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Comparison by 35S Radiotracer Methods of Hydrodesulfurization Behavior for Molybdenum, Cobalt–Molybdenum and Nickel–Molybdenum Catalysts Supported on γ-Alumina and High Specific Surface Area Titania

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The differences between MoS_2, CoMoS and NiMoS HDS catalysts supported on γ-alumina and high SSA titania are investigated based on the results of [^{35}S]DBT HDS experiments. Previous studies of MoS_2 and CoMoS are reviewed, discussed and compared with new results for NiMoS. Introduction of Ni or Co to MoS_2/Al_2O_3 catalysts classically yields a significant increase in HDS performance. Irrespective of the promoter, an increase in S_0, the number of labile sulfur atoms, is observed. In contrast, k_{RE}, the H_2S liberation rate constant, plotted as a function of the Ni/Mo ratio, presents a volcano profile on Ni-promoted catalysts, but k_{RE} reaches a plateau from low Co/Mo ratios on Co-promoted catalysts. The 'TiMoS' phase, which is formed *in-situ* during HDS on Mo/TiO_2 catalysts, promotes sulfur mobility and makes Mo/TiO_2 catalysts more active than Mo/Al_2O_3 catalysts. Nevertheless, CoMo/TiO_2 catalysts are less active than CoMo/Al_2O_3 catalysts because further promotion of 'TiMoS' phase with Co might yield excessive weakening of the metal–sulfur bonds, and/or some Co atoms might be 'lost' in the TiO_2 matrix without interacting with MoS_2. In contrast, introduction of Ni to Mo/TiO_2 catalysts yields significant increases in both k_{RE} and S_0. The NiMo/TiO_2 catalysts exhibit HDS performances close to those of Al_2O_3-supported catalysts. Clearly catalytic behavior over Co- and Ni-promoted catalysts is different.

Keywords

Hydrodesulfurization, Dibenzothiophene, γ-Alumina, High surface area titania, Nickel molybdenum catalyst, Radiotracer method

1. Introduction

Enhancement of fuel quality for better environmental characteristics is dependent on improved performances of hydrodesulfurization (HDS) catalysts[1]. For example, the limit for sulfur of 50 ppm in light gas oils is now in effect in Japan, but will be decreased to 10 ppm by 2007. Therefore, present research is intended to rapidly develop more active and selective catalyst formulations[2]. Conventional HDS catalysts consist of MoS_2 slabs decorated by Ni or Co atoms ('NiMoS' or 'CoMoS' phase) supported on a carrier, usually γ-alumina. NiMoS or CoMoS-based catalyst performance can be improved by adding third elements such

as fluorine[3),4)], phosphorus[5)~11)] or boron[10)~17)]. The use of other active phases such as WS_2[18),19)], CrS_x[20)~24)], noble metals[20),22),25)~35)], as well as other carriers such as TiO_2 or mixed oxides[36)~55)] or carbon[56)] and zeolites[57),58)] has also been investigated. Titania carrier appears promising since the specific activity of MoS_2/TiO_2 catalysts for thiophene HDS was 4.4 times higher than that of MoS_2/Al_2O_3 catalysts[36)]. However, conventional titania support has low specific surface area and poor mechanical properties which are not suitable for catalytic applications. Recently, a new titania support, which has high specific surface area (SSA) of *ca.* 134 $m^2 \cdot g^{-1}$ and excellent mechanical properties, was successfully synthesized by Chiyoda Corp.[59),60)].

The titania support is believed to improve the HDS activity of non-promoted MoS_2 catalysts based on better Mo dispersion[38),41)] and easier sulfidation of the active phase[44)]. The use of TiO_2 also increases the mobility of the sulfur atoms[49),50)~52),54),55),61)]. The DBT HDS activity of the non-promoted MoS_2 phase can be increased by using high SSA titania support[50),54)]. Such MoS_2/TiO_2 catalysts are significantly

more active than MoS_2/Al_2O_3 catalysts. Nevertheless, the Co-promoted MoS_2 phase is much more active supported on alumina rather than on titania[52),55)].

The present study investigated the activity of NiMo catalysts supported on high SSA titania in terms of sulfur vacancies and sulfur mobility for $CoMoS/TiO_2$, $CoMoS/Al_2O_3$, $NiMoS/TiO_2$ and $NiMoS/Al_2O_3$, and proposes some possible solutions for improving the activity of titania-supported HDS catalysts.

2. Experimental

2. 1. Catalysts

The TiO_2 support (anatase) used in this study had a SSA of 134 $m^2 \cdot g^{-1}$ as supplied by Chiyoda Corp. The $NiMo/TiO_2$ and $CoMo/TiO_2$ catalysts were prepared by successive incipient wetness impregnations of molybdenum and nickel or cobalt. First, Mo/TiO_2 catalyst loaded with 16 wt% Mo, which is the optimal Mo loading[55)], was prepared: titania was impregnated with an aqueous solution containing the desired amount of ammonium heptamolybdate, followed by drying at 120°C for 3 h and calcining in air at 500°C for 3 h. Then, the Ni(or Co)Mo/TiO_2 catalyst was prepared by a step-by-step incipient wetness impregnation of the previously prepared Mo/TiO_2 catalyst. The Mo/TiO_2 catalyst underwent successive impregnations with an aqueous solution containing a given amount of cobalt or nickel nitrate hexahydrate. For each step, the amount of metal (Co or Ni, indicated as 'Me') equivalent to a Me/Mo molar ratio of 0.1 was impregnated and the procedure was repeated until the desired Me/Mo ratio was reached. After each impregnation step, the obtained solids were dried at 120°C for 3 h and then calcined in air at 500°C for 3 h. MeMo catalysts supported on alumina were similarly prepared from the optimal Mo/Al_2O_3 catalyst loaded with 16 wt% MoO_3 (alumina SSA: 256 $m^2 \cdot g^{-1}$). The amounts of deposited molybdenum and nickel or cobalt were checked by X-ray fluorescence measurements with an EDX-800 spectrometer (Shimadzu Corp.).

