[Regular Paper]

Hydrodesulfurization of Dibenzothiophene Catalyzed by Supported Metal Carbonyl Complexes (Part 5) Catalysts for Hydrodesulfurization Prepared from Alumina-supported Ruthenium Carbonyl-Alkali Metal Hydroxide Systems

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In hydrodesulfurization of dibenzothiophene (DBT) catalyzed by sulfided alumina-supported ruthenium compounds, the effects of addition of alkali metal hydroxide on the catalytic activity and product selectivity were investigated. When sodium hydroxide was added to catalysts derived from alumina-supported $\text{Ru}_3(\text{CO})_{12}$, the conversion of DBT remarkably increased from 44 to 71%. It was essential to obtain the high catalytic activity and, therefore, that after the reaction of $\text{Ru}_3(\text{CO})_{12}$ with sodium hydroxide, in advance, to give a ruthenium hydride $\text{Na}[\text{HRu}_3(\text{CO})_{11}]$, the hydride was supported on alumina. By the reaction of RuCl_3 , $\text{Ru}(\text{acac})_3$ (acac=acetylacetonate) and $\text{Ru}_3(\text{CO})_{12}$ with cesium hydroxide and products supported on alumina, the activity increased in the order $\text{RuCl}_3\text{-CsOH}/\text{Al}_2\text{O}_3 < \text{Ru}(\text{acac})_3\text{-CsOH}/\text{Al}_2\text{O}_3 < \text{Ru}_3(\text{CO})_{12}\text{-3CsOH}/\text{Al}_2\text{O}_3$. When the amount of addition of alkali metal hydroxides increased in the alumina-supported ruthenium carbonyl system, the conversion of DBT increased and reached the maximum at $\text{M}/\text{Ru}=2$ ($\text{M}=\text{Na}$ or Cs). Further addition of cesium decreased the activity. In $\text{Ru}_3(\text{CO})_{12}\text{-}n\text{CsOH}/\text{Al}_2\text{O}_3$ systems, biphenyl was produced selectively. In order to elucidate these phenomenon, the measurements of NO chemisorption and X-ray photoelectron spectroscopy (XPS) before and after HDS were performed. The addition of cesium to $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ increased the amount of NO chemisorption, indicating that the sulfided catalysts still had many coordinatively unsaturated sites. XP spectra showed that addition of appropriate amounts of cesium would stabilize ruthenium sulfide on alumina, even in pressurized hydrogen. Catalysts derived from a $\text{Ru}_3(\text{CO})_{12}\text{-6CsOH}/\text{Al}_2\text{O}_3$ system showed activities comparable to that of $\text{Co-Mo}/\text{Al}_2\text{O}_3$.

1. Introduction

The recent air pollution in urban areas is one of serious problems in the world and deep hydrodesulfurization (HDS) of light gas oil and development of the new catalysts for this purpose are needed extensively. One method to prepare HDS catalysts with higher activity is to improve the traditional alumina-supported CoMo, NiMo and NiW catalysts by expanding the surface area of alumina and increasing the metal loading. An alternative is to develop new generation of catalysts which have the properties different from that of the present Co, Ni, Mo and W-based catalysts. Since Pecoraro and Chianelli¹⁾ have given a clue to the novel catalysts by reporting that ruthenium sulfide

is most active for HDS of dibenzothiophene (DBT) among the transition metal sulfides, much attention was focused on HDS catalyzed by ruthenium sulfide, over the last decade²⁻¹⁰⁾. Lacroix *et al.*²⁾ confirmed that unsupported RuS_2 was most active, even in a flow system for HDS of dibenzothiophene (DBT), among the transition metal sulfides. Vrinat *et al.*³⁾ reported, on HDS of thiophene, that $\text{Ni}_x\text{Ru}_{1-x}\text{S}$ and $\text{Co}_x\text{Ru}_{1-x}\text{S}$ among the mixed sulfide solid solutions¹¹⁾, prepared from RuS_2 and CoS_2 or NiS_2 , exhibited activities higher than that of RuS_2 , CoMoS or NiMoS.

