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NOTE

Hydrodesulfurization of Dibenzothiophene Catalyzed by Alumina-Supported Ruthenium Carbonyl Complexes in a Pressurized Flow System

Ruthenium sulfide has been found to be most active for hydrodesulfurization (HDS) of thiophenes as well as hydrogenation and hydrodenitrogenation among transition metal sulfides (1–9). When ruthenium sulfide is supported on alumina, silica, or zeolite with high surface area, highly dispersed ruthenium sulfide formed on the supports would increase the catalytic activity per a ruthenium atom. Several researchers have already reported HDS using supported ruthenium sulfides. In these works, $[Ru(NH_3)_6]^+$ (4), $Ru_3(CO)_{12}$, $RuCl_3$ (2, 4, 7), and Ru(III) acetate (6) supported on alumina, zeoliate, carbon (8, 9), etc., were used as catalyst precursors in HDS of thiophene, benzothiophene, or dibenzothiophene. Although these HDS reactions were performed under an atmospheric pressure, the activity of the catalysts derived from supported ruthenium in a pressurized flow system have not yet been understood.

On the other hand, although the catalysts prepared from supported metal carbonyl complexes are found to be active in many catalytic reactions (10–14), there are few examples where the catalysts derived from supported metal carbonyls were applied to HDS of thiophenes. We have already reported that the catalysts derived from supported anionic molybdenum carbonyls are more active in HDS of DBT than conventional sulfided molybdena alumina and one derived from alumina-supported neutral molybdenum hexacarbonyl (15, 16). In the course of our study, we were interested in the reactivity of supported anionic ruthenium carbonyls in HDS of DBT.

In the present study, HDS of DBT catalyzed by ruthenium catalysts is investigated in a pressurized flow reactor. The reactivity of the catalyst derived from an alumina-supported $Ru_3(CO)_{12}$-ethanethiol(EtSH)-triethylamine(Et_3N) system, where $Ru_3(CO)_{12}$ reacts EtSH and Et_3N to give an anionic ruthenium carbonyl complex with metal–sulfur bonds, is compared with those of catalysts derived from alumina-supported $Ru_3(CO)_{12}$, $Ru(acac)_3$ (acac, acetylacetonate), and $RuCl_3$. It is found that the catalyst derived from an alumina-supported anionic ruthenium carbonyl is the most active for HDS of DBT.

Commercially available $Ru_3(CO)_{12}$, Ru(acac, acetylacetonate)$_3$, $RuCl_3 \cdot nH_2O$ (n = 2–4) (Nippon Chemcat), triethylamine (NEt_3), ethanethiol (EtSH), and xylene (Kishida Chemicals) were used without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Alumina (Japan Ketjen) was γ-alumina supplied as a 1/32 extrudate which was crushed and screened to provide 0.84- to 1.19-mm granules. Alumina was dried under vacuum as 350°C for 4 h prior to use and stored in Ar atmosphere. Hydrogen and nitrogen (99.99%) were obtained from Tohei Chemicals. Hydrogen sulfide in hydrogen (H_2S 3%) was obtained from Takachio Chemicals. Typical preparation method was as follows: 0.084 g of $Ru_3(CO)_{12}$ was reacted with 0.020 g of NEt_3 and 0.012 g of EtSH in THF under reflux for 30 min (Ru : N : S = 2 : 1 : 1) to give a brown solution. Then, 0.46 g of Al_2O_3 was added into the solution and stirred for 2 h. Solvent was removed *in vacuo*. $Ru_3(CO)_{12}/Al_2O_3$, $Ru(acac)_3/Al_2O_3$, and $RuCl_3/Al_2O_3$ systems were prepared similarly. These samples were used without dilution.

A catalyst precursor was placed into a pressurized fixed-bed flow reactor (10 mm I.D. × 300 mm), heated at 5°C/min and activated at 300°C under a flow of H_2, N_2, or H_2S in H_2 (H_2S 3%) for 2 or 3 h. When $RuCl_3/Al_2O_3$ was used, presulfidation with H_2S in H_2 (H_2S 3%) was performed at 400°C for 3 h. After the treatment, the reactor was adjusted to 300°C and was pressurized by hydrogen. Then, the solution containing DBT was supplied to the feed pump (Kyowa Seimitsu KHD-16). HDS of DBT was carried out under the following conditions: temperature, 300°C; 50 kg/cm^2; H_2 18 l/h; LHSV, 14 h^{-1}; initial concentration of DBT, 1.0 wt%; and catalyst, 0.5 g. Reaction products were analyzed by gas chromatography with a FID detector (Shimadzu GC-9A) using a OV-1 capillary column (I.D. 0.25 × 50 mm).

