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Development of new catalysts for deep hydrodesulfurization of gas oil

Kohichi Segawa*, Kazushige Takahashi, Shinobu Satoh

Department of Chemistry, Faculty of Science and Technology, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan

Abstract

TiO_2–Al_2O_3 composite supports have been prepared by chemical vapor deposition (CVD) over γ-Al_2O_3 substrate, using $TiCl_4$ as the precursor. High dispersion of TiO_2 overlayer on the surface of Al_2O_3 has been obtained, and no cluster formation has been detected. The catalytic behavior of Mo supported on Al_2O_3, TiO_2 and TiO_2–Al_2O_3 composite has been investigated for the hydrodesulfurization (HDS) of dibenzothiophene (DBT) and methyl-substituted DBT derivatives. The conversion over the Mo catalysts supported on TiO_2–Al_2O_3 composite, in particular for the HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) is much higher than that of conversion obtained over Mo catalyst supported on Al_2O_3. The ratio of the corresponding cyclohexylbenzenes/biphenyls is increased over Mo catalyst supported on TiO_2–Al_2O_3 composite support. This means that the reaction rate of prehydrogenation of an aromatic ring rather than the rate of hydrogenolysis of C–S bond cleavage is accelerated for the HDS of DBT derivatives. The Mo/TiO_2–Al_2O_3 catalyst leads to higher catalytic performance for deep HDS of gas oil. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrodesulfurization; Gas oil; Chemical vapor deposition

1. Introduction

Recently, the interest in the deep hydrodesulfurization (HDS) of gas oil has been renewed due to the stricter regulations concerning the sulfur content in diesel oil. In order to protect the global environment, many industrialized countries have lowered the limit of the sulfur content of gas oil to 0.05% in the middle of 1990s, and will have lowered the limit to 0.005% (50 ppm) in the near future. To meet this assignment, the development of a suitable catalyst for the deep HDS of gas oil is a very important subject.

When gas oil was desulfurized with a conventional HDS catalyst, the most refractory sulfur compounds were found to be dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), and 4,6-DMDBT [1]. Fig. 1 shows the FPD chromatogram of Arabian light middle distillates before and after HDS processing. There are many different kinds of sulfur compounds are present in the gas oil fraction, such as alkyl-substituted benzothiophene (BT) and DBT derivatives. It is obvious that the DBT derivatives still remain even in the product oil. Therefore, DBT, 4-MDBT and 4,6-DMDBT are the key sulfur compounds for HDS in the gas oil fraction and it is thus difficult to desulfurize this fraction. To reduce the sulfur content of the previous 0.25% gas oils to the new 0.05% standards, 75% of the refractory species will have to be desulfurized, preferably without altering any of the other components of the gas oil, which constitute more than 98% of the total gas oil. Therefore, in order to achieve deep HDS, it is essential to desulfurize DBT derivatives effectively.

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* Corresponding author. Tel.: +81-3-3238-3452;
fax: +81-3-3238-4350.
E-mail address: k-segawa@sophia.ac.jp (K. Segawa).

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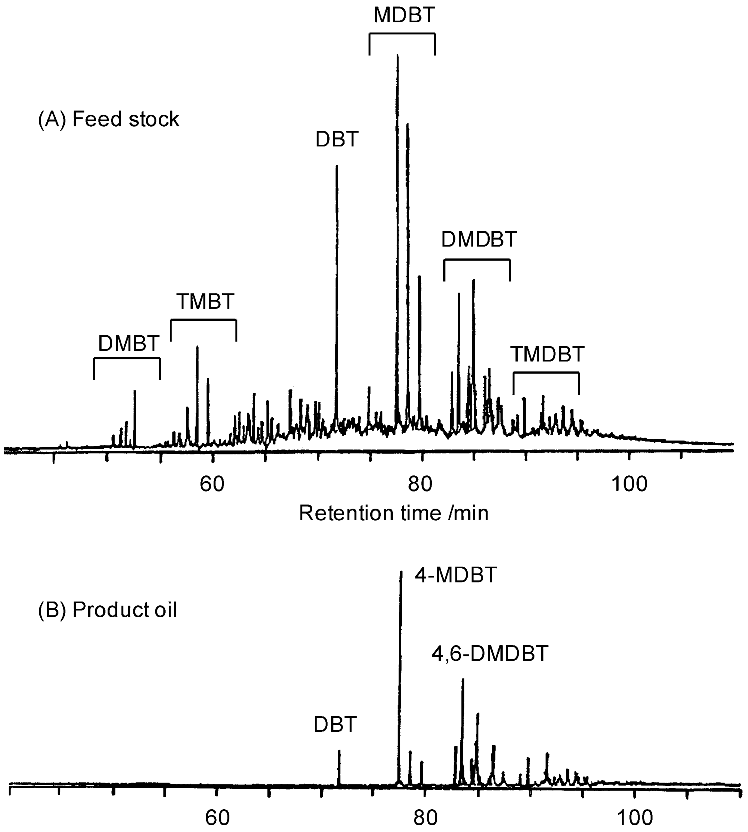
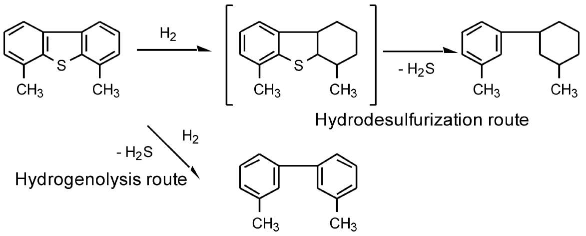