It can be expected that the deposition of ruthenium sulfide onto supports with large surface areas, such as alumina, silica, silica-alumina, zeolite etc., increases catalytic activity per ruthenium atom. This approach is also economical because ruthenium is one of noble metals. Some groups

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have already performed HDS catalyzed by supported ruthenium sulfide. Harvey and Matheson reported HDS of benzothiophene with catalysts derived from $[\text{Ru}(\text{NH}_3)_6]^+$, $\text{Ru}_3(\text{CO})_{12}$ and RuCl_3 supported on alumina and zeolite in a batch system⁴. Mitchell *et al.* performed HDS of thiophene with the catalyst derived from alumina-supported Ru(III) acetate⁵. Kuo *et al.*⁶ and De Los Reyes *et al.*⁷ used catalysts derived from alumina-supported RuCl_3 and $\text{Ru}_3(\text{CO})_{12}$ in HDS of thiophene. With these catalysts, the HDS activity was rather low probably because sulfidation of ruthenium species was incomplete and that RuS_2 on alumina is unstable in hydrogen atmosphere. Chary *et al.*⁸ compared $\text{RuS}_2/\text{Al}_2\text{O}_3$ with $\text{MoS}_2/\text{Al}_2\text{O}_3$ in HDS of thiophene and O_2 chemisorption. These HDS reactions, however, were performed in atmospheric pressure, and so far the activities of the catalysts derived from the supported ruthenium in a pressurized flow system have not yet been clarified in comparison with those of Co-Mo/ Al_2O_3 and Ni-Mo/ Al_2O_3 . Recently, Davis *et al.*⁹ reported on HDS of coal-derived naphtha catalyzed by alumina-supported metal sulfides in a pressurized flow system.

On the other hand, it was reported that catalysts prepared from supported metal carbonyl complexes are active in many catalytic reactions¹²⁻¹⁴, such as hydrogenation of olefin¹², Fischer-Tropsch reactions¹³, metathesis of olefin¹⁴ etc. Their reactivities in the HDS of thiophenes, especially DBT, which is a key compound in desulfurization of heavier feedstock, such as light oil, have been scarcely investigated. Recently, there have been only a few examples of catalysts, derived from supported molybdenum carbonyls, being active in HDS of thiophenes^{15,16}. The authors have also reported that catalysts derived from supported anionic molybdenum carbonyls, in HDS of DBT, are more active than conventional sulfided supported catalysts¹⁷⁻¹⁹. In the course of this study, the authors became interested in the activity of supported ruthenium carbonyls in HDS of DBT. It has been reported, however, that catalyst derived from supported $\text{Ru}_3(\text{CO})_{12}$ showed activity lower than that from supported RuCl_3 ^{4,6,7}, for HDS of thiophene. The authors tried to prepare anionic metal carbonyl complexes with a metal-sulfur bond, because these complexes were effective for HDS of DBT catalyzed by supported molybdenum carbonyls. It was found that catalyst derived from the alumina-supported anionic ruthenium carbonyl was the most active for HDS of DBT, among catalysts derived from alumina-supported $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{acac})_3$ (acac=acetylacetonate) and RuCl_3 ²⁰.

In the present study, HDS of DBT, catalyzed by alkali-promoted ruthenium catalysts, has been investigated in a pressurized flow reactor. The activity of the catalyst derived from the alumina-supported $\text{Ru}_3(\text{CO})_{12}$ -alkali metal hydroxide system, where $\text{Ru}_3(\text{CO})_{12}$ reacts with alkali metal hydroxide to give an anionic ruthenium hydride complex $\text{M}[\text{HRu}_3(\text{CO})_{11}]$ (M=alkali metal), is compared with that of catalysts derived from alkali promoted alumina-supported $\text{Ru}(\text{acac})_3$ and RuCl_3 . It was found, that the addition of alkali metal remarkably increased the activities of ruthenium catalysts, and that the catalyst derived from the alumina-supported anionic ruthenium carbonyl is the most active for HDS of DBT. Characterization of ruthenium catalysts by means of NO chemisorption and XPS measurement was also performed. Preliminary results appear in the literature²¹.

