1. Introduction

Fuel cell systems are important to improve energy utilization efficiency1). Fuel cells for power generation commonly use hydrogen as fuel produced by the reforming of natural gas. Sulfur compounds contained in natural gas must be removed to avoid the deterioration of reforming catalyst2). Consequently, hydrodesulfurization (HDS) is used as a general industrial desulfurization technology15). However, the operation conditions of the HDS process are unsuitable for a stationary fuel cell co-generation system, because high pressure hydrogen and high temperature are required.

Adsorptive desulfurization (ADS) can also easily remove the sulfur compounds contained in the fuels16),17). ADS is operated at ordinary temperatures and allows frequent start-up and shut-down cycles. Residential fuel cell systems incorporating the ADS process have been already commercialized in Japan since 2009. However, the used adsorbent must be replaced approximately every year due to the limits of adsorption capacity. In Europe and North America, natural gas is transported and distributed directly by pipeline17), and the natural gas may contain various sulfur compounds, such as thiols, sulfides, carbonyl sulfide, or hydrogen sulfide (H2S). Consequently, specific absorbents are required for each type of sulfur compound, so the ADS process is unsuitable for the desulfurization of pipeline natural gas. Therefore, the development of easy and efficient methods for sulfur removal from pipeline natural gas are required instead of the HDS and ADS processes.

Recently, we have focused on a new desulfurization process; the catalytic decomposition desulfurization (CDDS)18~20) process that decomposes sulfur compounds to hydrogen sulfide over catalyst, and the resul-
tant hydrogen sulfide is removed using a sulfur absorbent such as zinc oxide. This CDDS process needs no hydrogen addition as required in the HDS process. Use of preheating from the reforming process can combine the CDDS reactor with the reformer, leading to low operation costs.

Conversion of dimethyl sulfide (DMS, (CH3)2S) into other sulfur compounds has been reported by several research groups. Methanethiol (CH3SH) can be produced from DMS and H2S over γ-Al2O3 at 450-550 °C21). The activity of the thiolation reaction over γ-Al2O3-based catalysts at 400-450 °C was improved by using a support of phosphorus on Al2O322,23). The identical reaction occurs over WO3/ZrO2 as other catalysts24). DMS decomposition over Y-type zeolite at 450-500 °C produced ethanethiol (C2H5SH) and some hydrocarbons25). However, direct decomposition of DMS into H2S has not been reported. Recently, we studied various oxide-supported metal-based catalysts for DMS decomposition, and found that 10 wt% NiO/γ-Al2O3 catalyst prepared by the impregnation method exhibits high activity for this reaction20).

The present study investigated the catalytic decomposition of DMS to H2S in the moderate temperature range below 400 °C over 10 wt% NiO/γ-Al2O3 in more detail. In particular, we examined the sulfurization treatment effect of 10 wt% NiO/γ-Al2O3 catalyst on its catalytic performance for DMS decomposition. Moreover, we investigated the sulfurization behavior of NiO/γ-Al2O3 catalyst in the H2S stream using in-situ XAS analysis.

2. Experimental

2.1. Catalyst Preparation

A γ-Al2O3 support material was obtained by calcination at 600 °C for 2 h of boehmite (α-Al(OOH), aluminum hydroxide) supplied by Sasol Japan K.K. The Ni species were introduced by the conventional impregnation method20,26). A predetermined amount of γ-Al2O3 support was mixed with distilled water in an eggplant flask followed by addition of a predetermined amount of metal nitrate solution. Nickel nitrate (II) hexahydrate (Kanto Chemical Co., Inc.) was used as a starting material for the Ni species. The metal loading amount was adjusted to 10 wt% as the metal. The solution was stirred and evaporated to dryness under reduced pressure in a water bath at 80 °C. The obtained powder sample was dried at 110 °C overnight and then calcined in air at 500 °C or 800 °C for 2 h. The prepared catalysts were molded and crushed to particle size of 150-250 μm for use in the DMS decomposition activity test. The prepared catalysts are denoted as NiAl-T, where T shows the calcination temperature.

