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RESEARCH NOTE

Elucidation of Behavior of Sulfur on Mo Catalysts Supported on TiO_2 with Various Surface Areas Using ^{35}S Tracer Methods

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A series of Mo catalysts supported on TiO_2 with various surface areas were prepared. In hydrodesulfurization (HDS) of dibenzothiophene (DBT) the activities of the series of catalysts were estimated. The results show that the activities of the series of catalysts increased linearly with the surface areas of TiO_2 supports. The sulfur mobility on the sulfided Mo/TiO_2 catalysts under the reaction conditions was elucidated by a ^{35}S radioisotope tracer method using ^{35}S-labeled DBT. The results suggest that the sulfur exchange rate constants (k_{RE}) were approximately the same for all catalysts at a given temperature and that the amount of labile sulfur (S_0) increases linearly with the surface area of TiO_2 supports. The sulfidation states of the series of catalysts were also investigated by a ^{35}S radioisotope pulse tracer method using ^{35}S-labeled H_2S. The results indicate that in spite of the coverage of Mo species on TiO_2 support, the sulfidation of TiO_2 support would still occur at 300°C. The sulfided catalysts could be reduced under H_2 atmosphere. © 2002 Elsevier Science (USA)

1. INTRODUCTION

The need for better hydrodesulfurization catalysts to fulfill the more strict environmental restrictions imposed on the sulfur content of transport fuels has prompted the researchers in the field to look for more active and selective catalyst formulations (1). Several studies suggested that changing the support into titania (2–4) or alumina–titania mixed oxides (5–8) have shown promising results. However, titania usually has low surface area and seems unsuitable for industrial application. To take advantage of the high activity of titania-supported Mo catalysts and the excellent surface area of alumina, alumina–titania mixed oxides have also been proposed as HDS catalytic supports. Although significant activity increase is observed for the catalysts supported on alumina–titania mixed oxides compared with that of alumina-supported catalysts, HDS activity close to that of titania-supported catalyst is difficult to obtain (9–11). Recently, a titania support suitable for a catalyst having a surface area in the range of 80–200 m^2/g was reported (12), which makes the use of titania support possible in industrial catalysts.

In previous work (13), the authors investigated reaction mechanisms and sulfidation states of TiO_2 supports with various surface areas under the typical HDS reaction conditions. The object of the present work is to study the effect of surface area of TiO_2 supports on the HDS mechanism and sulfidation states when TiO_2 supports are almost covered with a monolayer of molybdenum. A ^{35}S radioisotope tracer method using ^{35}S-labeled dibenzothiophene (DBT), which can give information about the behavior of sulfur on the working catalyst (14–16), was used to elucidate the sulfur mobility on the sulfided Mo/TiO_2 catalysts under the reaction conditions. Moreover, a ^{35}S radioisotope pulse tracer method using ^{35}S-labeled H_2S, which can exactly determine the sulfidation state of the catalyst (17), was used to investigate the sulfidation and reduction state of Mo/TiO_2 catalysts.

2. EXPERIMENTAL

2.1. Catalysts

The $TiO_2(18)$ and $TiO_2(70)$ supports used in this study are reference catalysts of JRC-TIO-2 and JRC-TIO-1 supplied from the Catalysis Society of Japan; the $TiO_2(120)$ support was supplied by the Deqing Chemical Technology Co. (China) (12). All TiO_2 supports used here were anatase. The numbers in parentheses represent the surface areas of the supports, which are 18, 70, and 120 $m^2\ g^{-1}$, respectively. The Mo/TiO_2 catalysts were prepared by a conventional impregnation method: the TiO_2 support was impregnated with an aqueous solution of ammonium heptamolybdate as required. This was followed by drying at 120°C for 3 h and calcination in air at 500°C for 15 h. MT(x) means Mo catalyst supported on a TiO_2 support with a surface area of $x\ m^2\ g^{-1}$.