2. Experimental

2.1. Materials

Commercially available $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{acac})_3$ (acac=acetylacetonate), $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ($n=2-4$) (Nippon Chemcat), alkali metal hydroxides (LiOH, NaOH, KOH, RbOH and CsOH), sodium salts (NaI, Na_2S , NaHCO_3 , $\text{NaC}_2\text{H}_3\text{O}_2$, and NaHSO_3), xylene and decalin (Kishida Chemicals) were used without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Alumina was gamma-alumina supplied from Japan Ketjen Co., Ltd. (260 m²/g) which was crushed and screened to provide 0.84- to 1.19-mm granules used in this work. Alumina was dried under vacuum at 350°C for 4 h prior to use and stored in Ar atmosphere. Commercial Co-Mo/ Al_2O_3 was supplied from Japan Ketjen Co., Ltd. (KF-124: MoO_3 , 12.3 wt%; CoO , 3.8 wt%; 274 m²/g). Hydrogen, nitrogen (99.99%) and hydrogen sulfide were obtained from Tohei Chemicals. Hydrogen sulfide in hydrogen (H_2S 3%) and nitrogen monoxide (NO) were obtained from Takachiho Chemicals. NO was washed by condensing in a trap filled with solid KOH at -196°C before use.

2.2. Catalyst Preparation

2.2.1. $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{acac})_3$ or $\text{RuCl}_3\text{-MOH}/\text{Al}_2\text{O}_3$ (M=Li, Na, K, Rb or Cs) and $\text{Ru}_3(\text{CO})_{12}\text{-NaX}$ or $\text{Na}_2\text{Y}/\text{Al}_2\text{O}_3$ (X=I, HCO_3 , $\text{C}_2\text{H}_3\text{O}_2$, HSO_3 ; Y=S)

0.13 mmol of $\text{Ru}_3(\text{CO})_{12}$ (0.39 mmol of $\text{Ru}(\text{acac})_3$ or RuCl_3) and 0-1.2 mmol of an alkali metal salt were dissolved in methanol or distilled water (5 ml) and stirred at 25°C for 30 min. After the reaction, 0.46 g of gamma- Al_2O_3 (>20 mesh) was

added into the reaction mixture and stirred for 2 h. Solvent was removed *in vacuo*.

2. 2. 2. $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$, $\text{Ru}(\text{acac})_3/\text{Al}_2\text{O}_3$, and $\text{RuCl}_3/\text{Al}_2\text{O}_3$

0.084 g of $\text{Ru}_3(\text{CO})_{12}$ was dissolved in THF. 0.46 g of Al_2O_3 was added to the solution and stirred for 2 h. The solvent was removed *in vacuo*.

In the preparation of $\text{Ru}(\text{acac})_3/\text{Al}_2\text{O}_3$, methanol was used as the solvent. In $\text{RuCl}_3/\text{Al}_2\text{O}_3$, distilled water was used as the solvent. Although ruthenium trichloride was purchased in $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ($n=2-4$), the amount of ruthenium was weighed with $n=3$. Other procedures were the same as those for $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$.

2. 2. 3. $\text{RuCl}_3/\text{Al}_2\text{O}_3 + \text{NaOH}$

$\text{RuCl}_3/\text{Al}_2\text{O}_3$ prepared above was calcined at 450°C for 24 h to prevent RuCl_3 dissolving into a solvent ($\text{RuCl}_3/\text{Al}_2\text{O}_3$ in 2. 2. 2. was not calcined). Then, the $\text{RuCl}_3/\text{Al}_2\text{O}_3$ was suspended in methanol and 0.39 mmol of NaOH was added. After the mixture was stirred for 2 h, methanol was removed *in vacuo*.

