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Elucidation of Sulfidation State and Hydrodesulfurization Mechanism on TiO_2 Catalysts Using ^{35}S Radioisotope Tracer Methods

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The hydrodesulfurization (HDS) activities of sulfided TiO_2 with various surface areas were characterized under the typical HDS reaction conditions. The results showed that HDS activities increased linearly with increasing surface area of TiO_2, suggesting that the surface sulfide TiS_2 is the active phase of the HDS reaction on sulfided TiO_2 catalyst. The sulfidation states of TiO_2 with various surface areas were investigated using a ^{35}S radioisotope pulse tracer method. The results showed that the Ti atoms on the surface of TiO_2 could be completely sulfided to TiS_2 at 400°C, whereas the sulfidation of Ti atoms in the bulk of TiO_2 would occur slowly at 500°C. When the sulfided TiO_2 was reduced in H_2 at 400°C, TiS_2 was reduced to the sulfidation state $TiS_{1.5}$, leading to the formation of Ti^{3+} ions and sulfur anion vacancies. Moreover, HDS reaction mechanisms on sulfided TiO_2 catalysts under the reaction conditions were elucidated by a ^{35}S radioisotope tracer method using ^{35}S-labeled dibenzothiophene (DBT). The results showed that less labile sulfur was detected on the sulfided TiO_2 catalysts, suggesting that the HDS mechanism on TiO_2 catalysts was very different from that on Mo-based catalysts. © 2001 Academic Press

Key Words: **TiO_2 catalyst; ^{35}S radioisotope tracer method; hydrodesulfurization.**

1. INTRODUCTION

The need for better hydrodesulfurization (HDS) catalysts to comply with increasingly strict environmental regulations has promoted research on the use of new supports and active phases to improve the performance of HDS catalysts (1). Among the new supports, titania (2–4) and alumina–titania mixed oxides (5–8) have shown promising results. Compared with conventional supports such as Al_2O_3 and SiO_2, TiO_2 support can be easily reduced to Ti^{3+} by H_2 even at low temperature (9). It is well known that a strong metal–support interaction (SMSI) will occur on TiO_2-supported group VIII metals after high-temperature reduction (10), which plays important roles as follows: (1) Metals dispersed on TiO_2 support as thin pillbox structures or composite clusters were significantly more stable than on other supports (11). (2) A special interface between metal and partially reduced TiO_2 support was formed that includes a metal atom, a Ti^{3+} ion, and an anion vacancy (12, 13). (3) Electron migration from the support to metal occurred and the extra electrons saturated the unfilled *d* orbitals of the metal atoms (14). (4) Partially reduced TiO_2 migrated to the surface of metals (15, 16).

Despite all the previous studies, an explanation for the substantial difference in HDS activity between alumina- and titania-supported catalysts has not yet been elucidated, since the increase in activity when using TiO_2 as a support cannot be completely explained by differences in dispersion or sulfidation of the active metallic species (17–19). Therefore, as a specific property described above, it can be inferred that the role of TiO_2 in HDS catalysts is not only that of a conventional support but, more importantly, that of an electronic promoter of the molybdenum sulfide phase (20). It is proposed here that to explain the previous activity results, the titania particles present on the surface of the support have to play an active role in the HDS reaction mechanism. So it becomes important for the authors to characterize the HDS activity of TiO_2 support under the typical HDS reaction conditions first and, further, the sulfidation and reduction state of TiO_2 support.

In the present work, the HDS activities on TiO_2 supports of various surface areas were characterized under the typical HDS reaction conditions. A ^{35}S radioisotope pulse tracer method using $H_2{}^{35}S$, which can exactly determine the sulfidation state of the catalyst (21), was used to investigate the sulfidation and reduction states of TiO_2 supports. Moreover, a ^{35}S radioisotope tracer method using ^{35}S-labeled dibenzothiophene (DBT), which can give information about the behavior of sulfur on the catalyst (22–26), was used to elucidate the HDS reaction mechanism on the sulfided TiO_2 catalyst under reaction conditions.

2. EXPERIMENTAL

2.1. Catalysts

TiO_2(18) and TiO_2(70) catalysts used in this study are Japanese reference catalysts JRC-TIO-2 and JRC-TIO-1;

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TiO_2(120) catalyst is supplied by Deqing Chemical Technology Company (China). The numbers in parentheses represent the surface areas of the catalysts, which are 18, 70, and 120 m^2/g, respectively. All of the catalysts (anatase) were calcined at 500°C for 12 h.

