[Note]

Characterization of CoMo–Al₂O₃ Catalyst by Combination Technique of Temperature-programmed Sulfiding and Electron Spin Resonance (TPS–ESR)

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CoMo–Al₂O₃ catalyst was characterized with a combination technique of temperature-programmed sulfiding (TPS) and electron spin resonance (ESR). The behavior of the MoO₃ loaded over the surface of Al₂O₃ obtained from TPS has been compared with that of Mo⁵⁺ observed with ESR at isothermal and elevated temperatures. The Mo⁶⁺ in the MoO₃ supported is easily reduced with H₂S + H₂ under very mild conditions and transformed into Mo⁵⁺ as an intermediate. This Mo⁵⁺ peak drastically decreased around 200°C with H₂S desorption, and H₂ consumption appeared simultaneously in the TPS profile. These results suggest that the Mo⁵⁺ species observed with ESR associates with sulfur from H₂S.

1. Introduction

CoMo–Al₂O₃ has been used as a hydrotreating catalyst for petroleum fractions because of its high activities for hydrodesulfurization (HDS) and hydrogenation. In most cases, the catalyst in the active state has a metal sulfide structure because of the treatment with hydrogen and sulfur-containing compounds before reaction. The correlation between reaction activity and the sulfiding behavior provides fundamental information for HDS and hydrocracking catalyst characterization.

The temperature-programmed sulfiding (TPS) method has been developed to investigate the sulfiding behavior of the HDS catalyst and it has been recognized as a useful technique for catalyst characterization^{1)~5)}. Although the sulfiding process of the catalyst can be observed with this method, still some uncertainty remains about the sulfiding mechanism. Moreover, but slight attention has been paid to the phenomena of TPS at low sulfiding temperatures.

The ESR has also been recognized as a useful catalyst-characterization technique. A large number of ESR studies of Mo species in HDS catalysts have been carried out^{6)~11)}, because Mo is one of the typical loading metals for HDS catalysts, and Mo provides ESR active species as Mo⁵⁺ from/to the ESR inactive species (for example Mo⁶⁺ or Mo⁴⁺) after sulfiding. In

this report, the ESR method is employed together with TPS in order to gain deep insight into the sulfiding behavior of the catalyst.

2. Experimental

2.1. Preparation of CoMo–Al₂O₃

CoMo–Al₂O₃ was prepared by impregnation technique. A mixture of aqueous solutions of ammonium heptamolybdate and cobalt nitrate was impregnated into the powder of γ -Al₂O₃. The amounts of the metals loaded were 15 wt% Mo as MoO₃ and 4 wt% Co as CoO. The resulting sample was dried at 120°C overnight before it was finally calcined at 400°C overnight in air.

2.2. Measurement of TPS

Temperature-programmed sulfiding (TPS) experiments were carried out with the TPS equipment (Model TP-2000) supplied by Ohkura Riken Co., Ltd., Japan. Prior to TPS measurements, the catalyst (0.15 g) was heated in the TPS reactor at 400°C for 2 h in a stream of dry air (30 ml/min) through a moisture trap. After the catalyst was cooled to room temperature, air was replaced and purged with argon (flow rate: 30 ml/min). Sulfiding gas (H₂S : H₂ : Ar = 2 : 42 : 56) (flow rate: 18 ml/min) was then introduced to start TPS. The catalyst was heated up to 1030°C with a temperature raising rate of 10°C/min. Effluents from the reactor were monitored by TCD and UV detectors.

2.3. Combination of TPS and ESR

Prior to performing the ESR measurements, the pro-

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Scheme 1 Temperature-programmed Sulfiding Condition of Catalyst for ESR

Fig. 1 TPS Profile of CoMo-Al₂O₃ Catalyst

file of TPS was obtained by the method described in 2.2. The catalyst sample was installed in a quartz reactor, which was used as TPS reactor and as *in-situ* ESR sample tube without exposure to air, and the ESR signal was obtained.

The ESR measurements were carried out using a JEOL RE1X spectrometer, which was operated in the X-band microwave frequency. For the determination of *g*-value, DPPH was used as a standard material. The ESR spectra of the catalysts in the reactor were obtained under Ar atmosphere at room temperature by step(a) and by step(b).

(a) Temperature-programmed sulfiding – ESR: The catalyst sample exposed and sulfided in a H₂–H₂S–Ar mixture at various temperatures in the range from room temperature to 600°C was brought to the ESR cavity and Mo⁵⁺ signal was measured. This procedure is summarized in Scheme 1.

(b) Isothermal sulfiding – ESR: The catalyst sample for characterization with ESR was carried out by isothermal sulfiding at 30°C for a time from 10 to 60 min. This procedure is summarized in Scheme 2.