Fig. 1. FPD chromatogram of gas oil before and after HDS processing: (A) Arabian light middle distilate, (B) product oil after HDS (S: 0.05%).

Two reaction pathways for the HDS of alkyl-substituted DBT are proposed, they are illustrated in Scheme 1 [1,2]. The direct sulfur abstraction (hydrogenolysis route) leads to 4,6-dimethyl-BP, whereas prehydrogenation is forming dimethyl-hexahydro-DBT as an intermediate (HDS route), which is desulfurized to the corresponding cyclohexylbenzene (CHB) derivatives. Furthermore, it is known that hydrogenation of neighboring phenyl groups reduces the steric hindrance caused by the methyl groups.



Scheme 1. Reaction pathways in HDS of 4,6-DMDBT.

In the petroleum refining industry, γ-alumina (γ-Al_2O_3) supported molybdenum oxide catalysts promoted with cobalt or nickel have been widely used for the HDS of sulfur compounds. A new catalyst is required to desulfurize DBT, 4-MDBT and 4,6-DMDBT efficiently, these sulfur compounds are the keys to achieve deep HDS of gas oil. Recently, TiO_2-supported molybdena catalysts have attracted increasing attention, because of their higher reducibility to a lower valence state of molybdenum and their higher catalytic activity for HDS, as well as for hydrocracking, compared to Al_2O_3 supported materials [3–5]. Various studies have focused on the characterization of molybdenum species supported on TiO_2, using several experimental techniques such as Raman spectroscopy, XPS and temperature programmed reduction (TPR) [6–11]. The formation of the active sites when MoO_3 changes to MoS_2 by sulfurization has been elucidated by Arnoldy et al. [12]. Nishijima et al. [13] and Shimada et al. [14] have investigated molybdenum catalysts supported on Al_2O_3, TiO_2, SiO_2 and MgO by means of extended X-ray absorption fine structure (EXAFS), XPS and Raman spectroscopy. They reported the presence of different molybdenum species on the surface of the supports investigated. However, pure TiO_2 supports have very small specific surface areas compared to γ-Al_2O_3, and it is difficult to make pellets. Furthermore, the active anatase structure possesses only low thermal stability. This makes TiO_2 support alone is unsuitable for industrial applications. Coating of the surface of commercially available γ-Al_2O_3 with TiO_2 may lead to TiO_2–Al_2O_3 composite supports which could help to overcome the disadvantages of pure TiO_2 supports [15–19]. We could prepare some new types of catalyst support for deep HDS, e.g., TiO_2–Al_2O_3 composite supports have been prepared by chemical vapor deposition (CVD) over γ-Al_2O_3 substrate, using $TiCl_4$ as the precursor. The Mo catalyst supported on TiO_2–Al_2O_3 composite showed much higher HDS activity for DBT than that of the catalyst supported on conventional γ-Al_2O_3 support.

2. Experimental

2.1. Preparation of TiO_2–Al_2O_3 supports and Mo catalysts

TiO_2 was supplied by Degussa (P-25, $51\,m^2\,g^{-1}$) and the γ-Al_2O_3 support was provided by Nikki (N611-N, $186\,m^2\,g^{-1}$). The TiO_2–Al_2O_3 composite supports were prepared by CVD method of $TiCl_4$ on γ-Al_2O_3 [15–17], according to the following procedure: 2 g of γ-Al_2O_3 (12–24 mesh) substrate was placed in a quartz tubular reactor and pretreated for 2 h at 773 K in oxygen flow. The substrate was then exposed to $TiCl_4$ (WAKO) vapor (0.43 kPa) at 473 K, when $TiCl_4$ was mixed with N_2 as carrier gas. The decomposition time was varied between 0.5 and 20 h, in order to obtain different loadings of TiO_2. Afterwards, the sample was hydrolyzed by water vapor (2.30 kPa) with N_2 as carrier gas at 473 K for 2 h. Calcination was carried out under O_2 flow for 2 h at 773 K. The supported Mo catalysts used in this study were prepared by an impregnation method. Impregnation was performed at 323 K for 100 h, using an aqueous solution of ammonium heptamolybdate (0.004 M) over the support. After impregnation, all materials were dried at 373 K for 10 h and calcined at 773 K for 10 h in air.