2. 2. Apparatus and Procedure

The catalysts were packed in a reactor and pre-sulfided under a flow of 5% H_2S/95% H_2 (5 $l \cdot h^{-1}$, 0.1 MPa, 400°C). The reactor was then cooled to room temperature and pressurized with hydrogen. The reactant solution (DBT dissolved in decalin) was fed into the reactor pre-heated at the desired reaction temperature using a high-pressure liquid pump (Kyowa Seimitsu, KHD-16). Typical HDS reaction conditions were as follows: H_2 flow rate 25 $l \cdot h^{-1}$, WHSV 28 h^{-1}, reaction pressure 5 MPa, and concentration of DBT in decalin 1.0 wt%. The liquid products were collected every 15 min and analyzed using a gas chromatograph equipped with a FID detector (Shimadzu-17A, Shimadzu Corp.) and a commercial capillary column

(DB-1). The same reaction conditions were used to characterize the solid catalyst properties with the [^{35}S]DBT radioisotope tracer method, as described elsewhere[62),63)].

The rate constants (k_{HDS}) of the pseudo-first-order reactions of HDS of DBT were determined using the following equation:

$$k_{HDS} = -(F/W) \ln(1 - x) \qquad (1)$$

where k_{HDS} is the rate constant of HDS ($mol \cdot h^{-1} \cdot g_{cat}^{-1}$), x is the conversion of DBT, F is the feed rate of the reactant ($mol \cdot h^{-1}$), and W is the weight of catalyst (g). Although the temperature conditions of HDS were different for the TiO_2-supported catalysts and Al_2O_3-supported catalysts, these temperatures were considered to be within the allowable range for comparison.

3. Results and Discussion

3. 1. Non-promoted MoS_2 Catalysts Supported on Al_2O_3 and High SSA TiO_2

Various differences have been observed between the catalytic behavior of non-promoted Mo/Al_2O_3 and Mo/TiO_2 HDS catalysts. In our previous studies, the catalytic results obtained in the reaction of HDS of DBT over Mo/TiO_2-based catalysts were interpreted based on the properties of the so-called 'TiMoS' phase[51),52),54)], which is formed under HDS working conditions. In this catalytic system, the titania support acts as a promoter of the MoS_2 phase[64)], even if some points are controversial[65)].

Density functional theory (DFT) calculations combined with ^{35}S experiments results showed that the metallic edge of the MoS_2 particles is the active site in HDS on non-promoted catalysts[63)]. On the metallic edge, the sulfur-replenished HDS active sites are dynamically reconstructed (regeneration of coordinatively unsaturated sites) by elimination of an H_2S molecule via a mechanism that is fully described elsewhere[63),66)]. We obtained very good agreement between the activation energy of the H_2S liberation reaction from the metallic edge of MoS_2 calculated by DFT of about 50 $kJ \cdot mol^{-1}$ and the experimental finding of about 42 $kJ \cdot mol^{-1}$ [63)]. However, the DFT calculations were performed for MoS_2 crystallites, whereas the experiments were performed on MoS_2 catalysts supported on Al_2O_3. Thus, the good agreement between experimental results and calculated values implicitly suggests that the interaction between the Al_2O_3 carrier and the MoS_2 active phase is not very strong or not important for the catalytic behavior of the supported MoS_2 active phase.

Geometrical considerations suggest that there may be no fundamental difference in morphology for the MoS_2 phase supported on alumina or titania[61)]. **Figure 1** shows the Arrhenius plots for k_{RE}, the rate constant of the H_2S liberation reaction obtained from ^{35}S radiotracer
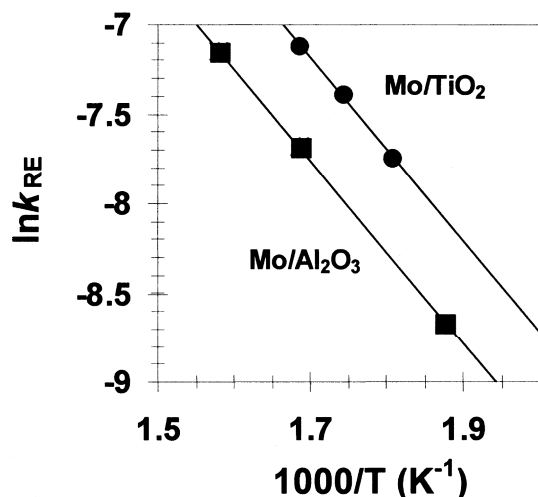
Al₂O₃ SSA: 256 m²·g⁻¹; TiO₂ SSA: 134 m²·g⁻¹; Catalysts loaded with 16 wt% MoO₃.

Fig. 1 Arrhenius Plots for the H₂S Liberation Reaction over MoS₂ Supported on Alumina (from Ref. 63) and Titania (from Ref. 54)
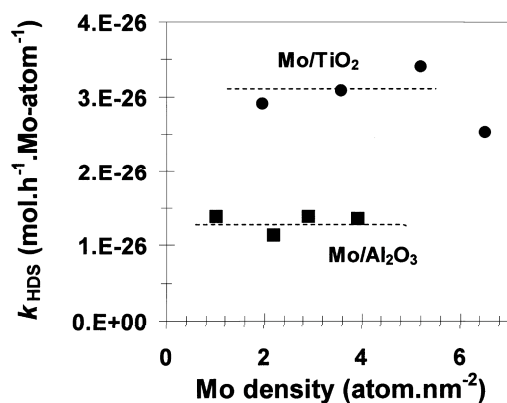
DBT: 1 wt%; Reaction temperature: 320°C; Al₂O₃ SSA: 256 m²·g⁻¹; TiO₂ SSA: 134 m²·g⁻¹.

