[Review Paper]

Characterization of Co–Mo/Al₂O₃ Hydrodesulfurization Catalyst by ¹²⁹Xe NMR Spectroscopy

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The present study evaluated ¹²⁹Xe NMR spectroscopy for the analysis of Co–Mo/Al₂O₃ hydrodesulfurization catalyst. This study also reconsidered the conventional interpretation of ¹²⁹Xe NMR spectroscopy that had been used for zeolite micropore analysis. The chemical shift δ of an observed ¹²⁹Xe NMR peak varied nonlinearly against the amount of adsorbed xenon N for sulfided Mo/Al₂O₃ catalyst. In contrast, δ was almost constant against N for dried catalyst. This result suggests that the nonlinear variation of δ against N is mainly caused by electronic interactions between xenon and coordinatively unsaturated sites on the edge of MoS₂ crystallites. In addition, the xenon diffusibility δ_0 calculated from ¹²⁹Xe NMR spectra gradually increased with sulfidation temperature and approached the maximum value at more than 673 K, indicating that δ_0 is closely related to the formation of MoS₂ crystallites on the surface. δ_0 became gradually larger with the cobalt loading and reached the maximum value at 5.7 mass% for sulfided Co–Mo/Al₂O₃ catalyst. On the other hand, δ_0 increased from 0 mass% to 2.4 mass% and was almost constant at more than 2.4 mass% for sulfided Co/Al₂O₃ catalyst. This observation is mainly caused by the differences in the magnetic susceptibility between Co–Mo/Al₂O₃ catalyst and Co/Al₂O₃ catalyst after sulfidation. In other words, the formation of the antiferromagnetic Co–Mo–S phase causes increased magnetic susceptibility that greatly affects δ_0 . The slight decrease of δ_0 at 7.3 mass% for sulfided Co–Mo/Al₂O₃ catalyst is closely related to the formation of Co₉S₈ prior to that of the Co–Mo–S phase. These findings strongly suggest that δ_0 obtained from ¹²⁹Xe NMR spectroscopy is a sensitive indicator of the amount of the Co–Mo–S phase. Furthermore, the relative hydrodesulfurization activity of various Co–Mo/Al₂O₃ catalysts was roughly correlated with δ_0 . This result also demonstrates that ¹²⁹Xe NMR spectroscopy is useful for analysis of the Co–Mo–S phase on Co–Mo/Al₂O₃ hydrodesulfurization catalyst.

Keywords

¹²⁹Xe NMR, Cobalt molybdenum catalyst, Sulfidation, Co–Mo–S phase, Magnetic susceptibility, Hydrodesulfurization

1. Introduction

Hydrodesulfurization of petroleum fractions such as diesel is becoming more and more important in the petroleum refining industry to satisfy environmental protection requirements. Hydrodesulfurization processes have widely utilized cobalt (or nickel) promoted molybdenum catalysts for many years. In the case of Co–Mo catalyst, sulfidation treatment greatly enhances the hydrodesulfurization activity. Previous studies using ⁵⁷Co Mössbauer spectroscopy proposed that the so-called “Co–Mo–S phase” was formed by sulfidation and functioned as the catalytic active site for hydrodesulfurization^{1,2)}. In the Co–Mo–S phase model, cobalt atoms are highly dispersed on the surface and located on the edges of stacked MoS₂ crystallites, together with other cobalt species such as Co₉S₈ which

are inefficient in hydrodesulfurization. A previous study using EXAFS (extended X-ray absorption fine structure) of the local structure of the Co–Mo–S phase reported that cobalt atoms were coordinated to sulfur atoms in a square pyramidal structure similar to millerite³⁾. A recent study investigated the NO adsorption behavior and the magnetic properties of model Co–Mo sulfide catalysts and proposed a cobalt sulfide dinuclear cluster model as an alternative structure for the Co–Mo–S phase^{4,5)}. This model is closely related to the antiferromagnetic property of cobalt in the Co–Mo–S phase⁶⁾ and mainly corresponds with other findings using *ab initio* DFT (density functional theory) calculations of the Co–Mo–S phase⁷⁾. Several properties of the sulfided Co–Mo catalyst, such as the detailed structure of the Co–Mo–S phase, have not been clarified, and a novel technique for structural analysis of the Co–Mo–S phase is now necessary.

Recently, we applied ¹²⁹Xe NMR (nuclear magnetic

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resonance) spectroscopy to the characterization of Co-Mo/Al₂O₃ hydrosulfurization catalysts in order to investigate the state of cobalt in the Co-Mo-S phase^{8)~10)}. ¹²⁹Xe NMR spectroscopy is one of the most powerful techniques for analysis of microporous materials such as zeolites. Pioneering applications of ¹²⁹Xe NMR spectroscopy to zeolite analysis were investigated at the beginning of the 1980's^{11),12)}, and ¹²⁹Xe NMR spectroscopy has since been widely used as an analytical method for zeolite micropores. Xenon atoms frequently collide with other atoms in the micropores at ambient temperatures in the case of zeolites. These collisions cause electronic distortion of xenon atoms and greatly affect the chemical shifts of observable ¹²⁹Xe NMR peaks. Therefore, ¹²⁹Xe NMR spectroscopy generally reflects the electronic interactions between xenon and other atoms in the micropores and provides valuable information about the micropore structure. We previously obtained several types of information about structural destruction of USY zeolite under hydrothermal conditions using ¹²⁹Xe NMR spectroscopy¹³⁾. Recently, hyperpolarized xenon has been also applied to ¹²⁹Xe NMR spectroscopy for the enhancement of NMR signal intensity^{14),15)}.

