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Application of ^{129}Xe NMR Spectroscopy to Analysis of Co-Mo/ Al_2O_3 Hydrodesulfurization Catalyst—Effect of Sulfidation on ^{129}Xe NMR Spectra—

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The effect of sulfidation on ^{129}Xe NMR spectra of Co-Mo/ Al_2O_3 hydrodesulfurization catalysts was investigated. Before sulfidation, catalysts containing cobalt such as Co/ Al_2O_3 and Co-Mo/ Al_2O_3 showed remarkable ^{129}Xe NMR peak broadening, whereas one sharp ^{129}Xe NMR peak was observed for Mo/ Al_2O_3 and Al_2O_3 , mainly caused by the paramagnetic effect of cobalt oxides such as CoAl_2O_4 and CoO . In contrast, after sulfidation, the remarkable broadening of the ^{129}Xe NMR peak did not occur. We consider that the paramagnetic effect of cobalt was much reduced due to the transformation of paramagnetic oxides such as CoAl_2O_4 and CoO into antiferromagnetic sulfides such as the Co-Mo-S phase and Co_9S_8 . In addition, XPS of the sulfided catalysts showed that the Co 2p binding energy of the sharp peak for Co-Mo/ Al_2O_3 was 0.7 eV higher than that for Co/ Al_2O_3 . This result strongly suggests that cobalt was mainly present as the Co-Mo-S phase on the surface and is closely related to the observation that the ^{129}Xe NMR peak of sulfided Co-Mo/ Al_2O_3 was shifted further downfield in comparison with sulfided Mo/ Al_2O_3 . ^{129}Xe NMR spectroscopy is sensitive to the formation of the Co-Mo-S phase on Co-Mo/ Al_2O_3 hydrodesulfurization catalyst.

Keywords ^{129}Xe NMR, Cobalt molybdenum catalyst, Sulfidation, Peak broadening, Magnetic property, Co-Mo-S phase**1. Introduction**

^{129}Xe NMR (nuclear magnetic resonance) spectroscopy is one of the most powerful methods for the structural analysis of microporous materials such as zeolites. In general, the mobile exchange between adsorbed xenon atoms in micropores is extremely fast at ambient temperatures, so only one peak is observed by ^{129}Xe NMR spectroscopy. The chemical shift δ of the ^{129}Xe NMR peak is mainly dependent on various collisions between xenon and other atoms in the micropores^{1,2}. More frequent collisions will cause downfield shift of the peak and increase in δ due to electronic distortion of the xenon atoms. In the case of microporous materials, δ increases linearly with the amount of adsorbed xenon N because the number of collisions between xenon atoms in the micropores directly increases with N . The electronic interaction between xenon and strong adsorption sites, *e.g.*, bivalent or trivalent cations in the micropores also causes further downfield shift of the peak. However, δ then varies nonlinearly with N , and is expressed inversely proportional to N^2 .

Recently, we investigated the application of ^{129}Xe NMR spectroscopy to analysis of Al_2O_3 -supported

molybdenum catalysts^{3,4}. In the case of Mo/ Al_2O_3 , the term of xenon diffusibility δ_0 calculated from the ^{129}Xe NMR spectrum was sensitive to both the molybdenum loading and the sulfidation temperature³. This result suggests that δ_0 is a useful parameter for the analysis of stacked MoS_2 crystallites. Furthermore, in the case of Co-Mo/ Al_2O_3 , δ_0 gradually increased with Co/Mo ratio and reached the maximum value at a certain Co/Mo ratio⁴. We deduced that this behavior is mainly caused by the formation of the Co-Mo-S phase indicating antiferromagnetism. Both the stacked MoS_2 crystallite and the Co-Mo-S phase are important active sites in the hydrodesulfurization of petroleum fractions^{5,6}. Therefore, ^{129}Xe NMR spectroscopy may be a powerful tool for the analysis of Mo/ Al_2O_3 or Co-Mo/ Al_2O_3 hydrodesulfurization catalysts which contain mesopores or macropores as well as microporous materials such as zeolites.

