

# Novel hydrodesulfurization catalysts derived from a supported rhodium carbonyl complex -Effect of the support on the catalytic activity and the sulfur behavior

Jeayoung Lee, Atsushi Ishihara\*, Franck Dumeignil, Eika W. Qian, Toshiaki Kabe

*Department of Chemical Engineering, Tokyo University of Agriculture & Technology, Nakacho, Koganei, Tokyo 184-8588, Japan*

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## Abstract

The dibenzothiophene hydrodesulfurization (HDS) reactions were carried out over alumina, titania, silica and silica-alumina supported rhodium complex catalysts. First, a series of catalysts containing 1 wt.% Rh was prepared and tested. Whilst in the case of the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst we did not observe any significant variation of the activity with the pretreatment, in the case of the titania, the silica and the silica-alumina supported catalysts, the pre-reduction treatment resulted in an activity twice as high as that obtained after the pre-sulfiding treatment. The use of the various supports slightly affected the overall HDS activity as well as the products selectivities. Whilst the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited the highest biphenyl (BP) selectivity, the Rh/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst exhibited the highest dibenzothiophene conversion. The Rh supported on TiO<sub>2</sub>, SiO<sub>2</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts gave high cyclohexylbenzene (CHB) yields, indicating high hydrogenation abilities. Further, the effect of the Rh loading was studied on the titania and the silica supports. Unlike the other supports for which the activity stabilized for Rh loadings higher than 0.5–1.0 wt.%, the DBT conversions of the SiO<sub>2</sub>-supported Rh catalysts increased up to 4 wt.% Rh, exhibiting the highest HDS activity. To precisely elucidate the effect of the pre-activation method on the sulfidation state and on the HDS activity, the 4 wt.% Rh/SiO<sub>2</sub> catalyst was placed under HDS working conditions and [<sup>35</sup>S]DBT HDS tracer experiments were performed. We found that, whilst the amount of labile sulfur (S<sub>OA</sub>) present on the surface of the prereduced catalyst was slightly lower than that observed for the presulfided catalyst, the labile sulfur atoms created on the prereduced catalyst exhibited a significantly greater mobility (*k*<sub>RE</sub>). This increase in sulfur mobility induced by the reduction pretreatment facilitated the active sites regeneration during the reaction, which led to an enhancement of the HDS catalytic activity.

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## 1. Introduction

The air pollution caused by the diesel exhaust fumes has dangerously increased in big city areas. Thus, much attention is now focused on the development of more efficient depollution processes aiming at cleaning light gas oils such as the deep hydrodesulfurization (HDS) process. In order to achieve a sufficient HDS level, it is not only essential to develop new hydrodesulfurization catalysts but also to elucidate the HDS reaction mechanism [1,2]. Among the large number of new catalytic formulations reported in the literature, the non-supported ruthenium sulfides were found

to exhibit particularly remarkable properties in the dibenzothiophene HDS reaction [3–7]. Further, some research groups conducted the HDS reaction over ruthenium sulfide supported on various carriers such as alumina [8–11], carbon [12–14], zeolites [15–19], MgF<sub>2</sub> [20] and amorphous silica-alumina [21]. All these efforts improved the HDS ability of the Ru sulfide catalysts. Especially, the alkali promoted Ru catalysts exhibited HDS activities comparable to those of the conventional Co-Mo catalysts [22].

On the other hand, the rhodium in the metallic state is known to be one of the most active catalysts for the hydrogenation of carbon monoxide. The hydrogenation of CO over supported Rh catalysts has been studied for many years to produce chemical feedstocks from synthesis gas. Some studies dealt with the CO<sub>2</sub> hydrogenation over supported Rh catalysts for the synthesis of methane [23–25] or for

\* Corresponding author. Tel.: +81-42-388-7228;  
fax: +81-42-388-7228.

E-mail address: [atsushii@cc.tuat.ac.jp](mailto:atsushii@cc.tuat.ac.jp) (A. Ishihara).

the synthesis of methanol and acetic acid [26,27]. Recently, the performance of rhodium sulfide catalysts in HDS reaction was investigated. It was found that rhodium sulfide exhibits a relatively high activity compared to the sulfides of the other transition metal elements [3]. Indeed, Harris and Chianelli [28] found that for very low metal loadings, carbon-supported rhodium and iridium sulfides exhibited activities even higher than the ruthenium one, while similar results were also reported by Vissers et al. [29]. Moreover, Sugioka et al. showed that rhodium and platinum-palladium supported on an ultra-stable Y (USY) zeolite, and platinum supported on HZSM-5 and a mesoporous silicate exhibited a higher activity than a commercial Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst [30]. We also reported that an alumina supported rhodium carbonyl complex exhibited very interesting HDS catalytic properties for low Rh loadings, as the activity calculated per metal atom was much higher than that of a conventional Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst [31]. Further, using a radio-tracer [<sup>35</sup>S]DBT HDS method it was shown that a larger number of active sites (labile sulfur atoms) was formed on the Rh catalysts than on the Ru catalysts, thus explaining the higher HDS activity of the former. Nevertheless, an increase in the Rh loading did not lead to a catalyst with the expected performance, as the high specific activity was not maintained for high Rh loadings.

These results suggested that it is possible to further optimize highly active metal carbonyl-based catalysts performance by complexation of the precursor and subsequent modification of the support. Therefore, in the present research we decided to investigate the effect of the carrier on the DBT HDS activity of supported rhodium carbonyl complexes.

Thus, the present paper deals with the influence of the carrier (alumina, titania, silica and silica-alumina) on the DBT HDS catalytic properties of a rhodium carbonyl supported complex. In the first part, we studied the effect of the support, the metal amount and the catalyst activation method on the DBT HDS activity. In the second part, the sulfur behavior on a catalyst that exhibited interesting properties (the silica supported catalyst) was interpreted by a radiotracer [<sup>35</sup>S]DBT HDS method described elsewhere [32–35]. The amount of labile sulfur atoms and the H<sub>2</sub>S release rate constant were determined on the catalyst activated by pre-sulfiding and by pre-reduction.