Volumetric measurements of NO and CO chemisorption were carried out in a conventional Pyrex glass high vacuum adsorption system. A typical procedure was as follows: samples of 250 mg were placed in a glass reactor, heated at 5°C/min and activated at 300°C under a flow of H_2, N_2, or 3% H_2S/H_2 (30 ml/min) for 2 or 3 h. After this treatment, samples were evacuated at 300°C under

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TABLE 1

Hydrodesulfurization of Dibenzothiophene Catalyzed by Alumina-Supported Ruthenium Carbonyls[a]

Run	Catalyst	Conv. of DBT (%)	Selec. for BP (%)	NO[e] Chemisorption ($\times 10^2$ μmol/g-cat)	CO[e] chemisorption ($\times 10^2$ μmol/g-cat)
1	$RuCl_3/Al_2O_3$	29	80	1.4	0.4
2	$Ru(acac)_3/Al_2O_3$[b]	32	71	1.7	0.9
3	$Ru_3(CO)_{12}/Al_2O_3$	44	86	1.8	0.7
4	$Ru_3(CO)_{12}$–NEt_3–EtSH/Al_2O_3	48	90	1.8	0.9
5	$Ru_3(CO)_{12}$–NEt_3–EtSH/Al_2O_3[c]	47	87	2.1	1.0
6	$Ru_3(CO)_{12}$–NEt_3–EtSH/Al_2O_3[d]	50	86	2.6	1.2

[a] React. temp. 300°C, 50 atm, LHSV 14 h^{-1}, H_2 18 l/h, Cat 0.5 g, Ru 8.0 wt%; presulfided by H_2S in H_2 (H_2S 3%) at 300°C (Runs 2–6) and at 400°C (Run 1).

[b] acac, acetylacetonate.

[c] Activated by H_2 at 300°C.

[d] Activated by N_2.

[e] Amounts of irreversible chemisorption are given.

vacuum (10^{-3} Torr) for 1 h and then cooled to 25°C. Adsorption of NO or CO was always carried out at 25°C. More details were described in the previous paper (15, 16).

After NO chemisorption and HDS reaction, the XP spectra of the sampled catalyst was measured without exposing the catalyst to air. The XPS was recorded on a Shimadzu ESCA-850 photoelectron spectrometer using Mg*Kα* radiation. Before XPS measurement, etching, i.e., sputtering by argon ion, was carried out by an ion gun equipped with ESCA-850 to obtain the clean surface (condition: 2 kV, 20 mA). The binding energies (BE) were referenced to the O1s band at 532.0 eV.

Catalysts derived from alumina-supported ruthenium compounds were active for HDS of DBT. The catalytic activity reached the steady state within 3 h and was kept constant for over 10 h. Products were biphenyl (BP) and cyclohexylbenzene (CHB). The conversion of DBT and the selectivity for BP at reaction time 3 h are shown in Table 1. When $RuCl_3$ and $Ru(acac)_3$ were used, conversions of DBT were about 30% (Runs 1 and 2). The use of $Ru_3(CO)_{12}$ increased the conversion of DBT in Run 3 (44%). The effect of the amount of Ru on the conversion of DBT and the selectivity for BP was investigated in the $Ru_3(CO)_{12}/Al_2O_3$ system as shown in Fig. 1. The conversion of DBT increased linearly up to 8 wt% of Ru and only slightly above 8 wt% to reach 60% at 24 wt%. Further loading of Ru decreased the conversion. Selectivity for BP decreased with increasing the amount of Ru. The results show that the high dispersion of ruthenium can be maintained up to 8 wt% of Ru. When an anionic ruthenium carbonyl complex (*vide infra*) formed by the reaction of $Ru_3(CO)_{12}$ with ethanethiol (EtSH) and triethylamine (NEt_3) was supported on alumina and activated by H_2S/H_2, H_2 or N_2 ($Ru_3(CO)_{12}$–NEt_3–EtSH/Al_2O_3 system in Runs 4–6), the catalytic activities were higher than catalysts derived from alumina-supported $RuCl_3$, $Ru(acac)_3$, and $Ru_3(CO)_{12}$ and the conversion of DBT was 47–50%. Selectivities for BP in the cases of organometallic compounds were nearly 90% and also higher than those in other ones.