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 (1 g) was presulfided with a mixture of 5 vol% H_2S in H_2 flowing at 5 liters h^{-1}, 0.1 MPa. After presulfidation, the reactor was cooled to room temperature and then pressurized with hydrogen. A decalin solution of DBT was fed into the reactor at the reaction temperature with a high-pressure liquid pump (Kyowa Seimitsu KHD-16). Typical reaction conditions were: H_2 flow rate 25 liters 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 radioisotope tracer method was carried out under the same conditions and ^{35}S-labeled DBT was synthesized as described in the previous paper (23).

2.2.2. Sulfidation of TiO_2 catalysts 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 (21) and ^{35}S-labeled hydrogen sulfide ($H_2{}^{35}S$) was prepared as described in Ref. (21). One tenth gram of catalyst was used. A pulse of ca. 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 Carbsorb every 10 min was measured with a liquid scintillation counter (Beckman LS-6500, Beckman, Co. Ltd.) as described elsewhere (23, 24).

2.2.3. Reduction of sulfided TiO_2 catalysts. To investigate the sulfidation state under H_2 atmosphere, the catalysts sulfided with $H_2{}^{35}S$ as described in Section 2.2.2 were subsequently reduced with H_2 carrier gas. After the sulfidation procedure, the catalyst was cooled in a N_2 carrier gas stream to the reduction temperature and was pressurized to 0.5 MPa with H_2 carrier gas. The $H_2{}^{35}S$ released was absorbed by Carbsorb every 15 min and the radioactivity was measured with a liquid scintillation counter.

2.2.4. Electron spin resonance (ESR) study. ESR spectra were recorded with a JES-RE2X spectrometer, operating in X-band mode and connected to a personal computer for data handling. Spectra were recorded at 298 K and atmospheric pressure. Mn sample ($g_1 = 2.034$, $g_2 = 1.981$) was used as a standard for g-value determination.

3. RESULTS AND DISCUSSION

3.1. *HDS of DBT on TiO_2 Catalysts*

3.1.1. HDS activities on sulfided TiO_2 catalysts. The HDS activities on sulfided TiO_2 catalysts of various surface areas were investigated at several temperatures when the HDS activities reached a steady state. The catalysts were presulfided at 400°C for 3 h. Rate constants (k_{HDS}) of the pseudo-first-order reaction for HDS of DBT for the catalysts were determined using the equation

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

where k_{HDS} is the rate constant for HDS (mol h^{-1} g cat^{-1}), x is the conversion of DBT, F is the feed rate of reactant (mol h^{-1}), and W is the weight of the catalyst (g cat). Figure 1 shows that k_{HDS} on TiO_2 catalysts increased linearly with surface area at each temperature. An increase in the surface area means an increase in the amount of surface TiS_2; therefore, it can be concluded that the linear increase in HDS activity with surface area could be attributed to the increase in total number of active sites of TiS_2. The apparent activation energies for HDS of DBT on TiO_2 catalysts, which were estimated from Arrhenius plots, were almost the same, 27 ± 1 kcal/mol.

3.1.2. Effect of presulfidation conditions on HDS activities. The HDS activities on TiO_2(70) catalysts under different presulfidation conditions were investigated at 320–390°C to clarify the effect of presulfidation conditions on HDS activity. Presulfidation was carried out under different conditions as follows: (1) without sulfidation, (2) sulfidation at 400°C for 3 h, (3) sulfidation at 500°C for 24 h. Figure 2 shows the Arrhenius plots of the TiO_2(70) catalysts. The catalyst sulfided at 400°C shows the highest HDS activity. Lower HDS activity was obtained when

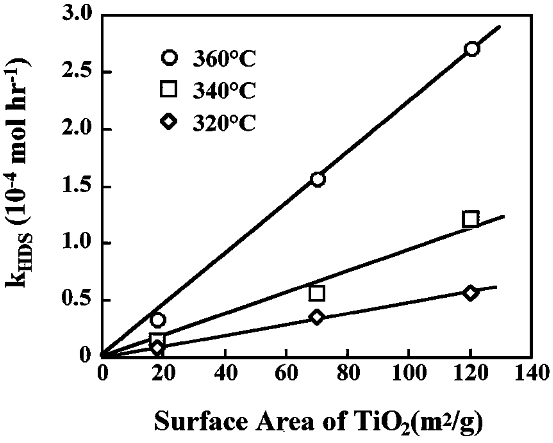

FIG. 1. Effect of surface area of TiO_2 catalysts on HDS activities after sulfidation at 400°C.