## 2. Experimental

### 2.1. Materials

Commercially available triethyl amine (NEt<sub>3</sub>), ethyl alcohol and decalin (purity: ~98%) (Kishida Chemicals) were used without further purification. Hexarhodium hexadecacarbonyl (Rh<sub>6</sub>(CO)<sub>16</sub>) was supplied from Aldrich Chem. Co. Ltd. The  $\gamma$ -alumina supplied by Nippon Ketjen Co. Ltd., was crushed and screened to obtain 0.84–1.19 mm

grains. SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (JRC-SAL2), SiO<sub>2</sub> (JRC-SIO4) and TiO<sub>2</sub> (JRC-TIO1) were supplied by the Catalysis Society of Japan. Table 1 shows the BET surface areas of the supports together with the amount of impregnated rhodium. In order to remove the moisture and the adsorbed impurities, the supports were dried under vacuum at 350 °C during 4 h and stored under Ar atmosphere prior to use. Hydrogen (99.99%) and hydrogen sulfide in hydrogen (H<sub>2</sub>S: 5.0%) were obtained from Tohei Chemicals. All the scintillation solvents used for the radioactivity measurements were supplied by Packard Japan.

### 2.2. Preparation of the Rh<sub>6</sub>(CO)<sub>16</sub>-NEt<sub>3</sub> based catalysts

In order to prepare a catalyst containing 1 wt.% Rh, 0.0086 g of Rh<sub>6</sub>(CO)<sub>16</sub> and NEt<sub>3</sub> (Rh:N = 2:1) were introduced into a 50 ml reactor before being dissolved in ethyl alcohol (10 ml). After stirring the mixture at 70 °C for 1 h, the system was cooled down to room temperature. Then, 0.495 g of Al<sub>2</sub>O<sub>3</sub> was added into the solution and stirred for 2 h. Finally, the solvent was removed in vacuum. Various catalysts were prepared by modulation of the rhodium content as well as the use of various carriers, always keeping the Rh/N ratio equal to 2 (Table 1 gives an overview of the prepared catalysts).

All the catalysts were called 'XRh/Y', X being the Rh wt.% and Y being the carrier (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> or SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>).

### 2.3. Characterization of the prepared catalysts

Powder X-ray diffraction (XRD) spectra were recorded on a Rigaku RINT 2000 apparatus using a Cu K $\alpha$  radiation ( $\lambda = 0.15405$  nm). The Debye–Scherrer equation was used to estimate the mean size of the Rh particles.

Transmission electron microscopy (TEM) photographs were taken on a CM 300/STEM microscope working at an accelerating voltage of 250 kV. The samples were crushed before being slurried with methanol and deposited on a copper grid, which was subsequently set in the microscope. The micrographs were recorded with a magnification of 175,000–255,000. EDX analysis was also carried out to confirm that the particles observed by TEM on the Rh/SiO<sub>2</sub> catalyst consisted of Rh.

Hydrogen adsorption was performed in a conventional glass vacuum system (static method). The vacuum was

Table 1  
Description of the synthesized catalysts and their subsequent pre-activation treatments

Support (m <sup>2</sup> g <sup>-1</sup> )	Pretreatment (3 h)	Rh content (wt.%)
Al <sub>2</sub> O <sub>3</sub> (256)	H <sub>2</sub> S (400), H <sub>2</sub> (400)	1
TiO <sub>2</sub> (73)	H <sub>2</sub> S (400), H <sub>2</sub> (400)	0.5, 1, 2
SiO <sub>2</sub> (347)	H <sub>2</sub> S (400), H <sub>2</sub> (400)	1, 4
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (560)	H <sub>2</sub> S (400), H <sub>2</sub> (400)	1

attained using an oil diffusion pump in line with a mechanical pump (primary vacuum). The pressure was measured by a manometer. Samples (2 g) were pre-reduced in situ in a flow of hydrogen at 400 °C for 3 h in a manner similar to that used for the activity tests. The hydrogen uptakes were determined at  $25 \pm 1$  °C on the reduced and evacuated samples.

#### 2.4. Apparatus and experimental procedure

##### 2.4.1. HDS activity

The HDS experiments were carried out in a fixed-bed flow reactor (8 mm × i.d. 300 mm). The catalysts were activated by pre-sulfiding with a mixture of 5 vol.% H<sub>2</sub>S/H<sub>2</sub> or by pre-reduction in 99.9% H<sub>2</sub> for 3 h at 300 or 400 °C. After the catalyst pretreatment, the reactor was cooled down to room temperature and then pressurized with hydrogen. A decalin solution of DBT was then fed by using a high-pressure liquid pump (Kyowa Seimitsu KHD-16). The DBT HDS reactions were carried out under the following conditions: H<sub>2</sub> flow rate: 12.5 l·h<sup>-1</sup>; WHSV: 28 h<sup>-1</sup>; reaction pressure: 5 MPa; concentration of DBT in decalin: 1.0 wt.%; catalyst weight: 0.5 g. The liquid products were collected every 15 min and analyzed by a gas chromatograph equipped with an FID detector (Shimadzu-17A, Shimadzu Co. Ltd.) and a capillary column (DB-1).

##### 2.4.2. The [<sup>35</sup>S]DBT HDS radioisotope tracer method

We selected the reaction conditions as follows: catalyst weight: 1 g; H<sub>2</sub> flow rate: 25 l·h<sup>-1</sup>; WHSV: 28 h<sup>-1</sup>; pressure: 5 MPa; concentration of DBT in decalin: 1.0 wt.%; reaction temperature: 300 °C. Before each experiment the catalyst was pre-sulfided with a 5 vol.% H<sub>2</sub>S in H<sub>2</sub> or pre-reduced in 99.9% H<sub>2</sub> at 400 °C for 3 h. The liquid product was collected from a gas/liquid separator. The produced H<sub>2</sub>S was absorbed by bubbling through a commercial basic scintillation solution (Carbosorb, Packard Co. Ltd.). Both liquid product and absorbed H<sub>2</sub>S solution samples were collected every 15 min. The radioactivities of the unreacted [<sup>35</sup>S]DBT in the liquid phase and the produced [<sup>35</sup>S]H<sub>2</sub>S quantity were measured by a liquid scintillation counter (Beckman, LS-6500) [32]. A typical [<sup>35</sup>S]DBT HDS operation procedure is as given further:

1. A decalin solution of 1 wt.% [<sup>32</sup>S]DBT is pumped into the reactor until the DBT conversion becomes constant (about 3 h).
2. Then, the reactant solution is replaced by a 1 wt.% [<sup>35</sup>S]DBT (9000 dpm/g) solution. The [<sup>35</sup>S]DBT HDS reaction is performed until the amount of released [<sup>35</sup>S]H<sub>2</sub>S stabilizes at a constant value (about 2–4 h).
3. The [<sup>35</sup>S]DBT solution is then replaced by decalin. The decalin flow is maintained during about 3 h.
4. Finally, the [<sup>32</sup>S]DBT solution is re-introduced and the reaction is pursued for 4–5 h.

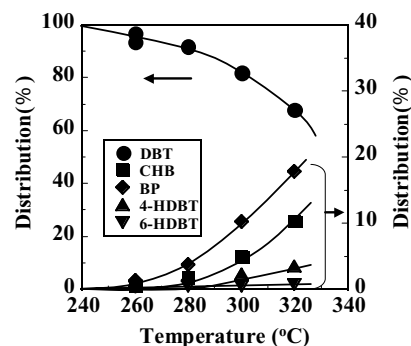


Fig. 1. Products distribution for 1Rh/TiO<sub>2</sub> presulfided at 400 °C for 3 h.

### 3. Results and discussion

#### 3.1. Effect of the support on the DBT HDS activity

##### 3.1.1. Activity of the presulfided 1 wt.% Rh catalysts

Fig. 1 shows the activity and the selectivity results of the DBT HDS reaction performed over the 1Rh/TiO<sub>2</sub> catalyst preactivated by sulfiding (in a 5.0% H<sub>2</sub>S/H<sub>2</sub> mixture at 400 °C during 3 h). The main products were cyclohexylbenzene (CHB) and biphenyl (BP), while some minor co-products such as tetrahydrodibenzothiophene (4-HDBT) and hexahydrodibenzothiophene (6-HDBT) were also formed. When the temperature increased, the DBT concentration decrease was accompanied with an increase in the yield of all the products. Similar experiments were performed over all the catalysts. Fig. 2 summarizes the conversions obtained for the presulfided 1 wt.% Rh catalysts supported on alumina, silica, titania and silica-alumina. The Rh/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited the highest HDS activity, which was twice as high as that of the silica, the silica-alumina and the titania supported catalysts. For these experiments, the activity was measured from the lowest temperature (260 °C) to the highest (320 °C) by steps of 20 °C. In the last stage of the reaction, the activity was measured again after decreasing the temperature to 260 °C in order to check about a possible catalyst deactivation. Whilst in the case of the Al<sub>2</sub>O<sub>3</sub> carrier the activity returned to its initial value, in the case

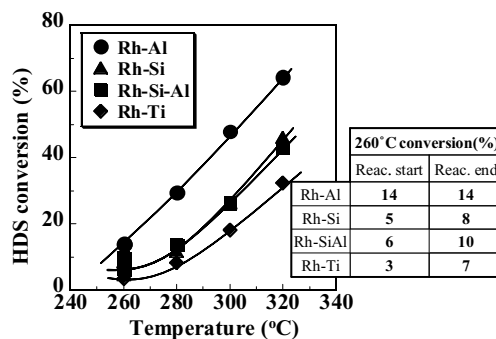


Fig. 2. Effect of the support on the DBT conversion for 1 wt.% Rh containing catalysts activated by pre-sulfidation.

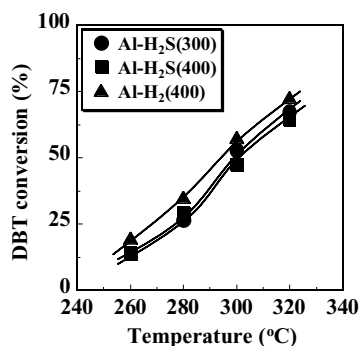


Fig. 3. Effect of pre-activation treatment on DBT HDS activity of the 1Rh/Al<sub>2</sub>O<sub>3</sub> catalyst.

of the other carriers surprisingly the reevaluated activity was about twice as high as the initial one (see the Table inserted in Fig. 2). These results suggested that the active phase supported on silica, silica-alumina and titania was progressively modified under the HDS experimental conditions (high H<sub>2</sub> pressure), resulting in better catalytic performance.

### 3.1.2. Influence of the catalyst pre-activation method on the HDS catalytic performances

According to the results presented in Section 3.1.1, we decided to investigate the effect of the catalyst pretreatment on the DBT HDS activity. The activity of the pre-reduced catalysts was measured and then compared with the activity obtained after pre-sulfiding. Fig. 3 shows the influence of the pretreatment conditions on the activity of the 1 wt.% Rh/Al<sub>2</sub>O<sub>3</sub> catalyst. For this catalyst, the pretreatment modifications did not induce any significant variation in the HDS activity, as expected from the results presented in Fig. 2. On the other hand, as shown in Fig. 4, the pre-reduced 1 wt.% Rh catalysts supported on titania, silica and silica-alumina catalysts gave an activity about twice as high as that obtained after a conventional sulfiding pretreatment. In contrast, it has been previously shown that Ru/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> catalysts exhibit a higher HDS activity after a pre-sulfiding pretreatment rather than after a pre-reduction treatment. Generally, the species active in HDS are formed upon

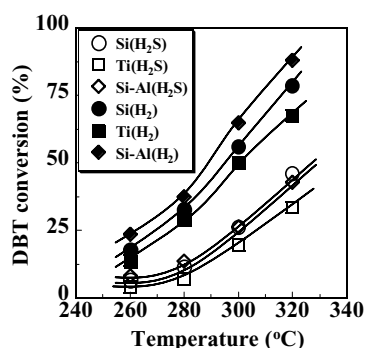


Fig. 4. Effect of pre-activation treatment on DBT HDS activity of the 1Rh/TiO<sub>2</sub>, the 1Rh/SiO<sub>2</sub> and the 1Rh/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts.