The present study investigated the effect of sulfidation on ^{129}Xe NMR spectroscopy of Co-Mo/ Al_2O_3 hydrodesulfurization catalyst. Before sulfidation, both cobalt and molybdenum are generally present as the oxide form on the Al_2O_3 surface. After sulfidation, these elements are mainly transformed into the sulfide form. Presumably this sulfidation process remarkably changes the magnetic property of the elements. At ambient temperature, cobalt oxides such as CoO and

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Table 1 Elemental Analysis and the BET Specific Surface Area of the Catalysts

Sample	Co [mass%]	Mo [mass%]	Specific surface area [m ² /g]
Al ₂ O ₃	—	—	340
Mo/Al ₂ O ₃	—	13	272 (207)*
Co/Al ₂ O ₃	3.3	—	291 (287)*
Co-Mo/Al ₂ O ₃	3.6	12	266 (192)*

* Values of the specific surface area in parentheses were measured after sulfidation.

Co₃O₄ are paramagnetic, whereas the Co-Mo-S phase is antiferromagnetic^(7),8). Both Mo³⁺ and Mo⁵⁺ are paramagnetic whereas both MoO₃ and MoS₂ are diamagnetic. Paramagnetic compounds cause various NMR phenomena such as peak broadening and loss of peak intensity. The presence of paramagnetic elements such as cobalt ions induced strong peak broadening in ³¹P and ²⁷Al MAS NMR spectroscopy of CoMoP/Al₂O₃ catalysts due to magnetic dipole interactions and reduction in relaxation times⁽⁹⁾. Such effects are mainly caused by the proximity of the paramagnetic element to the NMR nucleus⁽¹⁰⁾. In the case of ¹²⁹Xe NMR spectroscopy, if xenon frequently interacts with paramagnetic compounds on the surface, the effects will be remarkable on the ¹²⁹Xe NMR spectrum. Therefore, the application of ¹²⁹Xe NMR spectroscopy to analysis of catalysts containing paramagnetic compounds requires further examination. The present study investigated the effect of the magnetic property of cobalt or molybdenum, as affected by sulfidation, on the ¹²⁹Xe NMR spectroscopy of Co-Mo/Al₂O₃ catalysts.

2. Experimental

2.1. Catalyst Preparation

Extruded γ -Al₂O₃ was used as the catalyst support. The model Mo/Al₂O₃ catalyst was prepared by the incipient wetness impregnation method using an aqueous solution of ammonium heptamolybdate. After impregnation, the material was dried at ambient temperature and then calcined at 773 K for 4 h in air. In addition, two model Al₂O₃-supported cobalt catalysts, a Co-Mo/Al₂O₃ catalyst and a Co/Al₂O₃ catalyst, were prepared by impregnating the Mo/Al₂O₃ catalyst and the Al₂O₃ support, respectively, with cobalt nitrate solution, followed by drying at ambient temperature and calcining at 773 K for 4 h in air. **Table 1** shows the elemental analysis and the BET specific surface area of the catalysts prepared in this study. The BET specific surface area was measured before and after the sulfidation pretreatment carried out in the following ¹²⁹Xe NMR spectroscopy.

2.2. Characterization

Prior to ¹²⁹Xe NMR spectroscopy, the catalyst was sulfided with a mixture of 5 vol% H₂S and H₂ for 3 h at

673 K under atmospheric pressure in a glass reactor connected to the NMR tube. The sulfidation temperature was increased at about 2.5 K/min. The pretreatment apparatus has been already shown elsewhere⁽³⁾. After the sulfidation, the catalyst was transferred from the reactor to the NMR tube without exposure to air. In addition, the prepared catalysts and the Al₂O₃ support were dried in helium at 673 K for 3 h and then used for the following ¹²⁹Xe NMR measurement in order to investigate the effect of sulfidation.

After the pretreatment, the xenon adsorption isotherm on the catalyst or the Al₂O₃ support was measured at ambient temperature (298 K). Then, ¹²⁹Xe NMR spectra of the pretreated catalysts under 120 kPa xenon adsorption pressure were recorded using a JNM CMX 400 spectrometer (JEOL) with a single pulse sequence at ambient temperature. ¹²⁹Xe NMR measurement without MAS used observed frequency of 110.726 MHz, pulse width of $\pi/4$ flip angle, recycle time of 1 s and number of accumulations between 1000 and 4000. The chemical shifts were determined relative to xenon gas extrapolated to zero pressure⁽¹¹⁾.