The catalyst derived from the activation of a $Mo(CO)_6$–NEt_3–EtSH/Al_2O_3 system and the conventional sulfided molybdena–alumina showed the conversions of DBT, 43 and 38%, respectively. The selectivities for BP in molybdenum systems were lower than 80% (15, 16). Ruthenium catalysts derived from $Ru_3(CO)_{12}$–NEt_3–EtSH/Al_2O_3 and $Ru_3(CO)_{12}/Al_2O_3$ systems showed the higher catalytic activity and selectivity for BP than molybdenum-based catalysts.

FTIR spectra of $Ru_3(CO)_{12}$–NEt_3–EtSH/Al_2O_3 and $Ru_3(CO)_{12}/Al_2O_3$ systems are shown in Fig. 2. Alumina-supported $Ru_3(CO)_{12}$ showed IR absorptions at 2058, 2020, and 1998 cm^{-1} which are similar to IR absorptions

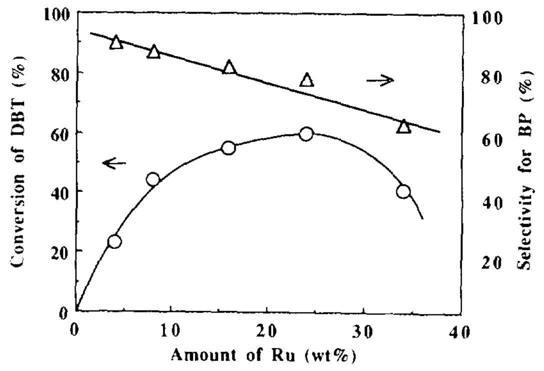

FIG. 1. Effect of amount of Ru on the conversion of DBT.

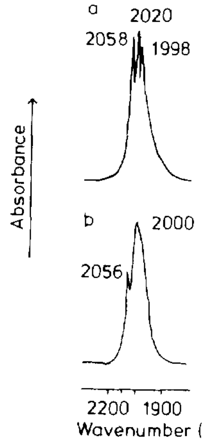

FIG. 2. FTIR measurement of supported ruthenium carbonyls: (a) $Ru_3(CO)_{12}/Al_2O_3$, (b) $Ru_3(CO)_{12}$–NEt_3–$EtSH/Al_2O_3$.

of $Ru_3(CO)_{12}$ itself. $Ru_3(CO)_{12}$ reacted with NEt_3 and EtSH to give a complex which have IR absorptions at 2060 (weak) and 2002 (vs) cm^{-1} in a THF solution. This indicates that an anionic trinuclear ruthenium complex would be formed in this reaction. When this complex was supported on Al_2O_3, IR absorptions at 2056 (medium) and 2000 (vs, broad) cm^{-1} were observed. Although a small amount of the initial complex reacted with alumina, it can be assumed that most of the anionic species with the original structure remained on alumina. Since hydrogenolysis and thermolysis of these species on Al_2O_3 revealed the high conversion of DBT, it can be deduced that the reaction of $Ru_3(CO)_{12}$ with NEt_3 and EtSH formed a complex with a ruthenium–sulfur bond and that hydrogenolysis and thermolysis of the complex supported on Al_2O_3 produced the highly dispersed ruthenium species with sulfur which is active for HDS of DBT. The amounts of adsorbed NO and CO are also listed in Table 1. The amounts of adsorbed NO and CO in the catalysts derived from a $Ru_3(CO)_{12}$–NEt_3–$EtSH/Al_2O_3$ system were larger than the others. This also confirms the formation of highly dispersed ruthenium species from $Ru_3(CO)_{12}$–NEt_3–$EtSH/Al_2O_3$ systems.

