caused the reduction of sulfated ion (SO₄²⁻) to sulfide ion (S²⁻). As described in catalytic performance over the Co/SO₄²⁻/Al₂O₃ in **Fig. 1(b)**, the propane conversion was increased with time on stream. In order to consider the relationship between the catalytic performance and S²⁻ species on the catalyst, XPS analyses were performed over the Co/SO₄²⁻/Al₂O₃ catalyst after 20, 50 and 200 min reaction. To evaluate the amount of S²⁻ species on the catalyst, the ratio of the area of S²⁻ and SO₄²⁻ species to the area of Al³⁺ was calculated and summarized in **Table 3**. From **Table 3**, the ratio of SO₄²⁻/Al³⁺ had no tendency. The ratio of SO₄²⁻/Al³⁺ on the catalyst after 20 min reaction was largely decreased, compared to that on the catalyst before the dehydrogenation. During the reaction, the sulfated ion (SO₄²⁻) species were reduced and/or desorbed from the catalyst. Such phenomena might cause a large decrease of the ratio of SO₄²⁻/Al³⁺. Additionally, the ratio of SO₄²⁻/Al³⁺ did not become a constant value even if the progress of the reaction. On the other hand, the ratio of S²⁻/Al³⁺ has the tendency, which was slightly increased with time on stream. Since the catalytic activity was increased with time on stream (**Fig. 1(b)**), the activity might be related with sulfide ion (S²⁻), excluding sulfated ion (SO₄²⁻) species.

Fig. 6 XPS Spectra of (a) Co_{2p} and (b) S_{2p} for Co/Al₂O₃ and Co/SO₄²⁻/Al₂O₃ Catalysts before the Dehydrogenation

Fig. 7 XPS Spectra of (a) Co_{2p} and (b) S_{2p} for Co/Al₂O₃ and Co/SO₄²⁻/Al₂O₃ Catalysts after the Dehydrogenation of Propane

Table 3 Summary of Al_{2p} and S_{2p} for Co/SO₄²⁻/Al₂O₃ Catalyst with Reaction Time

Reaction time [min]	SO ₄ ²⁻ area [-]	S ²⁻ area [-]	Al ³⁺ area [-]	Area ratio of SO ₄ ²⁻ to Al ³⁺ [-]	Area ratio of S ²⁻ to Al ³⁺ [-]	Propylene yield [%]
0	2894	-	66818	0.0433	-	-
20	517	135	111823	0.0046	0.0012	6.9
50	630	198	77843	0.0081	0.0025	11.5
200	356	235	61002	0.0058	0.0039	18.3

The oxidation state of the reduced sulfur species was further analyzed by XANES measurement in detail. **Figure 8** showed S K-edge XANES spectrum of the Co/SO₄²⁻/Al₂O₃ catalyst before and after the dehydrogenation. The peak for the S⁶⁺ in standard CoSO₄ closely matched with the observed peak at 2481.8 eV in the Co/SO₄²⁻/Al₂O₃ catalyst before the dehydrogena-

tion. The absorption at 2481.8 eV was attributed to the transition of S_{1s} core level electrons to t₂^{*} of S_{3p} orbital²³⁾. Good agreement between the standard sample and the catalyst before the dehydrogenation indicated that the sulfur species was present as sulfated ion (SO₄²⁻). On the other hand, XANES spectrum of the catalyst after the dehydrogenation was coincident with the CoS

standard sample including CoSO_4 . The peaks at 2470.8 eV and 2481.8 eV were corresponded to sulfide ion (S^{2-}) and sulfated ion (SO_4^{2-}) species, respectively. The first prominent absorption at 2470.8 eV was derived from the transition of S_{1s} core level electrons to un-occupied S_{3p} σ^* antibonding hybridized with Co_{3d} (e_g) orbital²⁴. From XANES results, the CoS and CoSO_4 were present on the surface of the $\text{Co}/\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ catalyst during the dehydrogenation.

Figure 9 displays a STEM image and an elemental mapping of the $\text{Co}/\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ catalyst after reaction. From the mapping, the S species was slightly detected. In addition, the mapping shapes of the S species almost fit with the dispersed state of the Co component. The result indicated that Co-S bond was formed by the reaction atmosphere. The formed CoS species would have an important role on the propane dehydrogenation.

