Development of Highly Active Hydrodesulfurization Catalysts and Effective Usage of Hydrogen Sulfide

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This paper deals with the author's systematic studies concerning development of highly active hydrodesulfurization catalysts and effective usage of hydrogen sulfide produced in the hydrodesulfurization process. The author and associates found that reduced metal ion-exchanged Y zeolites (Me°Y) such as Ni°Y and Co°Y have tremendous possibilities as highly active hydrodesulfurization catalysts for treatment of petroleum feedstocks. The author also revealed that hydrogen sulfide has some possibilities for effective usage in the production of hydrogen, and as hydrogen donating agent for unsaturated hydrocarbons, promoter for certain kinds of heterogeneous catalytic reactions and modifying agent for solid surfaces, and so forth.

1. Introduction

Hydrodesulfurization of petroleum feedstocks is one of the important processes in the petroleum industry to produce clean fuels. $\text{CoMo}/\text{Al}_2\text{O}_3$ and $\text{NiMo}/\text{Al}_2\text{O}_3$ catalysts have been widely used in hydrodesulfurization process of petroleum. However, recently, the development of catalysts for hydrodesulfurization of petroleum, which are much more active than $\text{CoMo}/\text{Al}_2\text{O}_3$ and $\text{NiMo}/\text{Al}_2\text{O}_3$ catalysts, have been claimed in the petroleum industry to produce lower sulfur content fuels, prompted by serious problems of air pollution by SO_x (and NO_x) caused by burning fossil fuels, which are being aggravated on global scale.

On the other hand, in the hydrodesulfurization process of petroleum, large amounts of hydrogen sulfide are produced, which are finally converted into elementary sulfur and water by Claus process. Since hydrogen sulfide formed in the hydrodesulfurization process is wasted as effluent, the possibilities of the effective usage of hydrogen sulfide would become of great importance from an economic view point.

The author and associates have been systematically investigating the catalytic hydrodesulfurization of organic sulfur compounds over various solid catalysts in order to develop highly active hydrodesulfurization catalysts and, also, the effective usage of hydrogen sulfide, including the recovery of hydrogen from hydrogen sulfide using heterogeneous catalytic technique.

This paper describes the results of our systematic studies, with respect to the development of highly active hydrodesulfurization catalysts and the effective

usage of hydrogen sulfide as a total system embodying hydrodesulfurization process of petroleum.

2. Development of Highly Active Hydrodesulfurization Catalysts

2.1 Catalytic Activity of Reduced Metal Y Zeolites for Hydrodesulfurization of Thiophene

The author and associates have studied catalytic cracking of organic sulfur compounds such as aliphatic thiols and sulfides over various solid catalysts to clarify effective catalysts for the cracking of organic sulfur compounds. We found that solid acid catalysts such as silica-alumina, alumina, solid phosphoric acid, metal fluorides and zeolites were effective for the cracking of organic sulfur compounds^{1)~14)}. We, therefore, concluded that solid acid catalysts are effective for the cracking of organic sulfur compounds and that acid site of solid acid catalysts acts as active site for the cracking of organic sulfur compounds. Furthermore, we found that nickel or molybdenum supported on acidic carriers such as silica-alumina and alumina showed high catalytic activity for the hydrodesulfurization of thiophene^{15)~17)}. From these results, we concluded that bifunctional catalysts, which have the nature of both metal and solid acid catalysts, are effective for hydrodesulfurization of thiophene, and high dispersion of metal particles is also an important factor of highly active hydrodesulfurization catalysts. The author and associates focused attention to reduced metal ion-exchanged Y zeolites (Me°Y).

It is generally accepted that the metal ions in MeY zeolites are reduced by hydrogen into highly

dispersed zero valent metal particles, which form a new acidic hydroxyl groups, *i.e.*, Brönsted acid site, according to the following equation:

where $(\text{O}^--\text{Zeol})_x$ and $\text{H}^+\text{O}^--\text{Zeol}$ represent the zeolite lattice and the surface acidic hydroxyl groups, respectively.

Since it has been revealed that the reduced MeY zeolites (Me^0Y) act as bifunctional catalysts in hydrocracking of hydrocarbons, we expected that reduced MeY zeolites would also act as effective hydrodesulfurization catalysts for removal of organic sulfur compounds. Thus, we investigated the hydrodesulfurization of thiophene over various Me^0Y zeolites for the purpose of development of highly active hydrodesulfurization catalysts for treatment of petroleum feedstocks¹⁸⁾⁻²³⁾.

