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Catalysis Today 45 (1998) 293–298

CATALYSIS TODAY

Hydrodesulfurization of dibenzothiophenes over molybdenum catalyst supported on TiO_2–Al_2O_3

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Abstract

Composite types of TiO_2–Al_2O_3 supports, which are γ-aluminas coated by titania, have been prepared by chemical vapor deposition (CVD), using $TiCl_4$ as a precursor. Then supported molybdenum catalysts have been prepared by an impregnation method. As supports, we employed γ-alumina, anatase types of titania, and composite types of TiO_2–Al_2O_3 with different loadings of TiO_2. We studied the conversion of Mo from oxidic to sulfidic state through sulfurization by X-ray photoelectron spectroscopy (XPS). The obtained spectra unambiguously revealed the higher reducibility from oxidic to sulfidic molybdenum species on the TiO_2 and TiO_2–Al_2O_3 supports compared to that on the Al_2O_3 support. Higher TiO_2 loadings of the TiO_2–Al_2O_3 composite support led to higher reducibility for molybdenum species. Furthermore, the catalytic behavior of supported molybdenum catalysts has been investigated for hydrodesulfurization (HDS) of dibenzothiophene (DBT) and methyl-substituted DBT derivatives. The conversion over the TiO_2–Al_2O_3 supported Mo catalysts, in particular for the 4,6-dimethyl-DBT, is much higher than that obtained over Al_2O_3 supported Mo catalyst. The ratio of the corresponding cyclohexylbenzene (CHB)/biphenyl (BP) derivatives is increased over the Mo/TiO_2–Al_2O_3. This indicates that the prehydrogenation of an aromatic ring plays an important role in the HDS of DBT derivatives over TiO_2–Al_2O_3 supported catalysts. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Hydrodesulfurization; Titania–alumina support; Chemical vapor deposition; Mo catalyst

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 fuel. The Japanese government decided to lower the limit of the sulfur content from 0.2–0.05 wt% in 1997 in order to protect the environment from diesel emissions. To meet this assignment, the development of a suitable catalyst for the deep HDS is a very urgent subject. Taking cost requirements into consideration, a reaction temperature below 623 K and a reaction pressure of H_2 below 3.5 MPa would be preferable.

In the petrochemical industry, γ-alumina supported molybdenum catalysts promoted by cobalt or nickel have been widely used for HDS of sulfur compounds. Recently, TiO_2 supported molybdena catalysts have attracted more and more attention, because of their higher reducibility to a lower valence state of molybdenum and their higher catalytic activity for HDS [1–5] compared to alumina supported molybdenum catalysts [6]. However, TiO_2 supports have no pore system. Their specific surface areas are very small compared to those of alumina, and it is difficult to

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PII: S0920-5861(98)00232-6

make pellets out of such materials [6]. Furthermore, the active anatase structure possesses only low thermal stability. This makes TiO_2 support alone unsuitable for industrial applications. In order to overcome these drawbacks, we prepared composite types of TiO_2–Al_2O_3 supports, which were titania over-layers coated on alumina supports, by chemical vapor deposition (CVD) using $TiCl_4$ as precursor [7,8].

4-methyl-DBT (4-MDBT) and 4,6-dimethyl-DBT (4,6-DMDBT) are key sulfur compounds in the gas oil fraction and they are difficult to desulfurize [9–15]. Nevertheless, in order to achieve deep HDS, it is essential to desulfurize these molecules. In the present work, we therefore focused on the composite types of TiO_2–Al_2O_3 supports with different loadings of TiO_2. To examine the catalytic activity of the TiO_2–Al_2O_3 supported Mo catalysts, we studied the HDS of dibenzothiophene (DBT) derivatives, such as DBT, 4-MDBT and 4,6-DMDBT, under mild reaction conditions. Furthermore, we investigated by means of X-ray photoelectron spectroscopy (XPS) the catalyst conditions before and after sulfiding.

2. Experimental

The composite types of TiO_2–Al_2O_3 supports were prepared by CVD method, using $TiCl_4$ as precursor [16,17]. γ-alumina was exposed to $TiCl_4$ vapor (0.43 kPa) at 473 K. Here $TiCl_4$ was mixed with N_2 as carrier gas. 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 loadings of titania were determined by X-ray fluorescence analysis (XRF). Using X-ray diffraction (XRD) analysis, we examined whether the TiO_2 precipitations were formed or not. The supported molybdena catalysts used in this study were prepared by an impregnation method, using an aqueous solution of ammonium heptamolybdate. Impregnation was performed at 323 K. After impregnation, all materials were calcined at 773 K for 10 h in air. As a support, we used γ-Al_2O_3 provided by NIKKI, TiO_2 (anatase) provided by Degussa, and the composite types of TiO_2–Al_2O_3 stated above.