However, ¹²⁹Xe NMR spectroscopy has seldom been utilized for surface analysis of Al₂O₃-supported catalysts such as Co-Mo/Al₂O₃ catalyst. Al₂O₃-supported catalyst contains an irregular distribution of micropores only on the surface of Al₂O₃, in marked contrast with the zeolites which contain regular distributions of micropores. This fact suggests that xenon diffusibility in Al₂O₃-supported catalysts is quite different from that in the zeolites. Therefore, application of ¹²⁹Xe NMR spectroscopy to Al₂O₃-supported catalysts will require further investigations into the conventional interpretation for ¹²⁹Xe NMR data of zeolites^{11),12),16),17)}. In the present study, we assumed that any interaction between xenon and active sites such as the Co-Mo-S phase would be reflected in the ¹²⁹Xe NMR spectra, and so investigated the application of ¹²⁹Xe NMR spectroscopy to analysis of Co-Mo/Al₂O₃ hydrosulfurization catalysts.

2. Principles of ¹²⁹Xe NMR Spectroscopy

The important features of xenon as applied to ¹²⁹Xe NMR spectroscopy are that the ¹²⁹Xe isotope is an ideal nucleus for NMR measurements, and the electronic condition of xenon is sensitive to interactions between xenon and other atoms. The spin number *I* of ¹²⁹Xe is 1/2, so no peak broadening caused by the quadrupolar interaction appears in the NMR spectrum. In addition, the natural abundance of ¹²⁹Xe is much higher (26.44%) than that of ¹³C (1.11%), and the absolute NMR sensitivity of ¹²⁹Xe is about 30 times higher than that of ¹³C. The atomic diameter of xenon is relatively

large (0.44 nm) and the electronic condition of xenon is susceptible to the surroundings, whereas xenon is an 'inert' gas. In fact, the ¹²⁹Xe chemical shift is extremely sensitive to the xenon density¹⁸⁾. The dependence of the ¹²⁹Xe chemical shift on the xenon density is almost linear within 10 MPa xenon pressure and is mainly caused by the number of collisions between xenon atoms. These collisions easily change the electronic condition of xenon, so ¹²⁹Xe NMR spectroscopy reflects any interaction between xenon and other atoms.

¹²⁹Xe NMR spectroscopy of microporous materials at ambient temperatures generally observes only one peak at the mean position because mobile exchanges between xenon atoms adsorbed on active sites are extremely fast in micropores. This phenomenon often makes detailed analysis of ¹²⁹Xe NMR spectra difficult. High resolution NMR spectroscopy, such as liquid-state NMR spectroscopy, generally observes several peaks, and the chemical shift of each peak directly reflects molecular structural information about the functional groups, the coordination number and the conformation. In contrast, ¹²⁹Xe NMR spectroscopy does not directly provide valuable information about the micropore structure, and the observed peak needs to be further analyzed on the basis of the conventional interpretation^{11),12),16),17)}. In practice, the chemical shift δ of the observed peak is plotted against the amount of adsorbed xenon per unit weight of the sample *N*. The plot of δ against *N* is useful for evaluation of various terms characteristic of the micropore structure and is here described as the ' δ -*N* plot'.

Previous studies^{11),12),16),17)} investigated the δ -*N* plot of zeolites and demonstrated that δ could be represented as the sum of three characteristic terms:

$$\delta = \delta_0 + \delta_{Xe} + \delta_E \quad (1)$$

where δ_0 mainly depends on the xenon diffusibility, *i.e.*, collisions between xenon and other atoms in a micropore. In general, δ_0 is constant against the xenon density; δ_{Xe} originates from collisions among xenon atoms in a micropore and is directly dependent on the xenon density; and δ_E represents the presence of strong adsorption sites such as bivalent or trivalent cations and is inversely proportional to the xenon density in contrast with δ_{Xe} . In other words, these three terms have quite different dependences on the xenon density. This feature is applicable to the practical analysis of the δ -*N* plot because the xenon density is generally correlated with *N*. For example, the intercept and the slope of the linear section of the δ -*N* plot corresponds to δ_0 and $d\delta_{Xe}/dN$, respectively. The nonlinear term δ_E can be represented as ' k/N ', where *k* is a constant characteristic of the strong adsorption sites interacting with xenon electronically. When $d\delta_{Xe}/dN$ is represented as ' α ', Eq. (1) can be rewritten as follows:

$$\delta = \delta_0 + \alpha N + k/N \quad (2)$$

In addition, a previous study on ¹²⁹Xe NMR spectroscopy

1: Drying in helium; 2: sulfidation at 373 K; 3: sulfidation at 473 K; 4: sulfidation at 573 K; 5: sulfidation at 673 K; 6: sulfidation at 773 K.