The catalytic activities of reduced MeY zeolites in the hydrodesulfurization of thiophene were examined at 400 °C using the pulse reaction method. The catalytic activities of various Me^0Y zeolites for the hydrodesulfurization of thiophene at 400 °C are shown in Fig. 1. It was found that some of the Me^0Y zeolites such as Ni^0Y , Co^0Y , Ag^0Y and Cu^0Y were active in the hydrodesulfurization of thiophene. The products of hydrodesulfurization of thiophene over these Me^0Y zeolites consisted of hydrogen sulfide and low molecular weight hydrocarbons such as methane,

ethylene, propylene, butenes and butanes. The order of maximal catalytic activity of Me^0Y was as follows:

The catalytic activities of Me^0Y zeolites except those of Co^0Y decreased gradually as pulse number progressed. For hydrodesulfurization of thiophene over Co^0Y , the maximal activity was observed at some pulse number after the first pulse. However, the initial activity of Co^0Y at the first pulse was remarkably enhanced by pretreatment with 2 ml of hydrogen sulfide as shown in Fig. 1. This result is closely related to the activity of MeY zeolites enhanced by pretreatment with hydrogen sulfide in acid-catalyzed reactions described in later section 3.4. The order of catalytic activity of Me^0Y matches the order of H_2 -adsorptive ability of these metals, excepting iron and chromium. It was, therefore, found that the catalytic activity of Me^0Y for hydrodesulfurization of thiophene is mainly controlled by the difference in H_2 -adsorptive ability of metals in Me^0Y zeolites.

On the other hand, we examined the activity of hydrogen Y zeolite (HY) for the desulfurization of thiophene at 400 °C¹⁹⁾. The result was positive. The main desulfurization product was hydrogen sulfide, but a trace amount of unidentified carbonaceous compound had also formed. The conversion of thiophene on HY decreased as the pulse number progressed, and finally it became zero as shown by dotted line in Fig. 1. This result indicates that the Brönsted acid site acts as another active site in hydrodesulfurization of thiophene over reduced MeY zeolites. The author and associates concluded, therefore, that both H_2 -adsorptive ability of metals and the Brönsted acid site are necessary for highly active Me^0Y hydrodesulfurization catalysts.

The catalytic activity of Me^0Y zeolites in the hydrodesulfurization of thiophene decreased as pulse number progressed. The decreased catalytic activity of Me^0Y , relative to pulse number, was regenerated by calcination at 500 °C in an oxygen stream. This result indicates that the cause of catalyst deactivation of Me^0Y with progression of pulse number is the accumulation of carbonaceous deposits on the catalyst surface. The catalyst deactivation of Ni^0Y and Co^0Y with progress of pulse number was remarkably improved by increasing calcination temperature of NiY and CoY in air prior to reduction. NiY and CoY calcined at 800 °C showed no catalytic activity, however, because crystal structure of zeolite had

Fig. 1 Catalytic Activities of Reduced Metal Y Zeolites (Me^0Y) for Hydrodesulfurization of Thiophene at 400 °C (Numbers in parentheses represent the percentage of ion-exchange.)

Fig. 2 Comparison of Catalytic Activities of Ni°Y and Co°Y with Those of Various Kinds of Catalysts for Hydrodesulfurization of Thiophene at 400°C

been destroyed.

Since Ni°Y and Co°Y calcined at 700 °C and 600 °C (Ni°Y-700 and Co°Y-600), respectively, showed high and relatively stable catalytic activity in hydrodesulfurization of thiophene, the catalytic activities of these two Me°Y zeolites were compared with those of nickel and molybdenum catalysts supported on silica-alumina (Ni-SiO₂·Al₂O₃ and Mo-SiO₂·Al₂O₃) and commercially available CoMo/Al₂O₃ catalysts (Girdler G-35 and Ketjenfine K-125) to explore the possibility of utilizing the Me°Y zeolites as industrial hydrodesulfurization catalysts. The activities of various solid catalysts for hydrodesulfurization of thiophene under same experimental conditions are shown in Fig. 2. It was found that the Ni°Y-700 and Co°Y-600 showed higher catalytic activities than those of Ni-SiO₂·Al₂O₃, Mo-SiO₂·Al₂O₃ and commercially available Mo based hydrodesulfurization catalysts, as shown in Fig. 2²⁰. From these results, the author and associates concluded that there is a possibility of using Me°Y zeolites as highly active hydrodesulfurization catalysts for the treatment of petroleum feedstocks.