3. Results and Discussion

3.1. TPS of CoMo–Al₂O₃ Catalyst

Figure 1 shows the TPS profile of the CoMo–Al₂O₃ catalyst, which clearly shows consumption and desorp-

tion peaks of H₂S and H₂. Moreover, the profile is almost similar to that observed by Moulijn *et al.*²⁾. The first desorption of H₂S, adsorbed physically on the catalyst, was recognized at 120°C. After this desorption, H₂S was consumed at temperatures up to 200°C. A marked consumption of H₂ occurred in a relatively sharp peak at around 220°C while H₂S was simultaneously released. The sulfiding mechanism from the evidence above in the low-temperature region has been explained as follows²⁾. The dominant reaction at low-temperature stage occurs with the exchange between O and S on Mo⁶⁺ ions. Subsequently, the reduction of Mo⁶⁺ takes place by the rupture of the Mo–S bonds, together with the formation of elemental sulfur. This sulfur is catalytically reduced to H₂S at *ca.* 230°C. Therefore, H₂S predominates during low-temperature sulfiding, while H₂ plays as a reductant of elemental sulfur. According to their sulfiding mechanism, no direct evidence of elemental sulfur formation is given, although monitoring for H₂O formation has been carried out, that is, the TPS method cannot detect the reduction of Mo⁶⁺ followed by the formation of elemental sulfur because the resultant sulfur will be strongly adsorbed to the support. This implies that elemental sulfur formation does not consequently change the gas composition.

3.2. ESR of Sulfurized CoMo–Al₂O₃ Catalyst

It is easily concluded from the evidence that Mo⁶⁺ alters the lower valence species such as Mo⁵⁺, Mo⁴⁺, and so on, during the H₂S+H₂ treatment. Therefore, the detection of Mo⁵⁺ by ESR is useful at various sulfiding temperatures because Mo⁵⁺ is ESR active species, while Mo⁶⁺ and Mo⁴⁺ are ESR inactive species. ESR spectra of CoMo–Al₂O₃ catalyst are shown in Fig. 2. The ESR measurements were carried out in argon atmosphere for the pretreated catalyst, followed by Scheme 1. ESR signals with the *g*-value of 1.96 were assigned as Mo⁵⁺^{12),13)}. Sulfiding of CoMo–Al₂O₃ at room temperature gave a strong Mo⁵⁺ ESR spectrum as seen in Fig. 2a. The low-temperature sulfiding mechanism of MoO₃ proposed by Moulijn *et al.*²⁾ did not suggested the formation of Mo⁵⁺, but the formation of substantial amounts of Mo⁵⁺ was observed in X-Ray Photoelectron Spectroscopy (XPS)¹⁴⁾ and ESR⁶⁾ studies. The intensity of the Mo⁵⁺ peak observed at 30°C (a in Fig. 2) was almost the same as that observed at 200°C (b in Fig. 2). The intensity decreased considerably with increasing sulfiding temperature from 250 to 400°C (c–e in Fig. 2). Its possible explanation is that Mo⁵⁺ is further reduced to Mo⁴⁺, which has been assigned as MoS₂ in this sulfiding temperature region²⁾.

3.3. TPS-ESR of CoMo–Al₂O₃ Catalyst

To elucidate the formation process of Mo⁵⁺ species during sulfiding, the Mo⁵⁺ ESR peak intensity was monitored at 30°C as a function of exposure time (*i.e.*, isothermal condition) and monitored also at elevating

Temperature-programmed sulfiding temperature (TPS temp.) of a-e corresponds to those points in Fig. 1.

Fig. 2 Mo^{5+} ESR Spectra of $\text{CoMo-Al}_2\text{O}_3$ Catalyst after Temperature-programmed Sulfiding at Various Temperatures

Scheme 2 Isothermal Sulfiding Condition of Catalyst for ESR

temperature by means of TPS technique. The results are shown in Fig. 3.

Isothermal sulfiding at 30°C: At the isothermal sulfiding stage, ESR spectra of $\text{CoMo-Al}_2\text{O}_3$ were measured according to the treatment of Scheme 2. As shown in the TPS profile at the isothermal sulfiding stage in Fig. 3, the adsorption peak of H_2S appeared just after the introduction of the sulfiding gas. This adsorption was almost completed nearly within 20 min. Although H_2S was adsorbed physically on the catalyst surface under this condition, some part of the adsorbed H_2S was consumed by sulfiding of MoO_3 because the ESR intensity of Mo^{5+} drastically increased with the exposure time. The peak intensity was saturated within 60 min. If this sulfiding is attributed to the O-S exchange mechanism of $\text{MoO}_3^{(2)}$, H_2O must be produced on the catalyst⁽²⁾. Unfortunately, the production of H_2O at low-temperature sulfiding stages could not be confirmed by TPS method and by TPS-ESR method.