Fig. 1 ^{129}Xe NMR Spectra of Pretreated $\text{Mo}/\text{Al}_2\text{O}_3$ Catalyst (Mo: 9.0 mass %) under 120 kPa Xenon Pressure

copy of Ni^{2+}Y zeolites reported that the term of xenon diffusibility δ_0 could be represented as the sum of three terms¹⁹:

$$\delta_0 = \delta_W + \delta_A + \delta_M \quad (3)$$

where δ_W is dependent on collisions between xenon and the micropore; and δ_A arises from collisions between xenon and other molecules such as H_2O present or adsorbed on the micropore surface. In other words, these two terms mainly reflect the xenon diffusibility on the surface, whereas δ_M reflects magnetic interactions between xenon and other atoms such as Ni^{2+} and therefore depends on the magnetic property of adsorption sites on the surface. In the case of $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalyst, δ_M is closely related to the magnetic susceptibility of cobalt. The present study applied these interpretations to ^{129}Xe NMR spectroscopy of $\text{Co-Mo}/\text{Al}_2\text{O}_3$ hydrosulfurization catalysts to investigate the validity for analysis of the Co-Mo-S phase.

3. ^{129}Xe NMR Analysis of $\text{Mo}/\text{Al}_2\text{O}_3$ Catalyst

In general, a sulfur anion vacancy, *i.e.*, a coordinatively unsaturated site (CUS), is formed on the edge of stacked MoS_2 crystallites by sulfidation of $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst and functions as an active site for hydrosulfurization^{20,21}. TEM (transmission electron microscope) of sulfided $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst shows that MoS_2 crystallites are highly dispersed on the Al_2O_3 surface^{22,23}. However, TEM of the rough Al_2O_3 surface cannot generally detect small MoS_2 crystallites (less than about 1 nm)²⁴, so the hydrosulfurization activity of the catalyst does not necessarily correlate with TEM observations. Therefore, the present study evaluated ^{129}Xe NMR spectroscopy for the analysis of MoS_2 crystallites on sulfided $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst.

Figure 1 shows ^{129}Xe NMR spectra of $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst (Mo: 9.0 mass %) sulfided at various temperatures (373 K–773 K) or dried in helium at 673 K. All spectra were measured under 120 kPa xenon pressure at

1: Drying in helium; 2: sulfidation at 373 K; 3: sulfidation at 473 K; 4: sulfidation at 573 K; 5: sulfidation at 673 K; 6: sulfidation at 773 K.

Fig. 2 δ - N Plots Obtained from ^{129}Xe NMR Spectra of Pretreated $\text{Mo}/\text{Al}_2\text{O}_3$ Catalyst (Mo: 9.0 mass %)

Table 1 Quantitative XPS Analysis of $\text{Mo}/\text{Al}_2\text{O}_3$ Catalyst (Mo: 9.0 mass %) Sulfided at Various Temperatures

Sulfidation temperature [K]	XPS analysis	
	$\text{Mo}^{4+}/(\text{Mo}^{4+} + \text{Mo}^{6+})$ [%]	S/Mo [mol/mol]
373	42.5	1.03
473	44.1	1.20
573	53.6	1.35
673	78.6	1.88
773	83.3	1.85

ambient temperature. Only one peak was observed and assigned to xenon interacting with the catalyst surface. For the sulfided catalysts, the peak shifted further downfield and became broader with higher sulfidation temperature. In general, more frequent collisions between xenon and other atoms cause such downfield shift and broadening of the peak. Therefore, the formation of MoS_2 crystallites increases both inhibition and irregularity in xenon diffusion on the surface⁸.

Figure 2 shows the δ - N plots of these catalysts. For the dried catalyst, δ was almost constant against N . Only δ_0 is independent of N in Eq. (1), whereas both δ_{Xe} and δ_{E} are dependent on N . The dependency of these terms on N demonstrates that both δ_{Xe} and δ_{E} are almost negligible for the dried catalyst. In contrast, for the sulfided catalysts, δ varied nonlinearly at low N . In particular, the curvature of the δ - N plot became larger at more than 473 K. This behavior arises from the increase of δ_{E} that represents the interactions between xenon and strong electric fields. Table 1 shows the quantitative XPS (X-ray photoelectron spectroscopy) analysis of sulfided catalysts. Both the $\text{Mo}^{4+}/(\text{Mo}^{4+} + \text{Mo}^{6+})$ ratio and the S/Mo ratio calculated from the XPS analysis increased with sulfidation temperature, whereas the S/Mo ratio became almost constant at more than 673 K. Such XPS results indicate that molybde-

Fig. 3 Relationship between δ_0 Obtained from δ - N Plots and the Sulfidation Temperature for Sulfided Mo/Al₂O₃ Catalyst (Mo: 9.0 mass%)

num is transformed from oxides into sulfides, *i.e.*, MoS₂ crystallites, with higher sulfidation temperature. Therefore, we consider that the growth of δ_E is closely related to the formation of MoS₂ crystallites. In particular, CUS on the edge of MoS₂ crystallites strongly attracts the xenon electrons. The electronic interaction between CUS and xenon causes the increase of δ_E , so that the nonlinear variation in the δ - N plot is observed. Sulfidation at 373 K is insufficient for the formation of MoS₂ crystallites containing CUS, so that δ_E , arising from the electronic interaction between CUS and xenon and causing the nonlinear variation in the δ - N plot, becomes a little smaller.