Table 2  
DBT HDS activity over 1 wt.% Rh catalysts

Catalysts	Conversion (%)		BP yield (%)		CHB yield (%)		H/M <sup>a</sup>
	A <sup>b</sup>	B <sup>c</sup>	A <sup>b</sup>	B <sup>c</sup>	A <sup>b</sup>	B <sup>c</sup>	
Al <sub>2</sub> O <sub>3</sub>	57	48	53	45	2.9	0.9	0.12
TiO <sub>2</sub>	50	18	30	10	16.5	5.0	0.07
SiO <sub>2</sub>	56	26	40	19	13.5	4.0	0.29
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	65	26	36	14	26.0	6.6	Not determined

<sup>a</sup> H/M: hydrogen/metal (reduction under H<sub>2</sub> at 400 °C for 3 h and then evacuation at 400 °C for 1 h).

<sup>b</sup> Catalysts pre-reduced at 400 °C for 3 h.

<sup>c</sup> Catalysts pre-sulfided at 400 °C for 3 h.

sulfidation [3]. However, obviously in the case of the 1 wt.% Rh catalysts supported on titania, silica and silica-alumina, the pre-reduction treatment gave better results than the pre-sulfidation treatment. As shown in Fig. 3, the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst pre-reduced at 400 °C gave better catalytic results than the one pre-reduced at 300 °C, whilst usually a high pretreatment temperature is not preferable because the possibility of sintering of the noble metals is increased. Table 2 presents detailed results for all the catalysts loaded with 1 wt.% Rh and working at 300 °C. In all the cases, the major products were found to be BP and CHB. The catalytic activities of the catalysts activated by pre-sulfiding decreased in the order Al<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> ≥ SiO<sub>2</sub> > TiO<sub>2</sub>. However, the activity of the pre-reduced catalysts decreased in the order SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> > Al<sub>2</sub>O<sub>3</sub> ≥ SiO<sub>2</sub> > TiO<sub>2</sub>. In this case, the HDS activity was only moderately affected by the carriers. Nevertheless, among them the rhodium supported silica-alumina catalyst gave the highest DBT conversion and the highest CHB yield. That means that the rhodium species supported on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> have a higher ability to hydrogenate the aromatic rings of DBT. Indeed, tetrahydrodibenzothiophene (4-HDBT) and hexahydrodibenzothiophene (6-HDBT), which are hydrogenated products, are easier to desulfurize than DBT (the rate of HDS of 4-HDBT or 6-HDBT has been reported to be four times as high as that of DBT [36]). The same observation have also already been reported for a Ru<sub>3</sub>(CO)<sub>12</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst [37].

Then, to examine the relation between the particle size and the HDS activity, we measured the hydrogen adsorption of the 1 wt.% rhodium supported alumina, titania and silica catalysts. As shown in Table 2, the H/M ratio was clearly influenced by the support. The H/M ratio obtained for 1Rh/TiO<sub>2</sub> was low (0.07) and the mean particle size was found to be about 16 nm. Particles of such size would be easily detectable by XRD. However, the XRD spectra did not exhibit any characteristic feature of well-ordered Rh crystallites. This kind of phenomenon on Rh/TiO<sub>2</sub> catalysts can be explained by the SMSI (strong metal-support interactions) [38]. Neither 1Rh/Al<sub>2</sub>O<sub>3</sub> nor 1Rh/SiO<sub>2</sub> showed high dispersion. However, their HDS activities were higher than those of 8 wt.% Ru<sub>3</sub>(CO)<sub>12</sub> catalysts [37] supported on alumina

(44%), titania (33%) and silica alumina (62%) with much higher metal loadings. From this result and the results shown in Table 2, we can deduce that the particle size difference cannot explain the differences of catalytic performance. Further, in the case of the supported ruthenium carbonyl systems, the BP yield decreased in the order  $\text{Al}_2\text{O}_3$  (38%) >  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (36%) >  $\text{TiO}_2$  (22%) >  $\text{SiO}_2$  (17%) [37]. In contrast, the BP yields for Rh-based catalysts decreased in the order  $\text{Al}_2\text{O}_3$  (53%) >  $\text{SiO}_2$  (40%) >  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (36%) >  $\text{TiO}_2$  (30%) when the catalysts were prerduced.

### 3.1.3. Effect of the Rh loading on the DBT HDS activity

The effect of the Rh loading on the HDS activity was studied to improve the activity. The results are presented in Fig. 5. For comparison, a few results previously reported for Rh/ $\text{Al}_2\text{O}_3$  catalysts [31] are also shown in Fig. 5. The DBT conversion over the Rh/ $\text{Al}_2\text{O}_3$  catalysts increased linearly up to 0.5–1 wt.% and leveled off. The DBT conversion of the Rh/ $\text{TiO}_2$  catalysts increased up to about 1 wt.% Rh, similarly to the Rh/ $\text{Al}_2\text{O}_3$  catalysts. The DBT conversion of the Rh/ $\text{SiO}_2$  catalyst increased up to 4 wt.% Rh, and 4 wt.% Rh/ $\text{SiO}_2$  exhibited the highest HDS conversion. These results demonstrate the fact that not only the intrinsic activity of a metal but also the capacity of a support for metal loading is very important to obtain a high global conversion.