Fig. 2 k_{HDS} by Mo Atom as the Function of Mo Density on Mo/TiO₂ Catalysts (from Ref. 54) and Mo/Al₂O₃ Catalysts (from Ref. 63)

experiments, over MoS₂ catalysts supported on Al₂O₃ and TiO₂. The value of k_{RE} indicates the reactivity of one active site on a catalyst[62),63)]. The activation energy deduced for MoS₂/TiO₂ catalysts is the same as that previously determined for MoS₂/Al₂O₃ catalysts[63)] of about 42 kJ·mol⁻¹. Despite these similarities between MoS₂/Al₂O₃ and MoS₂/TiO₂ catalysts, the reactivity differs between the MoS₂ phases supported on Al₂O₃ and TiO₂. The promotion effect on MoS₂/TiO₂ catalysts is evidenced in **Fig. 2**, with a specific DBT HDS activity per atom of molybdenum of 2.4 times greater over the TiO₂ support than over the Al₂O₃ support. The results of the ³⁵S radiotracer experiments previously
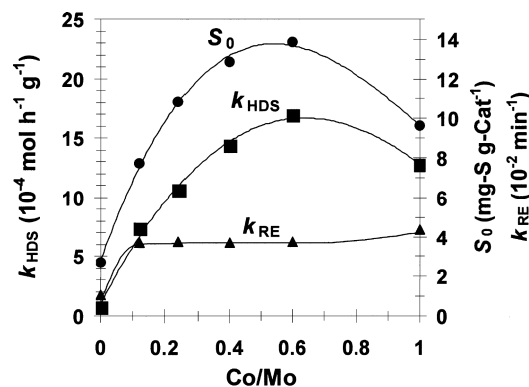
Al₂O₃ SSA: 256 m²·g⁻¹.

Fig. 3 Effect of the Co/Mo Ratio during DBT (1 wt%) HDS at 260°C over a CoMo/Al₂O₃ Catalyst Loaded with 16 wt% MoO₃ on S_0 and k_{RE} (adapted from Ref. 67)

showed that using TiO₂ instead of Al₂O₃ as a support for MoS₂ catalysts leads to increased sulfur mobility with k_{RE} about twice higher on titania, whereas the number of labile sulfur atoms is similar at iso-loading of Mo[54)].

In brief, the increase in sulfur mobility makes the MoS₂/TiO₂ catalysts more active than the MoS₂/Al₂O₃ catalysts through formation of the 'TiMoS' phase[54)].

3. 2. Co-promoted MoS₂ Catalysts Supported on Al₂O₃ and High SSA TiO₂

As a basis for comparison of the new results obtained over NiMo/TiO₂ catalysts, the main results of our previous investigations on Co-promoted CoMo/TiO₂[52),55)] and CoMo/Al₂O₃ catalysts are summarized here[67)]. Similarly to CoMo/Al₂O₃ catalysts (**Fig. 3**)[67)], the DBT HDS activity of CoMo/TiO₂ catalysts increases with addition of cobalt up to an optimal Co/Mo ratio and then decreases for higher ratios (**Fig. 4**)[55)]. The results of the [³⁵S]DBT HDS analysis show that the increase in activity caused by Co introduction to MoS₂/TiO₂ catalysts is mainly due to an increase in S_0, the amount of labile sulfur atoms. In contrast to the case of CoMo/Al₂O₃ catalysts (**Fig. 3**), only a very limited increase in k_{RE}, the H₂S release rate constant, is observed by Co introduction to MoS₂/TiO₂ catalysts (**Fig. 4**).

Co introduction to MoS₂/Al₂O₃ catalysts results in a significant combined effect of k_{RE} and S_0 increases. S_0, the amount of labile sulfur on a working catalyst, indicates the number of active sites on the catalyst[62),63)]. Therefore, whereas MoS₂/TiO₂ catalysts are more active than MoS₂/Al₂O₃ catalysts, the extent of the synergic effect induced by introduction of cobalt is much larger for MoS₂/Al₂O₃ catalysts than for MoS₂/TiO₂ catalysts. Indeed, CoMoS/Al₂O₃ catalysts are much more active in HDS than CoMoS/TiO₂ catalysts[55)].

In the so-called 'TiMoS' phase, the electronic density on molybdenum atoms is modified (injection of 3d elec-
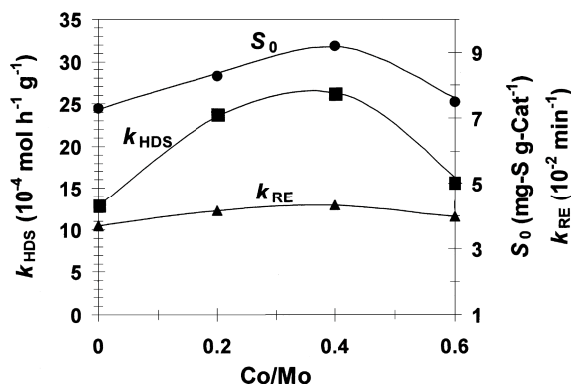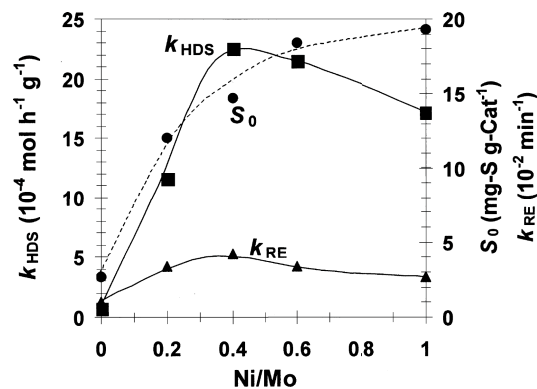
TiO₂ SSA: 134 m²·g⁻¹.

Fig. 4 Effect of the Co/Mo Ratio during DBT (1 wt%) HDS at 300°C over a CoMo/TiO₂ Catalyst Loaded with 16 wt% MoO₃ on S_0 and k_{RE} (adapted from Ref. 55)

Al₂O₃ SSA: 256 m²·g⁻¹.