Prior to XPS (X-ray photoelectron spectroscopy), the catalyst was sulfided with a mixture of 5 vol% H₂S and H₂ for 10 min at 573 K under atmospheric pressure in a glass reactor. The sulfidation temperature was increased at about 5 K/min. The reactor (not shown in this paper) was set up with an infrared image furnace and directly connected to the sample introduction chamber (less than 1×10^{-4} Pa) of the XPS machine. After the sulfidation, the catalyst was purged with a helium stream for more than 1 h and evacuated with a rotary vacuum pump at ambient temperature. Then, the sulfided catalyst was transferred from the reactor to the sample introduction chamber in a vacuum (less than 1×10^{-3} Pa). The XPS measurement of the sulfided catalyst was carried out with a XPS-7000 spectrometer (Rigaku) using monochromated Al K α radiation (14 kV, 350 W) in a high vacuum (less than 1×10^{-6} Pa). In the XPS measurement, the pass energy was adjusted to 23.5 eV, and the Al 2p binding energy (74.7 eV) of γ -Al₂O₃ was used as the reference value for the purpose of compensation for sample charge. After the XPS measurement, peak deconvolution of the Mo 3d XPS of the sulfided catalyst was carried out for quantitative analysis of the state of molybdenum.

Powder XRD (X-ray diffraction) patterns of the catalysts were recorded on a RINT-2500V diffractometer (Rigaku) using monochromated Cu K α radiation (50 kV, 300 mA). XRD measurement of the catalyst was carried out before or after sulfidation. The sulfided catalysts were previously used in the ¹²⁹Xe NMR measurement.

○: dried Mo/Al₂O₃; ●: sulfided Mo/Al₂O₃; □: dried Co/Al₂O₃; ■: sulfided Co/Al₂O₃; ◇: dried Co-Mo/Al₂O₃; ◆: sulfided Co-Mo/Al₂O₃; △: dried Al₂O₃.

Fig. 1 Xenon Adsorption Isotherms on Sulfided or Dried Samples at 298 K (1 Torr = 133.322 Pa)

3. Results

3.1. ¹²⁹Xe NMR Analysis

Figure 1 shows the xenon adsorption isotherms (298 K) on the various catalysts sulfided or dried at 673 K. Neither sulfidation nor cobalt addition had much effect on the xenon adsorption isotherm for Mo/Al₂O₃ and Co-Mo/Al₂O₃. This result suggests that the amount of adsorbed xenon is mainly dependent on the content of molybdenum. Our recent studies showed that the amount of adsorbed xenon is strongly affected by the molybdenum loading and little influenced by the Co/Mo ratio if the molybdenum loading is constant^(3,4). Therefore, we consider that the xenon adsorption isotherm is mainly controlled by the adsorption interaction between xenon and molybdenum species on the surface. In addition, the specific surface area of the samples containing molybdenum became much smaller after sulfidation (**Table 1**). This finding suggests that the decrease in the specific surface area was compensated for by the sulfidation effect, *i.e.*, the adsorption interaction between xenon and stacked MoS₂ crystallites. As a result, the amount of adsorbed xenon remained approximately constant before and after the sulfidation. In contrast, the xenon adsorption isotherm for Co/Al₂O₃ shifted downward in comparison with Al₂O₃, and both sulfidation and drying had little effect. In this respect, the specific surface area of Co/Al₂O₃ was much smaller than that of Al₂O₃ and changed little with sulfidation (**Table 1**). Therefore, the amount of adsorbed xenon was mainly dependent on the specific surface area for Co/Al₂O₃, in the absence of the adsorption interaction between xenon and molybdenum species on the surface.

Figure 2 shows ¹²⁹Xe NMR spectra of the dried catalysts under 120 kPa xenon adsorption pressure. One sharp peak at very similar chemical shift was observed

1: Al₂O₃; 2: Mo/Al₂O₃; 3: Co/Al₂O₃; 4: Co-Mo/Al₂O₃.

Fig. 2 ¹²⁹Xe NMR Spectra of Dried Samples under 120 kPa Xenon Adsorption Pressure

1: Al₂O₃; 2: Mo/Al₂O₃; 3: Co/Al₂O₃; 4: Co-Mo/Al₂O₃.

Fig. 3 ¹²⁹Xe NMR Spectra of Sulfided Samples under 120 kPa Xenon Adsorption Pressure

in the spectrum of Al₂O₃ and Mo/Al₂O₃. However, the peak intensity of Mo/Al₂O₃ was larger than that of Al₂O₃. This result corresponds with the observation that the amount of adsorbed xenon on Mo/Al₂O₃ was larger than that on Al₂O₃ (**Fig. 1**). In contrast, remarkable peak broadening was observed in the spectra of Co/Al₂O₃ and Co-Mo/Al₂O₃. This peak broadening was probably caused by the paramagnetic cobalt oxides such as CoO and Co₃O₄ present on the surface. This interaction was negligible in the case of Al₂O₃ and Mo/Al₂O₃ not containing cobalt, and as a result the ¹²⁹Xe NMR peak remained sharp.