The micrographs obtained for the Rh/ $\text{SiO}_2$  catalysts are shown in Fig. 6. The Rh particles appeared as black dots

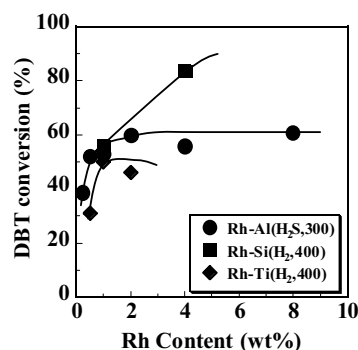
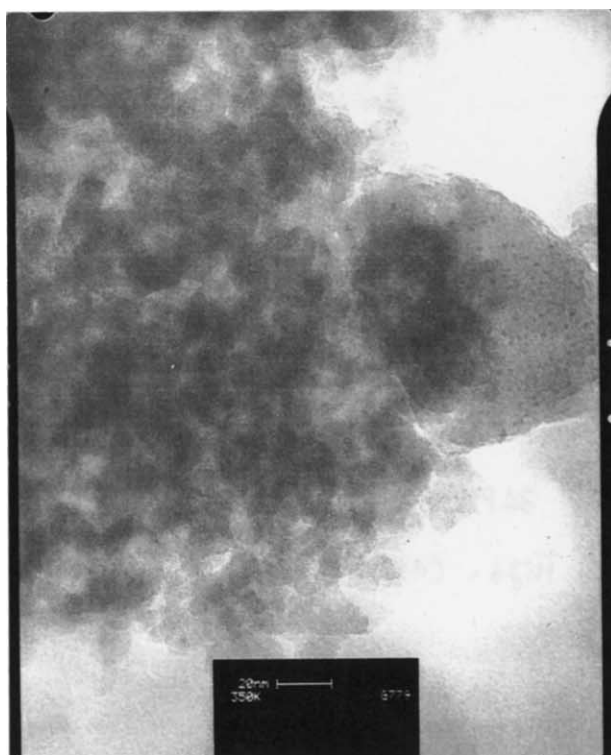
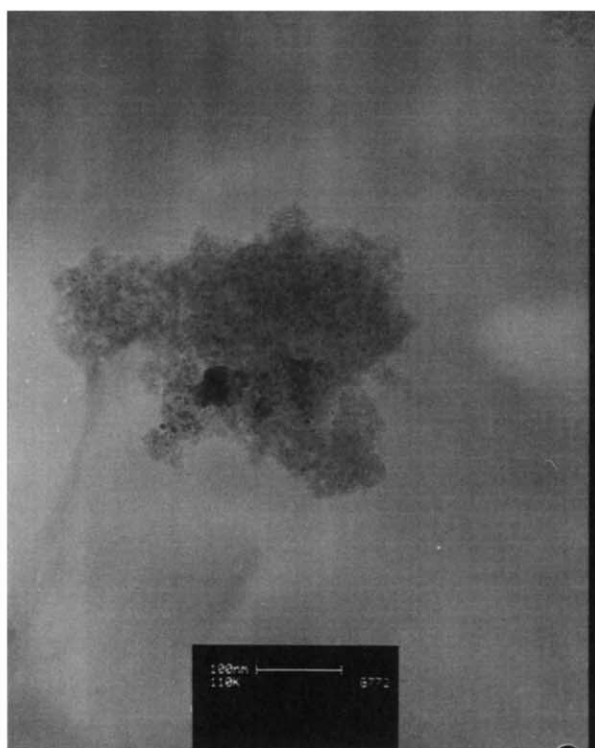


Fig. 5. Effect of the Rh content on the DBT conversion at 300°C.

(because of their higher electron density) of a few nanometers, while  $\text{SiO}_2$  was observed as a greyish background (confirmed by EDX analysis). For 1Rh/ $\text{SiO}_2$ , a uniform distribution of the small Rh particles (< 3 nm) was observed. The 4Rh/ $\text{SiO}_2$  catalyst exhibited larger Rh particles (< 8 nm). It indicates that the Rh particle size was affected by the Rh concentration, in agreement with the findings previously reported for Rh/ $\text{Al}_2\text{O}_3$  catalysts [31]. In the latter case, the size of the particles increased, and thus the DBT conversion leveled off for Rh > 0.5 wt.%. Although the DBT conversion of the Rh/ $\text{SiO}_2$  catalysts increased up to 4 wt.% Rh, the intrinsic activity for one Rh atom might decrease.



(a) 1wt%Rh/ $\text{SiO}_2$



(b) 4wt%Rh/ $\text{SiO}_2$

Fig. 6. Transmission electron micrograph of Rh/ $\text{SiO}_2$  catalysts (reduced at 400°C for 3 h).

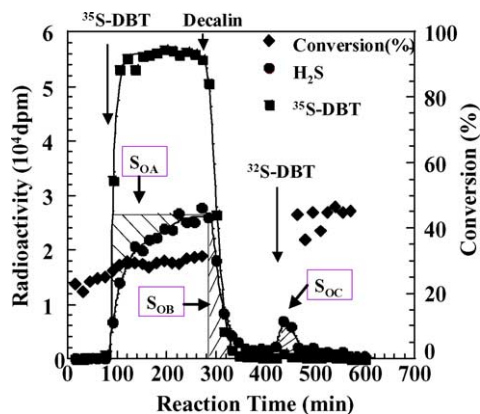


Fig. 7. Change in radioactivity of unreacted  $[^{35}\text{S}]\text{DBT}$  and released  $[^{35}\text{S}]\text{H}_2\text{S}$  with reaction time (4Rh/SiO<sub>2</sub> presulfided catalyst).

### 3.2. Study of the sulfur behavior on the 4Rh/SiO<sub>2</sub> catalyst during the HDS working conditions using a $^{35}\text{S}$ tracer method