In addition, for the sulfided catalysts, δ did not become larger with increased N at all. This result shows that δ_{Xe} , the term directly proportional to N , can be considered as negligible in Eq. (1). δ_{Xe} is dependent on collisions between xenon atoms in the micropore. For Mo/Al₂O₃ catalyst, the micropores are irregularly distributed on only the surface of Al₂O₃, and so the micropore volume is quite small. In this case, few xenon atoms are adsorbed in a micropore, and so xenon atoms seldom collide with each other, which reduces δ_{Xe} remarkably. This behavior is little observed in the ¹²⁹Xe NMR spectroscopy of zeolites. In other words, the δ - N plot of sulfided Mo/Al₂O₃ catalyst can be simplified as follows:

$$\delta = \delta_0 + k/N \quad (4)$$

The present study calculated the term δ_0 by fitting the δ - N plot (Fig. 2) into Eq. (4). Figure 3 shows the relationship between δ_0 and the sulfidation temperature. δ_0 gradually increased with sulfidation temperature and approached the maximum value at more than 673 K. This observation roughly corresponds to the quantitative XPS data shown in Table 1. Therefore, δ_0 , as well as δ_E , are closely related to the formation of MoS₂ crystallites. δ_0 can be represented as the sum of δ_w , δ_A and δ_M . In this case, δ_w is almost constant with increasing sulfidation temperature because sulfidation

Fig. 4 ¹²⁹Xe NMR Spectra of Sulfided Mo/Al₂O₃ Catalysts with Various Molybdenum Loadings under 120 kPa Xenon Pressure

has little effect on the surface structure of Al₂O₃. The Mo/Al₂O₃ catalyst contains few paramagnetic elements such as cobalt and nickel, so δ_M can be considered as negligible. Consequently, δ_0 mostly depends on δ_A that depends on collisions between xenon and other molecules, *e.g.* MoS₂ crystallites, on the surface.

For sulfided Mo/Al₂O₃ catalyst, we propose the following interpretation: molybdenum is increasingly sulfided, so more frequent collisions between xenon and MoS₂ crystallites cause increase of δ_A . On the other hand, for the dried catalyst, δ_0 was about 76 ppm and much smaller than that for the sulfided catalyst. This observation also demonstrates that the increase of δ_0 depends on whether MoS₂ crystallites are formed on the surface. In other words, drying of the catalyst is unlikely to cause the formation of MoS₂ crystallites, which collide with xenon frequently and contribute to the increase of δ_A . Consequently, both δ_0 and δ_E are sensitive to the formation of MoS₂ crystallites on the surface. In particular, δ_0 is dependent on the sulfidation state of molybdenum on the surface, whereas δ_E is mainly related to the amount of CUS on the edge of MoS₂ crystallites. These findings strongly suggest that detailed analysis of the δ - N plot is useful for characterization of MoS₂ crystallites on sulfided Mo/Al₂O₃ catalyst.

Figure 4 shows ¹²⁹Xe NMR spectra of sulfided Mo/Al₂O₃ catalysts with various molybdenum loadings (0–12 mass%) measured under 120 kPa xenon pressure at ambient temperature. The peak shifted further downfield and became gradually broader with higher molybdenum loading. This behavior is similar to the observation that the ¹²⁹Xe NMR peak greatly depends on the sulfidation temperature. Therefore, we deduce that higher molybdenum loading causes more inhibition and more irregularity in xenon diffusion on the surface because of more collisions between xenon and MoS₂ crystallites. Figure 5 shows the δ - N plots of these catalysts. Except for dried Al₂O₃, δ varied nonlinearly at low N . In addition, the curvature of the δ - N plot became gradually larger with higher molybdenum load-

Values indicate molybdenum loading on the catalysts.

Fig. 5 δ - N Plots Obtained from ^{129}Xe NMR Spectra of Sulfided Mo/Al₂O₃ Catalysts with Various Molybdenum Loadings

Fig. 6 Relationship between δ_0 Obtained from δ - N Plots and the Molybdenum Loading for Sulfided Mo/Al₂O₃ Catalysts

ing. As discussed above, the nonlinear variation in the δ - N plot for sulfided Mo/Al₂O₃ catalyst is mainly caused by electronic interactions between xenon and CUS on the edge of MoS₂ crystallites. In other words, CUS functions as a strong adsorption site and attracts the xenon electrons. In this case, an increase in MoS₂ crystallites causes more adsorption interactions between xenon and CUS, and so δ_E becomes larger.

δ_0 was calculated by fitting the δ - N plot into Eq. (4) assuming that δ_{Xe} can be considered as negligible in Eq. (1). **Figure 6** shows the relationship between δ_0 and molybdenum loading. δ_0 became gradually larger with higher molybdenum loading. As discussed above, δ_0 for sulfided Mo/Al₂O₃ catalysts mostly depend on δ_A . Therefore, higher molybdenum loading causes more collisions between xenon and MoS₂ crystallites on the surface and so increases δ_A . These findings almost correspond to the interpretation that the formation of MoS₂ crystallites by the sulfidation increases δ_A .

4. ^{129}Xe NMR Analysis of Co-Mo/Al₂O₃ Catalyst

The preceding findings demonstrated that ^{129}Xe

1: Dried Al₂O₃; 2: Mo/Al₂O₃; 3: Co/Al₂O₃; 4: mixture of Mo/Al₂O₃ and Co/Al₂O₃; 5: Co-Mo/Al₂O₃.

Fig. 7 ^{129}Xe NMR Spectra of Various Sulfided Catalysts and Dried Al₂O₃ under 120 kPa Xenon Pressure

NMR spectroscopy is applicable to analysis of sulfided Mo/Al₂O₃ catalysts which contain mesopores and macropores as well as microporous materials such as zeolites. Therefore, ^{129}Xe NMR spectroscopy is likely to be useful for analysis of the Co-Mo-S phase on the surface. The present study tried to apply ^{129}Xe NMR spectroscopy to analysis of sulfided Co-Mo/Al₂O₃ catalyst.