2.2. HDS reaction of methyl-substituted DBT

The HDS reaction was carried out in a fixed bed high-pressure flow reactor, consisting of a 0.5-in. stainless steel tube packed with 250-mg catalyst mixed with quartz sand. Before the reaction, the catalysts were dried at 773 K for 5 h under oxygen stream and presulfided with a mixture of H_2S (5%) and H_2 for 2 h at 573 K under atmospheric pressure. After purging of excess H_2S by nitrogen stream at 573 K for 0.5 h, H_2 and the reaction mixture were supplied to the reactor.

The reactant methyl-substituted DBT derivatives were synthesized as described in the literature [20]. All reaction mixtures used in this study were diluted in *n*-dodecane. The initial content of sulfur was 0.05% and the reaction temperature was 573 K (H_2 pressure: 3 MPa, H_2 flow rate: $0.2\,dm^3\,min^{-1}$, LHSV: 12.08–$16.07\,h^{-1}$). The liquid products collected from a gas–liquid separator were analyzed by GC (Hitachi G-3000) and GC–MS (GC: Hewlett Packard 5890 Series II, MS: Nihondenshi JMS-SX 102A). The activity of the catalysts under investigation was estimated by the conversion of the DBT derivatives and by the ratio of the products after reaching steady state.

2.3. Characterization of the supports and the catalysts

Nitrogen adsorption measurements were performed at 77 K on a BEL Japan BELSORP, 28SA, to determine the specific surface area. As pretreatment, 200 mg of support were placed in a quartz tube and evacuated for 6 h at 573 K. The pore volume and the pore size distribution were obtained by the Dollimore–Heal method [21].

XPS measurements were carried out at room temperature to investigate the state of molybdenum on the surface of the different supports. Data were collected before and after sulfiding for 2 h at 673 K, with 5% H_2S diluted in H_2 as carrier gas. The data were taken on a Surface Science Laboratory SSX-100 spectrometer, using monochromized Al Kα-radiation (1486.6 eV) and the C (1 s) binding energy (285.5 eV) was taken as reference. Before measuring, all samples have been evacuated and pretreated at 573 K.

3. Results and discussion

Gas oil refining currently operates at moderate temperatures (610–640 K) and hydrogen pressures of 3.5–5.0 MPa, usually with CoMo/Al_2O_3 catalysts. These conditions are unable to achieve the 0.05% specification of gas oil. Thus, there is a continuing need for new HDS technology, particularly in the areas of developing more active catalysts and novel process options that can meet the new standards at lower pressures with present equipment.

3.1. Preparation of TiO_2–Al_2O_3 composite supports

A novel catalyst support for deep HDS, such as TiO_2–Al_2O_3 composite supports, have been prepared by CVD over γ-Al_2O_3 substrate, using $TiCl_4$ as the precursor. We assume that TiO_2 covers the surface of the γ-Al_2O_3 support mainly without forming aggregates or precipitation during the preparation of TiO_2–Al_2O_3 composite supports. The IR spectra for stretching vibrations of hydroxyl group (υ_{OH}) of γ-Al_2O_3 and TiO_2–Al_2O_3 composite supports with different loadings of TiO_2 are displayed in Fig. 1. The TiO_2 loadings were increased with increasing deposition time of $TiCl_4$ precursor [16]. Before CVD treatment, OH stretching bands of γ-Al_2O_3 appear at 3762, 3723 and 3680 cm^{-1}. They correspond to hydroxyl stretching vibrations of Al–OH groups. Even at low TiO_2 loadings (2.3%), the band at 3762 cm^{-1} has almost disappeared, while the bands at 3723 and 3680 cm^{-1} are not significantly affected at very low TiO_2 coverage. Nevertheless, a further increase of the TiO_2 loading, up to a total amount of 11 wt.% leads to a strong decrease of the integral intensities of all observed stretching bands. This might be due to the fact that the Al_2O_3 surface is not completely covered. With regard to a closed packing of TiO_2 and under the assumption of a TiO_2 monolayer, the surface of the γ-Al_2O_3 support would be completely covered at loadings of about 15 wt.% titania. Nevertheless, higher loadings of TiO_2 may lead to a more complete elimination of hydroxyl bands on the alumina surface. The comparison of the surface composition and the total amount of TiO_2 unambiguously reveal that the TiO_2 overlayer is highly dispersed on the surface of the γ-Al_2O_3 support, and that Al–OH groups are substituted by Al–O–Ti groups after calcination at 773 K.