2.2. DMS Decomposition Activity Test

The DMS decomposition test was carried out in a fixed bed flow reactor under atmospheric pressure. Catalyst 500 mg was set in a quartz tube (I.d. 6 mm) and the reaction gas mixture (10 ppm DMS/N2 balance) was fed into the catalyst bed at the total flow rate of 500 cm3 min–1 at a predetermined temperature. Sulfur compounds and hydrocarbons in the effluent gas were analyzed using a gas chromatograph equipped with a hydrogen flame photometric detector (GC-FPD, Shimadzu Corp., GC-14BPF) and a gas chromatograph with a flame ionization detector (GC-FID, Shimadzu Corp., GC-8AIF). To separate the gaseous products, a 1,2,3-TCEP 25 % Shimalite 80/100 AW-DMCS-ST G-5278 column (Shinwa Chemical Industries Ltd.) and a BX-10 column (GL Sciences Inc.) were used for GC-FPD and GC-FID, respectively.

Prior to the DMS decomposition activity test, sulfurization treatment was carried out at 500 °C in 1000 ppm H2S/N2 or 100 ppm DMS/N2 as the sulfur source. The treatment time was selected to supply the sulfur species in the gas in only the amount sufficient to sulfurize the metal component contained in the catalyst. Specifically, the gas was passed for a predetermined period until the molar ratio of Ni : S = 1 : 2 was reached. After that, N2 was circulated at 500 cm3 min–1 for 62.67 h to remove the physically adsorbed sulfur component. Subsequently, the DMS decomposition activity test was performed at the temperature range of 200-400 °C (temperature lowering process, cooling rate: 5 °C min–1, holding time: 30 min).

2.3. Catalyst Characterization

2.3.1. X-ray Diffraction (XRD)

To identify the crystalline structure of the Ni based catalysts, powder XRD analysis was performed using a Rigaku Ultima IV instrument equipped with a Cu Kα radiation source. Acceleration voltage and current were 40 kV and 40 mA, respectively, and measurements were conducted with scanning speed of 2.0° min–1 and step size of 0.01° step–1.

2.3.2. X-ray Photoelectron Spectroscopy (XPS)

For the NiAl-500 catalyst as-prepared and after sulfurization treatment at 500 °C by H2S and DMS, XPS measurement was performed to obtain the S2p peak spectra using an ULVAC-PHI Inc. ESCA 1600 equipped with Mg Kα radiation source (hν = 1253.6 eV) operated at 15 kV and 10 mA. The obtained spectra were calibrated relative to the position of the Al2p peak with a binding energy of 74.8 eV.

2.3.3. X-ray Absorption Spectroscopy (XAS)

For the Ni based catalysts, the Ni K-edge X-ray absorption near edge structure (XANES) was measured at the BL14B2 beamline at SPring-8, Japan. Each sample was mixed with an appropriate amount of boron nitride (BN), press-molded, and set in a normal measurement folder or an in-situ measurement cell (sample pellet diameter 7 mm). The sulfurized catalyst samples were sealed in an Al bag to prevent exposure to the
atmosphere after pre-treatment using 1000 ppm H\textsubscript{2}S/N\textsubscript{2} or 100 ppm DMS/N\textsubscript{2} and were used for the normal XAS measurement at room temperature. XANES measurements of NiS, Ni foil, and NiO as standard samples were also carried out at room temperature. The spectrum of the NiAl-800 sample was also measured at room temperature. The Ni species in the NiAl-800 sample were expected to have the identical local structure environment with those in the spinel-type oxide (NiAl\textsubscript{2}O\textsubscript{4}). For the \textit{in-situ} Ni K-edge XAS during the sulfurization process of NiAl-500, a special measuring cell that allows flow of gas and raising the temperature was used. The cell temperature was raised to 300, 400, and 550 °C under N\textsubscript{2} flow, and 50 ppm H\textsubscript{2}S/N\textsubscript{2} gas mixture was fed at 75 cm\textsuperscript{3} min\textsuperscript{-1} for 5 h; the spectra were collected continuously. In addition, \textit{in-situ} XAS measurement was applied to one sample of NiAl-800 after pre-reduction treatment in 10 % H\textsubscript{2}/N\textsubscript{2} (100 cm\textsuperscript{3} min\textsuperscript{-1}) at 550 °C for 1 h. The XAS measurement used a Si (111) monochromator which was continuously moved from 14.31° to 11.93°. The spectra were collected in the transmission mode using ion chambers filled with an Ar/N\textsubscript{2} mixture on the pelletized catalysts. The measurement time of one spectrum was ca. 30 s using a quick scan mode. For analysis of the obtained XANES spectra, background correction and normalization were carried out using the Athena and Artemis software\textsuperscript{27). Additionally, linear combination fitting (LCF) analysis for the obtained XANES spectra was performed using Athena to quantify the composition ratio of Ni components in the catalyst.