Figure 7 shows ^{129}Xe NMR spectra of various catalysts or dried Al₂O₃ under 120 kPa xenon pressure at ambient temperature. All catalysts were sulfided at 673 K and then utilized for the ^{129}Xe NMR measurement. For the Mo/Al₂O₃ catalyst (Mo: 13 mass%) and the Co/Al₂O₃ catalyst (Co: 3.3 mass%), a single peak was observed at 124 ppm and 105 ppm, respectively. The downfield shift of the peak is mainly caused by increased collisions between xenon and other atoms in the micropore¹²⁾. In this case, the diffusion of xenon is more restricted in the Mo/Al₂O₃ catalyst than that in the Co/Al₂O₃ catalyst. This result roughly corresponds with the observation that the peak of the Mo/Al₂O₃ catalyst was broader than that of the Co/Al₂O₃ catalyst. Broadening of a NMR peak generally represents a wider distribution of molecular environments and arises from increased irregularity in collisions between xenon and other atoms²⁵⁾. Therefore, xenon collides with other atoms such as MoS₂ crystallites on the surface more frequently and more irregularly in the Mo/Al₂O₃ catalyst, compared to the Co/Al₂O₃ catalyst. In other words, the effect of MoS₂ crystallites is larger than that of Co₉S₈ on the diffusion of xenon on the surface.

For a weight-balanced mixture of Mo/Al₂O₃ catalyst and Co/Al₂O₃ catalyst, two peaks were observed at 103 ppm and 127 ppm. The chemical shift of each peak was nearly equal to that of the Mo/Al₂O₃ catalyst or the Co/Al₂O₃ catalyst. This result implies that the downfield peak should be attributed to the Mo/Al₂O₃

1: 20 kPa; 2: 33 kPa; 3: 60 kPa; 4: 87 kPa; 5: 120 kPa.

Fig. 8 ^{129}Xe NMR Spectra of the Sulfided Mixture of $\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{Co}/\text{Al}_2\text{O}_3$ under Various Xenon Pressures

catalyst and the other peak to the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst. In addition, the appearance of the two peaks demonstrates that xenon atoms adsorbed on the $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst undergo little exchange with those adsorbed on the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst during the NMR measurement time (less than about 0.1 ms). In other words, the NMR measurement time is not long enough for exchange between xenon atoms adsorbed on each catalyst. On the other hand, only one peak was observed at 155 ppm for a $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalyst (Co: 2.2 mass%, Mo: 13 mass%). This result shows that cobalt is in close proximity to molybdenum on the surface. In other words, xenon interacts with both cobalt and molybdenum during the NMR measurement time, which represents rapid exchange of xenon atoms on the $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalyst, and as a result the observable peaks merge. However, the chemical shift of the peak moved further downfield compared with the mean position of the two peaks observed for the mixture. This observation suggests a remarkable change in the magnetic property due to the coexistence of cobalt with molybdenum and will be further discussed in the following sections.

Figure 8 shows the ^{129}Xe NMR spectra of the sulfided mixture under various xenon pressures. The upfield peak attributed to the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst became gradually smaller than the downfield peak attributed to the $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst with decreased xenon pressure. In particular, at less than 33 kPa, the relative intensity of the upfield peak obviously decreased in comparison with the downfield peak. This behavior is mainly caused by the difference in adsorption interactions between xenon and other atoms on the surface. In general, lower xenon pressure favors the stronger interactions between xenon and adsorption sites. Therefore, xenon tended to be adsorbed on the $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst rather than on the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst in the mixture, and as a result the peak attributed to the $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst was

Fig. 9 ^{129}Xe NMR Spectra of Sulfided $\text{Co-Mo}/\text{Al}_2\text{O}_3$ Catalysts with Various Cobalt Loadings under 120 kPa Xenon Pressure

larger at low xenon pressures. In other words, xenon has a stronger electronic interaction with CUS on the edge of MoS_2 crystallites on the $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst rather than with Co_9S_8 on the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst.

Figure 9 shows ^{129}Xe NMR spectra of sulfided $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalysts with various cobalt loadings (0–7.3 mass%) under 120 kPa xenon pressure at ambient temperature. The molybdenum loading was almost constant (*ca.* 13 mass%) and the Co/Mo ratio was 0 to 0.99. The observed peak gradually shifted downfield with the cobalt loading except for the highest cobalt loading (7.3 mass%). This downfield shift of the peak demonstrated that the addition of cobalt greatly affected the electronic condition of xenon adsorbed on the surface. However, the peak width was almost constant at all cobalt loadings. The peak width is closely related with irregularity in collisions between xenon and other atoms. Therefore, the irregularity in the diffusion of xenon on the surface was little affected by the cobalt loading, in contrast with the findings that increased molybdenum loading caused both downfield shift and broadening of the peak⁸⁾.

Figure 10 shows the δ - N plots of these catalysts. As for the sulfided $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts (**Fig. 2**), δ varied nonlinearly at low N and did not increase with higher N at all. This observation demonstrates that δ_{Xe} can be considered as negligible in Eq. (1) and as a result the δ - N plots of these catalysts can be represented as Eq. (4). In the case of sulfided $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalyst, the nonlinear variation in the δ - N plots, *i.e.*, the growth of δ_{E} , is presumably caused by electronic interactions between xenon and CUS on the edge of MoS_2 crystallites.