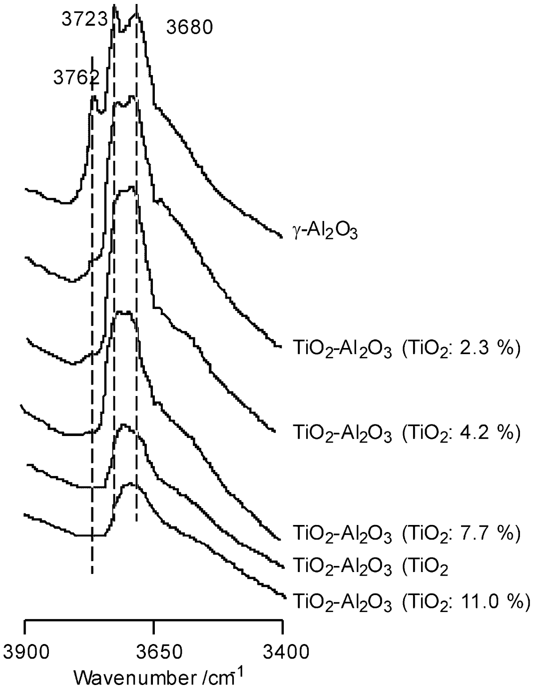


Fig. 2. IR spectra of Al–O–H stretching region of γ-Al_2O_3 and TiO_2–Al_2O_3 composite supports with different TiO_2 loadings.

Fig. 2 shows the pore size distribution obtained for γ-Al_2O_3 (N611-N: 186 $m^2\,g^{-1}$), TiO_2 (P-25: 55 $m^2\,g^{-1}$) and TiO_2–Al_2O_3 (TiO_2: 10.2%) composite supports which were prepared by CVD method over γ-Al_2O_3. It is obvious that pure TiO_2 possesses no pore system; the samples are composed of fine small particles. The crystal form is found to be anatase by XRD powder patterns. With regard to γ-Al_2O_3 and TiO_2–Al_2O_3 composite support, the average pore diameter is only slightly shifted to lower values than that of γ-Al_2O_3, whereas the distribution of the pore volume is not significantly affected by the coverage of Al_2O_3 with TiO_2. Thus, TiO_2 can be assumed to situate on the surface of the γ-Al_2O_3 support, and the incorporation of significant amounts of titanium

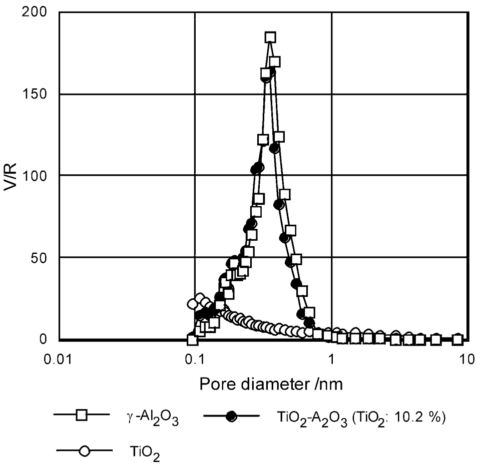


Fig. 3. Pore size distribution of γ-Al_2O_3, TiO_2, and TiO_2–Al_2O_3 composite support prepared by CVD method.

into the γ-Al_2O_3 matrix can, within the sensitivity of the investigation methods, be excluded. These results also reflect a homogeneous dispersion of TiO_2 overlayer on the surface of the Al_2O_3 support. The resulting composite TiO_2–Al_2O_3 composite support remains mesoporous, with a more or less monomodal pore size distribution and an average pore diameter of about 3.8 nm (Fig. 3).

3.2. HDS reactions of DBTs

Though it has long been known that the more highly condensed thiophene structures, such as DBT and especially their alkyl-substituted derivatives, have low HDS reactivity, it is only recently that study in this area has built up. Many of groups throughout the world are now actively seeking understanding of the fundamental causes of low reactivity and attempting to find means to avoid the problems. To elucidate the influence of the positions of methyl-groups on the conversion rate, we studied the HDS of a mixture of DBT, 2-methyl-DBT (2-MDBT) and 2,8-dimethyl-DBT (2,8-DMDBT), as well as that of other mixture of DBT, 4-MDBT and 4,6-DMDBT over Mo/Al_2O_3 catalysts on the different supports.

As already pointed out, the HDS of DBT derivatives leads to the corresponding substituted BP and CHB compounds (see Scheme 1). The product selectivity mainly depends on the reaction pathway. Prehydrogenation of neighboring phenyl groups leads to an intermediate, and then CHB derivatives are produced (HDS route). In contrast to that, the desulfurization without prehydrogenation (direct desulfurization route) leads to the corresponding BP products.