In the preceding discussion, we showed that compared to the classical sulfiding pretreatment, the reduction pretreatment resulted in the significant increase in the HDS activity of rhodium supported titania, silica and silica-alumina catalysts. The higher HDS performance on these prerduced Rh catalysts aroused interest in the sulfidation state of Rh during HDS working conditions. Thus, in order to elucidate precisely the observed activity difference between the reduction and the sulfiding pretreatments and to determine the Rh sulfidation state on the catalysts working under HDS conditions, a  $^{35}\text{S}$  tracer method was used.  $[^{35}\text{S}]\text{DBT}$  HDS was performed using the best catalyst (4Rh/SiO<sub>2</sub>) after pre-sulfiding or pre-reduction at 400 °C for 3 h. Fig. 7 shows the results obtained for the presulfided 4Rh/SiO<sub>2</sub> catalyst. Initially, a decalin solution of 1 wt.%  $[^{32}\text{S}]\text{DBT}$  was pumped into the reactor until the DBT conversion became constant. This solution was then replaced by a 1 wt.%  $[^{35}\text{S}]\text{DBT}$  solution, which was continuously fed into the reactor until the amount of produced  $[^{35}\text{S}]\text{H}_2\text{S}$  became constant. Just after the  $[^{35}\text{S}]\text{DBT}$  introduction, the radioactivity of the unreacted  $[^{35}\text{S}]\text{DBT}$  in the liquid product increased drastically and a steady state was immediately reached, whilst it took about 75 min to achieve a steady state in the radioactivity of the produced  $[^{35}\text{S}]\text{H}_2\text{S}$ . This result indicates that the sulfur taken from the DBT molecules is not directly released as hydrogen sulfide but is temporarily accommodated on the catalyst, which is consistent with the results obtained so far over Al<sub>2</sub>O<sub>3</sub>-supported molybdenum catalysts [32,33]. Next, after the  $[^{35}\text{S}]\text{H}_2\text{S}$  radioactivity reached the steady state, only decalin was fed into the reactor. The radioactivity due to  $[^{35}\text{S}]\text{DBT}$  decreased immediately, whilst the  $[^{35}\text{S}]\text{H}_2\text{S}$  radioactivity decrease was somewhat slow. This progressive decrease suggests that at least a part of the sulfur previously accommodated on the catalyst surface can react with hydrogen during the decalin introduction stage since Rh sulfide is unstable under high H<sub>2</sub> pressures. Therefore,

some sulfur atoms are liberated as hydrogen sulfide through the reduction of the active phase. Then, after the  $[^{35}\text{S}]\text{H}_2\text{S}$  radioactivity was no more detected, the  $[^{32}\text{S}]\text{DBT}$  solution was fed again into the reactor. The  $^{35}\text{S}$  atoms remaining on the catalyst were exchanged with  $^{32}\text{S}$  atoms taken from the  $[^{32}\text{S}]\text{DBT}$  molecules. This resulted in further  $[^{35}\text{S}]\text{H}_2\text{S}$  liberation. After the last  $[^{32}\text{S}]\text{DBT}$  solution introduction, the HDS activity exhibited a value twice as high as the initial one. This phenomenon, which was not observed on alumina-supported molybdenum catalysts [34], was consistent with the activity change presented in Fig. 2. This result indicates that whilst molybdenum sulfide is stable under a high hydrogen pressure, both Rh sulfide based catalysts and Ru sulfide based catalysts [36] are not. It is remarkable that in the case of the ruthenium sulfide catalysts, unlike in the case of the rhodium sulfide catalysts, the observed HDS activity decreases after the  $[^{32}\text{S}]\text{DBT}$  solution reintroduction. That means that for the ruthenium sulfide based catalysts, the sites responsible for the DBT HDS are denatured by reduction under the experimental conditions, whilst in the case of the Rh based sulfide catalysts the activity can be enhanced over adequate carriers under specific experimental conditions. From the results of the  $[^{35}\text{S}]\text{DBT}$  HDS experiments, we determined  $S_{0A}$ , the total amount of labile sulfur,  $S_{0B}$ , the amount of labile sulfur that can be removed by reduction under the experimental conditions, and  $S_{0C}$ , the amount of labile sulfur, which is hardly influenced by reduction phenomena (see Fig. 7). The results are presented in Table 3. We found that  $S_{0A}$  was close to the sum of  $S_{0B}$  and  $S_{0C}$ . In Table 3 we present also  $k_{RE}$ , the rate constant of  $[^{35}\text{S}]\text{H}_2\text{S}$  release which was determined by a method described elsewhere [32,33]. For comparison, the results previously obtained for Ru-Cs/Al<sub>2</sub>O<sub>3</sub> [39] and Rh-Cs/Al<sub>2</sub>O<sub>3</sub> catalysts [31] are also listed in Table 3. These parameters are very important to the characterization of the catalytic properties because  $S_{0A}$  is likely to represent the number of active sites present on the catalysts whilst  $k_{RE}$  is representative of the reactivity of one active site. The HDS activity of the prerduced 4Rh/SiO<sub>2</sub> catalyst during the  $[^{35}\text{S}]\text{DBT}$  HDS experiment was twice as high as that of the presulfided 4Rh/SiO<sub>2</sub> catalyst, confirming the results of the activity experiments. If we compare the effect of the pre-sulfiding and

Table 3  
Kinetic parameters on supported Rh and Ru catalysts

Catalysts	Conversion (%)	$S_{0A}$ (mg g <sub>cat</sub> <sup>-1</sup> )	$k_{RE} \times 10^{-2}$ (min <sup>-1</sup> ) <sup>a</sup>	$S_{0A}/S_{total}$ <sup>b</sup> (%)
4Rh/SiO <sub>2</sub> <sup>c</sup>	29.0	19.3	2.6	104
4Rh/SiO <sub>2</sub> <sup>d</sup>	58.0	15.2	6.0	82
4Rh-Cs/Al <sub>2</sub> O <sub>3</sub> <sup>e</sup>	53.8	12.2	3.6	65
4Ru-Cs/Al <sub>2</sub> O <sub>3</sub> <sup>e</sup>	125.8	7.3	3.7	29

<sup>a</sup>  $[^{35}\text{S}]\text{H}_2\text{S}$  release reaction rate constant.

<sup>b</sup>  $S_{total}$  is defined as the amount of total sulfur supposing that Rh and Ru are respectively fully sulfided in the Rh<sub>2</sub>S<sub>3</sub> and the Ru<sub>2</sub>S<sub>2</sub> forms.

<sup>c</sup> Pre-sulfidation at 400 °C.

<sup>d</sup> Pre-reduction at 400 °C.