To elucidate the effect of Co_9S_8 on ^{129}Xe NMR spectroscopy in detail, the present study investigated $\text{Co}/\text{Al}_2\text{O}_3$ catalysts with various cobalt loadings (0–7.7 mass%). **Figure 11** shows ^{129}Xe NMR spectra of sulfided $\text{Co}/\text{Al}_2\text{O}_3$ catalysts under 120 kPa xenon pressure at ambient temperature. At 0.8 mass%, the observed peak shifted about 20 ppm further downfield than at 0 mass%, *i.e.*, dried Al_2O_3 , and was little changed at more than 2.4 mass%. This behavior is quite dif-

Values indicate cobalt loading on the catalysts.

Fig. 10 δ - N Plots Obtained from ^{129}Xe NMR Spectra of Sulfided Co-Mo/ Al_2O_3 Catalysts with Various Cobalt Loadings

Fig. 11 ^{129}Xe NMR Spectra of Sulfided Co/ Al_2O_3 Catalysts with Various Cobalt Loadings under 120 kPa Xenon Pressure

ferent from the sulfided Co-Mo/ Al_2O_3 catalysts (Fig. 9) and strongly suggests that the state of cobalt is affected by whether molybdenum is present on the surface.

Figure 12 shows the δ - N plots of the sulfided Co/ Al_2O_3 catalysts and the dried Al_2O_3 . For the sulfided Co/ Al_2O_3 catalysts, δ varied nonlinearly at low N , whereas δ was almost constant against N for dried Al_2O_3 . The nonlinear variation of δ at low N represents increase of δ_E and is caused by strong interactions between xenon and adsorption sites. Since the sulfided Co/ Al_2O_3 catalyst generally contains few CUS, cobalt species such as Co_9S_8 presumably functioned as strong adsorption sites and had strong electronic interaction with xenon. In addition, at more than 2.4 mass%, the δ - N plot little changed against the cobalt loading. This behavior almost corresponds with the previous result (Fig. 11) and suggests a large difference in the state of cobalt between sulfided Co/ Al_2O_3 catalyst and sulfided Co-Mo/ Al_2O_3 catalyst.

Similarly for the sulfided Mo/ Al_2O_3 catalyst, δ_0 was calculated by fitting the δ - N plot of the sulfided cobalt catalysts (Figs. 10 and 12) into Eq. (4). Figure 13 shows the relationship between δ_0 and cobalt loading for these catalysts. For the sulfided Co-Mo/ Al_2O_3 catalyst, δ_0 became gradually larger with cobalt loading

■ : Co 0 mass% (dried Al_2O_3); ▲ : Co 0.8 mass%; ◆ : Co 2.4 mass%; □ : Co 3.9 mass%; △ : Co 5.8 mass%; ○ : Co 7.7 mass%.

Fig. 12 δ - N Plots Obtained from ^{129}Xe NMR Spectra of Sulfided Co/ Al_2O_3 Catalysts

Fig. 13 Relationship between δ_0 Obtained from δ - N Plots and the Cobalt Loading for Sulfided Co-Mo/ Al_2O_3 Catalysts and Sulfided Co/ Al_2O_3 Catalysts

and reached the maximum value at 5.7 mass%. δ_0 slightly decreased at 7.3 mass%. On the other hand, for sulfided Co/ Al_2O_3 catalyst, δ_0 increased from 0 mass% to 2.4 mass%, and was almost constant at more than 2.4 mass%. Therefore, the behavior of δ_0 against cobalt loading for sulfided Co-Mo/ Al_2O_3 catalyst is quite different from that for sulfided Co/ Al_2O_3 catalyst. The present study tried to investigate this observation further on the basis of the following interpretation. Only one type of Al_2O_3 was used as a catalyst support for these cobalt catalysts. This fact implies that the difference in the surface structure of Al_2O_3 between these catalysts is negligible and therefore δ_W is almost constant for all these cobalt catalysts.

δ_A is dependent on the collisions between xenon and other molecules on the surface. In the case of sulfided Mo/ Al_2O_3 catalyst, the MoS_2 crystallites on the surface are the main contributor to δ_A . In this study, the molybdenum loading of the sulfided Co-Mo/ Al_2O_3 cata-

Fig. 14 XRD Patterns of Sulfided Co/Al₂O₃ Catalysts with Various Cobalt Loadings

lysts was almost constant (*ca.* 13 mass%). In addition, our previous XPS study demonstrated that the sulfidation degree of molybdenum on the surface little changes with the cobalt loading⁹⁾. These findings strongly suggest that there is little difference in the formation of MoS₂ crystallites on the surface between sulfided Co-Mo/Al₂O₃ catalysts, and corresponds to the preparation of all Co-Mo/Al₂O₃ catalysts in this study by adding cobalt to only one type of Mo/Al₂O₃ catalyst. Therefore, δ_A is almost constant against cobalt loading for the sulfided Co-Mo/Al₂O₃ catalyst.

For the sulfided Co/Al₂O₃ catalysts, the cobalt loading is closely related to the amount of Co₉S₈ formed on the surface. In fact, XRD (X-ray diffraction) patterns of the sulfided Co/Al₂O₃ catalysts (**Fig. 14**) showed that the two peaks attributed to Co₉S₈ were remarkably larger at more than 3.9 mass%, which indicates the formation of Co₉S₈. Therefore, the number of collisions between xenon and Co₉S₈ on the surface probably increased with the cobalt loading. In the case of sulfided Mo/Al₂O₃ catalyst, higher molybdenum loading causes more collisions between xenon and MoS₂ crystallites and thus δ_A increased⁸⁾. However, δ_0 was almost constant at more than 2.4 mass%. If the number of collisions between xenon and Co₉S₈ has a great effect on δ_A , δ_0 should become larger with cobalt loading, in particular, at high cobalt loadings. Therefore, this result implies that more collisions between xenon and Co₉S₈ cause little increase in δ_A . In other words, δ_A is almost independent of the formation of Co₉S₈ on the surface.