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2.2. Apparatus and Procedure

2.2.1. Measurement of HDS activity. The HDS experiments were carried out with a fixed-bed reactor. The catalyst was presulfided with a mixture of 5 vol% H_2S in H_2 flowing at 5 L h^{-1}, 0.1 MPa. Typical reaction conditions were as follows: H_2 flow rate, 25 L h^{-1}; WHSV, 28 h^{-1}; reaction pressure, 5 MPa; concentration of DBT in decalin, 1.0 wt%. The liquid products were collected every 15 min and analyzed by gas chromatography with a FID detector (Shimadzu-17A, Shimadzu Co., Ltd.) and a commercial capillary column (DB-1).

A typical operation procedure using the [^{35}S]DBT radioisotope tracer method was carried out under the same conditions and described in previous work (18, 19).

2.2.2. Sulfidation of Mo/TiO$_2$ catalyst using ^{35}S-labeled H_2S. A ^{35}S radioisotope pulse sulfiding method was developed to investigate the sulfidation process. The pulse tracer apparatus is described elsewhere (17). A pulse of 30 vol% $H_2{}^{35}S$ in hydrogen was introduced into the fixed-bed reactor with a gas sampler (2.46 ml) every 10 min under N_2 carrier gas (0.5 MPa, 40 ml min^{-1}). The radioactivity of unreacted $H_2{}^{35}S$ absorbed by a commercially available basic scintillation solvent (carbsorb, Packard Japan Co., Ltd.) every 10 min was measured by a liquid scintillation counter (Beckman LS-6500, Beckman, Co., Ltd.) as described elsewhere (15, 16). In order to investigate the sulfidation state under H_2 atmosphere, after the sulfidation procedure, the catalyst was cooled in a N_2 carrier gas stream to the desired temperature and was pressurized to 0.5 MPa with H_2 carrier gas. The $H_2{}^{35}S$ released was better absorbed by carbsorb solvent and the radioactivity was measured every 15 min by a liquid scintillation counter.

3. RESULTS AND DISCUSSION

3.1. HDS Activities of Mo Catalysts Supported on TiO$_2$ with Various Surface Areas

In our previous study (13), HDS activities of sulfided TiO$_2$ supports with various surface areas were investigated under the typical HDS reaction conditions. The results showed that HDS activities increased linearly with increasing surface areas of the TiO$_2$ supports. It became interesting for the authors to investigate the HDS activities when monolayer dispersion of Mo was supported on the various TiO$_2$ supports. Recently we also reported that HDS activities increased linearly with added Mo content up to 6 wt% MoO$_3$ on TiO$_2$(70) support and then leveled off beyond this value, which means that the monolayer dispersion of Mo 4.2 atom nm^{-2} was obtained on TiO$_2$ support (20). Therefore, the monolayer dispersion of Mo 4.2 atom nm^{-2} was supported on TiO$_2$ supports with various surface areas (18, 70, and 120 m^2 g^{-1}), corresponding to 2, 6, and 10 wt% MoO$_3$, respectively. The relative HDS activities of Mo catalysts were investigated at different temperatures. Figure 1 shows the effect of the surface area of the TiO$_2$ supports on the HDS activities over Mo/TiO$_2$ catalysts at several reaction temperatures. The HDS catalytic activities of the catalysts increased linearly at every temperature with increasing surface area of the TiO$_2$ support. Although TiO$_2$ supports are active in HDS reaction, the HDS activities can be neglected since they are very low compared with those of Mo/TiO$_2$ catalysts (13). An increase in the surface area of the TiO$_2$ support means an increase in the amount of monolayer-dispersed MoO$_3$; therefore, it can be concluded that the linear increase in HDS activity with surface area could be attributed to the increase in the amount of active species of MoS$_2$. This result also implies that the monolayer dispersion of Mo 4.2 atom nm^{-2} is obtained on each TiO$_2$ support with various surface areas.