2.3.4. \textbf{Hydrogen-temperature Programmed Reduction (H\textsubscript{2}-TPR)}

H\textsubscript{2}-TPR measurement was performed using a Micromeritics BELCAT-A instrument. Prior to the measurement, the catalyst sample was preheated in air at 300 °C for 0.5 h and cooled to 50 °C in a He atmosphere. Subsequently, the sample was heated up to 900 °C in 4 % H\textsubscript{2}/Ar feed (30 cm\textsuperscript{3} min\textsuperscript{-1}) at 5 °C min\textsuperscript{-1}, and then was kept at 900 °C for 0.5 h.

3. Results and Discussion

3.1. \textbf{Effect of Calcination Temperature of NiO/Al\textsubscript{2}O\textsubscript{3} Catalyst}

The effect of the calcination temperature during the catalyst preparation on the structure of NiO/γ-Al\textsubscript{2}O\textsubscript{3} was examined. Figure 1 shows the XRD patterns of the NiO/γ-Al\textsubscript{2}O\textsubscript{3} catalysts calcined at 300-800 °C. The diffraction peaks derived from the NiO phase appeared at 2θ of ca. 43° and 63° for the catalysts with calcination at 300-600 °C ((a), (b), (c), and (d) in Fig. 1). The diffraction peaks derived from γ-Al\textsubscript{2}O\textsubscript{3} phase shifted to the lower angle and became sharper at higher calcination temperature, indicating the formation of NiAl\textsubscript{2}O\textsubscript{4} or Ni\textsubscript{x}Al\textsubscript{2}O\textsubscript{4}\textsubscript{1+x} partially lacking the Ni component. The diffraction peaks derived from NiAl\textsubscript{2}O\textsubscript{4} appeared at 2θ of ca. 32°, 37°, 45°, 60°, and 66° for the catalysts with calcination at 700 °C and 800 °C ((e) and (f) in Fig. 1). The peak at 2θ of ca. 32° and 60° became obviously stronger with higher calcination temperature, indicating that all peaks are derived from the NiAl\textsubscript{2}O\textsubscript{4} phase. In addition, the peak derived from NiO disappeared with calcination at 700 °C or above. Therefore, the NiO and γ-Al\textsubscript{2}O\textsubscript{3} components are converted into NiAl\textsubscript{2}O\textsubscript{4} by high temperature calcination.