Fig. 5 Effect of the Ni/Mo Ratio during DBT (1 wt%) HDS at 260°C over a NiMo/Al₂O₃ Catalyst Loaded with 16 wt% MoO₃ on S_0 and k_{RE} (adapted from Ref. 74)

trons of Ti^{3+} in the Mo 3d conduction band[64]), which increases the mobility of sulfur, *i.e.* decreases the strength of the Mo–S bonds. Therefore, further promotion of the 'TiMoS' phase with Co might yield unstable metal–sulfur bonds. This would generate inappropriate interactions between the sulfur compounds and the active phase[64]. ^{35}S radiotracer analysis shows that with introduction of Co, the increase in mobility of sulfur atoms located in bridging positions between cobalt and molybdenum is much lower over TiO₂ than over Al₂O₃[55]. In other words, the dynamic cycle of sulfur vacancy creation and replenishment cannot optimally occur.

Some cobalt atoms might also be 'lost' in the TiO₂ matrix without interacting with MoS₂, which could also partly explain the low HDS catalytic performances. Nevertheless, the volcano-type profiles for k_{RE} and S_0 in **Fig. 4** suggest that a conventional promotion effect occurs but is very weak. The slight increase in k_{HDS} observed in **Fig. 4** could be due to promotion of a small part of MoS₂ slabs that are not involved in the formation of the 'TiMoS' phase. Then, if only a part of the 'TiMoS' phase is decorated with Co atoms, the slight increase in k_{RE} can be interpreted as the mean value between the unmodified k_{RE} of the active sites of the Co-independent part of the 'TiMoS' phase, and the increase in k_{RE} of the few active sites belonging to the MoS₂ phase promoted by Co. As the amount of Co introduced increases, the 'TiMoS' phase is further decorated with Co, which results in the unstable metal–sulfur bond. Then, a decrease in k_{RE} is observed (**Fig. 4**, CoMo > 0.4), which was not the case for CoMoS/Al₂O₃ catalysts overloaded with Co (**Fig. 3**).
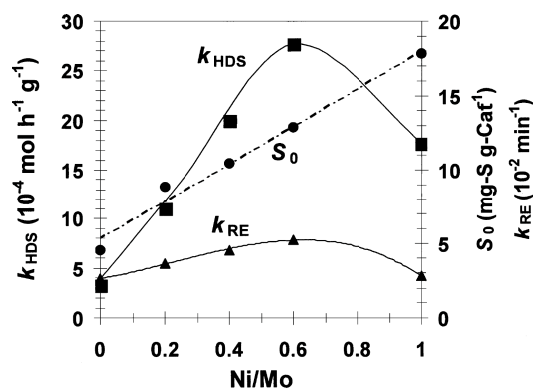
3. 3. Ni-promoted MoS₂ Catalysts Supported on Al₂O₃ and High SSA TiO₂

Similarly to the CoMo catalysts, a synergic effect is observed between Ni and Mo on alumina-supported

TiO₂ SSA: 134 m²·g⁻¹.

Fig. 6 Effect of the Ni/Mo Ratio during DBT (1 wt%) HDS at 280°C over a NiMo/TiO₂ Catalyst Loaded with 16 wt% MoO₃ on S_0 and k_{RE}

catalysts[68~73]. ^{35}S radiotracer analysis shows that the increase in activity caused by introduction of nickel to Mo/Al₂O₃ catalysts is due to a concerted increase in k_{RE} and S_0 (**Fig. 5**)[74].

Ni introduction also causes a substantial increase in activity of Mo/TiO₂ catalysts (**Fig. 6**). Indeed, k_{HDS} increased from a value of about 3×10^{-4} mol·h⁻¹·g⁻¹ for the Ni-free Mo/TiO₂ catalyst to about 28×10^{-4} mol·h⁻¹·g⁻¹ for the NiMo/TiO₂ catalyst with Ni/Mo = 0.6. Further, the value of S_0 increased linearly from about 4.5 mg-S·g_cat⁻¹ for Ni/Mo = 0 to about 18 mg-S·g_cat⁻¹ for Ni/Mo = 1. This behavior is clearly different from the low catalytic performances observed over Co-promoted MoS₂/TiO₂ catalysts (**3. 2.**). Although the value of S_0 increased up to Ni/Mo = 1, the activity decreased because k_{RE} at Ni/Mo = 1 decreased to half of the maximum, possibly due to further promotion of 'TiMoS' phase with Ni yielding the unstable

metal–sulfur bonds or the presence of excess Ni slowing the rate of sulfur elimination by the steric effect. In the former case, inappropriate interaction between the sulfur compounds and the active phase would occur resulting in a larger number of unreactive sites.

3. 4. Comparison between NiMo and CoMo Catalysts

Addition of Ni or Co promoter to the MoS_2 phase clearly affects the mechanism/kinetics of reconstruction of the active sites, but may also affect the nature of the active sites participating in the HDS reaction. The experimental activation energy of the H_2S departure reaction is 31 kJ·mol^{-1} on CoMoS/Al_2O_3 and 33 kJ·mol^{-1} on NiMoS/Al_2O_3 catalysts[75]. These values are lower than the about 42 kJ·mol^{-1} observed over non-promoted MoS_2/Al_2O_3 catalysts[63] or non-promoted MoS_2/TiO_2 catalysts (**Fig. 1**). For S atoms bridged between Co atoms, a mechanism implying H_2S departure from the metallic edge, *i.e.* a mechanism similar to that determined over non-promoted MoS_2/Al_2O_3 catalysts, can be excluded[75]. For cobalt-promoted Mo catalysts, the Co promoter prefers the sulfur edge[76),77)], which confirms that the promotion effect due to Co introduction on Mo-based catalysts cannot be achieved by directly transposing the results obtained for the non-promoted MoS_2 catalysts. In contrast, Ni in the nickel-promoted MoS_2 catalysts shows greater affinity for the metallic edge[76),77)], so the promotion effect might originate in the enhancement of the edge sites that are already the active sites for non-promoted catalysts. Further, this difference in the edge involved for each promoter addition is responsible for the different behaviors of hydrogen dissociation over the 'CoMoS' and 'NiMoS' phases[78]. Dissociation of hydrogen requires greater energy on the 'NiMoS' phase, but the adsorbed hydrogen species is more mobile than on the 'CoMoS' phase. However, the origin of the differences in catalytic behavior between 'CoMoS' and 'NiMoS' phases and the dynamic behavior during HDS reactions are not fully understood.