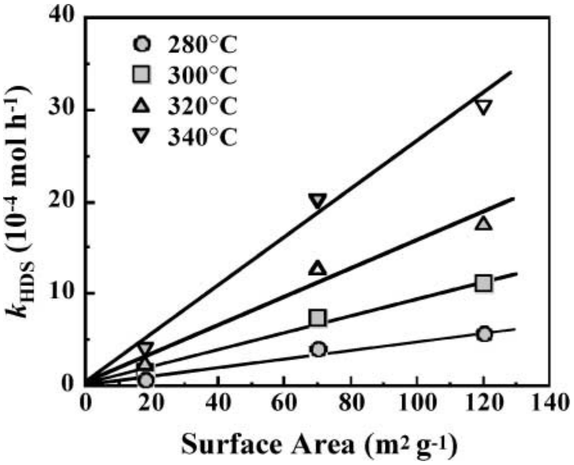

FIG. 1. Effect of surface area of TiO$_2$ support on HDS activities over Mo/TiO$_2$ catalysts at various temperatures.

According to Arrhenius plots, the apparent activation energies for HDS of DBT on TiO$_2$-supported catalysts were calculated. Despite the variance in Mo loadings, the apparent activation energies for all catalysts were almost the same, 22 ± 2 kcal/mol. This result suggested that there is essentially no difference in the mechanism of HDS reaction on TiO$_2$-supported Mo catalysts with various surface areas.

Several studies on the coverage of TiO$_2$ as a function of molybdenum content in sulfided catalysts have been performed (21–23). Most of the structural studies presented evidence that the MoS$_2$ crystallites in the sulfided state are present as a monolayer. It is generally found that coverage of titania by Mo species increases linearly with the Mo content up to a certain limit, above which it levels off. This indicates the formation of bulklike MoS$_2$ structures, the size of which is reported to increase somewhat with increasing molybdenum content.

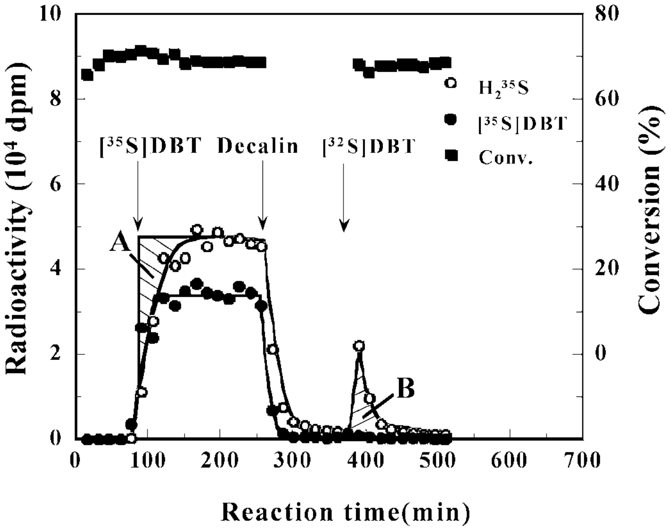

FIG. 2. Changes in the radioactivities of formed $H_2{}^{35}S$ and unreacted $[^{35}S]DBT$ with reaction time at 320°C over MT(120).

3.2. *Behavior of Sulfur on the Sulfided Mo/TiO$_2$ Catalyst*

Figure 2 shows a typical operation procedure of ^{35}S tracer method. The HDS reaction of $[^{35}S]DBT$ was carried over sulfided MT(120) catalyst at 320°C. Initially, a decalin solution of 1 wt% $[^{32}S]DBT$ was pumped into the reactor until the conversion of DBT became constant. Then a decalin solution of 1 wt% $[^{35}S]DBT$ was substituted for the $[^{32}S]DBT$ and reacted until the formation amount of $H_2{}^{35}S$ became constant. After $[^{35}S]DBT$ was introduced, the radioactivity of unreacted $[^{35}S]DBT$ in the liquid product increased and approached a steady state immediately. However, it took ca. 90 min to achieve a steady state in the radioactivity of the $H_2{}^{35}S$ produced. In order to determine the behavior of sulfur more accurately, the $[^{35}S]DBT$ solution was replaced by decalin solvent subsequently. It was observed that a portion of ^{35}S, denoted by the lined area A in Fig. 2, remained on the catalyst when decalin solvent was substituted for the reactant solution of $[^{35}S]DBT$. Even though the catalyst was reduced in an atmosphere of hydrogen, $H_2{}^{35}S$ was scarcely produced. This indicates that the sulfur accommodated on the catalyst could not be eluted without a supply of sulfur derived from HDS of DBT. When the reactant solution was replaced by $[^{32}S]DBT$ again, a portion of ^{35}S could be released again as $H_2{}^{35}S$, as shown in Fig. 2 (area B). This portion of ^{35}S was approximately equal to area A, which represented the total amount of labile sulfur (S_0) on the catalyst under this reaction condition. According to a method described in Ref. (16), the amount of labile sulfur can be calculated from the total radioactivity of the $H_2{}^{35}S$ released after $[^{32}S]DBT$ was reintroduced, i.e., shaded area B.