Figure 3 shows ¹²⁹Xe NMR spectra of the sulfided catalysts under 120 kPa xenon adsorption pressure, together with dried Al₂O₃. Little peak broadening occurred for Co/Al₂O₃ and Co-Mo/Al₂O₃, as for Mo/Al₂O₃ and Al₂O₃. This result suggests a remarkable change in the magnetic property of cobalt by sulfidation. The cobalt was presumably transformed into the Co-Mo-S phase or sulfides such as Co₉S₈. Both the Co-Mo-S phase and Co₉S₈ are antiferromagnetic and not paramagnetic⁽⁸⁾. Therefore, any interaction between

Lower and upper spectra were measured before and after sulfidation, respectively.

Fig. 4 Mo 3d XPS of Mo/Al₂O₃ and Co-Mo/Al₂O₃

xenon and these phases is unlikely to cause the remarkable broadening of the peak shown in **Fig. 2**. Such results imply that ¹²⁹Xe NMR is sensitive to the chemical state of cobalt. In addition, the ¹²⁹Xe NMR peak appeared at 170 ppm for Co-Mo/Al₂O₃, further downfield than the peaks for Co/Al₂O₃ and Mo/Al₂O₃. This result is closely related to the remarkable changes in the magnetic properties caused by the coexistence of cobalt with molybdenum on the surface. In general, if xenon simply interacts with both cobalt and molybdenum during the NMR measurement time (*ca.* 8×10^{-5} s), the ¹²⁹Xe NMR peak will appear at the mean position between the peaks observed on Co/Al₂O₃ and on Mo/Al₂O₃. Therefore, the further downfield shift of the peak for Co-Mo/Al₂O₃ suggests another interaction between xenon and cobalt or molybdenum. We recently suggested that the formation of the antiferromagnetic Co-Mo-S phase on the surface causes an increase in the magnetic susceptibility and consequent further downfield shift of the peak⁴. This result will be discussed again below.

3. 2. Surface Analysis by XPS

Figure 4 shows the Mo 3d XPS analyses of Mo/Al₂O₃ and Co-Mo/Al₂O₃. In general, the XPS findings reflect the chemical state of molybdenum on the surface. Before sulfidation, two peaks assigned to Mo 3d_{3/2} and Mo 3d_{5/2} were observed at 236.1 eV and 232.9 eV, respectively, corresponding to Mo⁶⁺ species such as MoO₃¹². The Mo 3d peak shape of Co-Mo/Al₂O₃ was almost identical with that of Mo/Al₂O₃. After sulfidation, another two peaks assigned to Mo 3d_{3/2} and Mo 3d_{5/2} were observed at 231.9 eV and 228.6 eV, respectively, overlapping with small Mo⁶⁺ 3d

peaks. These findings indicate that molybdenum was mostly transformed into Mo⁴⁺ species such as MoS₂¹³. As before sulfidation, the Mo 3d peak shape of the sulfided Co-Mo/Al₂O₃ was little different from that of the sulfided Mo/Al₂O₃. Therefore, we consider that the addition of cobalt to Mo/Al₂O₃ had little influence on the sulfidation of molybdenum on the surface. **Figure 5** and **Table 2** show peak deconvolution of the Mo 3d XPS results and the derived quantitative Mo 3d XPS analysis, respectively. The results indicate Mo⁵⁺ species were observed at around 230 eV for both Mo/Al₂O₃ and Co-Mo/Al₂O₃ after sulfidation¹⁴.