To elucidate the influence of the positions of methyl groups on the conversion rate in a mixture of different DBT derivatives, we studied the HDS for a mixture of DBT, 4-MDBT and 4,6-DMDBT (molar ratio: 1/1/1) over the Mo/Al_2O_3 catalysts (MoO_3: 6%). For comparison, the HDS for a mixture of DBT, 2-MDBT and 2,8-DMDBT (molar ratio: 1/1/1) has been performed under the same reaction conditions. The relative activity obtained at 573 K and a H_2 pressure of 3 MPa, for the HDS reaction of DBT derivatives over the Mo/Al_2O_3 catalysts under investigation are depicted in Table 1. As expected, the conversion for the different sulfur compounds increases as follows: DBT $>$ 4-MDBT $>$ 4,6-DMDBT. This leads to the assumption of a competitive mechanism between these sulfur compounds. The electron density at the sulfur atom is enhanced in the case of all methyl-substituted DBT derivatives. Nevertheless, concerning the direct desulfurization pathway, the steric hindrance retarding the C–S bond occurs only when the methyl groups are at 4 or 4,6 position. However, the relative activities of 2-MDBT and 2,8-DMDBT in a mixture with DBT are as follows: DBT $<$2-MDBT $<$2,8-DMDBT. Due to the higher electron density located at the sulfur atom of DBT, and the lower steric hindrance with active sites, the highest reaction rate over all catalysts under investigation was found for 2,8-DMDBT. The results suggest that the methyl migration from 4- and/or 6-positions of 4,6-DMDBT may enhance the HDS activity in order to avoid steric hindrance of the interaction between active sites for catalyst surfaces and the S atoms of DBT. To increase the isomerization activity

Table 1
Effect of substituent groups on DBT of HDS over MoS_2/Al_2O_3 (Mo: 6%) catalyst[a]

Substituent position	DBT	4-Methyl-DBT	4,6-Dimethyl-DBT
Relative activity	1.00	0.43	0.17
Substituent position	DBT	2-Methyl-DBT	2,8-Dimethyl-DBT
Relative activity	1.00	1.50	1.97

[a] Reaction conditions: reaction pressure 3 MPa, reaction temperature 573 K, LHSV 12–16 h^{-1}, H_2 flow rate 200 $cm^3\,min^{-1}$.

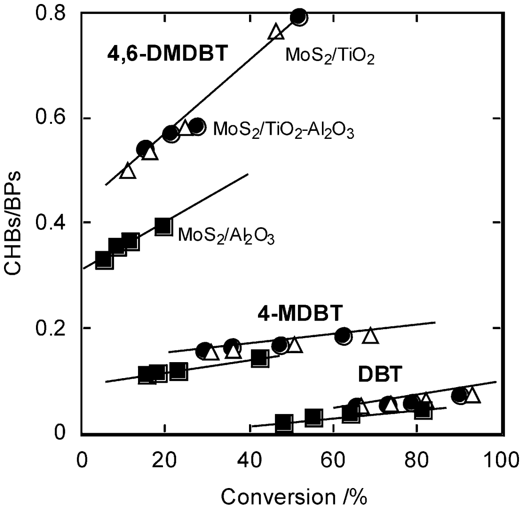


Fig. 4. Selectivity of cyclohexyl-benzene route versus hydrogenolysis route as a function of conversion of DBTs for HDS (Mo: 6%): reaction pressure 3 MPa, reaction temperature 573 K, LHSV 6–32 h^{-1}, H_2 flow rate 200 cm^3 min^{-1}.

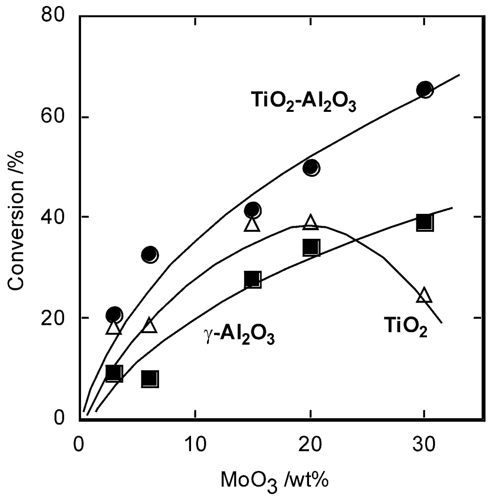


Fig. 5. HDS activities for 4,6-DMDBT as a function of Mo loadings: reaction pressure 3 MPa, reaction temperature 573 K, LHSV 12–16 h^{-1}, H_2 flow rate 200 cm^3 min^{-1}.

and/or hydrogenation activity over the HDS catalyst would be preferable for future developments of HDS catalyst.