To discuss the release process of $H_2{}^{35}S$ more accurately, the rate constant of $H_2{}^{35}S$ release (k_{RE}) from ^{35}S-labeled catalyst was determined. As reported previously (18), the release of $H_2{}^{35}S$ in the range of area B shown in Fig. 2 can be explained with respect to a first-order reaction and the rate constant of $H_2{}^{35}S$ release, k_{RE}, was determined.

The same radioisotope tracer experiments over MT(18) and MT(70) catalysts were also conducted at 320°C. By determining the amount of labile sulfur on the series of Mo/TiO$_2$ catalysts and the sulfur exchange rate constant in the HDS of DBT, the effect of surface area on the structure of sulfided catalysts was estimated. Since TiO_2 support can be sulfided under the reaction conditions (13), during determination of the amount of labile sulfur on Mo/TiO$_2$ catalysts, the value of S_0 originated from TiO_2 support was estimated. As reported in our previous study (13), the amounts of labile sulfur on TiO_2(70) and TiO_2(120) supports at 390°C were 0.52 and 0.96 mg-S/g-cat, respectively. Therefore, it can be concluded that in the present temperature range the value of S_0 originated from TiO_2 support can be negligible.

The amount of labile sulfur represents the number of active sites and the rate constant of H_2S release represents the mobility of active sites on the surface of the catalyst, i.e., the turnover frequency in the HDS reaction (24). In order to investigate the relationship among the HDS rate constant of DBT, the amount of labile sulfur, and the rate constant of sulfur exchange, the ^{35}S tracer experimental results at 320°C on Mo catalysts supported on various TiO_2 supports were performed and the results are shown in Fig. 3. It was observed that the amount of labile sulfur increased linearly with the surface area of TiO_2 support as well as the rate constant of HDS, although the sulfur exchange rate constant did not vary with the surface area of the support. Therefore, it can be concluded that at a given temperature, the increase in HDS activity with the surface area for this series of catalysts could be attributed to the increase in total number of active sites. Further, the activation energies of the HDS reaction and the exchange rate constant

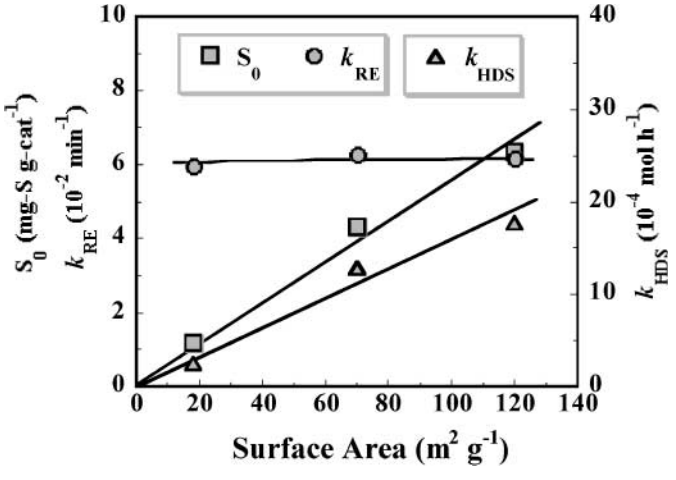

FIG. 3. Effect of surface area on S_0 and k_{RE} over Mo/TiO$_2$ catalysts at 320°C.