Figure 2 shows the results of H\textsubscript{2}-TPR analysis for the NiO/γ-Al\textsubscript{2}O\textsubscript{3} catalysts calcined at 500 °C (NiAl-500) and 800 °C (NiAl-800). The components of the TPR profiles were identified by peak-fitting, and Table 1 summarizes the reduction temperature of each peak. Four peaks labeled as Peaks I-IV were observed on the TPR profile for NiAl-500. The difference in the
The temperature of the reduction peak allows analysis of the ratio of Ni species to be reduced, the particle size, and the strength of interaction with the support. Peak I and Peak II reveal the reduction of NiO, and the difference in reduction temperature is considered to be resulted from the difference in the strength of interaction with the γ-Al2O3 and the particle size of NiO. Peaks III and IV are derived from NiAl2O4 or NiO, partially lacking the Ni component. Assuming that Peaks I and II are derived from NiO and Peaks III and IV are derived from NiAl2O4, NiAl-500 is presumed to be a composite of NiO and NiAl2O4 in the ratio of ca. 4 : 6 based on the ratio of their peak areas. In contrast, only one large peak (Peak IV) was confirmed at 778 °C for NiAl-800, indicating that Ni species exist in the state of NiAl2O4 or NiO, partially lacking the Ni component. This TPR result implies that the Ni component in NiAl-800 exists in the same local structure as the Ni component in the NiAl2O4 structure.

### Table 1: Peak Fitting Results of H2-TPR Profiles for NiAl-500 and NiAl-800

| Calcination temperature [°C] | Reduction peak temperature [°C] | Peak area fraction |
|-----------------------------|---------------------------------|-------------------|
|                             | Peak I | Peak II | Peak III | Peak IV |                      |
| 500                         | 445    | 534     | 627      | 728     | 0.14/0.30/0.32/0.24   |
| 800                         | -      | -       | -        | 778     | 0.00/0.00/0.00/1.00   |

a) As shown in Fig. 2.

Decomposition products CH3SH, H2S and CH4 were detected regardless of the sulfurizing agent. The formation behaviors of H2S and CH4 were similar for both catalysts; but formation of CH3SH was clearly larger for the DMS-sulfurized catalyst than that for the H2S-sulfurized catalyst. The present reaction tests also observed the formation of CH4. However, the observed amount of CH4 was smaller than that expected from the decomposition of the reactant DMS. The sulfur (S) balance and carbon (C) balance (influent gas/effluent gas) at each reaction temperature for the DMS decomposition reaction test shown in Fig. 3 is summarized in Fig. 4. For the catalysts sulfurized with H2S as shown in Fig. 3(A), the S balance was below 0.55 at reaction temperatures above 325 °C. Therefore, the amount of S components in the effluent gas was extremely small considering the amount of reacted DMS. Since the C balance was low at 0.19 at this temperature, the S component was presumably also accumulated during carbon deposition on the catalyst. In addition, the catalytic performance was lower below
275 °C, but the C balance and S balance were close to 1.0. In other words, the amounts of carbon deposition and S components were small in the low temperature range.

In contrast, the catalyst sulfurized with DMS as shown in Fig. 3(B) tended to have S balance larger than 1.0, and the C balance was lower than 1.0, at reaction temperatures above 325 °C. This implies that carbon and/or hydrocarbon species were deposited on the catalyst. Similarly, hydrocarbon species, such as \((\text{CH}_2)_n\), were probably deposited on the catalyst even during the sulfurization treatment with DMS. This indicates that accumulation of hydrocarbon species on the catalyst leads to increased \(\text{CH}_3\text{SH}\) in the effluent gas. Consequently, \(\text{CH}_3\text{SH}\) is considered to be formed by the reaction of \(\text{H}_2\text{S}\) and the hydrocarbon species present on the catalyst surface, with the former produced by the decomposition of DMS. In addition, the C and S balances were almost 1.0 below 275 °C. Therefore, deposition of S and C components was slight, and the decomposition reaction progressed in a nearly stoichiometric manner.