In order to examine the influence of the difference of supports on the reaction pathways of methyl-substituted DBT derivatives, the HDS reactions of a mixture of DBT derivatives were carried out with different contact times at 573 K and H_2 pressure of 3 MPa. In the course of this investigation, we used the composite types of TiO_2–Al_2O_3 support with titania loading of 10.2 wt.%, which showed the highest conversion in the Mo/TiO_2–Al_2O_3 system. The selectivity of CHB derivatives (CHBs/BPs) obtained over Mo catalysts as a function of conversion is illustrated in Fig. 4. In all the catalysts, the longer contact time led to the higher conversions of DBTs and to higher ratios of corresponding CHBs/BPs. Comparing the three sulfur compounds, we found that the sequence of CHBs/BPs increased in the following order: DBT $<$ 4-MDBT $<$ 4,6-DMDBT. This implies that, on the HDS of methyl-substituted DBT derivatives, the conversion to CHB derivatives is more important, because prehydrogenation of an aromatic ring reduces the steric hindrance by methyl groups. Therefore, the promotion of the HDS route leads to higher conversion of 4-MDBT and 4,6-DMDBT. For all the sulfur compounds, the ratios of CHBs/BPs obtained over Mo/TiO_2 and Mo/TiO_2–Al_2O_3 are higher than those obtained over Mo/Al_2O_3. Especially in the case of 4,6-DMDBT, the HDS route (see Scheme 1) over Mo/TiO_2 and Mo/TiO_2–Al_2O_3 are much higher than those obtained over Mo/Al_2O_3.

With regard to 4,6-DMDBT, the conversion rate over the different catalysts increases with increased Mo loadings (Mo: 3–30 wt.% as MoO_3), as are shown in Fig. 5. Concerning the conversions of 4,6-DMDBT, all catalysts revealed lower conversion rates than that of DBT, because of the lower reactivities of these compounds. However, the methyl-substituted CHB/BP ratios detected over the investigated catalysts are increased, whereas observed conversions are significantly higher over Mo/TiO_2 and Mo/TiO_2–Al_2O_3 than that of Mo/Al_2O_3. The most remarkable result is the very high catalytic activity of the TiO_2–Al_2O_3 supported molybdenum, reaching conversions of 65% for the HDS of 4,6-DMDBT at higher loading of Mo catalyst (Mo: 30% as MoO_3). On the other hand, over Mo/Al_2O_3, 4,6-DMDBT conversions of only 39% are obtained. The high conversions for the HDS of 4,6-DMDBT over Mo/TiO_2–Al_2O_3 can mainly be attributed to the high ratios of corresponding CHB/BP ratios, which become higher than those obtained over Mo/TiO_2 and Mo/Al_2O_3. In the case of Mo/TiO_2, the catalytic activity was also higher than that of Mo/Al_2O_3 at lower loading of Mo (Mo: 3–15% as MoO_3). However, at higher loading region, the HDS activities were retarded, due to the smaller specific area of support. This implies the hydro-desulfurization route to be more important for the HDS of 4,6-DMDBT over Mo/TiO_2–Al_2O_3 compared to the Al_2O_3 and TiO_2 supported Mo catalysts. As already pointed out above, prehydrogenation of an aromatic ring reduces the steric hindrance by methyl groups during the C–S bond scission and leads to the corresponding CHB derivatives.

Judged by the detected conversions discussed above, over TiO_2–Al_2O_3 and TiO_2 supported Mo catalysts, we conclude that the HDS route is much more important than the route of hydrogenolysis over the Mo/Al_2O_3 catalyst. According to Mochida and co-workers [22], the prehydrogenation of an aromatic ring leads to higher reactivities of 4-MDBT and 4,6-DMDBT. These results in comparably high conversions for the HDS of 4-MDBT and 4,6-DMDBT over the Mo catalysts supported on the TiO_2–Al_2O_3 composite material. In agreement with Kabe and co-workers [23], the reactivity of the sulfur compounds under investigation decreases in the order: 2,8-DMDBT > 2-MDBT > DBT > 4-MDBT > 4,6-DMDBT. This is true for all investigated catalysts.

3.3. *Characterization of Mo catalysts supported on TiO_2–Al_2O_3 composite*

Molybdenum XPS investigations have been performed in order to elucidate the state of molybdenum sites on the TiO_2–Al_2O_3 composite support. The results obtained by the Mo 3d XPS spectra for calcined and sulfided Mo/Al_2O_3, Mo/TiO_2, and Mo/TiO_2–Al_2O_3, crystalline MoO_3 and crystalline MoS_2 powder are illustrated in Fig. 6. The peaks obtained for Mo/Al_2O_3 (B) are much broader than those obtained for crystalline MoO_3 (A), Mo/TiO_2 (C), and Mo/TiO_2–Al_2O_3 (D). Nevertheless, the state of the molybdenum species on the TiO_2–Al_2O_3 composite support can be regarded as a state to Mo/TiO_2. The broadening of the 3d XPS peaks might be caused by strong interactions between Mo and the support, as well as by structural distortions. TiO_2 loadings of 10.2 wt.% provide Mo species, which are more similar to the Mo species present on pure TiO_2 supports than to molybdenum supported on Al_2O_3.