^{35}S radiotracer analysis shows differences in behavior according to the promoter on alumina supports. For CoMo catalysts, the maximum activity corresponds to the maximum in S_0, as the value of k_{RE} is almost constant irrespective of the Co/Mo ratio. Indeed, k_{RE} quickly reaches a maximum after introduction of a small quantity of Co (from Co/Mo = 0.1; **Fig. 3**). In contrast, for NiMo catalyst, the maximum activity corresponds to the maximum in k_{RE}, which exhibits a volcano-type profile when plotted as a function of Ni/Mo ratio (**Fig. 5**), whereas the value of S_0 increases in the whole range of studied Ni/Mo ratios.

Using TiO_2 as the carrier instead of Al_2O_3, the difference in catalytic behaviors between the 'CoMoS' phase and the 'NiMoS' phase is even more pronounced. The activity of CoMoS/TiO_2 catalysts is much lower than that of NiMoS/TiO_2 catalysts (**Figs. 4** (300°C) and **6** (280°C)). The slight increase in activity observed on the CoMo/TiO_2 catalysts is only due to the creation of a small quantity of labile sulfur atoms. Unlike the case of Al_2O_3-supported catalysts, the value of k_{RE} is almost unmodified by cobalt addition. This effect was discussed in **3. 2.** In contrast, addition of Ni to the Mo/TiO_2 catalysts leads to a progressive increase in k_{RE} together with a linear increase in S_0, similar to the results using the Al_2O_3 carrier. There is a clear promotion effect of Ni for Mo/TiO_2 catalysts, in contrast with the results for Co-promoted Mo/TiO_2 catalysts. However, the NiMo/TiO_2 catalysts are still not sufficiently competitive in terms of HDS activity compared to the NiMo/Al_2O_3 catalysts. Indeed, a working temperature of 280°C is necessary to reach a k_{HDS} of *ca.* 25×10^{-4} mol· h^{-1}·g^{-1} for the TiO_2-supported NiMo catalysts (**Fig. 6**) whereas a temperature of only 260°C is needed for the Al_2O_3-supported catalysts (**Fig. 5**). Similar to CoMo/TiO_2 catalysts, further promotion of the 'TiMoS' phase with Ni might yield unstable metal–sulfur bonds, which would also generate inappropriate interactions between the sulfur compounds and the active phase. However, this negative effect may be weaker compared with the Co case.

3. 5. Approaches for Increasing the Performances of TiO_2 Supported HDS Catalysts

3. 5. 1. Use of Nano-structured TiO_2 Supports

The main limitation of the TiO_2 carrier is the difficulty in obtaining high SSA solids. The titania support used in this study has exceptional properties with large SSA and excellent mechanical properties. Use of the high SSA TiO_2 support yields Mo/TiO_2 catalysts with higher activity than conventional Mo/Al_2O_3 catalysts for the HDS of DBT. Nevertheless, higher SSA is not the important factor in the formation of highly active Co-doped Mo/TiO_2 catalysts. For CoMo/Al_2O_3 sol-gel based catalysts, slight morphological modification of the sol-gel alumina support yields substantial increases in activity[79]. Similar efforts may optimize the structure of TiO_2 supports specifically destined for HDS applications. Recently, a nano-structured TiO_2 (*ca.* 350 m^2·g^{-1}) was used as a support for CoMo catalysts and the activity in DBT HDS of the CoMo/TiO_2 catalyst was about twice that of a CoMoP/Al_2O_3–SiO_2 commercial catalyst[80]. In contrast to our findings, a large promotion effect of the Co atoms was observed for the activity of the MoS_2 phase supported on TiO_2. Such excellent performance was attributed to better dispersion of the Co and Mo atoms together with better interaction between Co and Mo and consequent better sulfidability of the supported oxo-species.

Mesoporous titania with high SSA can be obtained by various techniques, such as template-directed assembly based on the triblock-copolymer template method[81] or the amine surfactant-mediated template method[82].

Investigations of such carriers with modification and optimization seems promising.

3. 5. 2. Use of TiO$_2$–Al$_2$O$_3$ Mixed Oxides

The use of aluminia–titania carriers may be an approach for improving the efficiency of titania-carrier based catalysts[83)~88)]. NiMo/TiO$_2$–Al$_2$O$_3$ catalysts are more active than NiMo/Al$_2$O$_3$ catalysts in the HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) due to better hydrogenation ability[84),88)], which is a crucial parameter in the case of 4,6-DMDBT HDS[89),90)]. Further, NiMo/TiO$_2$–Al$_2$O$_3$ catalysts are also more active in the HDS of DBT and 4-methylbenzothiophene (4-MDBT) than NiMo/Al$_2$O$_3$ catalysts[88)]. In contrast, CoMo/TiO$_2$–Al$_2$O$_3$ catalysts have low activities in the HDS of DBT compared to CoMo/Al$_2$O$_3$ catalysts, which is attributed to the formation of CoMoO$_4$[83)]. Optimization of the TiO$_2$–Al$_2$O$_3$ mixed oxides used as supports may improve the activities of the derived HDS catalysts. In particular, synthesis methods such as those proposed in **3. 5. 1.** for TiO$_2$ supports provide possible approaches to optimization.

3. 5. 3. Use of NiCoMo Active Phase

Another way of improving TiO$_2$-supported HDS catalysts would be to design NiCoMo/TiO$_2$ catalysts. Correct choice of the preparation conditions will increase the value of k_{RE} of NiCoMo catalysts to greater than that of the corresponding NiMo and CoMo catalysts[91)]. As Ni and Co have different promotion effects, optimization of such HDS catalysts supported on TiO$_2$ or TiO$_2$–Al$_2$O$_3$ may provide synergic effects.