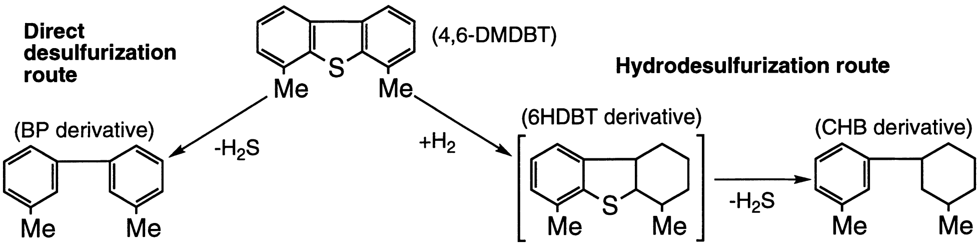
The HDS reaction of the mixture of dibenzothiophenes was carried out in a fixed bed high pressure flow reactor. Before the reaction, the catalysts were presulfided with a mixture of 5% H_2S and H_2 for 2 h at 573 K under atmospheric pressure. After pretreatment, H_2 and reaction mixture were supplied to the reactor. The used methyl-substituted dibenzothiophene derivatives were synthesized as described in the literature [18]. All reaction mixtures used in this study were diluted in *n*-dodecane (DBT:4-MDBT:4,6-DMDBT=1:1:1), and the initial content of sulfur was 0.05 wt%. The reaction conditions were as follows: reaction temperature 573 K, H_2 pressure 3 MPa, H_2 flow rate 0.2 $dm^3\ min^{-1}$, LHSV 6.04–32.14 h^{-1}. The liquid products collected from a gas-liquid separator were analyzed by GC and GC-MS.

The catalysts have been characterized by XPS. XPS measurements were carried out at room temperature in order to investigate the state of molybdenum species on the surface of the different supports. Data were collected before and after sulfiding for 2 h at 573 K, with a mixture of 5% H_2S and H_2. We used the C (1s) binding energy (285.0 eV) as reference.

3. Results and discussion

In this study, the HDS of methyl-substituted DBT derivatives led to the formation of corresponding substituted biphenyl (BP) and cyclohexylbenzene (CHB) compounds as liquid products. The product selectivity mainly depends on the reaction pathway, as illustrated in Scheme 1. Prehydrogenation of neighboring phenyl groups leads to the formation of hexahydrodibenzothiophene (6HDBT) as an intermediate, and then CHB derivatives are produced (hydrodesulfurization route) [19]. In contrast, direct sulfur abstraction without prehydrogenation leads to the formation of corresponding BP products (direct desulfurization route) [19].

The HDS reactions of a mixture of DBT, 4-MDBT, and 4,6-DMDBT were carried out at 573 K and H_2 pressure of 3 MPa. Fig. 1 shows the results of HDS over Mo catalysts. As for all sulfur compounds, the catalytic activity of Mo/TiO_2–Al_2O_3 increases with the amount of TiO_2 loaded on the γ-alumina surface. Thus Mo/TiO_2–Al_2O_3 with titania loadings of 10.2 wt% shows the highest conversion in the composite types of TiO_2–Al_2O_3 support. With regard to DBT, the conversion rates over Mo catalysts with different supports increase as follows: Mo/Al_2O_3<Mo/



Scheme 1. Reaction pathways in HDS of methyl substituted dibenzothiophene (4,6-DMDBT).