<sup>e</sup> Pre-sulfidation at 300 °C.

the pre-reduction shown in Table 3 for the 4Rh/SiO<sub>2</sub> catalyst, we can see that the former pretreatment led to a higher S<sub>0A</sub> of 19.3 mg/g-cat (i.e. a Rh sulfiding percentage of 100% if we consider that sulfidation is complete when Rh<sub>2</sub>S<sub>3</sub> is formed), whilst the latter gives a S<sub>0A</sub> of 15.2 mg/g-cat (i.e. a Rh sulfiding percentage of 82%) on the working catalyst. In other words the presulfided catalyst exhibited more labile sulfur atoms than the prerduced one. Mangnus et al. [41] also investigated the sulfidation state of Rh/Al<sub>2</sub>O<sub>3</sub> catalysts using TPR experiments, was found that Rh/Al<sub>2</sub>O<sub>3</sub> catalysts could be easily sulfided into Rh<sub>2</sub>S<sub>3</sub>. Then, Rh<sub>2</sub>S<sub>3</sub> could be further reduced under a H<sub>2</sub>S/H<sub>2</sub> atmosphere poor in H<sub>2</sub>S via intermediate steps, i.e. the reduction of Rh<sub>2</sub>S<sub>3</sub> into RhS<sub>0.89</sub> followed by reduction into Rh<sup>0</sup>. On the other hand, our results of the tracer experiment indicated that the Rh<sub>2</sub>S<sub>3</sub> species (presulfided Rh catalyst) are rather likely to be greatly preserved for long reaction times (at least 5 h) even in the presence of an atmosphere with a low H<sub>2</sub>S/H<sub>2</sub> ratio (calculated at about  $4.3 \times 10^{-4}$ ) at a relatively low temperature. However, the activity tests showed that the Rh<sub>2</sub>S<sub>3</sub> reduction proceeded at high reaction temperature (320 °C) and also during the decalin introduction step of the tracer experiments (i.e. when the H<sub>2</sub>S/H<sub>2</sub> ratio is equal to 0). Further, this indicates also that the metallic Rh present on the prerduced catalysts was easily sulfided by the sulfur atoms of DBT or by the hydrogen sulfide produced by the DBT HDS. In the case of the sulfiding pretreatment, the active phase was progressively reduced to give the same state as the one obtained at the steady state for a catalyst pretreated by reduction. In other words, irrespective of the pretreatment the sulfidation of the active phase might produce a steady state determined by the H<sub>2</sub>S/H<sub>2</sub> composition in the reactor.

When we examine the *k*<sub>RE</sub> obtained for both pretreatments, we can see that the one measured after pre-reduction is more than twice as high as that induced by pre-sulfiding, with a value of  $6.0 \times 10^{-2} \text{ min}^{-1}$  for the former and  $2.6 \times 10^{-2} \text{ min}^{-1}$  for the latter (Table 3). This means that the higher activity obtained after pre-reduction is not due to an increase in the labile sulfur amount (potential active sites number increase), because this latter quantity rather exhibits the tendency to decrease under such a treatment. In fact, this result suggests that the increase in activity is rather due to a greater reaction turnover number over the formed catalytic sites, i.e. a higher H<sub>2</sub>S release rate constant.

If now we compare the results of the present study with those conducted with other noble metal catalysts supported on alumina carrier and further improved by the addition of Cs (Rh-Cs and Ru-Cs catalysts), we can make the following points:

- The Rh supported on silica catalyst is the most efficient among the catalysts presented in Table 3. Its activity is even a slightly higher than that of the Rh-Cs catalyst supported on alumina.
- The Rh based catalysts superiority over the Ru based ones can be explained by the amount of labile sulfur atoms.

Table 4  
Evaluation of sulfidation state on various catalysts using <sup>35</sup>S pulse tracer method

Catalyst	Sulfidation of metal sulfide	S <sub>0</sub> , S <sub>0A</sub> <sup>*</sup> /S <sub>total</sub>
Mo/Al <sub>2</sub> O <sub>3</sub>	MoS <sub>2</sub>	<75% in MoS <sub>2</sub>
Co-Mo/Al <sub>2</sub> O <sub>3</sub>	CoS MoS <sub>2</sub>	<60% in MoS <sub>2</sub>
Ni-Mo/Al <sub>2</sub> O <sub>3</sub>	NiS MoS <sub>2</sub>	<40% in MoS <sub>2</sub>
Pt-Pd/Al <sub>2</sub> O <sub>3</sub>	PtS <sub>0.25</sub> PdS <sub>0.25</sub>	100%
Ru Cs/Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	RuS <sub>2</sub>	30%
Rh Cs/Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	Rh <sub>2</sub> S <sub>3</sub>	66%
Rh/SiO <sub>2</sub> <sup>c</sup>	Rh <sub>2</sub> S <sub>3</sub>	82%
Rh/SiO <sub>2</sub> <sup>d</sup>	Rh <sub>2</sub> S <sub>3</sub>	104%

<sup>a</sup> After pre-sulfiding at 300 °C (Ru 4 wt.%).

<sup>b</sup> After pre-sulfiding at 300 °C (Rh 4 wt.%).

<sup>c</sup> After pre-reduction at 400 °C (Rh 4 wt.%).

<sup>d</sup> After pre-sulfiding at 400 °C (Rh 4 wt.%).

Indeed, the amount of labile sulfur on the Rh based catalysts was at least 65% of the accommodated total sulfur (S<sub>total</sub>) while that of the Ru-Cs catalyst was only 29% of the accommodated total sulfur.

Table 4 shows the sulfidation states observed over various catalysts. The results obtained during DBT HDS reactions in previous studies [40] were compared with the ones obtained for the Rh/SiO<sub>2</sub> catalyst in the present study. The Mo present in a Ni-Mo and a Co-Mo catalyst was fully sulfided into MoS<sub>2</sub> and 40–75% of the sulfur was labile. Similarly to the Ni-Mo system, the Ru of a Ru-Cs catalyst was fully sulfided (into RuS<sub>2</sub>) but the labile sulfur represented only 30% of the total sulfur. Though the sulfided state of the Pt-Pd catalyst was only PtS<sub>0.25</sub>-PdS<sub>0.25</sub>, the percentage of mobile sulfur reached 100%. In brief, in these catalytic systems, when the active metal is stoichiometrically fully sulfided (Co-Mo, Ni-Mo and Ru-Cs systems), the percentage of labile sulfur atoms is not so high, and when 100% of labile sulfur is reached (Pt-Pd system) the sulfidation percentage is low. In contrast, the Rh-based catalyst could be fully sulfided into Rh<sub>2</sub>S<sub>3</sub> whilst exhibiting a satisfactory labile sulfur percentage (active sites) of about 66–100%.