4. Conclusion

Modification of HDS catalysts can yield changes in H$_2$ dissociation and/or adsorbed H species mobility, and changes in sulfur mobility. Both effects are linked since the mobility of sulfur involves departure of H$_2$S molecules. The effect of Co and Ni introduction into MoS$_2$ catalysts involves different modifications of the behavior of the active phase (and probably different MoS$_2$ edges). In particular, the ^{35}S analyses suggest that dynamic sulfur mobility during HDS is enhanced by introduction of Ni or Co on MoS$_2$/Al$_2$O$_3$ catalysts, but this effect is only observed with the Ni promoter in the case of MoS$_2$/TiO$_2$ catalysts. For Co-promoted MoS$_2$/TiO$_2$ catalysts, the conjugated effects of Ti^{3+} promotion ('TiMoS' phase) and the Co promoter yield inadequate metal–sulfur interaction by over-weakening the metal–sulfur bonds. While the Ni promotion seems to weaken the promotion effect of the 'TiMoS' phase with simultaneous creation of conventional 'NiMoS,' the negative effect may be weaker compared with the Co case.

References

1) Central Environment Council, Future Policy for Motor Vehicles Exhaust Emissions Reduction (7th Report), Japanese Ministry of the Environment, July 29, 2003.
2) Kabe, T., Ishihara, A., Qian, E. W., "Hydrodesulfurization and Hydrodenitrogenation," Kodansha Scientific, Tokyo, Wiley-VCH, New York (1999).
3) Muralidhar, G., Massoth, F. E., Shabtai, J., *J. Catal.*, **85**, 44 (1984).
4) Kwak, C., Lee, J. J., Bae, J. S., Choi, K., Moon, S. H., *Appl. Catal. A: General*, **200**, 233 (2000).
5) Fierro, J. L. G., López-Agudo, A., Esquivel, N., López Cordero, R., *Appl. Catal.*, **48**, 353 (1989).
6) Mangnus, P. J., van Veen, J. A. R., Eijbouts, S., de Beer, V. H. J., Moulijn, J. A., *Appl. Catal.*, **61**, 99 (1990).
7) Jian, M., Prins, R., *Catal. Lett.*, **35**, 193 (1995).
8) Quartararo, J., Fernandez, C., Guelton, M., Rigole, M., Amoureux, J. P., Grimblot, J., *J. Mater. Chem.*, **9**, 2637 (1999).
9) Iwamoto, R., Grimblot, J., *Adv. Catal.*, **44**, 417 (1999).
10) Ferdous, D., Dalai, A. K., Adjaye, J., *Appl. Catal. A: General*, **260**, (2), 137 (2004).
11) Ferdous, D., Dalai, A. K., Adjaye, J., *Appl. Catal. A: General*, **260**, (2), 153 (2004).
12) Ramírez, J., Castillo, P., Cedeño, L., Cuevas, R., Castillo, M., Palacios, J. M., López-Agudo, A., *Appl. Catal. A: General*, **132**, 317 (1995).
13) Bautista, F. M., Campelo, J. M., Garcia, A., Luna, D., Marinas, J. M., Moreno, M. C., Romero, A. A., *Appl. Catal. A: General*, **170**, 159 (1998).
14) Li, C., Chen, Y.-W., Yang, S.-J., Wu, J.-C., *Ind. Eng. Chem. Res.*, **32**, 1573 (1993).
15) Tsai, M.-C., Chen, Y.-W., Kang, B.-C., Wu, J.-C., Leu, L. J., *Ind. Eng. Chem. Res.*, **30**, 1801 (1991).
16) Dubois, J. L., Fujieda, S., *Catal. Today*, **29**, 191 (1996).
17) Dumeignil, F., Sato, K., Imamura, M., Matsubayashi, N., Payen, E., Shimada, H., submitted to *Appl. Catal. A: General*, (2006).
18) Breysse, M., Bachelier, J., Bonnelle, J. P., Cattenot, M., Cornet, D., Decamp, T., Duchet, J. C., Durand, R., Engelhard, P., Frety, R., Gachet, C., Geneste, P., Grimblot, J., Gueguen, C., Kasztelan, S., Lacroix, M., Lavalley, J. C., Leclercq, C., Moreau, C., de Mourgues, L., Olive, J. L., Payen, E., Portefaix, J. L., Toulhoat, H., Vrinat, M., *Bull. Soc. Chim. Belg.*, **96**, 829 (1987).
19) Vissenberg, M. J., van der Meer, Y., Hensen, E. J. M., de Beer, V. H. J., van der Kraan, A. M., van Santen, R. A., van Veen, J. A. R., *J. Catal.*, **198**, 151 (2001).
20) Pecoraro, T. A., Chianelli, R. R., *J. Catal.*, **67**, 430 (1981).
21) Ledoux, M. J., Michaux, O., Agostini, G., Panissod, P., *J. Catal.*, **102**, 275 (1986).
22) Lacroix, M., Bourtafa, N., Guillard, C., Vrinat, M., Breysse, M., *J. Catal.*, **120**, 473 (1989).
23) Qian, E. W., Kawano, T., Funato, A., Ishihara, A., Kabe, T., *Phys. Chem. Chem. Phys.*, **3**, 261 (2001).
24) Dumeignil, F., Amano, H., Wang, D., Qian, E. W., Ishihara, A.,

160

Kabe, T., *Appl. Catal. A: General*, **249**, (2), 255 (2003).

25) Vrinat, M., Lacroix, M., Breysse, M., Mosoni, L., Roubin, M., *Catal. Lett.*, **3**, 405 (1989).

26) Shabtai, J., Nag, N. K., Massoth, F. E., *J. Catal.*, **104**, 413 (1987).

27) Lu, K., Kuo, Y. J., Tatarchuk, B. J., *J. Catal.*, **116**, 373 (1989).

28) De Los Reyes, J. A., Vrinat, M., Geantet, C., Breysse, M., *Catal. Today*, **10**, 645 (1991).

29) Ishihara, A., Nomura, M., Kabe, T., *J. Catal.*, **150**, 212 (1994).

30) Raje, A. P., Liaw, S.-J., Davis, B. H., *Appl. Catal.*, **150**, 297 (1997).

31) Ogawa, Y., Toba, M., Yoshimura, Y., *Appl. Catal. A: General*, **246**, (2), 213 (2003).