Figure 6 shows the Co 2p XPS analyses of Co/Al₂O₃ and Co-Mo/Al₂O₃. Before sulfidation, a broad peak appeared at around 781.5 eV with an additional shoulder peak at higher binding energies, corresponding to cobalt oxides¹⁵. The Co 2p peak shape of Co-Mo/Al₂O₃ was similar to that of Co/Al₂O₃. After sulfidation, another sharp peak appeared at around 778 eV together with the peak corresponding to cobalt oxides. However, the Co 2p binding energy was 778.4 eV for Co-Mo/Al₂O₃ and slightly higher than 777.7 eV for Co/Al₂O₃. In this case, the C 1s binding energy for Co-Mo/Al₂O₃ was 284.7 eV and almost equal to 284.8 eV for Co/Al₂O₃, demonstrating that the charge correction using the Al 2p binding energy (74.7 eV) was almost valid. Therefore, the 0.7 eV difference in Co 2p binding energy between Co/Al₂O₃ and Co-Mo/Al₂O₃ is not negligible. The Co 2p binding energy of the Co-Mo-S phase is about 0.5 eV higher than that of Co₉S₈¹⁶. Similarly, the Co 2p binding energy of the Co-Mo-S phase is 0.9 eV higher than that of CoS_x/Al₂O₃ or Co₉S₈¹⁷. On the basis of these observations,

Fig. 5 Peak Deconvolution of Mo 3d XPS of Sulfided Mo/Al₂O₃ and Sulfided Co-Mo/Al₂O₃

Table 2 Quantitative Mo 3d XPS Analysis of the Sulfided Catalysts

Sample	Mo ⁴⁺	Mo ⁵⁺	Mo ⁶⁺
Mo/Al ₂ O ₃	228.7 62	230.2 17	233.1 21
Co-Mo/Al ₂ O ₃	228.7 61	230.0 17	233.1 22

The peak position (eV) (upper) and percentage abundance (%) (lower) of Mo species are shown.

our Co 2p XPS result strongly suggests that the Co-Mo-S phase is formed on the surface of the sulfided Co-Mo/Al₂O₃.

3.3. XRD Analysis

Figure 7 shows the XRD patterns of the catalysts before the sulfidation. For Co/Al₂O₃, several sharp peaks appeared, denoted by asterisks in the figure and corresponding to CoAl₂O₄ or CoO, with broad peaks corresponding to Al₂O₃. In contrast, for Co-Mo/Al₂O₃, no sharp peaks appeared, as for Mo/Al₂O₃. These findings suggest that the dispersion of cobalt on Co-Mo/Al₂O₃ is much larger than that on Co/Al₂O₃. Therefore, we believe that the presence of molybdenum on the surface has a great influence on the dispersion of cobalt in the sequential impregnation method, although the present study did not establish any mechanism for this result.

Figure 8 shows the XRD patterns of the sulfided catalysts. For Co/Al₂O₃, two obvious peaks appeared at 30° and 52°, denoted by asterisks in the figure and corresponding to Co₉S₈. On the other hand, for Mo/Al₂O₃ and Co-Mo/Al₂O₃, a broad peak and a shoulder peak appeared at *ca.* 58° and *ca.* 33°, respectively, denoted by circles in the figure and characteristic of

MoS₂. In particular, no peaks corresponding to Co₉S₈ appeared in the XRD pattern of Co-Mo/Al₂O₃. This result demonstrates that little formation of Co₉S₈ crystallites occurred on Co-Mo/Al₂O₃ after sulfidation, so cobalt was dispersed as other species, such as the Co-Mo-S phase.

4. Discussion

Sulfidation has a large effect on the ¹²⁹Xe NMR spectra as shown in Figs. 2 and 3. The main effect is broadening of the ¹²⁹Xe NMR peak corresponding to the interaction between xenon and other atoms. Remarkable broadening of the ¹²⁹Xe NMR peak was observed before sulfidation for catalysts containing cobalt such as Co/Al₂O₃ and Co-Mo/Al₂O₃, mainly caused by the magnetic property of cobalt on the surface. XRD showed that cobalt in Co/Al₂O₃ is mainly present as CoAl₂O₄ or CoO (Fig. 7), before sulfidation. These cobalt species are paramagnetic, and cause the broadening of the ¹²⁹Xe NMR peak. For Co-Mo/Al₂O₃ before sulfidation, XRD showed no peaks corresponding to CoAl₂O₄ or CoO due to the high dispersion of cobalt. However, the Co 2p XPS result (Fig. 6) showed that cobalt is present as oxides on the surface, similarly to Co/Al₂O₃. Therefore, we consider that the paramagnetic effect of cobalt oxides such as CoO and Co₃O₄ also causes the remarkable broadening of the ¹²⁹Xe NMR peak on Co-Mo/Al₂O₃ before sulfidation.