Further, whilst S<sub>0A</sub> and *k*<sub>RE</sub> observed on the presulfided Rh-Cs/Al<sub>2</sub>O<sub>3</sub> catalyst were lower than those observed on the prerduced Rh/SiO<sub>2</sub> catalyst (Table 3), the former exhibited a catalytic activity similar to that of the latter. This suggests that there are some catalytic sites on the presulfided Rh-Cs/Al<sub>2</sub>O<sub>3</sub> catalyst that are not involved in the conventional sulfur accommodation process responsible for the activity. These particular sites could be of the same type as the ones present on a Pt-Pd catalytic system. Fig. 8 shows the DBT HDS mechanism proposed over the Rh sulfide catalyst. First, the sulfur of the presulfided Rh catalyst is reduced by the hydrogen of the gas phase to form coordinative unsaturated site (CUS) (Fig. 8A). The sulfur atoms taken from the DBT molecules in the reactant solution can then replenish the prerduced Rh catalyst. In this case the sulfur atom of a DBT molecule is adsorbed on the previously formed CUS (Fig. 8B) before desorption of the reaction product (Fig. 8C).

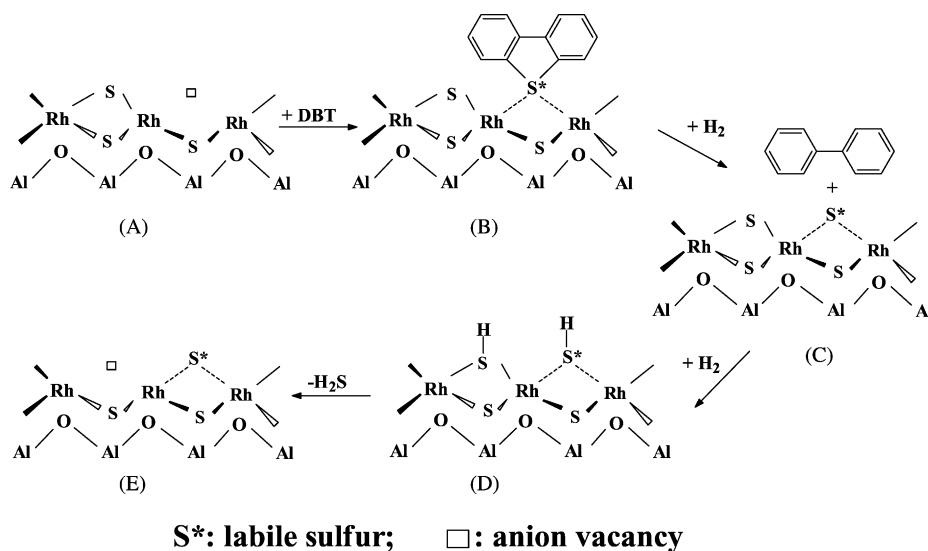


Fig. 8. DBT HDS reaction mechanism over sulfided Rh/Al<sub>2</sub>O<sub>3</sub> catalysts.

A new CUS is then formed by H<sub>2</sub>S liberation through the mechanism proposed in Fig. 8D and E. The position of the newly formed CUS (in Fig. 8E) differs from that of the initial CUS (Fig. 8A). Such a mechanism assumes that all the sulfur present on the catalyst can be exchanged during the reaction. Therefore, for the presulfided Rh/SiO<sub>2</sub> catalyst exhibiting a high S<sub>0</sub> value, the prevailing species in the steady state is likely to be B or C with the additional presence of some CUS progressively created by reduction with the time on stream. On the other hand, since the prerduced Rh/SiO<sub>2</sub> catalyst exhibits a lower S<sub>0</sub> value than the one observed on the presulfided catalyst, the steady state is likely to be A or E where CUS is present.

#### 4. Conclusion

The DBT HDS properties of titania, silica, alumina and silica-alumina supported rhodium complex catalysts were studied. A first series of experiments in which the catalysts were loaded with 1 wt.% Rh showed the superiority of the alumina supports over the other ones when the catalysts are pretreated by a conventional sulfiding procedure. Nevertheless, in this series of experiments, an unusual phenomenon was observed for the titania, silica and silica-alumina supports. Indeed, whilst in the case of the alumina support the used catalyst activity was almost the same as that of the fresh one, an increase in activity was observed for the catalysts prepared with all the other supports when the time on stream increased. For Ru supported catalysts, the inverse tendency was observed; i.e. the activity was decreased by a reduction treatment without DBT. Thus the experimental conditions greatly affected the activity because of the Rh-sulfide species reducibility under high H<sub>2</sub> pressures. Irrespective of the pretreatment conditions, the HDS activity of the alumina supported catalyst did not significantly vary; however, the

reduction pretreatment induced a drastic increase in the activity of the catalysts prepared with the other supports. The Rh/Al<sub>2</sub>O<sub>3</sub> catalyst gave the highest BP selectivity and the Rh supported TiO<sub>2</sub>, SiO<sub>2</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts gave high CHB yields; the Rh/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst showed the highest DBT conversion and the highest CHB yield. The rhodium catalyst supported on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> showed a higher ability to hydrogenate the aromatic rings of DBT inducing good DBT HDS performance (4-HDBT and 6-HDBT, which are hydrogenation products, are easier to desulfurize into CHB than DBT into BP). The DBT conversions of the Rh/SiO<sub>2</sub> catalysts increased up to a 4 wt.% Rh loading and exhibited the highest HDS activity. The [<sup>35</sup>S]DBT HDS tracer experiments showed that, whilst the amount of labile sulfur atoms was lower on the working prerduced catalyst than on the presulfided one, the former exhibited a higher H<sub>2</sub>S release ability. As a result, a higher activity of the prerduced catalyst was attained.

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