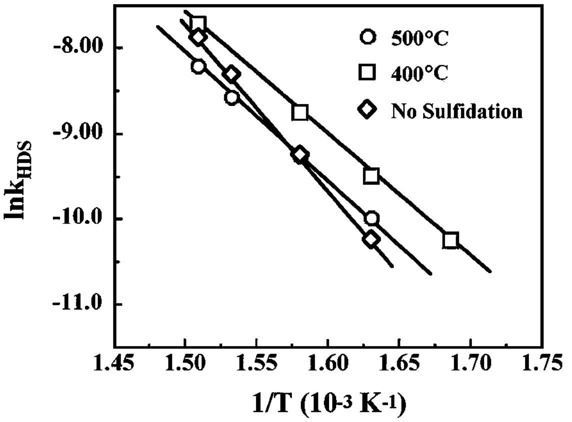

FIG. 2. Arrhenius plots of TiO_2(70) catalysts under various sulfidation conditions.

the catalyst was sulfided at 500°C, while almost the same apparent activation energies, 27 ± 1 kcal/mol, were observed on the catalysts sulfided at 400 and 500°C. When the HDS reaction was carried out on TiO_2 catalyst without sulfidation, lower HDS activity and higher apparent activation energy (37 ± 1 kcal/mol) were obtained.

3.2. Sulfidation of TiO_2 Catalysts Using ^{35}S-Labeled H_2S

Figure 3 shows the change in radioactivity of eluted $H_2{}^{35}S$ during the sulfidation of TiO_2(70) at various temperatures. The radioactivities of unreacted $H_2{}^{35}S$ at 200, 300, and 400°C increased with the number of pulses introduced and approached a constant, equal to the radioactivity in the pulse introduced. When the sulfidation temperature was increased to 500°C, $H_2{}^{35}S$ seemed to accumulate on the TiO_2(70) catalyst slowly, and the radioactivity of unreacted $H_2{}^{35}S$ barely reached the radioactivity in the pulse introduced. The amounts of sulfur incorporated into the catalyst could be calculated from the radioactivity of $H_2{}^{35}S$ released as described in Ref. (21). Similar sulfidation experiments with TiO_2(18) and TiO_2(120) using $H_2{}^{35}S$ pulse were carried out to investigate the sulfidation state of TiO_2 catalysts of various surface areas. Similar results were obtained and the amounts of sulfur at each temperature are summarized in Table 1. The degree of sulfidation was used to evaluate the extent of sulfidation of the catalyst, which was defined as the ratio of the amount of sulfur uptake to total sulfur on the surface when all surface TiO_2 was transformed into TiS_2. In crystal TiO_2 (anatase), 33.6 Å^3 is occupied by each Ti (with associated oxygen atoms), equivalent to an effective area of 10.4 Å^2 (27). According to this, the amount of surface TiO_2 species can be calculated from the surface area of the catalysts. Therefore, when only the surface of TiO_2 is sulfided, the total amounts of sulfur on the surfaces of TiO_2(18), TiO_2(70), and TiO_2(120) are 18.4, 71.7, and 123 mg/g cat, respectively.

TABLE 1

Amounts of Sulfur (mg S/g cat) in the Sulfidation and Reduction Processes on TiO_2 Catalysts

	Sulfidation				Reduction		
Catalyst	200°C	300°C	400°C	500°C	300°C	400°C	500°C
TiO_2(18)	2.2	11.3	18.9	34.8	5.3	8.5	10.1
TiO_2(70)	6.6	45.0	73.0	83.4	11.6	20.4	24.6
TiO_2(120)	10.5	74.2	124	133	17.2	32.3	36.7

To better understand the sulfidation state of TiO_2 catalysts of various surface areas, the amounts of sulfur incorporated into the TiO_2 catalysts at each temperature are plotted in Fig. 4 and the degrees of sulfidation of the TiO_2 catalysts are shown in Fig. 5. The amounts of sulfur that accumulated on the TiO_2 catalysts increased with increasing temperature. At 200°C sulfidation of the catalysts occurred, but TiO_2 catalysts were sulfided mainly at 300 and 400°C, and

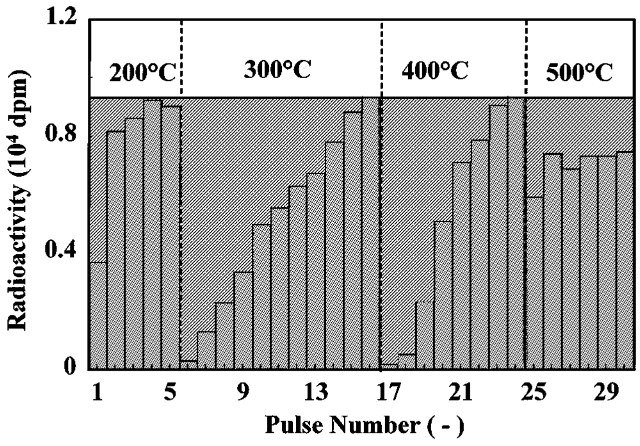

FIG. 3. Sulfidation of TiO_2(70) catalyst with $H_2{}^{35}S$ pulse at various temperatures.