of sulfur for this series of catalysts are very similar to each other. Therefore, it can be considered that there is no difference in the mechanism of HDS and the nature of the active sites within these catalysts. At the same time, this result also indicates similar intrinsic structure and morphology in the dispersion of MoO_3 on TiO_2 supports with various surface areas. Moreover, it was observed that the sulfur exchange rate did not vary with the surface area and that the HDS rate constants of DBT on the catalysts paralleled the amount of labile sulfur. Therefore, it was suggested that the effect of the surface area of TiO_2 support on the activity of the catalyst is due to the increase in the number of active sites rather than to a change in the nature of the active sites.

3.3. Sulfidation of Mo/TiO_2 Catalysts Using ^{35}S-Labeled H_2S

Figure 4 shows the changes in radioactivity of eluted $H_2{}^{35}S$ during the sulfidation of Mo/TiO_2 catalysts with various surface areas. For each catalyst, the radioactivity of unreacted $H_2{}^{35}S$ at 100 and 200°C approached a constant value, equal to the radioactivity of the pulse introduced, while at 300 and 400°C, $H_2{}^{35}S$ was accumulated by the catalysts slowly and it seems difficult to approach the radioactivity in the pulse introduced. The amount of sulfur incorporated into the catalyst could be calculated by subtracting the radioactivity of released $H_2{}^{35}S$ from the total radioactivity introduced (the darker area) (17). The results from this calculation are presented in Table 1. As reported in our previous study (13), TiO_2 support was difficult to sulfide at 200°C, at 300°C the sulfidation of TiO_2 support occurred rapidly and Ti atoms on the surface of TiO_2 support could be almost sulfided to TiS_2 at 400°C. For MT(18), MT(70), and MT(120) catalysts, the total amount of sulfur was calculated to be 9.7, 29.1, and 43.3 mg-S/g-cat, respectively. As shown in Table 1, the uptake amount of sulfur at 300°C for each Mo/TiO_2 catalyst exceeded substantially the total amount of sulfur, indicating that the sulfidation of TiO_2 supports began to occur at 300°C.

The Mo/TiO_2 catalysts sulfided by ^{35}S-labeled H_2S were then reduced by H_2 carrier gas to investigate the sulfidation state under H_2 atmosphere. The amounts of released sulfur for all catalysts at each temperature were also listed in Table 1. It was proposed that about one-fourth of the amount of sulfur accumulated by the TiO_2 support would be released under H_2 atmosphere at 400°C, which is due to the reduction of the sulfide TiS_2 (13). When monolayer dispersion of MoO_3 was loaded onto TiO_2, the reduction of sulfided Mo/TiO_2 catalysts also occurred. We reported