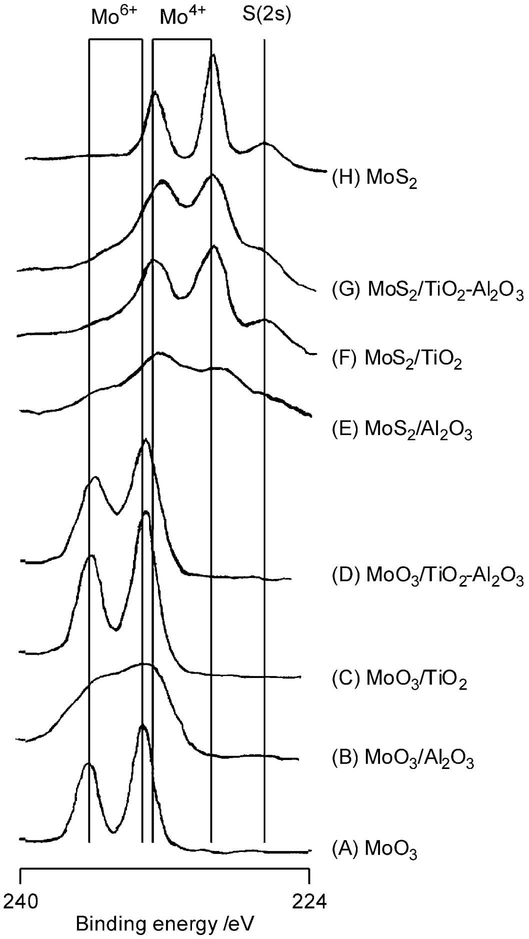


Fig. 6. XPS spectra of oxidic and sulfied Mo (Mo: 6%) on Al_2O_3, TiO_2, and TiO_2–Al_2O_3 (TiO_2: 10.2%).

After sulfurization, the Mo(VI)-species have strongly decreased. The binding energies for crystalline MoS_2 (H) are 233.0 eV ($3d_{3/2}$) and 229.9 eV ($3d_{5/2}$). The spectra of sulfided MoO_3 on the different supports can also be assigned to MoS_2 species, whereas Mo(VI) species are still present. As already obtained for the calcined materials, sulfided Mo/Al_2O_3 (E) reveals broader binding energy distributions than MoS_2, Mo/TiO_2 (F) and Mo/TiO_2–Al_2O_3 (G). This might be caused by the same reasons as mentioned above. However, the binding energies ($3d_{5/2}$) of the sulfided catalysts

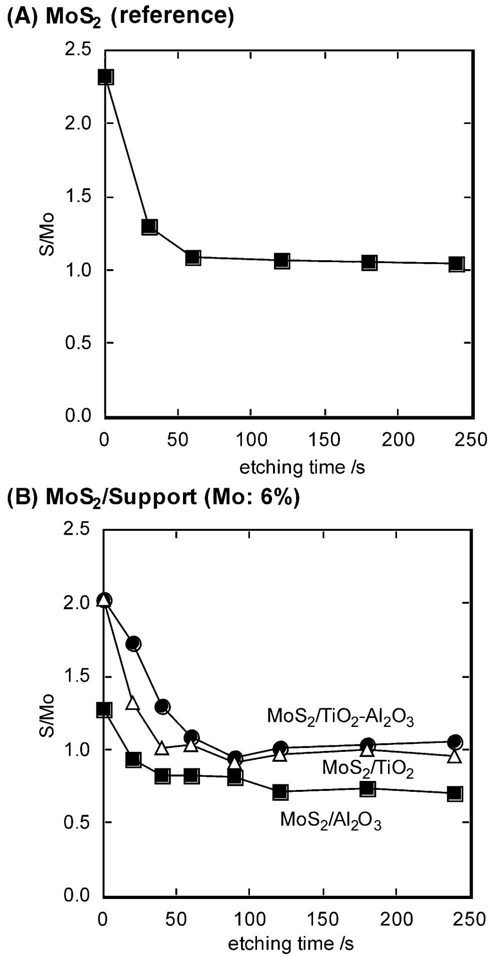


Fig. 7. Mo/S ratios on XPS spectra of MoS_2/Al_2O_3, MoS_2/TiO_2, and MoS_2/TiO_2–Al_2O_3 (TiO_2: 10.2%) as a function of Ar etching time.

increase as follows: $Mo/Al_2O_3 < Mo/TiO_2\text{-}Al_2O_3 = Mo/TiO_2$.