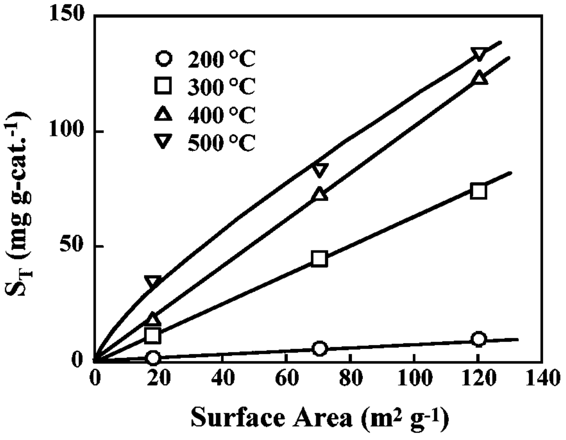

FIG. 4. Effect of surface area of TiO_2 catalysts on amount of sulfur uptake at various temperatures.

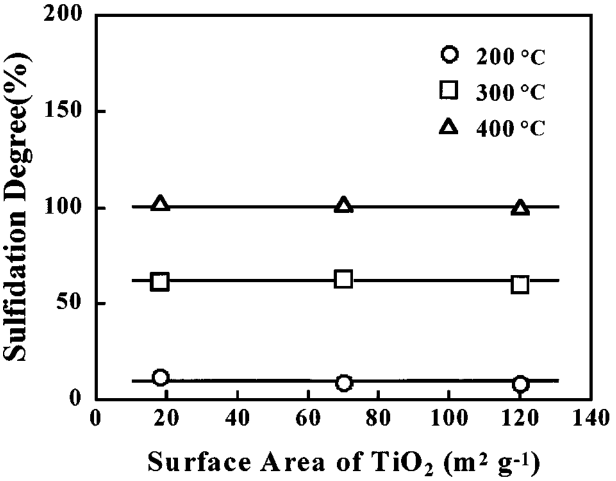

FIG. 5. Effect of surface area of TiO_2 catalysts on sulfidation degree at various temperatures.

at 500°C the sulfidation process continued slowly. At 200, 300, and 400°C, the amount of sulfur that accumulated on TiO_2 increased linearly with increasing surface area, while at 500°C the linear relationship could not be observed on the TiO_2 catalysts. These results show that the same kinds of sulfides are formed on the catalysts up to 400°C and the sulfidation kinetics changes at 500°C. As shown in Fig. 5, the degree of sulfidation did not change with increasing surface area at 200, 300, and 400°C. The degree of sulfidation for all catalysts at 400°C was almost 100%, corresponding to the sulfidation state when all of the surface Ti is present as TiS_2. This indicates that the surface TiO_2 of all catalysts of various surface areas could be sulfided to the stoichiometric TiS_2 state at 400°C, and that the sulfidation of bulk TiO_2 would occur slowly at 500°C.

As obtained above, the HDS activities on TiO_2 catalysts after sulfidation at 400°C increased linearly with surface area. This can be explained by the fact that the surface TiS_2 species, which has been suggested to act as the active phase in HDS reaction, increased linearly with the surface area of TiO_2 catalysts after the sulfidation at 400°C. At 500°C sulfidation of bulk TiO_2 occurred, and the oversulfidation may have led to the decrease in surface area, which means a decrease in the amount of surface TiS_2 and HDS activity. For the unsulfided TiO_2 catalyst it is proposed that the sulfidation of TiO_2 would lead to high apparent activation energy in the HDS reaction. According to the calculation, when a DBT conversion of 20% was obtained, 0.03 vol% of H_2S was formed under the reaction conditions, which is expected to lead to the sulfidation of TiO_2. At lower temperature it was difficult for sulfidation of the TiO_2 catalyst to occur and lower HDS activity was obtained, while at 390°C sulfidation of the TiO_2 catalyst occurred immediately and a HDS activity close to that of the sulfided TiO_2 could be obtained.