2. 2. 4. $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3 + 3\text{NaOH}$

$\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ prepared above was suspended in water and 0.39 mmol of NaOH was added. After the mixture was stirred for 2 h, water was removed *in vacuo*.

2. 2. 5. $3\text{NaOH}/\text{Al}_2\text{O}_3 + \text{Ru}_3(\text{CO})_{12}$

0.39 mmol of NaOH and 0.46 g of Al_2O_3 were stirred for 2 h in methanol. After methanol was removed *in vacuo*, 5 cc of THF was added. Into the resulted suspension was added 0.13 mmol of $\text{Ru}_3(\text{CO})_{12}$ and the mixture was stirred for 2 h. The solvent was removed *in vacuo*.

2. 3. Apparatus and Reaction Procedures

A catalyst precursor was placed in a pressurized fixed-bed flow reactor (10 mm ID×300 mm), heated at 5°C/min and activated at 300°C under a flow of H_2S in H_2 (H_2S 3%) for 3 h. For the activation of the catalyst, H_2 , N_2 , H_2S (100%), H_2S in N_2 (H_2S 50%) or H_2S in H_2 (H_2S 50%) was also used instead of H_2S in H_2 (H_2S 3%). When $\text{RuCl}_3/\text{Al}_2\text{O}_3$ 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 with hydrogen. Then, the solution containing DBT was supplied with a feed pump (Kyowa Seimitsu KHD-16). HDS of DBT was carried out under the following conditions: temperature, 300°C; 50 kg/cm²; H_2 18 l/h; WHSV, 16.5 h⁻¹; initial concentration of DBT in xylene, 1.0 wt%; catalyst, 0.5 g; Ru 8 wt%. The weight of the catalyst includes the weights of metal and support. Conversion of DBT reached a steady state within about 3 h. Then samples of products were collected from a gas-liquid separator, four

times per hour. No sign of catalyst deactivation was observed during the 10 h run.

When Co-Mo/ Al_2O_3 was used, presulfidation was performed at 400°C for 3 h. HDS of DBT was carried out under the following conditions: 200-260°C; 50 kg/cm², H_2 18 l/h; WHSV 70 h⁻¹; DBT Concentration of DBT in decalin, 1.0 wt%; Catalyst, 0.2 g. HDS of DBT catalyzed by the $\text{Ru}_3(\text{CO})_{12}$ -6CsOH/ Al_2O_3 system was also carried out under the same conditions.

2. 4. Analytical

Reaction products were analyzed by gas chromatography with a FID detector (Shimadzu GC-9A) using a G-100 column (ID 1.2 mm; film thickness 1.0 μm; length 40 m) supplied from Chemicals Inspection & Testing Institute or an OV-1 capillary column (ID 0.25 mm×50 m).

2. 5. Infrared Measurement

FTIR spectra of catalyst precursors were recorded on FT/IR-5300, Japan Spectroscopic Co., Ltd.

2. 6. NO Chemisorption and XPS Measurement

Volumetric measurements of NO chemisorption were carried out in a conventional Pyrex glass high vacuum adsorption system. A typical procedure was as follows: Each samples of 250 mg was placed in a glass reactor, heated at 5°C/min and activated at 300°C under a flow of 3% $\text{H}_2\text{S}/\text{H}_2$ (30 ml/min) for 3 h. After this treatment, the sample was evacuated at 300°C under vacuum (10^{-3} Torr) for 1 h and then cooled to 25°C. For $\text{RuCl}_3/\text{Al}_2\text{O}_3$, the sample was sulfided at 400°C for 3 h, evacuated at 400°C for 1 h and then cooled to 25°C. Adsorption of NO was always carried out at 25°C as follows: For each sample, an adsorption isotherm was determined between 30 and 200 Torr, allowing 1 h for equilibration of the gas with the sample at each measurement point. Extrapolation of each isotherm to zero pressure provided the measure of the total amount of gas adsorbed. After a first isotherm, the sample was evacuated under vacuum (10^{-3} Torr) at 25°C for 1 h. After this treatment, a second isotherm was obtained. The difference in the uptakes between the first (total adsorption) and the second (reversible adsorption) isotherm was assumed to be the amount of the irreversibly chemisorbed NO.