Fig. 3 TPS Profile and Mo^{5+} ESR Peak Intensity of $\text{CoMo-Al}_2\text{O}_3$ Catalyst at Isothermal Sulfiding and Temperature-programmed Sulfiding Stage

Temperature-programmed sulfiding from 30 to 200°C: The Mo^{5+} peak intensity entirely was unchanged for this temperature region as shown in Fig. 3. On the other hand, H_2S was consumed without H_2 consumption. This H_2S consumption at about 180°C has been successfully explained as O-S exchange of $\text{MoO}_3^{(2)}$. The O-S exchange reaction of MoO_3 over this temperature region is not associated with the formation and reduction of the Mo^{5+} species.

Temperature-programmed sulfiding from 200 to 600°C: In Fig. 3, a drastic decrease in the Mo^{5+} species was observed above 220°C. In addition, H_2S desorption and H_2 consumption peaks appeared simultaneously in the TPS profile. The Mo^{5+} ESR peak was observed just after the flow of sulfiding gas ($\text{H}_2\text{S} + \text{H}_2$) at 30°C and decreased with the desorption of H_2S at about 220°C. The reduction process of Mo^{6+} must take account of the following paths:

Therefore, our results suggest that (i) Mo^{5+} species observed with ESR are associated with the sulfur from H_2S , (ii) Mo^{6+} species are reduced to Mo^{5+} species by H_2S producing $\text{Mo}^{5+}\text{-S}$ species, and (iii) $\text{Mo}^{5+}\text{-S}$ species are reduced to Mo^{4+} species by the release of sulfur. It has been explained that desorbed H_2S is produced with the reduction of elemental sulfur, which is formed by sulfiding of MoO_3 at low-sulfiding temperatures^(2,15-17). However, H_2S is produced not only from the reduction of isolated elemental sulfur but also from the reduction of the sulfur associated with the Mo^{5+} species. It seems that the $\text{Mo}^{5+}\text{-S}$ bond strength over the surface of Al_2O_3 may be very weak, and the sulfur

associated with the Mo^{5+} species is easily reduced at the temperature required for elemental sulfur reduction. On the other hand, Muijsers *et al.* have studied different states of sulfur and molybdenum occurring during sulfidation by XPS, and they have observed the presence of disulfide ligands and substantial amounts of Mo^{5+} during an early stage of the sulfiding by XPS¹⁴⁾. In their experiments, the Mo^{5+} species have been observed with S_2^{2-} after sulfiding at low temperatures (25-125°C), and both species have disappeared almost completely above 200-250°C. Our results from the combination technique of TPS-ESR agree with those of the XPS studies of Muijsers *et al.*

It is well known that Mo^{5+} species observed with ESR are not necessarily the same as those observed by XPS^{18)~20)}. This is one of the answers relevant to the site and role of the active species of the catalyst for given reactions such as hydrodesulfurization and hydrogenation. More concrete discussions on the results of this study will come about with further investigation.

4. Conclusions

The reduction mechanism of MoO_3 in the sulfiding process of $\text{CoMo-Al}_2\text{O}_3$ was studied with the combined system of TPS and TPS-ESR methods. The Mo^{5+} species, one of the resultant species of Mo^{6+} reduction, was produced during sulfiding at 30°C and suddenly reducing at 220°C and associating with H_2S desorption and H_2 consumption. The Mo^{5+} is reduced to a Mo species with a lower valence like Mo^{4+} over a narrow temperature range in temperature-programmed sulfiding. These results obtained using the ESR technique could be one piece of evidence that the Mo^{5+} species associates with sulfur.

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要 旨

昇温硫化-ESR 併用法 (TPS-ESR 法) を用いた CoMo-Al₂O₃ 触媒のキャラクタリゼーション

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昇温硫化法 (Temperature-Programmed Sulfiding; TPS) と電子スピン共鳴法 (ESR) を併用することにより, CoMo-Al₂O₃ 触媒のキャラクタリゼーションを行った。Al₂O₃ 上に担持された MoO₃ の昇温硫化挙動を等温および昇温硫化過程における Mo⁵⁺ ESR ピーク強度と比較した。アルミナ上に担持された MoO₃

の Mo⁶⁺ は, 極めて温和な条件下で H₂S+H₂ 混合ガスにより還元され Mo⁵⁺ となり, さらにこの Mo⁵⁺ ESR ピークは 200℃ 付近で H₂S の放出, H₂ の消費を伴い急激に低下する。ESR で観測される Mo⁵⁺ 種が硫黄原子と結合しているものと考えられる。

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Keywords

Cobalt molybdena alumina, Characterization, Sulfiding mechanism, ESR, Temperature-programmed sulfiding, Catalyst