3.3. *Reduction of Sulfided TiO_2 Catalysts*

To investigate the sulfidation state under a H_2 atmosphere, after sulfidation with $H_2{}^{35}S$ at 500°C, as described in Section 3.2, the catalysts were subsequently reduced by H_2 at various temperatures. Figure 6 shows the change in radioactivity of $H_2{}^{35}S$ released during the reduction of sulfided TiO_2(70). No release of $H_2{}^{35}S$ was detected at 200°C which means that reduction of TiS_2 did not occur. The reduction of sulfided TiO_2(70) catalyst began at 300°C and occurred rapidly at 400°C; at 500°C the reduction process continued slowly. Similar reduction experiments were carried out on TiO_2(18) and TiO_2(120) catalysts after sulfidation at 500°C and similar results were obtained. The amounts of sulfur released at each temperature during the reduction process are also summarized in Table 1. For each catalyst, the amount of sulfur released up to 400°C was about one-fourth the total amount of sulfur that accumulated on the catalyst at 500°C. This indicates that one-fourth of the sulfur accumulated on the catalyst could be reduced by H_2 and released as $H_2{}^{35}S$ at 400°C. That is, under H_2 atmosphere at 400°C the sulfided TiO_2 corresponded to the sulfidation state $TiS_{1.5}$ and Ti was present in the stoichiometric Ti^{3+} state. When the reduction temperature was increased to 500°C, $H_2{}^{35}S$ was released slowly, which indicates that further reduction to $Ti_{1+x}S_2$ occurred at 500°C slowly. This observation is quite important since the HDS reaction on TiO_2 catalyst was carried out under a H_2 atmosphere and the Ti^{3+} species should play an important role in the HDS mechanism.

3.4. *ESR Study of Reduced TiS_2 Species*

Since it is proposed that TiS_2 was present in the stoichiometric Ti^{3+} state after the reduction treatment at 400°C, electron spin resonance analysis was further used to confirm the presence of Ti^{3+} species. Figure 7 shows the ESR spectra

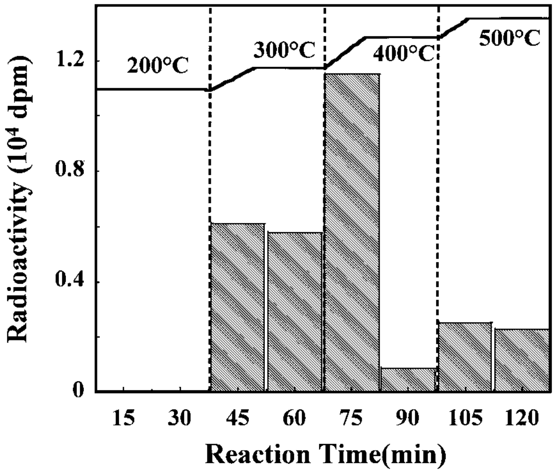

FIG. 6. Reduction of sulfided TiO_2(70) catalyst in H_2 at various temperatures.

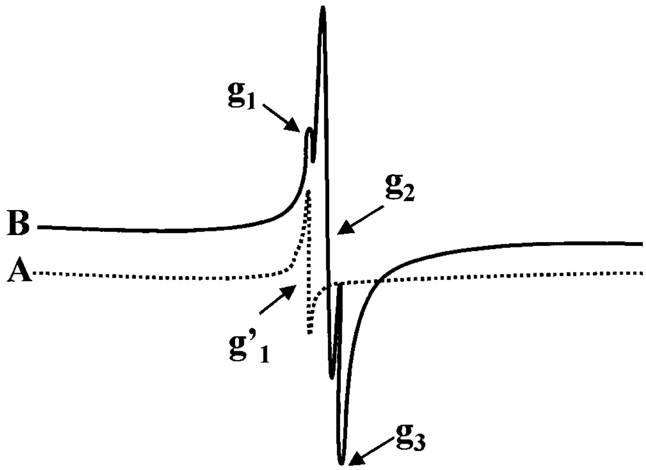

FIG. 7. Electron spin resonance spectra of sulfided TiO_2(70) catalysts after reduction with H_2 at 400°C: (A) sulfided at 400°C for 3 h; (B) sulfided at 500°C for 24 h.