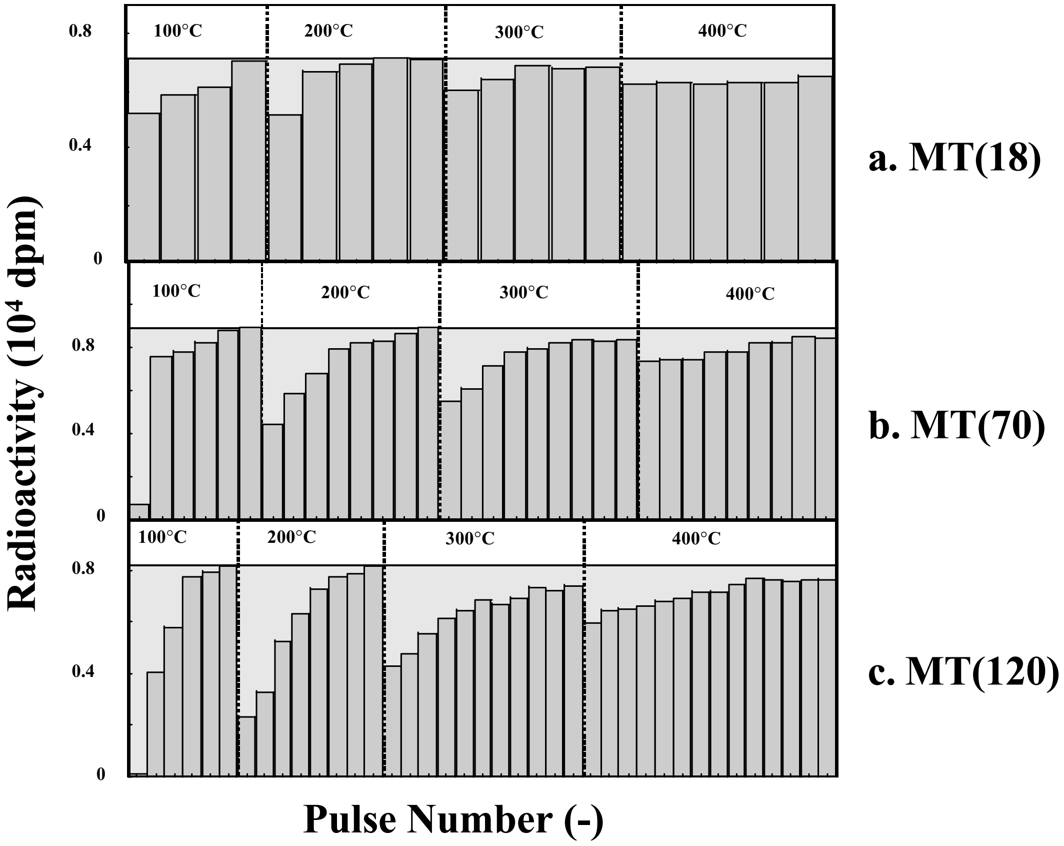

FIG. 4. Sulfidation of Mo/TiO_2 catalysts with $H_2{}^{35}S$ pulse at various temperatures.

TABLE 1

The Uptake and Released Amount of Sulfur on Mo/TiO_2 Catalysts (mg-S g-cat^{-1})

	Sulfidation				Reduction		
Catalysts	100°C	200°C	300°C	400°C	200°C	300°C	400°C
MT(18)	4.0	7.8	10.6	15.3	0.4	2.3	4.5
MT(70)	12.1	25.3	38.9	49.1	1.8	5.8	10.2
MT(120)	16.7	35.6	57.9	74.4	2.2	9.7	17.9

that sulfidation of TiO_2 support with H_2S will lead to the formation of TiS_2 and TiS_2 can be reduced to Ti^{3+} easily under hydrogen atmosphere. Our ESR results (13) indicate that the reduction of TiS_2 will lead to the formation of free electrons trapped in sulfur vacancies. When TiO_2 support is covered by the dispersion of MoO_3, the sulfidation of TiO_2 support will also occur. Wei *et al.* (25) also reported that TiO_2 support in Mo-based catalysts could be sulfided according to the TPS results. Sulfided Mo/TiO_2 catalysts can be reduced by H_2, which is attributed to the reduction of TiS_2.

4. CONCLUSIONS

From the above results the following conclusions were obtained. The HDS activities on the Mo/TiO_2 catalysts increased linearly with the surface areas of TiO_2 supports, which means that monolayer dispersion of 4.2 atom nm^{-2} MoO_3 was obtained on all TiO_2 supports. It was found that the amount of labile sulfur increased linearly with the surface area of the TiO_2 support, that the sulfur exchange rate constants were approximately the same at a given temperature, and that the apparent activation energies of HDS reactions were 22 ± 2 kcal mol^{-1} for all catalysts. These results suggest that the mechanism of HDS and the nature of the active sites did not vary with the surface area of the support and that the effect of the surface area of the TiO_2 support on the activity of the catalyst is due to the increase in the number of active sites rather than to a change in the nature of the active sites. When monolayer dispersion of MoO_3 metals was supported on TiO_2, the sulfidation of TiO_2 support would also occur at 300°C and the sulfided Mo/TiO_2 catalyst can be reduced under H_2 atmosphere.

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