Sulfidation resulted in slight broadening of the ¹²⁹Xe NMR peak in the spectra of the Al₂O₃-supported molybdenum catalysts such as Mo/Al₂O₃ and Co-Mo/Al₂O₃, compared with Co/Al₂O₃ and dried Al₂O₃. We previously found that an increase of molybdenum load-

Lower and upper spectra were measured before and after sulfidation, respectively.

Fig. 6 Co 2p XPS of Co/Al₂O₃ and Co-Mo/Al₂O₃

1: Al₂O₃; 2: Mo/Al₂O₃; 3: Co/Al₂O₃; 4: Co-Mo/Al₂O₃. Asterisks in the figure indicate CoAl₂O₃ or CoO.

Fig. 7 XRD Patterns of Samples before Sulfidation

ing on Mo/Al₂O₃ caused gradual broadening of the ¹²⁹Xe NMR peak³⁾. The broadening of the peak is closely related to a growth of irregularity in collisions between xenon and molybdenum species and this conclusion is also applicable to the present findings. However, the Mo 3d XPS (Fig. 4) showed that molybdenum is mainly transformed into sulfides after sulfidation. Moreover, the quantitative Mo 3d XPS analy-

sis (Table 2) suggested that a small amount of Mo⁵⁺, associated with Al₂O₃ as an oxysulfidic intermediate^{14),18)}, is present on the surface in addition to a large amount of Mo⁴⁺ as MoS₂ and Mo⁶⁺ as residual MoO₃. In general, Mo⁵⁺ species are paramagnetic, so the slight broadening of the ¹²⁹Xe NMR peak on Mo/Al₂O₃ and Co-Mo/Al₂O₃ is probably caused by both the irregularity in collisions between xenon and molybdenum species

1: Al_2O_3 ; 2: $\text{Mo}/\text{Al}_2\text{O}_3$; 3: $\text{Co}/\text{Al}_2\text{O}_3$; 4: $\text{Co-Mo}/\text{Al}_2\text{O}_3$. Circles and asterisks in the figure indicate MoS_2 and Co_9S_8 , respectively.

Fig. 8 XRD Patterns of Samples after Sulfidation

and by the formation of Mo^{5+} species.

Sulfidation resulted in the appearance of a sharp peak at 105 ppm for sulfided $\text{Co}/\text{Al}_2\text{O}_3$. XRD (**Fig. 8**) showed that cobalt is mainly transformed into antiferromagnetic Co_9S_8 , whereas the Co 2p XPS result showed that cobalt oxides are still present after sulfidation (**Fig. 6**). In general, XRD analyzes the bulk particle of the sample, whereas XPS analyzes only the surface of the sample. ^{129}Xe NMR spectroscopy is affected by the magnetic properties of all cobalt species in the sample, and so tends to correlate with XRD rather than XPS. Therefore, we consider that sulfidation causes a marked decrease in paramagnetic cobalt oxides so the sharp ^{129}Xe NMR peak is observed without remarkable broadening caused by the paramagnetic effect of cobalt. Similarly, no remarkable broadening of the ^{129}Xe NMR peak occurred for sulfided $\text{Co-Mo}/\text{Al}_2\text{O}_3$, in contrast with dried $\text{Co-Mo}/\text{Al}_2\text{O}_3$. XRD detected no peaks corresponding to cobalt species such as Co_9S_8 (**Fig. 8**). The Co 2p XPS of sulfided $\text{Co-Mo}/\text{Al}_2\text{O}_3$ (**Fig. 6**) showed that the binding energy of the sharp peak was *ca.* 778 eV, indicating that cobalt was mainly transformed into sulfides, probably the Co-Mo-S phase or Co_9S_8 . Cobalt sulfides are generally antiferromagnetic and not paramagnetic⁸⁾. Therefore, we conclude that the transformation of cobalt oxides into cobalt sulfides by sulfidation drastically decreased the paramagnetic effect which caused the remarkable broadening of the ^{129}Xe NMR peak.

Finally, the Co 2p XPS analysis showed that the binding energy of the sharp peak for sulfided Co-Mo/

Al_2O_3 was 0.7 eV higher than that for sulfided $\text{Co}/\text{Al}_2\text{O}_3$, strongly suggesting that cobalt was mainly present as the Co-Mo-S phase on the surface of sulfided $\text{Co-Mo}/\text{Al}_2\text{O}_3$. This result corresponds with the conclusion that the formation of the Co-Mo-S phase on the surface causes further downfield shift of the ^{129}Xe NMR peak in comparison with sulfided $\text{Mo}/\text{Al}_2\text{O}_3$. Formation of the antiferromagnetic Co-Mo-S phase on the surface increases the magnetic susceptibility so the ^{129}Xe NMR peak shifts downfield due to an increase in the δ_0 term representative of xenon diffusibility⁴⁾. Therefore, we suggest that ^{129}Xe NMR spectroscopy is useful for the analysis of the Co-Mo-S phase on the Co-Mo/ Al_2O_3 hydrodesulfurization catalyst.