recorded at atmospheric pressure and room temperature for TiO_2 samples. Sample A was sulfided at 400°C for 3 h and then reduced by H_2 at 400°C for 2 h under the reaction conditions; sample B was sulfided at 500°C for 24 h and then reduced by H_2 at 400°C for 2 h under the reaction conditions. As obtained above, only the surface of TiO_2 was sulfided for sample A, and sulfidation of bulk TiO_2 occurred for sample B. A significant ESR signal ($g'_1 = 2.004$) was detected in sample A. From the position of the ESR this signal is assigned to the free electrons trapped in sulfur vacancies of TiS_2. For sample B, the signal for free electrons ($g_1 = 2.004$) was also observed and new stronger signals appeared in the lower field of the spectrum ($g_2 = 1.989$ and $g_3 = 1.966$). According to Ref. (28), the new signals are assigned to subsurface Ti^{3+} ions from the position of the ESR. The detection of Ti^{3+} signal at atmospheric pressure and room temperature is unusual due to the presence of oxygen. Angelo *et al.* (29) also reported that the ESR signal of Ti^{3+} was detected at atmospheric pressure and room temperature after treating TiO_2 with H_2O_2. From the ESR results, it is concluded that due to the reduction of TiS_2, the surface free electrons trapped in sulfur vacancies and the subsurface Ti^{3+} ion will be formed. When only surface TiO_2 is sulfided to TiS_2 at 400°C, the reduction treatment leads to the formation of surface free electrons trapped in sulfur vacancies; when the subsurface TiO_2 is also sulfided to TiS_2 at 500°C, the subsurface Ti^{3+} ion will be formed after reduction treatment. As compared with conventional Al_2O_3 support, TiO_2 can be easily reduced under hydrogen atmosphere and temperature (30, 31), although partial reduction of TiO_2 only results in the formation of electrons that can be trapped in forming Ti^{3+} ions detectable by ESR at liquid-nitrogen temperature (77 K) (28). These Ti^{3+} ions are preferably located at the surface of TiO_2 and can be reoxidized easily in the presence of oxygen. TiO_2 (anatase), characterized by UV–vis diffuse resolution electron microscopy (DRS), presents as a semiconductor with an energy gap near 3.0 eV. On the other hand, according to previous studies, an exchange reaction between sulfur and the oxygen of TiO_2 can easily take place (32). Changes in the electrical conductivity of TiO_2 in a H_2S environment also gave an effective indication of the presence of this exchange (33). That is, sulfidation of TiO_2 with H_2S will lead to the formation of TiS_2, which is a narrow-gap semiconductor, the energy gap of which has been measured to be as low as 0.2 eV (34, 35). Therefore, compared with TiO_2, TiS_2 can be reduced more easily under hydrogen atmosphere and the Ti^{3+} ions formed in TiS_2 are more stable. In fact, it has been reported that TiS_2 takes a metal character by reduction to $Ti_{1+x}S_2$ (36). Ramirez *et al.* (20) also reported that in the case of TiO_2-supported hydrotreating catalysts, after sulfidation and under reaction conditions, where the catalyst is under a high hydrogen partial pressure, TiO_2 can be reduced and sulfided in part. Moreover, under these conditions the reduced titanium oxide and titanium sulfide species will have nearly metal conductivity, the latter having a narrow-gap semiconductor property. It is also suggested that the sulfur on sulfided TiO_2 could be hydrogenated to H_2S and that this ability for sulfur hydrogenation is equivalent to the ability of creating sulfur vacancies and must be related to HDS activity.

3.5. *Behavior of Sulfur on the Sulfided Catalysts in HDS of [^{35}S]DBT*

HDS of [^{35}S]DBT was performed to investigate the behavior of sulfur on sulfided TiO_2 catalysts in the steady state. Figure 8 shows a typical operation of the ^{35}S tracer method. The HDS of [^{35}S]DBT was carried out on a sulfided TiO_2(120) catalyst at 390°C. Initially, a decalin solution of 1 wt% [^{32}S]DBT was pumped into the reactor until the conversion of DBT became constant. A decalin solution of 1 wt% [^{35}S]DBT was then substituted for the [^{32}S]DBT and

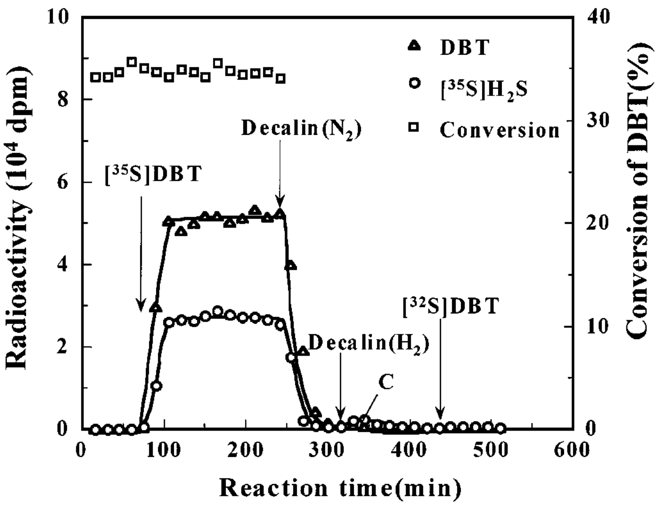

FIG. 8. Change in the radioactivity of unreacted ^{35}S-DBT and released H_2 ^{35}S with reaction time at 390°C over TiO_2(120) sulfided at 500°C.