3.3 Change in Crystalline Phase of Catalyst by Sulfurization Treatment

Figure 5 shows the XRD patterns of the catalyst before and after the reaction test with sulfurization treatment by \(\text{H}_2\text{S}\) or DMS. The XRD pattern of the catalyst before sulfurization treatment showed diffraction peaks derived from the NiO phase at 2θ of ca. 43° and 63°. In addition, the peaks derived from the \(\gamma\)-\(\text{Al}_2\text{O}_3\) phase or the NiAl\(_2\text{O}_4\) phase appeared at 2θ of ca. 37°, 45-46°, 60-61°, and 66-67° as shown in (a) in Fig. 5. The XRD patterns of the catalysts after the sulfurization treatments and the DMS decomposition activity tests ((b) and (c) in Fig. 5) showed the NiO phase had disappeared and the NiS phase was formed, irrespective of the sulfurization agent.

XPS analysis also confirmed that NiS was formed on the catalyst surface as shown in Fig. 6. No clear difference was found with the sulfurization gas. Therefore, we suppose that the active sites for DMS decomposition involved the NiS component regardless of the gas used for the sulfurization of NiO/\(\gamma\)-\(\text{Al}_2\text{O}_3\) catalyst.

3.4 Local Structure of Ni Species in Catalyst by XAS Analysis

The Ni K-edge XANES spectra of the catalysts with calcination at 500 °C (NiAl-500) before and after the sulfurization treatment with \(\text{H}_2\text{S}\) and DMS at 500 °C are shown in Fig. 7(A). The spectrum of NiAl-500 before sulfurization in (a) in Fig. 7(A) showed a white line peak at 8346 eV, indicating the transition of inner core electrons to empty orbitals. In addition, a small pre-edge peak appeared at around 8328 eV, which is attributed to the electric quadrupole transition from the 1s orbit to the 3d orbit\(^{31}\). The Ni K-edge XANES spectra of the reference samples: (a) NiO, (c) Ni foil, and (d) NiS, are shown in Fig. 7(B) as well as the spectrum of (b) NiAl-800. NiAl-800 exhibited almost the same spectrum as NiAl\(_2\text{O}_4\) as reported\(^{32}\)
cates that the Ni species contained in the catalyst with calcination at 800 °C before sulfurization is present with similar local fine structure as the Ni component in the NiAl2O4 spinel structure. In contrast, the spectrum of NiAl-500 did not match any of the reference samples. This suggests that the Ni species in NiAl-500 consists of several Ni based components. Therefore, we applied LCF analysis to the XANES spectrum of NiAl-500 assuming the four components of NiO, NiAl-800 (equivalent to NiAl2O4), Ni foil, and NiS. Table 2 shows the calculated composition ratio of each component. No Ni foil (metallic Ni) or NiS were present in the sample before sulfurization, so these two components are negligible. NiAl-500 calcined at 500 °C contained a mixture of NiO and NiAl2O4 in a ratio of ca. 4 : 6. This result agrees with the result of TPR analysis (Fig. 2 and Table 1). Therefore, we conclude that the Ni component in the NiAl-500 catalyst occupies a large proportion of the NiAl2O4 spinel structure.

The Ni K-edge XANES spectra of the NiAl-500 with sulfurization by H2S or DMS are shown in (b) and (c) in Fig. 7(A), respectively. The spectrum of the DMS-treated sample was slightly broader at the XANES region compared to the H2S-treated sample. This implies that sulfurization of NiO to NiS progressed more in the DMS-treated sample. The results of LCF analysis for both samples are also summarized in Table 2. The formation ratio of NiS was larger for the DMS-treated sample than the H2S-treated sample. The ratio of the NiAl2O4 component was significantly lower in the DMS-treated sample. Presumably sulfurization by DMS facilitates sulfurization of the Ni component, and the final amount of sulfurized Ni component (NiS) is increased. However, the DMS decomposition activity of NiAl-500 was slightly higher for the H2S-treated catalyst than the DMS-treated catalyst as shown in Fig. 3. This may be due to the effect of active site coverage by the deposition of carbon or/and hydrocarbon species on the catalyst by DMS sulfurization.