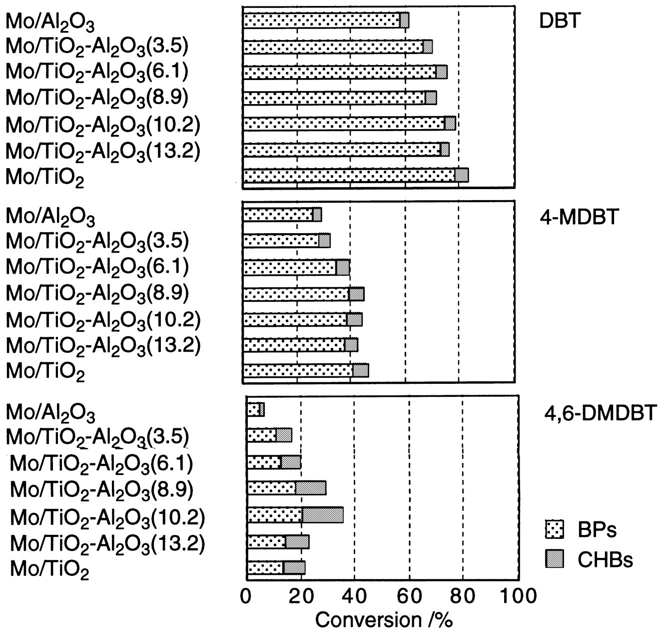


Fig. 1. Conversions obtained over Mo catalysts for the HDS of DBT, 4-MDBT and 4,6-DMDBT MoO_3: 6wt%, The number in parenthesis is TiO_2 /wt%, Pretreatment: 5%H_2S/95%H_2, 573 K, 2 h, Reaction temperature: 573 K, H_2 Pressure: 3 MPa, H_2 Flow rate: 200 cm^3 min^{-1}, LHSV: 12.08–16.07 h^{-1}.

TiO_2–Al_2O_3<Mo/TiO_2. In the case of DBT, most of the liquid products was BP, and only a little CHB was obtained. The conversions of 4-MDBT and 4,6-DMDBT were studied; all catalysts revealed lower conversion rates than that of DBT. This was because the reactivities of these compounds are lowered by the steric hindrance of their methyl groups [20]. With regard to 4-MDBT, the observed conversions are higher over Mo/TiO_2–Al_2O_3 and Mo/TiO_2 than over Mo/Al_2O_3. Also in the case of 4-MDBT, the liquid products are mainly methyl-substituted BP. However, most remarkable is the very high catalytic activity of the TiO_2–Al_2O_3 supported molybdenum for the HDS of 4,6-DMDBT. The observed conversion of 4,6-DMDBT over Mo/TiO_2–Al_2O_3 (10.2 wt% TiO_2) was higher than the conversions obtained over Mo/Al_2O_3 and even over Mo/TiO_2. The high conversion for the HDS of 4,6-DMDBT over Mo/TiO_2–Al_2O_3 can mainly be attributed to the high ratio of the corresponding CHB [15], which has become higher than those obtained over Mo/TiO_2 and Mo/Al_2O_3. This implies that the hydrodesulfurization route is more important for the HDS of 4,6-DMDBT over Mo/TiO_2–Al_2O_3.

To elucidate the influence of the difference of supports on the reaction pathways of methyl-substi-

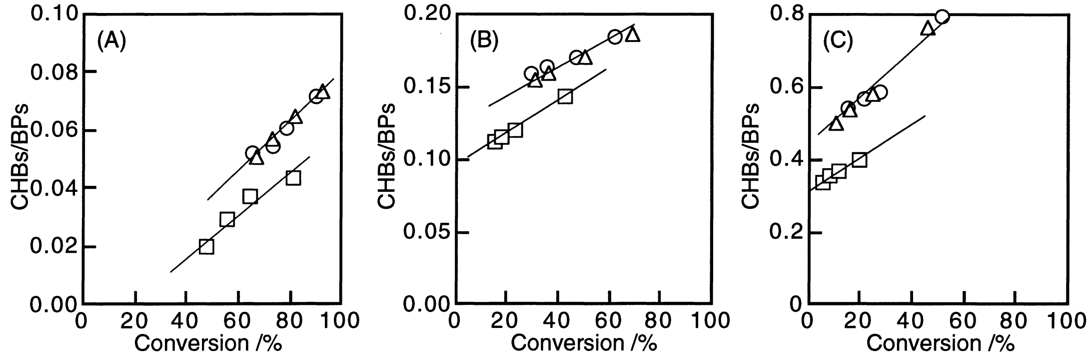


Fig. 2. Ratio of CHBs/BPs obtained over Mo catalysts as a function of the conversion. (A): DBT, (B): 4-MDBT, (C): 4,6-DMDBT,: Mo/Al_2O_3, □: Mo/TiO_2, △: Mo/TiO_2-Al_2O_3 Pretreatment: 5%H_2S/95%H_2,573 K,2 h, Reaction Temperature: 573 K, H_2 Pressure: 3 MPa, H_2 Flow rate: 200 cm^3 min^{-1}, LHSV: 6.04–32.14 h^{-1}, MoO_3: 6 wt%.