32) Venezia, A. M., La Parola, V., Deganello, G., Pawelec, B., Fierro, J. L. G., *J. Catal.*, **215**, 317 (2003).

33) Lee, J., Ishihara, A., Dumeignil, F., Qian, E. W., Kabe, T., *J. Mol. Cat.*, **213**, (2), 207 (2004).

34) Barrio, V. L., Arias, P. L., Cambra, J. F., Güemez, M. B., Pawelec, B., Fierro, J. L. G., *Catal. Commun.*, **5**, (4), 173 (2004).

35) Ishihara, A., Dumeignil, F., Lee, J., Mitsuhashi, K., Qian, E. W., Kabe, T., *Appl. Catal. A: General*, **289**, 163 (2005).

36) Ramírez, J., Fuentes, S., Diaz, G., Vrinat, M., Breysse, M., Lacroix, M., *Appl. Catal.*, **52**, 211 (1989).

37) Okamoto, Y., Maezawa, A., Imanaka, T., *J. Catal.*, **120**, 29 (1989).

38) Wei, Z. B., Xin, Q., Guo, X. X, Grange, P., Delmon, B., Yoshida, S., *Catal. Sci. Technol.*, **1**, 147 (1991).

39) Ramírez, J., Ruiz-Ramírez, L., Cedeno, L., Harle, V., Vrinat, M., Breysse, M., *Appl. Catal. A: General*, **93**, 163 (1993).

40) Trawczyñski, J., Walendziewski, J., *Appl. Catal. A: General*, **119**, (1), 59 (1994).

41) Wei, Z. B., Wei, C. D., Xin, Q., *Acta Physico-chemica Sinica*, **10**, 402 (1994).

42) Olguin, E., Vrinat, M., Cedeno, L., Ramírez, J., Borque, M., López-Agudo, A., *Appl. Catal. A: General*, **165**, 1 (1997).

43) Ramírez, J., Gutierrez, A., *J. Catal.*, **170**, 108 (1997).

44) Pophal, C., Kameda, F., Hoshino, K., Yoshinaka, S., Segawa, K., *Catal. Today*, **39**, 21 (1997).

45) Klimowa, T., Casados, D. S., Ramírez, J., *Catal. Today*, **43**, (1-2), 135 (1998).

46) Lecrenay, E., Sakanishi, K., Nagamatsu, T., Mochida, I., Suzuka, T., *Appl. Catal. B: Environ.*, **18**, 325 (1998).

47) Yoshinaka, S., Segawa, K., *Catal. Today*, **45**, 293 (1998).

48) Fujikawa, T., Idei, K., Ohki, K., Mizuguchi, H., Usui, K., *Appl. Catal. A: General*, **205**, 71 (2001).

49) Wang, D. H., Qian, E. W., Ishihara, A., Kabe, T., *J. Catal.*, **203**, 322 (2001).

50) Wang, D., Qian, E. W., Ishihara, A., Kabe, T., *Appl. Catal. A: General*, **224**, (1-2), 191 (2002).

51) Wang, D. H., Qian, E. W., Ishihara, A., Kabe, T., *J. Catal.*, **209**, 266 (2002).

52) Wang, D., Li, X., Qian, E. W., Ishihara, A., Kabe, T., *Appl. Catal. A: General*, **238**, (1), 109 (2003).

53) Barrio, V. L., Arias, P. L., Cambra, J. F., Güemez, M. B., Pawelec, B., Fierro, J. L. G., *Fuel*, **82**, (5), 501 (2003).

54) Ishihara, A., Dumeignil, F., Wang, D., Li, X., Arakawa, H., Qian, E. W., Inoue, S., Muto, A., Kabe, T., *J. Jpn. Petrol. Inst.*, **48**, (1), 37 (2005).

55) Ishihara, A., Dumeignil, F., Wang, D., Li, X., Arakawa, H., Qian, E. W., Inoue, S., Muto, A., Kabe, T., *Appl. Catal. A: General*, **292**, 5 (2005).

56) Pawelec, B., Mariscal, R., Fierro, J. L. G., Greenwood, A., Vasudevan, P. T., *Appl. Catal. A: General*, **206**, (2), 295 (2001).

57) Sugioka, M., Sado, F., Kurosaka, T., Wang, X., *Catal. Today*, **45**, 327 (1998).

58) Pérot, G., *Catal. Today*, **86**, 111 (2003).

59) Inoue, S., Kudou, H., Muto, A., Ono, T., Proceedings of 225th ACS National Meeting, 2003, p. 88.

60) Inoue, S., Muto, A., Kudou, H., Ono, T., Proceedings of 226th ACS National Meeting, 2003, p. 496.

61) Dumeignil, F., Wang, D., Li, X., Arakawa, H., Qian, E. W., Inoue, S., Muto, A., Kabe, T., Ishihara, A., *Res. Chem. Intermed.*, **31**, (9), 759 (2005).

62) Qian, E. W., Ishihara, A., Ogawa, S., Kabe, T., *J. Phys. Chem.*, **98**, 907 (1994).

63) Dumeignil, F., Paul, J.-F., Qian, E. W., Ishihara, A., Payen, E., Kabe, T., *Res. Chem. Intermed.*, **29**, (6), 589 (2003).

64) Ramírez, J., Macías, G., Cedeño, L., Gutiérrez-Alejandre, A., Cuevas, R., Castillo, P., *Catal. Today*, **98**, 19 (2004).

65) Arrouvel, C., Breysse, M., Toulhoat, H., Raybaud, P., *J. Catal.*, **232**, 161 (2005).

66) Paul, J.-F., Payen, E., *J. Phys. Chem. B*, **107**, 4057 (2003).

67) Qian, E. W., Ishihara, A., Okoshi, Y., Nakakami, W., Godo, M., Kabe, T., *J. Chem. Soc., Faraday Trans.*, **93**, 4395 (1997).

68) Beuther, H., Flinn, R. A., Mckinley, J. B., *Ind. Eng. Chem. Res.*, **51**, 1349 (1959).

69) Pratt, K. C., Sanders, J. V., Tamp, N., *J. Catal.*, **66**, 82 (1980).