3.5. Sulfurization Behavior of NiAl-500 by in-situ XAS Analysis

The temperature dependence of the structural change
of the Ni components in the NiAl-500 with sulfurization treatment was investigated to determine the optimum sulfurization temperature by in-situ XAS measurement for 5 h. We examined the change in the sulfurization behavior of the catalyst due to the difference in the Ni components (NiO and NiAl2O4). Figures 8(A), 8(B), and 8(C) shows the time series of in-situ Ni K-edge XANES spectra of NiAl-500 with H2S/N2 feed at 300, 400, and 550 °C, respectively. The pre-edge peak at 8328 eV was slightly increased and the white line peak at 8345 eV was decreased at all temperatures. In addition, the transformation proceeded faster at higher reaction temperatures. Furthermore, the presence of the isosbestic point was confirmed in the measurements at every temperature. This indicates that only one set of component changes occurs during the H2S feed. In other words, the chemical environment of the Ni species in the NiAl-500 catalyst continuously changes from NiO to NiS under the sulfurization condition.

Figures 9(A), 9(B), and 9(C) show the hourly changes in the composition ratio calculated by LCF analysis using the spectra shown in Figs. 8(A), 8(B), and 8(C), respectively. The composition ratio of the

| Sample          | NiAl2O4 | NiO   | Ni-foil | NiS   | R factor | Reduced \(\chi^2\) |
|-----------------|---------|-------|---------|-------|----------|------------------|
| As-prepared     | 0.589   | 0.387 | 0.024   | 0.000 | 0.000828 | 0.000212         |
| H2S treatment   | 0.466   | 0.094 | 0.000   | 0.440 | 0.001520 | 0.000327         |
| DMS treatment   | 0.196   | 0.000 | 0.000   | 0.845 | 0.000517 | 0.000100         |

Table 2 Results of LCF Analysis for NiAl-500 As-prepared and NiAl-500 after Sulfurization at 500 °C by H2S and DMS
NiAl-500 sample before sulfurization was NiO : NiAl2O4 of ca. 4 : 6. After the sulfurization, the ratio of each component had changed. NiO and NiAl2O4 were decreased and NiS was increased with sulfurization time at all temperatures. Therefore, the sulfurization reaction proceeds at every temperature, and was more prominent at higher temperatures. The decrease in NiO was larger than that in NiAl2O4, indicating that NiO is more easily sulfurized.

3.6 Effect of Pre-reduction Treatment on the Sulfurization Behavior of NiAl-500

To study the effect of the pre-reduction treatment, the changes in the in-situ Ni K-edge XANES spectrum of NiAl-500 during pre-reduction by H2 for 1 h and sulfurization by H2S for 5 h were measured as shown in Fig. 8(D). The composition change calculated with the LCF analysis is also shown in Fig. 9(D). The reduction treatment rapidly reduced the NiO in the catalyst to metallic Ni; but the Ni component in NiAl2O4 was only partially reduced to Ni. Therefore, the sulfurization reactivity was NiO > NiAl2O4, and the reactivities of Ni species to reduction by H2 were similar. In addition, the isosbestic point was confirmed during the sulfurization process for the catalyst with pre-reduction, suggesting that the sulfurization reaction of metallic Ni to NiS mainly proceeds. We conclude that suppression of the formation of NiAl2O4 after catalyst preparation is necessary to form a large amount of NiS through efficient sulfurization treatment.