On the basis of the above findings, we suggest that neither δ_w nor δ_A changes with the cobalt loading for these cobalt catalysts. Therefore, the behavior of δ_0 against the cobalt loading (**Fig. 13**) is mostly caused by δ_M . δ_M arises from differences in the magnetic susceptibility between the external reference and the sample. In the case of the cobalt catalyst, the chemical state of cobalt greatly contributes to δ_M . XRD showed that Co₉S₈ is generally formed by the sulfidation of Co/Al₂O₃ catalysts. Since δ_0 is almost constant at high

Fig. 15 XRD Patterns of Sulfided Co-Mo/Al₂O₃ Catalysts with Various Cobalt Loadings

cobalt loadings, the formation of Co₉S₈ caused little increase of δ_M . This result is closely related to the previous findings that the magnetic susceptibility of Co₉S₈ is extremely low and so makes few significant contributions to the magnetic moments^{6),26)}. In contrast, for the sulfided Co-Mo/Al₂O₃ catalyst, δ_0 was sensitive to the cobalt loading. This observation mainly reflects the variation of δ_M that arises from the magnetic susceptibility. Previous studies have reported that the Co-Mo-S phase indicates antiferromagnetism^{4)~6)}. In general, growth of antiferromagnetic compounds increases the magnetic susceptibility. Therefore, the antiferromagnetic Co-Mo-S phase is formed on the surface, and as a result the magnetic susceptibility becomes larger, which directly contributes to the increase of δ_M . In other words, the increase of δ_0 with cobalt loading is closely related to the formation of the antiferromagnetic Co-Mo-S phase, because δ_0 is mostly dependent on δ_M for these cobalt catalysts.

Figure 15 shows the XRD patterns of the sulfided Co-Mo/Al₂O₃ catalysts with various cobalt loadings. The two peaks attributed to Co₉S₈ were weak at 5.7 mass% and became remarkably stronger at 7.3 mass%, but did not appear at less than 3.8 mass%. This result demonstrates that Co₉S₈ was formed on the surface at more than 5.7 mass%. We consider that the formation of Co₉S₈ is closely related to the slight decrease of δ_0 at 7.3 mass% (**Fig. 13**). The formation of the Co-Mo-S phase causes increased magnetic susceptibility that greatly affects δ_M . As mentioned above, the effect of Co₉S₈ on δ_0 is negligible because δ_0 for the sulfided Co/Al₂O₃ catalyst is almost constant at high cobalt loading. Therefore, we deduce that the slight decrease of δ_0 for the sulfided Co-Mo/Al₂O₃ catalyst is mainly caused by the formation of Co₉S₈ prior to that of the Co-Mo-S phase. At high cobalt loadings, Co₉S₈ becomes the dominant cobalt species at the expense of the Co-Mo-S phase^{2),27)}. In other words, selective formation of Co₉S₈ causes a decrease of the Co-Mo-S phase, and as a result, δ_M that greatly contributes to δ_0 becomes smaller at high cobalt loadings.

Fig. 16 Relationship between δ_0 Obtained from δ - N Plots and Relative Hydrodesulfurization Activity for Various Co-Mo/Al₂O₃ Catalysts

Therefore, δ_0 measured by ^{129}Xe NMR spectroscopy is a sensitive parameter for the amount of the Co-Mo-S phase.

Finally, the relationship between δ_0 and the relative hydrodesulfurization activity of various Co-Mo/Al₂O₃ catalysts is shown in Fig. 16. The relative activity of the catalysts was roughly correlated with δ_0 , whereas both the physical properties and the metal contents were different between these catalysts. This result demonstrates that δ_0 reflects the state of active sites such as the Co-Mo-S phase. In particular, the relative activity became remarkably larger at $\delta_0 > 180$ ppm. This behavior was mainly caused by differences in the specific activity between the Co-Mo-S phase (Type I) and the Co-Mo-S phase (Type II). Previous studies reported that the specific activity of the Co-Mo-S phase (Type II) was much higher than that of the Co-Mo-S phase (Type I)^{28)~30)}. On the other hand, δ_M is mainly dependent on the amount of the Co-Mo-S phase, regardless of the type of the Co-Mo-S phase. Therefore, the remarkable increase in relative activity at $\delta_0 > 180$ ppm probably reflects formation of the Co-Mo-S phase (Type II) rather than the Co-Mo-S phase (Type I). These findings suggest that ^{129}Xe NMR spectroscopy is useful for evaluation of the Co-Mo-S phase on sulfided Co-Mo/Al₂O₃ catalysts.