XPS spectra were measured for samples used in NO chemisorption as catalysts before HDS and the results are shown in Table 2. In supported ruthenium catalysts, S2*p* spectra were observed at 162.5–162.9 eV and Ru3*p* 3/2 at 461.8–462.1 eV. Ru3*p* 3/2 spectrum of Ru(0) is observed at 461.1 eV while a Ru3*p* 3/2 spectrum of RuS_2 is observed at 462.7 eV. Mitchell *et al.* reported that catalysts derived from presulfidation of alumina-supported ruthenium (III) acetate showed the Ru3*p* 3/2 and S2*p* spectra at 461.1–461.2 and 162.2–162.6 eV, respectively, and contained Ru–S species and S^{2-} sulfide ion (6). They also reported that RuS_2 precipitated by H_2S from $RuCl_3$ in ethyl acetate showed spectra at 460.8 eV while $RuS_{0.6}$ from reduced $RuCl_3$ reacted with H_2/H_2S (10%) at 643 K, for 4 h at 461.6 eV. It is suggested that, in catalysts prepared here, the valence state of Ru is between Ru(0) and RuS_2 and that S^{2-} sulfide ions coordinated to the metal ions are present on the surface. However, the values of the binding energies in the catalysts are not so different as to distinguish one catalyst from the other. It has been pointed out that XPS is not a suitable technique to identify metallic ruthenium because Ru(0) binding energies are very close to those of RuS_2 (2).

Unambiguous differences were observed in comparison with the ratio of S/Ru in XP spectra. The sulfidation of $RuCl_3/Al_2O_3$ and $Ru(acac)_3/Al_2O_3$ systems proceeded under the conditions and the ratios of S/Ru were 2.31 and 1.51, respectively. However, a $Ru_3(CO)_{12}/Al_2O_3$ system containing Ru(0) species was not sulfided so much as $RuCl_3/Al_2O_3$ and $Ru(acac)_3/Al_2O_3$ systems and the ratio of S/Ru was 0.83. The ratios of S/Ru in the catalyst derived from H_2 treatment of a $Ru_3(CO)_{12}$–EtSH–Et_3N/Al_2O_3 system were 0.49 lower than that in a $Ru_3(CO)_{12}/Al_2O_3$ system. The result also confirms that a complex containing metal–sulfur bonds was formed at the preparation of the precursor. De Los Reyes *et al.* reported that the S/Ru ratio was 1.8 when $RuCl_3/Al_2O_3$ was presulfided under the condition: 15% H_2S/H_2, 673 K, 4h (2). On the other hand, it has been reported that the ratio of S/Ru of the catalyst derived from presulfidation (10% H_2S/H_2, 673 K, 1h) of ruthenium sponge is ca. 0.3 and that it is difficult to sulfide ruthenium metal to ruthenium sulfide (7). Our results were approximately consistent with these reports. The S/Ru ratio in our $Ru_3(CO)_{12}/Al_2O_3$ system was 0.83 higher than that (ca. 0.3) in ruthenium sponge reported by Kuo *et al.* (7), because Ru(0) species derived from the $Ru_3(CO)_{12}/Al_2O_3$ system was highly dispersed on alumina and could be effectively exposed to hydrogen sulfide.

De Los Reyes *et al.* reported that the catalysts prepared by the H_2S/N_2 (15%) and H_2S (100%) treatment of $RuCl_3/Al_2O_3$ showed 4.2 and 3.6 of S/Ru ratios in XPS, respectively, and the higher catalytic activity than the catalyst prepared by the H_2S/H_2 (15%) treatment. It was concluded that sulfidation under H_2S/N_2 without prereduction gave a well-sulfided and highly active RuS_2 supported catalyst (2). However, our results were significantly different from this. XP spectra of ruthenium catalysts after HDS of DBT were recorded and the results are also shown in Table 2. Although binding energies of the catalysts were shown at 162.4–162.8 (S2*p*) and 461.8–462.2 (Ru3*p* 3/2), it was difficult to distinguish one catalyst from the other as shown in the catalysts before HDS reaction. The interesting result could be found in the ratio of S/Ru. It was evident that the ratios of S/Ru after HDS were lower than those before HDS. The values of S/Ru decreased

TABLE 2

Characterization of Supported Ruthenium Catalysts by Means of XPS[a]