tuted 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 loadings of 10.2 wt%, which showed the highest conversion in the Mo/TiO_2–Al_2O_3. The ratios of corresponding CHB/BP obtained over Mo catalysts as a function of the conversion are illustrated in Fig. 2. In all the catalysts, the longer contact times led to the higher conversions of sulfur compounds and to higher ratios of corresponding CHB/BP. 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 convertion to CHB derivatives is more important, because prehydrogenation of an aromatic ring reduces the steric hindrance by methyl groups. Therefore, the promotion of the hydrodesulfurization 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, CHBs/BPs for Mo/TiO_2 and Mo/TiO_2–Al_2O_3 are much higher than that for Mo/Al_2O_3. The ratio of CHBs/BPs illustrated in Fig. 2 indicates the promotion of the prehydrogenation of an aromatic ring over Mo/TiO_2 and Mo/TiO_2–Al_2O_3. Due to the promotion of the hydrodesulfurization route, Mo/TiO_2 and Mo/TiO_2–Al_2O_3 have revealed higher conversion values than Mo/Al_2O_3, especially for the HDS of 4-MDBT and 4,6-DMDBT.

In order to elucidate the state of molybdenum species on the different supports, XPS investigations have been performed. The results obtained by the Mo 3d XPS spectra for oxidic state Mo/Al_2O_3, Mo/TiO_2, and Mo/TiO_2–Al_2O_3 are illustrated in Fig. 3. The Mo 3d peaks obtained for Mo/Al_2O_3 are much broader than those obtained for Mo/TiO_2 and Mo/TiO_2–Al_2O_3.

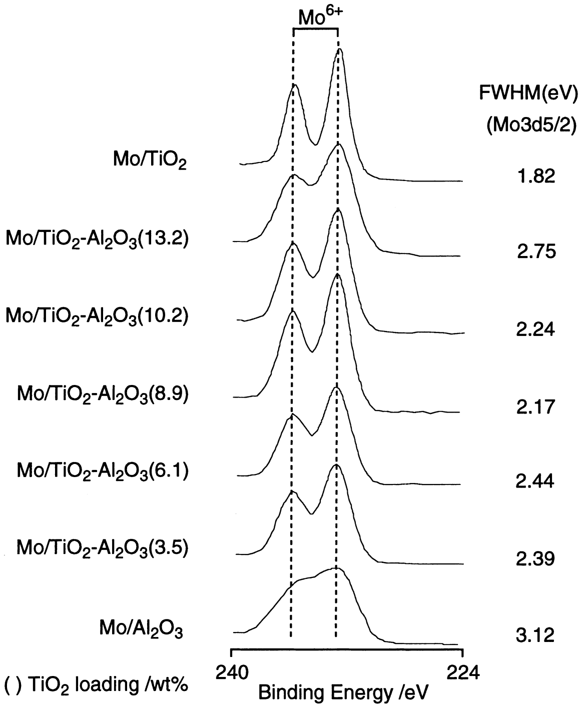


Fig. 3. Mo 3d XPS spectra of the unsulfided Mo catalysts with different TiO_2 loading.

This result indicates that the interactions between the Mo-species and the supports are different. The full widths at half-maximum (FWHM) derived from the corresponding Mo 3d5/2 XPS spectra are shown in Fig. 3. The spectrum obtained for Mo/TiO_2 reveals the lowest FWHM, whereas the spectrum obtained for Mo/Al_2O_3 shows the highest FWHM. Moreover, the results for the TiO_2–Al_2O_3 composite supports indicate that the amount of TiO_2 which covered on the γ-alumina surface significantly affects the FWHM obtained at the peaks in the Mo 3d XPS spectra. The FWHM of the Mo/TiO_2–Al_2O_3 catalysts is increased fundamentally with the amount of TiO_2, and then the catalysts with 8.9 wt% and 10.2 wt% TiO_2 reveals the lowest FWHM in the Mo/TiO_2–Al_2O_3. Furthermore, the state of the molybdenum species on the TiO_2–Al_2O_3 composite supports can be regarded as a transition state between the Mo/Al_2O_3 and Mo/TiO_2. This behavior of the state of the molybdenum species is nearly in agreement with similar behavior of HDS reactions of methyl-substituted DBT derivatives over supported molybdenum catalysts, as described earlier. The broadening of the Mo 3d XPS peaks might be caused by the strong interactions between Mo and supports. Therefore Mo/TiO_2–Al_2O_3 catalysts with 8.9 wt% and 10.2 wt% TiO_2 provide Mo species which are more similar to the Mo species presented on the pure anatase types of titania supports than to molybdenum supported on γ-alumina. The fact that Mo/TiO_2–Al_2O_3 catalysts with 13.2 wt% TiO_2 lead to higher FWHM of the Mo 3d2/5 XPS peak might be caused by the formation of TiO_2 precipitations detected by XRD.