reacted until the amount of $H_2{}^{35}S$ formed became constant. After [^{35}S]DBT was introduced, the radioactivity of the $H_2{}^{35}S$ produced increased and approached a steady state immediately, which means that sulfur exchange between ^{35}S and ^{32}S was not significant. To determine the behavior of sulfur more accurately, the carrier gas H_2 was replaced by N_2, and the [^{35}S]DBT solution was replaced by decalin solvent subsequently. During this process less release of $H_2{}^{35}S$ was detected. When the carrier gas N_2 was replaced by H_2 again, a small portion of ^{35}S was observed to be released as $H_2{}^{35}S$, as shown in Fig. 8 (area C). This indicates that the small amount of sulfur incorporated into the catalyst could be reduced under the H_2 atmosphere. When the reactant solution was replaced by [^{32}S]DBT again, less release of $H_2{}^{35}S$ was detected. The small portion of reduced ^{35}S, which represented the amount of sulfur exchanged on the catalyst, can be calculated from the total radioactivity of the $H_2{}^{35}S$ released in the range of area C. The same radioisotope tracer experiment was conducted over TiO_2(70) catalyst at 390°C and similar results were obtained. The amounts of sulfur exchanged on the TiO_2(120) and TiO_2(70) catalysts were 0.96 and 0.52 mg/g cat, which were about one-tenth of that on MoO_3/Al_2O_3 catalysts when similar HDS activities were obtained (25). This indicates that the HDS mechanism on TiO_2 catalyst is evidently different from that on Mo-based catalyst. It can be supposed that most of the sulfur released in HDS of DBT does not accumulate on the TiO_2 catalyst and less sulfur exchange occurs. It is suggested that the sulfur anion vacancies act as the active site on the sulfided TiO_2 catalyst and the sulfur of DBT is adsorbed on the sulfur anion vacancy and then desorbed as H_2S immediately without sulfur exchange.

3.6. *HDS Mechanism on TiO_2 Catalyst*

TiO_2 has shown a remarkable capability for both hydrogenation and desulfurization under the reaction conditions. This capability seems to be related to the electronic properties of the sulfided and reduced TiO_2 surface and, in particular, to the presence of sulfur anion vacancies in Ti^{3+} ions. As reported in our previous study using a ^{35}S tracer method (37), in the HDS reaction on Mo-based catalysts, the portion of sulfur in the Mo–S phase was labile and present as SH groups under the H_2 atmosphere. When H_2S formed and subsequently desorbed from the catalyst, an anion vacancy was generated. The sulfur in DBT occupied the S^{2-} anion vacancy and the carbon–sulfur bonds were cleaved; the sulfur remained on the catalyst as a Mo–S species and the old anion vacancy disappeared. Therefore, exchange between the sulfur in DBT and the sulfur on the catalyst occured, and as an intermediate, a sulfur anion vacancy was generated. According to the results obtained above, no sulfur exchange occurred on TiO_2 catalyst during the HDS reaction, which indicates that the reaction pathway is different from that for Mo-based catalysts. A hypothesis about the basic steps of the HDS process taking place on the TiO_2 is schematically illustrated in Fig. 9 and summarized in the following points:

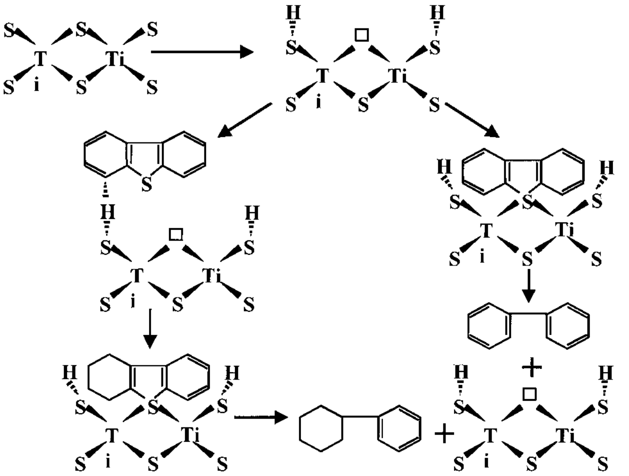

FIG. 9. Schematic view of the proposed HDS mechanism on TiO_2. □, Sulfur anion vacancy.