2.2 Mechanism of Hydrodesulfurization of Thiophene over Me°Y Zeolites

It was found that Ni°Y and Co°Y zeolites showed high catalytic activity in the hydrodesulfurization of thiophene. We investigated the mechanism of the hydrodesulfurization of thiophene over reduced NiY and CoY zeolites by use of infrared spectroscopic method^{21)~23)}.

The infrared spectra of thiophene adsorbed on reduced NiY at room temperature followed by

(a) NiY reduced at 450°C for 2 h. Ni°Y after thiophene adsorption at room temperature followed by evacuation at (b) room temp., (c) 120°C, (d) 200°C, (e) 300°C, (f) 400°C

Fig. 3 Effect of Heating on Infrared Spectra of Thiophene Adsorbed on Ni°Y

evacuation at different temperatures as shown in Fig. 3. A marked decrease in intensity of the strong band of acidic hydroxyl group at 3,640 cm⁻¹ was observed by adsorption of thiophene as shown in the spectra(b). It was revealed that there is strong interaction between acidic hydroxyl group on reduced NiY surface and adsorbed thiophene. In the spectra(b), the absorption band of stretching vibration of unsaturated (=CH-) and saturated (-CH₂-) of C-H groups at 3,100 cm⁻¹ and 2,960 cm⁻¹ and deformation vibration of C-H group at 1,450, 1,430 and 1,395 cm⁻¹ were observed. On the other hand, a strong band appeared at 1,620 and 1,495 cm⁻¹ in the adsorption of thiophene. These bands were assigned to the out-of-plane mode of C-H group of adsorbed thiophene ring and C=S double bond. As the evacuation temperature increased, intensities of following absorption bands of C=S double bond at 1,495 cm⁻¹, out-of-plane mode of C-H group in thiophene ring at 1,620 cm⁻¹, and C-H groups at 3,100, 2,960, 1,450, 1,430, 1,395 cm⁻¹ decreased, but a large and broad band near 1,580 cm⁻¹ had appeared. The broad band near 2,580 cm⁻¹ was assigned to the precursor of carbonaceous deposit, probably polyene species $\{CH=CH\}_n$ which result from polymerization of diene species. The band of hydroxyl group which disappeared at 3,640 cm⁻¹ by adsorption of thiophene had gradually regenerated as evacuation temperature was raised as shown in the spectra (c)–(f).

From the results of the infrared spectra of thiophene adsorbed on reduced NiY zeolite, we concluded that reaction mechanism in hydrodesulfurization of thiophene on reduced MeY zeolites is represented as shown below:

By this mechanism, thiophene is adsorbed on reduced Me^oY zeolites by strong interaction with acidic hydroxyl group, maintaining a planar structure. The acidic hydroxyl group, *i.e.*, Brönsted acid site, acts as the active site for cleavage of the C-S bond of the thiophene ring to form a reaction intermediate with C=S double bond like S=C=CH-CH=CH₂. Hydrogen is independently adsorbed dissociatively on the metal or metal sulfide particles. The adsorbed species with C=S double bond are hydrogenated or hydrocracked to form hydrogen sulfide and various hydrocarbon products such as methane, ethylene, propylene, butenes and butanes by the attack of hydrogen atom dissociated on metal or metal sulfide particles.

On the basis of this mechanism, much more active Me^oY catalysts for usage in the hydrodesulfurization of petroleum feedstocks could be prepared by loading metal or metal particles with high dispersion, which are extremely effective in hydrogenation of hydrocarbon species, in the presence of hydrogen sulfide, on strongly acidic zeolites.

3. Effective Usage of Hydrogen Sulfide

3.1 Recovery of Hydrogen by Catalytic Decomposition of Hydrogen Sulfide

Recently, some attempts have been made to recover hydrogen from hydrogen sulfide by catalytic decomposition of hydrogen sulfide³⁵⁾. It has been revealed that only MoS₂ and WS₂ act as catalyst in the decomposition of hydrogen sulfide³⁸⁾.