After sulfurization, most of the Mo^{6+} species have disappeared and the Mo^{4+} species have appeared. Furthermore, the spectra of sulfided molybdenum catalysts supported on the different supports can also be assigned to MoS_2 species. The ratios of S(2p)/Mo(3d) and $Mo^{4+}/(Mo^{4+}+Mo^{6+})$ for the different supports are shown in Table 1. Both S/Mo and $Mo^{4+}/(Mo^{4+}+Mo^{6+})$ ratios are clearly increasing as follows: Mo/Al_2O_3<Mo/TiO_2–Al_2O_3<Mo/TiO_2. With regard to Mo/TiO_2–Al_2O_3, higher TiO_2 loadings also lead to higher values for S/Mo and $Mo^{4+}/(Mo^{4+}+Mo^{6+})$ ratios. The ratios of $Mo^{4+}/(Mo^{4+}+Mo^{6+})$ also indicate that not all molybdenum has been sulfided to MoS_2 on the surfaces of all catalysts. However, these XPS investigations definitely reveal that the reducibility from the oxidic to sulfidic molybdenum species on the TiO_2 and TiO_2–Al_2O_3 composite supports is higher than that on the γf-Al_2O_3 support. The differences of reducibility might be caused by differences in the interactions between Mo species and the different supports. This is in agreement with the reason why FWHM at the peaks in the Mo XPS spectra are different. As already stated above, broad peaks in Mo 3d XPS spectra indicate strong interactions between Mo species and supports, which may lead to lower reducibilities of MoO_3 to MoS_2. The active sites of HDS reaction over molybdenum catalysts are the coordinatively unsaturated sites on the surface of MoS_2, and the formation of the active sites has occurred when MoO_3 changes to MoS_2 by sulfurization [21]. Therefore, the higher values for S/Mo and $Mo^{4+}/(Mo^{4+}+Mo^{6+})$ ratios obtained for Mo/TiO_2 and Mo/TiO_2–Al_2O_3 suggest that the number of active sites has increased on the surface of TiO_2 and TiO_2–Al_2O_3 composite supports, compared with Mo/Al_2O_3. This increase is one of the reasons for the high catalytic activity of HDS reaction over Mo/TiO_2 and Mo/TiO_2–Al_2O_3.

Table 1
Surface properties of the sulfided Mo catalysts derived from the Mo 3d XPS spectra

Catalyst	Mo	$Mo^{4+}/(Mo^{4+} + Mo^{6+})$
Mo/Al_2O_3	1.30	0.63
Mo/TiO_2–Al_2O_3 (3.5)	1.26	0.63
Mo/TiO_2–Al_2O_3 (6.1)	1.47	0.68
Mo/TiO_2–Al_2O_3 (8.9)	1.54	0.71
Mo/TiO_2–Al_2O_3(10.2)	1.63	0.71
Mo/TiO_2–Al_2O_3 (13.2)	1.65	0.79
Mo/TiO_2	1.74	0.82

Sulfurization: 5%H_2S/95%H_2, 573 K, 2 h, MoO_3 loading: 6.0 wt%, MoS_2 (S/Mo=2.29).
Values in parentheses correspond to the TiO_2 loading/wt%.

4. Conclusion

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 were much higher than that obtained over

Mo/Al_2O_3. $Mo/TiO_2–Al_2O_3$ with 10.2 wt% TiO_2 showed the highest catalytic activity in the $TiO_2–Al_2O_3$ supports. With regard to the HDS of 4,6-DMDBT, this catalyst revealed higher conversion than Mo/TiO_2. According to the high CHBs/BPs ratios obtained over $Mo/TiO_2–Al_2O_3$, the hydrodesulfurization route was promoted over the $TiO_2–Al_2O_3$ supports. XPS investigations of catalysts before and after sulfiding suggest that the interaction between Mo species and γ-Al_2O_3 is stronger than that between Mo and $TiO_2–Al_2O_3$, and also suggest that the reducibility from oxidic to sulfidic molybdenum species on the $TiO_2–Al_2O_3$ is higher than that on the γ-Al_2O_3 support. Therefore, the number of active sites has increased on the surface of $TiO_2–Al_2O_3$ supports. The present study suggests that the composite $TiO_2–Al_2O_3$ supports are able to overcome the disadvantages of the pure TiO_2 supports described above. Furthermore, $TiO_2–Al_2O_3$ supports are suitable candidates to substitute for γ-alumina in the deep HDS processes, because of providing higher catalytic activity for the HDS reaction of DBT derivatives than γ-alumina does.

Acknowledgements

This work has been carried out as a research project of The Japan Petroleum Institute commissioned by the Petroleum Energy Center with the subsidy of the Ministry of International Trade and Industry.

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