3.4. The Effect of Pre-reduction on Dehydrogenation Performance

As shown in **Fig. 1(b)**, the $\text{Co}/\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ catalyst had an induction period to show a high performance for dehydrogenation. The reason for the induction period was considered to be the formation of CoS species on

the catalyst as shown in the section 3.3. In order to form S^{2-} species on the $\text{Co}/\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ catalyst before the dehydrogenation, the pre-reduction was performed using 5 vol% H_2 stream (5 mL min^{-1}) at 600°C . **Figure 10** showed a propylene yield with time on stream over the $\text{Co}/\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ catalyst with and without the H_2 reduction. The propylene yield over the $\text{Co}/\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ catalyst without pre-reduction was increased with time on stream. On the other hand, there was no induction period over the $\text{Co}/\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ catalyst with pre-reduction. The pre-reduction might produce CoS species on the $\text{Co}/\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ catalyst, which displayed a good performance.

Based on the obtained results, the CoS species might be responsible for the dehydrogenation performance. Other researchers also reported the importance for metal sulfide for dehydrogenation of alkane. Wang *et al.* investigated that the metal sulfide catalyst for dehydrogenation of isobutane to isobutene²⁵. The metal sulfide catalyst showed a higher dehydrogenation performance in terms of selectivity, compared to the metal oxide catalyst. The sulfide catalyst was possible to activate C-H bond without C-C bond breaking, which suppressed the side reaction of cracking of isobutane. Resasco *et al.* studied the dehydrogenation of isobutane dehydrogenation over the sulfided Ni catalyst²⁶. The supported metallic nickel catalyzed the hydrogenolysis of isobutane, which resulted in extremely poor selectivity toward dehydrogenation product of isobutene. By sulfidation of the catalyst, the hydrogenolysis reaction was

Fig. 8 S K-edge XANES Spectra of Sulfur-containing Standard Materials and $\text{Co}/\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ Catalysts before and after the Dehydrogenation of Propane (DHP)

Fig. 10 Effect of H_2 Reduction on Propylene Yield over $\text{Co}/\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ Catalyst

Fig. 9 STEM-EDX Mapping of the $\text{Co}/\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ Catalyst after the Dehydrogenation of Propane (DHP)

suppressed. The saturation coverage of hydrogen was reduced on Ni due to a steric hindrance of sulfur on hydrogen adsorption site. Such an effect suppressed hydrogenolysis reaction, and produced a high selectivity to isobutene. Based on these results, the formed CoS species in this study might suppress the hydrogenolysis reaction of propane and propylene, which produced a high selectivity to the dehydrogenation product of propylene. Based on the above descriptions and our obtained data, the following reaction mechanism on the CoS species was suggested as a possible explanation. Propane would dissociatively adsorb on the CoS surface as the propyl intermediate, leaving the H bonded to a sulfide ion. The β -hydrogen in the propyl intermediate was subsequently withdrawn from the propyl intermediate. These hydrogen species combined to molecular hydrogen, and followed by desorbing to the gas phase. The produced π -bonded propylene intermediate would be desorbed from the CoS catalyst without a sequential progress of hydrogenolysis. The above reactions smoothly proceeded on the catalyst, which produced a high selectivity to propylene.

4. Conclusions

The sulfated catalyst showed a better selectivity and stability for the propane dehydrogenation, compared to the unsulfated catalyst, especially for the Co/SO₄²⁻/Al₂O₃ catalyst. The sulfated ion (SO₄²⁻) was present over the catalyst before the dehydrogenation, and reduced to sulfide ion (S²⁻) during the dehydrogenation reaction. The formed S²⁻ might work as the active site for the propane dehydrogenation.

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要 旨

プロパン脱水素反応のための硫酸処理した金属酸化物触媒における活性種

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ゾル-ゲル法で γ - Al_2O_3 を調製し、そこへ硫酸アンモニウムを投入することで硫酸処理した担体を用い、遷移金属 (Cr, Mn, Fe, Co, Ni, Cu) を担持した触媒を調製した。そして、プロパン脱水素反応に及ぼす硫酸処理の影響と活性種の調査を行った。担体に硫酸処理をしない触媒はプロピレン選択性が低かったが、硫酸処理した触媒は高いプロピレン選択性を示した。特に、Co 成分を担持した触媒が高選択的にプロピレンを生成した。また、安定性も改善されて、触媒劣化が抑制された。硫酸

処理した Co 触媒の反応前と反応後の触媒について物理化学的特性を評価し、触媒性能が向上した要因を検討した。XRD や Raman 測定の結果から、硫酸処理は触媒のバルク構造には影響を与えないことが分かった。XPS や XANES 測定から、反応前に SO_4^{2-} として担持された硫黄種は、反応中に S^{2-} に還元されることが分かった。活性の上昇とともに S^{2-} の量が増加していることから、 S^{2-} が活性種として機能し、選択的に脱水素反応を促進する一因と推測された。

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