Fig. 7B reveals S/Mo ratios of sulfided Mo/Al_2O_3, Mo/TiO_2–Al_2O_3, and Mo/TiO_2, as a function of Ar etching time. The S/Mo ratio of crystalline form of MoS_2 was about 2.3 before Ar etching, and equilibrated at about 1.0 at longer etching time, these values are shown in Fig. 7A as a reference. Similar observations of S/Mo ratios on Mo/TiO_2–Al_2O_3, and Mo/TiO_2 are shown in Fig. 7B. However, the equilibrated value of S/Mo on Mo/Al_2O_3 at longer etching time was 0.6, which value is much smaller than that of Mo/TiO_2–Al_2O_3 and Mo/TiO_2. The results suggest that the surface species of Mo after sulfiding treatment on Mo/TiO_2–Al_2O_3 and Mo/TiO_2 became to the MoS_2 like structure, which reflect the higher catalytic activities for HDS than that of Mo/Al_2O_3 catalyst. Nevertheless, in agreement with the calcined materials, the spectra of MoS_2 and of sulfided Mo/TiO_2–Al_2O_3 or Mo/TiO_2 are very similar, indicating the structure of surface MoS_2 to be also very similar (see Fig. 5). As already stated above, and in particular in the case of the Al_2O_3 support, there are still Mo(VI) species present and the sensitivity of the XPS technique used is not high enough to make any conclusion on the exact structural state of Mo on the surface of the different supports.

4. Conclusions

We prepared TiO_2–Al_2O_3 composite supports by CVD method. The HDS reactions of DBT, 4-MDBT, and 4,6-DMDBT were carried out over molybdenum catalysts. The conversion rates obtained over Mo/TiO_2–Al_2O_3 catalyst were much higher than that obtained over Mo/Al_2O_3. With regard to the HDS of 4,6-DMDBT, this catalyst revealed higher conversion than Mo/TiO_2. According to the higher CHBs/BPs ratios obtained over Mo/TiO_2–Al_2O_3, the HDS route was promoted than that of hydrogenorisis. XPS investigations of catalysts before and after sulfiding suggest that the interaction between Mo and Al_2O_3 is stronger than that between Mo and TiO_2–Al_2O_3 composite, and also suggest that the reducibility from oxidic to sulfidic Mo species on the TiO_2–Al_2O_3 composite is higher than that on the Al_2O_3 support. Therefore, the number of active sites for HDS has increased on the surface of TiO_2–Al_2O_3 composite supports.

References

[1] D.D. Whitehurst, T. Isoda, I. Mochida, Adv. Catal. 42 (1998) 345.
[2] K. Segawa, S. Satoh, Stud. Surf. Sci. Catal. 127 (1999) 129.
[3] K.Y.S. Ng, E. Gulari, J. Catal. 95 (1985) 33.
[4] Y. Okamoto, A. Maezawa, T. Imanaka, J. Catal. 120 (1989) 29.
[5] H. Shimada, T. Sato, Y. Yoshimura, J. Hirai, A. Nishijima, Shokubai 27 (1985).
[6] S. Matsuda, A. Kato, Appl. Catal. 8 (1983) 149.

[7] G. Muralidhar, F.E. Massoth, J. Shabtai, J. Catal. 85 (1984) 44.

[8] A. Fernandez, J. Leurer, A.R. Gonzales-Elipe, G. Munuera, H. Knozinger, J. Catal. 120 (1988) 489.

[9] D.S. Kim, Y. Kurusu, I.E. Wachs, F.D. Hardcastle, K. Segawa, J. Catal. 120 (1988) 325.

[10] R.B. Quincy, M. Houalla, A. Proctor, D.M. Hercules, J. Catal. 125 (1990) 214.

[11] J. Ramirez, R. Cuevas, L. Gasque, M. Vrinat, M. Breysse, Appl. Catal. 71 (1991) 351.

[12] P. Arnoldy, J.A.M. van den Heijkant, G.D. de Bok, J.A. Moulijn, J. Catal. 92 (1985) 35.

[13] A. Nishijima, H. Shimada, T. Sato, T. Yoshimura, J. Hiraishi, Polyhedron 5 (1986) 243.

[14] H. Shimada, T. Sato, Y. Yoshimura, J. Hiraishi, A. Nishijima, J. Catal. 120 (1988) 275.

[15] K. Segawa, M. Katsuta, F. Kameda, Catal. Today 29 (1996) 215.

[16] C. Pophal, F. Kameda, K. Hoshino, S. Yoshinaka, K. Segawa, Catal. Today 39 (1997) 21.

[17] S. Yoshinaka, K. Segawa, Catal. Today 45 (1998) 1998.

[18] A. Stranick, M. Houalla, D.M. Hercules, J. Catal. 125 (1990) 214.

[19] Z. Wei, Q. Xin, X. Guo, E.L. Sham, P. Granga, B. Delmon, Appl. Catal. 63 (1990) 305.

[20] R. Gerdil, E.A. Lucken, J. Am. Chem. Soc. 87 (2) (1965) 213.

[21] D. Dollimore, G.R. Heal, J. Appl. Chem. 14 (1964) 109.

[22] T. Isoda, X. Ma, I. Mochida, Sekiyu Gakkaishi 37 (1994) 368.

[23] Q. Zhang, A. Ishihara, T. Kabe, Sekiyu Gakkaishi 39 (1996) 410.