Run	Catalyst	Before HDS				After HDS			
		S2*p* (eV)	Ru3*p* 3/2 (eV)	Ru3*p*/Al[b]	S/Ru3*p*[b]	S2*p* (eV)	Ru3*p* 3/2 (eV)	Ru3*p*/Al[b]	S/Ru3*p*[b]
7	$RuCl_3/Al_2O_3$[c]	162.8	462.1	0.027	2.31	162.8	461.8	0.041	0.52
8	$Ru(acac)_3/Al_2O_3$[d]	162.5	461.9	0.035	1.51	162.8	462.2	0.026	0.97
9	$Ru_3(CO)_{12}/Al_2O_3$[d]	162.8	462.0	0.026	0.83	162.5	462.1	0.025	0.45
10	$Ru_3(CO)_{12}$–EtSH–Et_3N/Al_2O_3[e]	162.7	461.8	0.021	0.49	162.4	462.0	0.022	0.54

[a] XPS spectra were measured for samples used in HDS reaction of DBT. Before the measurement, the samples were sputtered by Ar+ ion for 10 min. Every binding energy was referenced to Oxygen O1s 232.0 eV.

[b] Ratio of peak areas between A12*p*, S2*p* and Ru3*p* 3/2.

[c] Presulfided by H_2S in H_2 at 400°C (H_2S 3%) for 3 h before HDS.

[d] Presulfided by H_2S in H_2 at 300°C (H_2S 3%) for 3 h before HDS.

[e] Hydrotreated by H_2 at 300°C for 2 h before HDS.

considerably in $RuCl_3/Al_2O_3$ and $Ru(acac)_3/Al_2O_3$ systems and slightly in a $Ru_3(CO)_{12}/Al_2O_3$ system, scarcely changed in a $Ru_3(CO)_{12}$–EtSH–Et_3N/Al_2O_3 system and seem to approach about 0.5. The result indicates that active ruthenium species on the catalyst are near metallic ruthenium rather than RuS_2 and that, whatever the precursor, the amount of sulfur remaining on the catalyst surface is very small at least under the conditions pressurized by H_2. Further, it can be assumed that the activation of a $Ru_3(CO)_{12}$–EtSH–Et_3N/Al_2O_3 system would give the surface structure near-active species before HDS reaction. Lacroix *et al.* reported that the ratios of S/Ru before and after HDS of DBT (flow system, 1 atm) were 2.2 and 1.87, respectively, in elemental analysis of bulk RuS_2 catalyst (3). It has also been reported that some Ru(0) species are present in the unsupported RuS_2 tested under high hydrogen pressures (17). These reports may support our results.

In summary, hydrodesulfurization of dibenzothiophene using catalysts derived from alumina-supported ruthenium compounds was performed and the following conclusions were obtained:

1. Catalysts prepared by the activation of $Ru_3(CO)_{12}$-triethylamine(NEt_3)-ethanethiol(EtSH)/Al_2O_3 systems where metal carbonyls were reacted with NEt_3 and EtSH to give anionic complexes with metal–sulfur bonds were found to be active for HDS of DBT.

2. When a $Ru_3(CO)_{12}$–NEt_3–EtSH/Al_2O_3 system was activated in a H_2S, H_2, or N_2 stream, the catalytic activity was higher than catalysts derived from alumina-supported $RuCl_3$, $Ru(acac)_3$ and $Ru_3(CO)_{12}$, or molybdena–alumina.

3. When Ru(0) complexes such as $Ru_3(CO)_{12}$, anionic ruthenium carbonyls, etc., were used, the selectivities for biphenyl (BP) were more than 86% which was also higher than that with the use of a conventional molybdena–alumina (71%).

4. From NO and CO chemisorptions, the differences between the conversions of DBT could be explained by dispersion of ruthenium on a support. It is deduced that the activation of a $Ru_3(CO)_{12}$–NEt_3–EtSH/Al_2O_3 system would give highly dispersed ruthenium species.

5. In XPS measurement of catalysts before HDS, it was confirmed that $Ru_3(CO)_{12}/Al_2O_3$ was difficult to be sulfided (0.83, S/Ru) while alumina-supported $RuCl_3$ and Ru $(acac)_3$ can be sulfided up to 2.31 and 1.51, S/Ru ratios, respectively.

6. After HDS, S/Ru ratios of the ruthenium catalysts decreased to ca. 0.5, indicating that, under pressurized conditions, ruthenium species on the catalysts were near reduced metals rather than ruthenium sulfide on alumina.

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