The author and associates investigated the decomposition of hydrogen sulfide over various MoS₂ based catalysts, using closed circulation system, to develop effective catalysts for recovery of hydrogen from hydrogen sulfide^{24)~26)}. The catalytic decomposition of hydrogen sulfide over various supported MoS₂ catalysts at 500 °C is shown in **Fig. 4**. It was found that MoS₂ supported on alumina showed the highest activity in the decomposition of hydrogen sulfide, and alumina was the most effective as carrier for MoS₂ catalyst.

(a): MoS₂/γ-Al₂O₃, (b): MoS₂/α-Al₂O₃, (c): MoS₂/quartz, (d): MoS₂/NaY, (e): MoS₂/γ-Al₂O₃-K

Fig. 4 Decomposition of Hydrogen Sulfide over Various Supported MoS₂ Catalysts at 500°C

(a): CoMo/Al₂O₃, (b): NiMo/Al₂O₃, (c): Mo/Al₂O₃, (d): quartz

Fig. 5 Decomposition of Hydrogen Sulfide over Mo Based Hydrodesulfurization Catalysts at 500°C

The catalytic decomposition of hydrogen sulfide over various commercially available Mo based hydrodesulfurization catalysts is shown in **Fig. 5**. It was revealed that sulfided CoMo/Al₂O₃ catalyst was effective in the recovery of hydrogen from hydrogen sulfide by the catalytic decomposition of hydrogen sulfide.

The author and associates also studied in more detail the catalytic decomposition of hydrogen sulfide over MoS₂ at 500 °C, in order to clarify the mechanism of catalytic decomposition of hydrogen sulfide over MoS₂ based catalysts. The catalytic decomposition of hydrogen sulfide over MoS₂ at 500 °C is shown in **Fig. 6**. Only slight increase of pressure of hydrogen over quartz sand at 500 °C was observed as shown in **Fig. 6**. The pressure of hydrogen, however, remarkably increased with

reaction time, it was observed, in the decomposition of hydrogen sulfide over MoS_2 evacuated at 500°C . The catalytic activity of MoS_2 was much greater enhanced by reduction with hydrogen at 500°C as shown in Fig. 6. The catalytic activity of MoS_2 was further enhanced with a raise in the reduction temperature as shown in Fig. 7. From these results, we concluded that coordinatively unsaturated site of MoS_2 , formed by evacuation or reduction at high temperatures, acts as the active site for the decomposition of hydrogen sulfide. On the basis of this conclusion, the authors advanced the following reaction mechanism in the catalytic decomposition of hydrogen sulfide over MoS_2 :

Fig. 6 Decomposition of H_2S over MoS_2 Catalyst at 500°C

Fig. 7 Effect of Reduction Temperature on the Catalytic Activity of MoS_2 for the Decomposition of H_2S

The authors also advanced a similar reaction mechanism for the decomposition of hydrogen sulfide over sulfided $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst, in which alumina and cobalt sulfide in the catalyst system act as promoter for MoS_2 ²⁶⁾.

3.2 Catalytic Hydrogenation of Olefins with Hydrogen Sulfide

The author and associates investigated the hydrogenation of olefins with hydrogen sulfide over sulfided $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst by use of a closed circulation system in order to develop alternative effective usage of hydrogen sulfide²⁷⁾.

The reaction of 1,3-butadiene with hydrogen sulfide at 200°C is shown in Fig. 8. It was found that hydrogenation of 1,3-butadiene to form various butene isomers occurred at 200°C . Butane was not formed, however, even after all 1,3-butadiene in gas phase had been completely consumed. This is unique phenomenon observed in the hydrogenation of 1,3-butadiene with hydrogen sulfide, as compared with hydrogenation of hydrogen.

The reaction of propylene with hydrogen sulfide at 400°C is shown in Fig. 9. Substantial amount

1,3-C₄H₆=25 Torr, H₂S=50 Torr

Fig. 8 Hydrogenation of 1,3-Butadiene with Hydrogen Sulfide over Sulfided $\text{Mo}/\text{Al}_2\text{O}_3$ Catalyst at 200°C

Fig. 9 Hydrogenation and Hydrogenolysis of Propylene with Hydrogen Sulfide over Sulfided Mo/Al₂O₃ Catalyst at 400°C

of propane and small amounts of methane and ethane were formed. These indicate that main reaction of propylene with hydrogen sulfide is hydrogenation of propylene, but the hydrogenolysis of propylene or propane also slightly proceeds at high temperatures. It was revealed that hydrogen sulfide acts as a hydrogen donating agent for olefins in the reaction of olefins with hydrogen sulfide over sulfided Mo/Al₂O₃ catalyst.