3.7 Comparison of DMS Decomposition Performance between NiAl-500 and NiAl-800

NiAl-500 and NiAl-800 catalysts were sulfurized by H2S at 500 °C, then used for the DMS decomposition test at 350 °C. In this reaction test, the catalyst 50 mg was set in the reactor and the reaction gas mixture (100 ppm DMS/N2 balance) was fed into the catalyst bed at a total flow rate of 200 cm3 min−1. Under these reaction conditions, the catalytic performance was evaluated under conditions that were 40 times more severe than the experimental conditions in Fig. 3. Changes in the effluent gas composition during the performance tests using both catalysts are shown in Fig. 10. For NiAl-500, ca. 60 ppm of DMS was detected immediately after the start of the reaction (Fig. 10(A)), meaning that DMS conversion was ca. 40 %. Subsequently, the concentration of DMS increased with reaction time and was maintained at ca. 86 ppm for a long time. Carbon species are deposited on the catalyst by the decomposition of DMS, leading to decreased DMS decomposition. In contrast, for NiAl-800, ca. 86 ppm of DMS was detected after the start of the reaction, and no significant change in the concentrations of DMS, CH3SH, H2S, and CH4 occurred for 30 h (Fig. 10(B)). According to the XAS analysis, the Ni component in
the NiAl-800 is located on the spinel structure of NiAl2O4, and is only slightly sulfurized to NiS. Therefore, the DMS decomposition activity of NiAl-800 was lower than that of NiAl-500.

4. Conclusions

Local structure change of the Ni species in 10 wt% NiO/γ-Al2O3 catalysts for the reaction of DMS decomposition to H2S was studied. The calcination and sulfurization conditions of the prepared catalyst affected the catalytic performance for DMS decomposition. The effect of the gas species used for the sulfurization treatment prior to the DMS decomposition test was also examined; the amount of decomposition products, especially CH3SH, were larger using DMS than H2S.

XRD and XPS analyses indicated that the active sites for DMS decomposition are the NiS component. Furthermore, XAS analysis revealed that NiO and NiAl2O4 of the Ni components were present in a ratio of ca. 4 : 6 in the catalyst with calcination at 500 °C, and can be sulfurized to NiS by sulfurization, but the Ni component in the NiAl2O4 spinel structure was less susceptible to sulfurization than NiO. In contrast, for the catalyst with calcination at 800 °C, Ni species were located on the spinel structure NiAl2O4, and the amount of Ni component that can be sulfurized was quite small. Therefore, we conclude that more Ni component is present as NiO than NiAl2O4 after the catalyst preparation results in greater amount of NiS after the sulfurization treatment, leading to higher DMS decomposition activity of the NiO/γ-Al2O3 catalyst.

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要 旨

ジメチルスルフィド分解用 NiO/γ-Al2O3触媒の活性サイトの局所構造解析—X線吸収分光分析を用いたNi種の硫化挙動—

霜田 直宏1,4, 小出 奈央1, 本間 徹生2, 中野 武雄1, 張 晋3, 脇田 英延3, 里川 重夫3

1) 成蹊大学理工学部物質生命理工学科, 180-8633 東京都武蔵野市吉祥寺北町3-3-1
2) (財) 高輝度光科学研究センター, 679-5198 兵庫県佐用郡佐用町児吉町1-1-1
3) パナソニック(株), 570-8501 大阪府守口市八雲中町3-1-1
4) (現在)徳島大学工学部応用化学科, 770-8506 徳島市南三島町2-1

含浸法により調製した NiO/γ-Al2O3触媒を用いたジメチルスルフィド (以下 DMS) の分解反応プロセスにおけるNi種の微細構造変化の検討を行った。調製触媒の焼結および硫化条件が触媒活性に影響を及ぼした。反応前に行う硫化処理として、H₂Sで硫化した場合の方が DMSで硫化した場合と比較して分解性能が高くなった。XRD, XPS 分析から活性点は NiS であることが確認された。さらに、硫化処理前後の Ni種の微細構造変化を in-situ XAS により分析した結果、800℃ 焼成触媒では Ni種が NiO と Ni₃Al₄O₉として約4:6の比で存在しており、硫化処理によって主に NiO が NiS へと硫化され、DMS分解反応の活性点となることが明らかとなった。一方、800℃ 焼成触媒では Ni種がほぼすべて Ni₃Al₄O₉として存在していた。そのため、硫化後に活性点である NiS 成分の生成量は少なく、800℃ 焼成触媒の DMS分解性能は低かった。