5. Conclusions

The present study investigated application of ^{129}Xe NMR spectroscopy to analysis of Co-Mo/Al₂O₃ hydrodesulfurization catalyst. We reconsidered the conventional interpretation of ^{129}Xe NMR spectroscopy for zeolite micropores. For sulfided Mo/Al₂O₃ catalyst, the chemical shift δ of the observed ^{129}Xe NMR peak varied nonlinearly against the amount of adsorbed xenon N . In particular, the curvature of the δ - N plot became larger after sulfidation at more than 473 K. In contrast, for dried Mo/Al₂O₃ catalyst, δ was almost con-

stant against N . This result implies that nonlinear variation of δ with N is mainly caused by electronic interactions between xenon and CUS on the edge of MoS₂ crystallites. In addition, the term of the xenon diffusibility δ_0 was calculated from the relationship between δ and N based on the assumption that xenon atoms seldom collide with each other in a micropore. δ_0 gradually increased with sulfidation temperature and approached the maximum value at more than 673 K. This result generally corresponds to the sulfidation state of molybdenum analyzed by XPS, and demonstrates that δ_0 is closely related to the formation of MoS₂ crystallites on the surface. Increased molybdenum loading also caused nonlinear variation of δ against N and gradual increase of δ_0 . This result also suggests that the formation of MoS₂ crystallites has a great effect detectable by ^{129}Xe NMR spectroscopy.

For sulfided Co-Mo/Al₂O₃ catalyst, δ_0 became gradually larger with higher cobalt loading and reached the maximum value at 5.7 mass%. δ_0 slightly decreased at 7.3 mass%. On the other hand, for sulfided Co/Al₂O₃ catalyst, δ_0 increased from 0 mass% to 2.4 mass%, and was almost constant at more than 2.4 mass%. Therefore, the behavior of δ_0 with cobalt loading is dependent on whether molybdenum is present on the surface, mainly due to differences in the magnetic susceptibility between Co-Mo/Al₂O₃ catalyst and Co/Al₂O₃ catalyst after sulfidation. In other words, formation of antiferromagnetic Co-Mo-S phase on sulfided Co-Mo/Al₂O₃ catalyst causes increased magnetic susceptibility that greatly affects δ_0 . The slight decrease of δ_0 at 7.3 mass% for sulfided Co-Mo/Al₂O₃ catalyst is closely related to the formation of Co₉S₈ prior to that of the Co-Mo-S phase. Therefore, Co₉S₈ tends to be formed at the expense of the Co-Mo-S phase at high cobalt loadings. These findings strongly suggest that δ_0 obtained from ^{129}Xe NMR spectroscopy is a sensitive measurement of the amount of the Co-Mo-S phase. Furthermore, the relative hydrodesulfurization activity of various Co-Mo/Al₂O₃ catalysts roughly correlated with δ_0 . This result demonstrates that δ_0 reflects the state of the active sites such as the Co-Mo-S phase. In particular, the relative activity became remarkably higher at $\delta_0 > 180$ ppm. We consider that this behavior mainly represents the formation of the Co-Mo-S phase (Type II) rather than the Co-Mo-S phase (Type I). Therefore, ^{129}Xe NMR spectroscopy is useful for evaluation of the Co-Mo-S phase on Co-Mo/Al₂O₃ hydrodesulfurization catalyst.

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要 旨

¹²⁹Xe NMR 法による Co-Mo/Al₂O₃ 水素化脱硫触媒のキャラクタリゼーション

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本研究では、¹²⁹Xe NMR 法を Co-Mo/Al₂O₃ 水素化脱硫触媒の解析に応用する検討を行った。この応用に際しては、ゼオライト細孔解析に用いられている従来の¹²⁹Xe NMR 法の解釈を再考した。硫化 Mo/Al₂O₃ 触媒では、観測された¹²⁹Xe NMR ピークの化学シフト δ が Xe 吸着量 N に対して非直線的に変化した。対照的に、乾燥処理した触媒では、 δ は N に対してほぼ一定であった。この結果は、 δ の N に対する非直線的な変化が Xe と MoS₂ 結晶のエッジに存在する配位不飽和サイトとの電子的な相互作用に主に起因していることを示唆している。さらに、¹²⁹Xe NMR スペクトルにより算出した Xe の拡散状態に起因する項 δ_0 は、硫化温度に伴って徐々に増加し、673 K 以上で最大値に近づいた。この結果は、 δ_0 が表面上における MoS₂ 結晶の形成と密接に関連していることを示している。また、硫化 Co-Mo/Al₂O₃ 触媒では、 δ_0 が Co 担持量に伴って徐々に大きく

なり、5.7 mass% で最大値に達した。これに対して、硫化 Co/Al₂O₃ 触媒では、 δ_0 は 0 mass% から 2.4 mass% で増加し、2.4 mass% 以上ではほぼ一定となった。この結果は、主に硫化後における Co-Mo/Al₂O₃ 触媒と Co/Al₂O₃ 触媒での磁化率の差異に起因している。すなわち、反強磁性的な Co-Mo-S 相の形成が、 δ_0 に大きな影響を及ぼす磁化率の増大を引き起こしている。また、硫化 Co-Mo/Al₂O₃ 触媒における 7.3 mass% での δ_0 のわずかな減少は、Co-Mo-S 相よりも Co₉S₈ が選択的に形成されることと密接に関連している。これらの検討結果は、¹²⁹Xe NMR 法より得られる δ_0 が Co-Mo-S 相の量に敏感なパラメータであることを強く示唆している。さらに、種々の Co-Mo/Al₂O₃ 触媒の相対脱硫活性が δ_0 とおおむね相関した。この結果もまた、¹²⁹Xe NMR 法が Co-Mo/Al₂O₃ 水素化脱硫触媒上の Co-Mo-S 相の解析に有用であることを示している。