In the previous section 3.1, the author and associates described that the coordinatively unsaturated site on MoS₂ surface acts as active site for catalytic decomposition of hydrogen sulfide. Thus, the author and associates concluded that the coordinatively unsaturated site of MoS₂ in the sulfided Mo/Al₂O₃ catalyst also acts as active site for the hydrogenation of olefins with hydrogen sulfide. We advanced the following mechanism for the hydrogenation of olefins with hydrogen sulfide over sulfided Mo/Al₂O₃ catalyst:

On the other hand, the hydrogenolysis of propylene also proceeded in the reaction of propylene with hydrogen sulfide over sulfided Mo/Al₂O₃ catalyst at 400 °C. It is supposed that

(a): without H₂S, (b): with H₂S, (c): without H₂S after evacuation at 500°C for 2 h

Fig. 10 Effect of Addition of Hydrogen Sulfide on the Catalytic Activity of Various Na Zeolites for the Cracking of *n*-Butane at 500°C

the hydrogenolysis of propylene at an elevated temperature is attributed to the attack of hydrogen radical or active hydrogen formed by the decomposition of hydrogen sulfide over MoS₂ surface, as in the case of liquefaction of coal with hydrogen sulfide over iron sulfide catalyst³⁸.

3.3 Promotive Effect of Hydrogen Sulfide for Hydrocarbon Conversions over Heterogeneous Catalysts

Recently, it has been revealed that some heterogeneous catalytic reactions are remarkably promoted by the presence of hydrogen sulfide³⁹. The author and associates studied the promotional effect of hydrogen sulfide on the cracking of *n*-butane over sodium zeolites (NaZ, Z=X, Y and A). It was found that hydrogen sulfide remarkably promotes the catalytic cracking of *n*-butane over NaZ^{28, 29}.

The catalytic cracking of *n*-butane over Na zeolites at 500 °C by use of a closed circulation system is shown in Fig 10. The Na zeolites showed very low activity in the cracking of *n*-butane at 500 °C in the absence of hydrogen sulfide. The cracking of *n*-butane over Na zeolites, however, were remarkably accelerated by the presence of hydrogen sulfide. After conducting the cracking reaction for 5 h, all components in the gas phase were evacuated for 2 h and then the cracking reaction without hydrogen sulfide was carried out again. These Na zeolites showed very low activity just as in the first run. This indicates that the promoting action of hydrogen sulfide is completely reversible. The products of *n*-butane cracking over these Na zeolites were C₁—C₃ hydrocarbons.

The isomerization of cyclopropane, which proceeds predominantly on the Brönsted acid site of solid acid catalysts, was carried out at 150 °C over these Na zeolites to gain more definite knowledge

(a): background evacuated at 500° for 2 h, (b): after introduction of hydrogen sulfide at 500°C, (c): after evacuation at 500°C

Fig. 11 IR Spectra of Hydrogen Sulfide Adsorbed on Various Na Zeolites

on promotional action of hydrogen sulfide. It was revealed that hydrogen sulfide considerably promotes the isomerization of cyclopropane over these Na zeolites at 150 °C and the order of enhancement of Na zeolites activity with hydrogen sulfide was comparable to that in the cracking of *n*-butane at 500 °C²⁸⁾. These results indicate that hydrogen sulfide which had coexisted in the reaction system formed new Brönsted acid site and the Brönsted acid site formed on Na zeolites promoted the cracking of *n*-butane and isomerization of cyclopropane.