a. Reduction of the TiS_2 on the catalyst under a H_2 atmosphere involves depletion of H_2S from the matrix and formation of sulfur anion vacancies with electrons entrapped as follows: $2TiS_2 + H_2 \rightarrow H_2S + 2TiS_{1.5}$.

b. Simultaneously, H_2 adsorbs on the surface of the catalyst and sulfur in the reduced $TiS_{1.5}$ phase is present as SH groups under the H_2 atmosphere.

c. Two pathway of DBT adsorption on the surface of the catalyst are proposed: DBT can be adsorbed on the hydrogenation active site (e.g., SH groups) or on the sulfur anion vacancies with the sulfur in DBT. In the former pathway, one benzene ring of DBT can be hydrogenated first and as an intermediate tetrahydrodibenzothiophene (4HDBT) is formed which can be detected in the products. Then the sulfur of 4HDBT is adsorbed on the sulfur anion vacancy and entrapment of the electron in the vacancy results in the carbon–sulfur bond cleavage, leading to the formation of CHB. The sulfur is desorbed as the generation of H_2S immediately and the sulfur anion vacancy remains on the catalyst. In the latter pathway, the sulfur in DBT is directly adsorbed on the sulfur anion vacancy and the carbon–sulfur bond is cleaved with the formation of BP. The sulfur is desorbed immediately and the sulfur anion vacancy remains on the catalyst.

The HDS activity of sulfided TiO_2 catalysts would be closely related to the existence of sulfur vacancies. SH groups also play an important role in the HDS reaction (38). Recently, Topsoe and Topsoe (39) postulated that SH groups and vacancies on sulfided Mo-based catalysts could interconvert and coexist in close proximity. As mentioned above, for Mo-based catalysts, H_2S is not formed directly from the sulfur in DBT, but from the sulfur on the catalyst with sulfur exchange. For TiO_2 catalysts, no sulfur exchange occurs and H_2S is formed directly from the sulfur in DBT.

Our previous study (40) suggested that hydrogenation and desulfurization of DBT take place at different active sites. Further, when BP is added to a solution of DBT at steady state of the HDS reaction on TiO_2 catalyst, no significant increase in the formation of CHB is observed. This means that CHB is formed mainly by hydrogenation of DBT prior to desulfurization. Compared with Mo-based catalysts, TiO_2 catalysts show ca. 50% higher CHB selectivity at 390°C, which means that TiO_2 catalysts have greater hydrogenation ability. The hydrogenation ability is suggested to be associated with the SH groups on the catalysts under a H_2 atmosphere. It is supposed that Ti–S bond energy in the reduced $TiS_{1.5}$ phase would be stronger than Mo–S bond energy in MoS_2. Therefore, the H atoms spilled over Ti–S are less stable than those over Mo–S and can be moved to DBT more easily, which means that DBT can be hydrogenated more easily on TiO_2 catalysts than on Mo-based catalysts.

CONCLUSIONS

From the above results it is possible to conclude that:

(1) The HDS activities on sulfided TiO_2 catalysts increased linearly with increasing surface area of TiO_2, suggesting that the sulfide TiS_2 is the active phase of the HDS reaction on sulfided TiO_2 catalyst. Sulfidation under different conditions will lead to different HDS activities.

(2) Ti atoms on the surface of TiO_2 could be completely sulfided to TiS_2 at 400°C, and the sulfidation of Ti atoms in bulk TiO_2 would occur slowly at 500°C. With increasing surface area of TiO_2 catalysts, the amount of sulfur that accumulated on TiO_2 increased linearly, while the degree of sulfidation remained constant up to 400°C. When the sulfided TiO_2 was reduced by H_2 at 400°C, TiS_2 was reduced to the sulfidation state $TiS_{1.5}$, leading to the formation of Ti^{3+} ions and sulfur anion vacancies.

(3) As for the HDS reaction mechanism on sulfided TiO_2 catalyst, it is suggested that the sulfur anion vacancies acted as the active site and that the sulfur of DBT was adsorbed on the sulfur anion vacancies and then desorbed as H_2S immediately without sulfur exchange under the reaction conditions.

In future work, we will try to analyze if titania acts as a promoter when molybdenum is supported on it and if it is capable of creating a synergetic effect with the molybdenum sulfided phases under the reaction conditions.

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