5. Conclusions

The present study investigated the effect of sulfidation on the ^{129}Xe NMR spectra of Al_2O_3 -supported catalysts such as $\text{Co-Mo}/\text{Al}_2\text{O}_3$. Before sulfidation, *i.e.*, after drying, the ^{129}Xe NMR peak was remarkably broad for the catalysts containing cobalt such as $\text{Co}/\text{Al}_2\text{O}_3$ and $\text{Co-Mo}/\text{Al}_2\text{O}_3$, whereas one sharp ^{129}Xe NMR peak was observed for $\text{Mo}/\text{Al}_2\text{O}_3$ and Al_2O_3 . This remarkable broadening of the peak is mainly caused by the paramagnetic effect of cobalt oxides such as CoAl_2O_4 and CoO . In contrast, after sulfidation, no remarkable broadening of the ^{129}Xe NMR peak was observed for these catalysts. We consider that cobalt was mostly transformed from paramagnetic oxides into antiferromagnetic sulfides such as the Co-Mo-S phase

and Co_9S_8 , thus greatly reducing the paramagnetic effect.

In contrast, one ^{129}Xe NMR peak was observed for $\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{Co-Mo}/\text{Al}_2\text{O}_3$ after sulfidation, with a little broadening of the peak in comparison with sulfided $\text{Co}/\text{Al}_2\text{O}_3$. This finding is probably caused by both irregularity in collisions between xenon and molybdenum species and by the formation of Mo^{5+} species, associated with Al_2O_3 as an oxysulfidic intermediate. One sharp ^{129}Xe NMR peak was observed for sulfided $\text{Co}/\text{Al}_2\text{O}_3$, in contrast with dried $\text{Co}/\text{Al}_2\text{O}_3$. XRD of sulfided $\text{Co}/\text{Al}_2\text{O}_3$ suggested that formation of Co_9S_8 caused a marked decrease in the paramagnetic effect of cobalt. Furthermore, XPS of the sulfided catalysts showed that the Co 2p binding energy of the sharp peak for $\text{Co-Mo}/\text{Al}_2\text{O}_3$ was 0.7 eV higher than that for $\text{Co}/\text{Al}_2\text{O}_3$. This result strongly suggests that cobalt was mainly present as the Co-Mo-S phase on the surface and closely related to downfield shift of the ^{129}Xe NMR peak of sulfided $\text{Co-Mo}/\text{Al}_2\text{O}_3$ in comparison with sulfided $\text{Mo}/\text{Al}_2\text{O}_3$. The present study showed that ^{129}Xe NMR spectroscopy is sensitive to the chemical state of cobalt species, especially the Co-Mo-S phase, Co_9S_8 and cobalt oxides, present on $\text{Co-Mo}/\text{Al}_2\text{O}_3$ hydrodesulfurization catalyst.