70) Ledoux, M. J., Hantzer, S., Guille, J., *Bull. Soc. Chim. Belg.*, **96**, 855 (1987).

71) Lecrenay, E., Sakanishi, K., Nagamatsu, T., Mochida, I., Suzuka, T., *Appl. Catal. B: Environ.*, **18**, (3-4), 325 (1998).

72) Robinson, W. R. A. M., van Veen, J. A. R., de Beer, V. H. J., van Santen, R. A., *Fuel Processing Technol.*, **61**, (1), 89 (1999).

73) Kabe, T., Aoyama, Y., Wang, D., Ishihara, A., Qian, E. W., Hosoya, M., Zhang, Q., *Appl. Catal. A: General*, **209**, (1-2), 237 (2001).

74) Qian, E. W., Hachiya, Y., Wang, D., Hirabayashi, K., Ishihara, A., Kabe, T., Okazaki, H., Adachi, M., *Appl. Catal. A: General*, **227**, 19 (2002).

75) Dumeignil, F., Paul, J.-F., Veilly, E., Qian, E. W., Ishihara, A., Payen, E., Kabe, T., *Appl. Catal. A: General*, **289**, (1), 51 (2005).

76) Schweiger, H., Raybaud, P., Toulhoat, H., *J. Catal.*, **212**, 33 (2002).

77) Sun, M., Nelson, A. E., Adjaye, J., *J. Catal.*, **226**, 32 (2004).

78) Sun, M., Nelson, A. E., Adjaye, J., *J. Catal.*, **233**, 411 (2005).

79) Dumeignil, F., Sato, K., Imamura, M., Matsubayashi, N., Payen, E., Shimada, H., *Appl. Catal. A: General*, **287**, 135 (2005).

80) Escobar, J., Toledo, J. A., Cortés, M. A., Mosqueira, M. L., Pérez, V., Ferrat, G., López-Salinas, E., Torres-García, E., *Catal. Today*, **106**, 222 (2005).

81) Choi, S. Y., Mamak, M., Coombs, N., Chopra, N., Ozin, G. A., *Advanced Functional Materials*, **14**, (4), 335 (2004).

82) Chen, H., Dai, K., Peng, T., Yang, H., Zhao, D., *Mater. Chem. Phys.*, **96**, 176 (2006).

83) Vrinat, M., Letourneur, D., Bacaud, R., Harle, V., Jouguet, B., Leclercq, C., *Stud. Surf. Sci. Catal.*, **127**, 153 (1999).

84) Saih, Y., Segawa, K., *Catal. Surf. Asia*, **7**, (4), 235 (2003).

85) Cecílio, A. A., Pulcinelli, S. H., Santilli, C. V., Maniette, Y., *J. Sol-Gel Sci. Technol.*, **31**, 87 (2004).

86) Grzechowiak, J. R., Wereszczako-Zelińska, I., Rynkowski, J., Ziołek, M., *Appl. Catal. A: General*, **250**, 95 (2003).

87) Gutiérez-Alejandre, A., Ramírez, J., Jiménez-del Val, I., Peñuelas-Galaz, M., Sánchez-Nerro, P., Torres-Mancerra, P., *Catal. Today*, **107-108**, 879 (2005).

88) Saih, Y., Nagata, M., Funamoto, T., Masuyama, Y., Segawa, K., *Appl. Catal. A: General*, **295**, 11 (2005).

89) Houalla, M., Nag, N. K., Sapre, A. V., Broderick, D. H., Gates, B. C., *AIChE J.*, **24**, 1015 (1978).

90) Houalla, M., Broderic, D. H., Sapre, A. V., Kag, N. K., de Beer, V. H. J., Gates, B. C., Kwart, H., *J. Catal.*, **61**, 523 (1980).

91) Qian, E. W., Hachiya, Y., Wang, D., Hirabayashi, K., Ishihara, A., Kabe, T., Okazaki, H., Adachi, M., *Appl. Catal. A: General*, **227**, 19 (2002).

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要　　旨

γ- アルミナ担持および高表面積チタニア担持モリブデン，コバルト-モリブデン，ニッケル-モリブデン水素化脱硫触媒挙動の[35]S トレーサー法に基づいた比較

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[^{35}S]DBT 水素化脱硫反応の結果に基づき，高表面積 TiO_2 担持および γ-Al_2O_3 担持 MoS_2，CoMoS，NiMoS 水素化脱硫触媒の反応特性を比較した。すでに我々が公表した MoS_2 および CoMoS 系触媒を用いて得た結果のまとめと，NiMoS 系触媒を用いた際の新結果との比較を行った。

MoS_2/Al_2O_3 触媒に Ni あるいは Co を添加すると，水素化脱硫反応が著しく促進する。プロモーターがどちらであっても，移動可能な硫黄量 (S_0) の増加が見られる。しかし，相異点もあり，Ni 助触媒を添加した MoS_2 触媒では，H_2S の放出速度定数 (k_{RE}) が Ni : Mo 比に対して火山形プロットになるのに対し，Co 助触媒においては，同定数は低い Co : Mo 比から横ばいになることが分かった。

脱硫反応時に Mo/TiO_2 触媒上に形成される TiMoS 相が硫黄の挙動を促進させるために，Mo/Al_2O_3 触媒に比べ Mo/TiO_2 触媒の活性が高い。しかし，CoMo/TiO_2 触媒は CoMo/Al_2O_3 触媒より活性が低い。その理由として考えられることは二つあり，(1) TiMoS 相と Co 助触媒の影響が同時に発生し，硫黄・金属間の結合が不安定となるためと，(2) Mo と Co 間の相互作用が十分に起こらないためである。また，Mo/TiO_2 触媒に Ni 助触媒を添加すると，k_{RE} および S_0 の値がともに増加することも分かった。この結果，TiO_2 担持 NiMo 触媒と Al_2O_3 担持 NiMo 触媒の脱硫能が近づいた。

[35]S アイソトープトレーサー法により，水素化脱硫触媒の反応特性に及ぼす Co の添加効果と Ni の添加効果は異なっていることが明らかとなった。

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