The infrared spectra of hydrogen sulfide adsorbed on these Na zeolites were examined in order to clarify the mechanism of formation of new Brönsted acid sites on Na zeolites with hydrogen sulfide adsorbed on these Na zeolites evacuated at 500 °C for 2 h, small absorption band of silanol group were observed at around 3,720 cm⁻¹, as shown in Fig. 11. After introduction of hydrogen sulfide (10 Torr) onto these Na zeolites at 500 °C, absorption band of acidic hydroxyl groups at around 3,640 and 3,550 cm⁻¹ were not observed but thiol (SH) group was observed at around 2,572 cm⁻¹, as shown in spectra(b). The absorption band of SH group, however, had completely disappeared by the evacuation of hydrogen sulfide in gas phase at 500 °C, as shown in spectra(c). From these results, the author and associates concluded that hydrogen sulfide is reversibly adsorbed on sodium ions in Na zeolite without dissociation, and hydrogen atom of SH group in the adsorbed hydrogen sulfide molecule on Na zeolites acts as the Brönsted acid sites in the cracking of *n*-butane and isomerization of cyclopropane as shown below:

It was revealed that hydrogen sulfide adsorbed reversibly on alkali metal ions in alkali metal zeolites forms new Brönsted acid sites and remarkably accelerates the catalytic hydrocarbon conversions on alkali metal zeolites. This specific property of hydrogen sulfide should be widely applicable for some processes in the petroleum industry.

3.4 Enhancement of Catalytic Activity and Selectivity by Pretreatment with Hydrogen Sulfide

The author and associates investigated the effect of pretreatment with hydrogen sulfide on various heterogeneous catalysts, and found that hydrogen sulfide adsorbed irreversibly on certain kinds of metal ion-exchanged zeolites (MeY) considerably enhances the catalytic activities of MeY in some acid-catalyzed reactions such as the cracking of cumene and hexane, disproportionation of toluene, dehydration of 2-propanol, isomerization of xylene, butene and cyclopropane, etc.^{30)~39)}

The catalytic activities of various MeY zeolites for cracking of cumene before and after the pretreatment with hydrogen sulfide at 300 °C using a pulse reactor are shown in Table 1. Activities of NaY, CaY, BaY, MgY, CrY and ZnY were hardly changed by the pretreatment with hydrogen sulfide, but those of CdY, NiY, CuY, AgY and CoY were remarkably enhanced by this treatment as shown in Table 1. It was revealed

Table 1 Initial Activities of Various Metal Ion-exchanged Y Zeolite Catalysts for Cumene Cracking at 300°C

H₂S pretreatment temperature=300°C, Amount of H₂S injection=2 ml (8.3×10⁻⁵ mol), Carrier gas flow rate=27 ml/min, Volume of cumene pulse=2 μl

Catalyst	%-Ion exchanged	$k_0 \times 10^{-2a)}$ [ml/g·min]	$k_t \times 10^{-2b)}$ [ml/g·min]	$k_t/k_0^c)$	$v \times 10^{4d)}$ [mol/g-cat]	HSAB ^{e)}
NaY	—	0	0	—	<0.1	H
CaY	73.8	5.1	5.1	1.0	<0.1	H
BaY	79.5	0	0	—	<0.1	H
MgY	69.2	4.6	4.5	1.0	<0.1	H
MnY	69.3	4.9	5.1	1.0	<0.1	H
PbY	90.6	0	0	—	<0.1	M
FeY	92.9	0	0	—	<0.1	H
CrY	98.3	0	0	—	<0.1	H
CdY	75.2	2.9	15.9	5.5	5.7	S
CuY	77.3	3.1	16.5	5.3	5.6	M
NiY	68.8	3.1	15.7	5.1	6.0	M
AgY	93.9	2.0	9.2	4.6	10.3	S
CoY	71.4	5.2	12.8	2.5	3.6	M
ZnY	78.6	12.9	17.1	1.3	<0.1	M

- a) : First-order rate constant before pretreatment with H₂S
b) : First-order rate constant after pretreatment with H₂S
c) : Ratio of activity increase
d) : Amount of H₂S adsorbed on MeY
e) : Hard and soft acid and base

that the affinity of metal ions in MeY for hydrogen sulfide is very important for the increase of catalytic activity of MeY by pretreatment with hydrogen sulfide. The symbols of HSAB(Hard and Soft Acids and Bases) are also shown in **Table 1**. According to HSAB concept, hydrogen sulfide is classified as soft base and it has tendency to combine with soft or medium metal ions. As can be seen in **Table 1**, all MeY zeolites, which activities were remarkably enhanced by pretreatment with hydrogen sulfide, contained soft or medium metal ions in MeY. Therefore, the author and associates concluded that marked increase in activity of MeY zeolites by the pretreatment with hydrogen sulfide is attributed to strong interaction of metal ions in MeY with hydrogen sulfide.