References

- 1) Ito, T., Fraissard, J., *J. Chem. Phys.*, **76**, 5225 (1982).
- 2) Ito, T., *Zeolite News Lett.*, **6**, 5 (1989).
- 3a) Hagiwara, K., Ebihara, T., Urasato, N., Fujikawa, T., *J. Jpn. Petrol. Inst.*, **48**, (2), 84 (2005).
- 3b) Hagiwara, K., Ebihara, T., Urasato, N., Fujikawa, T., *Appl. Catal. A: General*, **285**, 132 (2005).
- 4a) Hagiwara, K., Ebihara, T., Urasato, N., Fujikawa, T., *J. Jpn. Petrol. Inst.*, **48**, (3), 156 (2005).
- 4b) Hagiwara, K., Ebihara, T., Urasato, N., Fujikawa, T., *Appl. Catal. A: General*, **293**, 56 (2005).
- 5) Topsøe, N.-Y., Topsøe, H., *J. Catal.*, **84**, 386 (1983).
- 6) Topsøe, H., Candia, R., Topsøe, N.-Y., Clausen, B. S., Topsøe, H., *Bull. Soc. Chim. Belg.*, **93**, 783 (1984).
- 7) Topsøe, H., Topsøe, N.-Y., Sørensen, O., Candia, R., Clausen, B. S., Kallesøe, S., Pedersen, E., Nevald, R., *ACS Symp. Ser.*, **279**, 235 (1985).
- 8) Okamoto, Y., Kawano, M., Kawabata, T., Kubota, T., Hiromitsu, I., *J. Phys. Chem. B*, **109**, 288 (2005).
- 9) Kraus, H., Prins, R., *J. Catal.*, **170**, 20 (1997).
- 10) Blumberg, W. E., *Phys. Rev.*, **119**, 79 (1960).
- 11) Jameson, A. K., Jameson, C. J., Gutowski, H. S., *J. Chem. Phys.*, **59**, 4540 (1973).
- 12) Kameda, F., Hoshino, K., Yoshinaka, S., Segawa, K., *Sekiyu Gakkaishi (J. Jpn. Petrol. Inst.)*, **40**, (3), 205 (1997).
- 13) de Jong, A. M., Borg, H. J., van IJzendoorn, L. J., Soudant, V. G. F. M., de Beer, V. H. J., van Veen, J. A. R., Niemantsverdriet, J. W., *J. Phys. Chem.*, **97**, 6477 (1993).
- 14) Hensen, E. J. M., de Beer, V. H. J., van Veen, J. A. R., van Santen, R. A., *Catal. Lett.*, **84**, 59 (2002).
- 15) de Jong, A. M., de Beer, V. H. J., van Veen, J. A. R., Niemantsverdriet, J. W., *J. Vac. Sci. Technol. A*, **15**, 1592 (1997).
- 16) Alstrup, I., Chorkendorff, I., Candia, R., Clausen, B. S., Topsøe, H., *J. Catal.*, **77**, 397 (1982).
- 17) Okamoto, Y., Ochiai, K., Kawano, M., Kobayashi, K., Kubota, T., *Appl. Catal. A: General*, **226**, 115 (2002).
- 18) Fujikawa, T., Kato, M., Ebihara, T., Hagiwara, K., Kubota, T., Okamoto, Y., *J. Jpn. Petrol. Inst.*, **48**, (2), 114 (2005).

要 旨

^{129}Xe NMR の $\text{Co-Mo}/\text{Al}_2\text{O}_3$ 脱硫触媒分析への応用— ^{129}Xe NMR スペクトルに及ぼす硫化処理の影響—

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$\text{Co-Mo}/\text{Al}_2\text{O}_3$ 脱硫触媒の ^{129}Xe NMR スペクトルに及ぼす硫化処理の影響について検討を行った。硫化前においては、 $\text{Mo}/\text{Al}_2\text{O}_3$ や Al_2O_3 の場合、1種類のシャープな ^{129}Xe NMR ピークが現れたのに対し、 $\text{Co}/\text{Al}_2\text{O}_3$ や $\text{Co-Mo}/\text{Al}_2\text{O}_3$ などのコバルトを含む試料では、 ^{129}Xe NMR ピークが著しく広幅化した。これは、 CoAl_2O_4 や CoO などのコバルト酸化物の常磁性効果に主に起因している。対照的に、硫化後においては、 ^{129}Xe NMR ピークの顕著な広幅化はこれらの試料では見られなかった。これは、 CoAl_2O_4 や CoO などの常磁性酸化物から Co-Mo-S 相や Co_9S_8 などの反強磁性硫化物への変化によって、コバルトの常磁性効

果が大幅に減少したためと考えられる。さらに、硫化した触媒の XPS 結果から、 $\text{Co-Mo}/\text{Al}_2\text{O}_3$ における Co 2p のシャープなピークの結合エネルギーは、 $\text{Co}/\text{Al}_2\text{O}_3$ よりも 0.7 eV 高くなった。この結果は、コバルトが Co-Mo-S 相として表面上に存在していることを強く示唆しており、硫化 $\text{Co-Mo}/\text{Al}_2\text{O}_3$ の ^{129}Xe NMR ピークが硫化 $\text{Mo}/\text{Al}_2\text{O}_3$ に比べてより低磁場側にシフトしたと密接に関連している。この結果より、 ^{129}Xe NMR は $\text{Co-Mo}/\text{Al}_2\text{O}_3$ 脱硫触媒上における Co-Mo-S 相の形成に敏感であるといえる。