The infrared spectra of MeY (CdY, NiY, CuY, AgY, CoY and ZnY) after adsorption of hydrogen sulfide were examined to clarify the mechanism of enhancement effect of hydrogen sulfide on catalytic activities of these MeY zeolites. The infrared spectra of these MeY, before and after the adsorption of hydrogen sulfide, are shown in **Fig. 12**. In the background infrared spectra of these MeY, weak intensity absorption band of surface acidic hydroxyl groups, *i.e.*, Brönsted acid site, at 3,640 and 3,545 cm⁻¹, were observed. The intensities of these two acidic hydroxyl groups on all MeY were remarkably increased by the adsorption of hydrogen sulfide. The infrared spectra of newly formed hydroxyl groups on MeY had completely disappeared by the adsorption of pyridine, and the band of pyridinium ion at 1,545 cm⁻¹ was observed. These results indicate clearly that the newly formed hydroxyl groups on MeY, as well as those on HY zeolite, after adsorption of hydrogen sulfide have

Dotted line represents background of MeY.

R. T.: room temperature

Fig. 12 IR Spectra of Various MeY Zeolites after Adsorption of Hydrogen Sulfide

strong acidic nature.

From these results, the author and associates concluded that new Brönsted acid sites are formed on these MeY zeolites by the pretreatment with hydrogen sulfide³⁰⁾, and advanced the following mechanism for the formation of new Brönsted acid sites on MeY zeolites by the pretreatment with hydrogen sulfide:

By this mechanism, hydrogen sulfide is adsorbed on metal ion in MeY zeolites and dissociates to form acidic hydroxyl groups and metal sulfide particles.

Furthermore, the author and associates revealed that high activity and selectivity to *trans*-2-butene in the isomerization of 1-butene were obtained over sulfided metal ion-exchanged A zeolite (MeA) with hydrogen sulfide^{40,41}. The catalytic isomerization of 1-butene over CoA and sulfided CoA zeolites⁴⁰ at room temperature by use of a closed circulation system are shown in Fig. 13. CoA zeolites without sulfiding showed no catalytic activity in the isomerization of 1-butene. The catalytic activity of CoA zeolite, however, was remarkably enhanced by sulfiding with hydrogen sulfide at 300 °C as shown in Fig. 13. Enhanced activity of CoA zeolite was found to be higher than that of HY zeolite. The isomerization of 1-butene over sulfided CoA zeolite was highly selective for the formation of *trans*-2-butene. A selectivity of above 90% was obtained constantly during the reaction. The high activity of CoA zeolite enhanced by sulfiding with hydrogen sulfide might be attributed to the formation of new Brönsted acid site on CoA zeolite surface just as in the case of MeY zeolites³⁵. The high selectivity of sulfided CoA zeolite for the formation of *trans*-2-butene could be attributed to the action of shape selectivity of CoA zeolite with

Fig. 13 Catalytic Isomerization of 1-Butene over CoA and Sulfided CoA Zeolites at Room Temperature

Table 2 Hydrogenation of Various Olefins over Highly Active Sulfided Mo/Al₂O₃ Catalyst

Olefin	Reaction temp.[°C]	Reaction time[min]	Conversion [%]
Ethylene ^{a)}	0	5	100
	-47	15	100
	-75	15	100
Propylene ^{a)}	5	15	100
	-46	30	100
1-Butene ^{a)}	0	15	100
1,3-Butadiene ^{b)}	4	20	100
	-20	35	100

a) H₂ : olefin=10 Torr : 10 Torr

b) H₂ : olefin=20 Torr : 10 Torr; only butane was formed.

small pore diameter. That is to say, since the diffusion rate of *cis*-2-butene is two orders of magnitude lower than that of *trans*-2-butene, *cis*-2-butene can not easily diffuse from the super cage to the outer surface at room temperature, even if *cis*-2-butene is formed inside the super cage of sulfided CoA in the isomerization of 1-butene.

On the other hand, the author and associates tried to prepare highly active sulfided Mo/Al₂O₃ catalyst by sulfiding with hydrogen sulfide, and found that extremely high active sulfided Mo/Al₂O₃ catalyst for the hydrogenation of olefins could be prepared by sulfiding Mo/Al₂O₃ with hydrogen sulfide followed by evacuation under high vacuum (10⁻⁵ Torr) at high temperature (450 °C)⁴². The activity of sulfided Mo/Al₂O₃ catalysts followed by evacuation under 10⁻⁵ Torr at 450 °C for the hydrogenation of various olefins are shown in Table 2, and it can be seen that sulfided Mo/Al₂O₃ catalyst thus prepared showed extremely high activity in the hydrogenation of

various olefins, even at low temperatures. The author and associates concluded that the extremely powerful activity of highly active sulfided Mo/Al₂O₃ catalyst for use in the hydrogenation of olefins could be attributed to the formation of highly dispersed MoS₂ with low coordination number on sulfided Mo/Al₂O₃ catalyst. This method of preparation of highly active sulfided Mo/Al₂O₃ catalyst would be available for the development of highly active MoS₂ based hydrodesulfurization catalyst for the treatment of petroleum feedstocks.

4. Conclusion

In those systematic studies with respect to the catalytic hydrodesulfurization of organic sulfur compounds and the effective usage of hydrogen sulfide, the author and associates found that reduced MeY zeolites are powerful as highly active hydrodesulfurization catalysts for the treatment of petroleum feedstocks, and also revealed that hydrogen sulfide has many possibilities as useful chemicals for the petroleum industry.

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要 旨

高活性脱硫触媒の開発と副生硫化水素の有効利用

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新規の高活性脱硫触媒を開発することは、燃料油の燃焼により排出される硫黄酸化物を低減するために極めて重要である。一方、燃料油の脱硫では大量の硫化水素が副生する。現在副生する硫化水素はクラウス反応により単体硫黄と水とに変換され、単体硫黄のみが回収されている。しかし、経済的見地から、将来は副生する硫化水素を積極的に有効利用することも重要な課題となるものと考えられる。本総合論文では著者および共同研究者がこれまでに行ってきた高活性脱硫触媒の開発および副生硫化水素の有効利用に関する系統的研究を述べた。

著者らは新規の高活性脱硫触媒として水素還元処理した金属イオン交換 Y 型ゼオライト ($\text{Me}^{\circ}\text{Y}$) 触媒に注目し、脱硫反応のモデル反応であるチオフエンの水素化脱硫反応に対する種々の $\text{Me}^{\circ}\text{Y}$ 触媒の活性を検討した。この結果、 $\text{Ni}^{\circ}\text{Y}$ および $\text{Co}^{\circ}\text{Y}$ などの $\text{Me}^{\circ}\text{Y}$ 触媒はチオフエンの水素化脱硫反応に対して市販の $\text{CoMo}/\text{Al}_2\text{O}_3$ 系脱硫触媒よりも著しく高い活性を示した (Figs. 1, 2)。また、 $\text{Me}^{\circ}\text{Y}$ 上に吸着したチオフエンの赤外吸収スペクトルなどから、 $\text{Me}^{\circ}\text{Y}$ 触媒はチオフエンの水素化脱硫反応に対して二元機能触媒として作用することが明らかとなった (Fig. 3)。これらのことから、 $\text{Me}^{\circ}\text{Y}$ 系触媒は新規の

高活性脱硫触媒として高い可能性を有しているものと考えられた。

一方、アルミナ担持 MoS_2 系触媒は硫化水素の接触分解による水素生成に対して有効な触媒として作用し、硫化水素の接触分解による水素と硫黄の同時回収が可能であることが明らかとなった (Figs. 4~7)。また、硫化処理した $\text{Mo}/\text{Al}_2\text{O}_3$ 触媒上では硫化水素によるオレフィンの水素化が進行し、硫化水素による不飽和炭化水素の接触水素化反応が可能であることが明らかとなった (Figs. 8, 9)。さらに、非酸性のアルカリ金属ゼオライト触媒による炭化水素の接触転化反応において、反応系に硫化水素が共存すると転化反応が著しく促進されることがわかった (Figs. 10, 11)。最後に金属イオン交換ゼオライト触媒および担持 Mo 触媒を硫化水素で硫化処理すると、炭化水素の種々の反応に対する触媒機能が著しく向上することが明らかとなった (Tables 1, 2, Figs. 12, 13)。このように、脱硫反応で副生する硫化水素を不均一系触媒反応の技術を応用して、種々のプロセスに有効利用することが可能であることが明らかとなった。

Keywords

Hydrodesulfurization, Catalyst design, Y zeolite, Thiophene, Hydrogen sulfide