After NO chemisorption and HDS reaction, XPS of the sampled catalyst was measured without exposing the catalyst to air. Each sample was mounted on a sample holder with a commercially available conducting tape. The XPS was recorded on a Shimadzu ESCA-850 photoelectron spectrometer using Mg K α radiation. Before the XPS measurement, etching, *i.e.* sputtering by argon ion, was carried out by an ion gun equipped

with ESCA-850 to obtain a clean surface of ruthenium sulfide (conditions: 2 kV, 20 mA). In this procedure, it was regarded that adsorbed species on the catalysts such as carbon material, solvent, hydrogen sulfide etc. could be removed. Binding energies (BE) were referenced to the O1s band at 532.0 eV.

3. Results and Discussion

3.1. The Effects of the Addition of Alkali Metal Salts on the Hydrodesulfurization Reactivities of Alumina-supported Ruthenium Catalysts

Initially, the effects of the addition of NaOH to the alumina-supported ruthenium catalysts were investigated under the following condition: 300°C; 50 kg/cm²; H₂ 18 l/h; WHSV, 16.5 h⁻¹; initial concentration of DBT, 1.0 wt% in xylene; catalyst, 0.5 g. Alumina-supported ruthenium catalysts examined were active for HDS and products were biphenyl, cyclohexylbenzene and a trace amount of hexahydrodibenzothiophene. The results are shown in **Table 1**. In the absence of NaOH (runs 1-3), the catalytic activities of catalysts derived from alumina-supported ruthenium decreased in the order Ru₃(CO)₁₂>Ru(acac)₃>RuCl₃. When Ru₃(CO)₁₂ was reacted with NaOH and then supported on alumina (run 4), the catalytic activity remarkably increased and the conversion of DBT was 71%. At the preparation of the catalyst in this system, Ru₃(CO)₁₂ reacted with sodium hydroxide to give Na[HRu₃(CO)₁₁] quantitatively which was confirmed by FTIR (2076 (w), 2022 (vs), 1993 (s), 1964(m), 1642(w) cm⁻¹ in methanol²²). With the use of the Ru(acac)₃-NaOH/Al₂O₃ system, the activity slightly increased (run 5). When NaOH was added to the calcined RuCl₃/Al₂O₃, however, the conversion of DBT decreased (run 6). When Ru₃(CO)₁₂ and/or NaOH were supported on alumina in sequence (see experimental section), a

significant increase in the catalytic activity was not observed (runs 7, 8). This suggests that the location of sodium close to ruthenium species by the presulfidation of Na[HRu₃(CO)₁₁] supported on alumina may be intrinsic for high catalytic activity. The addition of NaOH increased the selectivity for BP in every catalyst, independent of the activity. Presence of NaOH seems to poison the active sites for hydrogenation of an aromatic ring, without affecting those for desulfurization. Further, the result indicates that the active sites for hydrogenation of an aromatic ring are different from those for hydrodesulfurization.

The effects of the addition of sodium salts other than NaOH were investigated and listed in **Table 2**. Use of sodium iodide decreased the catalytic activity and did not affect the selectivity for BP. The use of sodium hydrogen carbonate, sodium acetate and sodium hydrogen sulfite did not reveal any remarkable change in the catalytic activity, but slightly increased the selectivity for BP. While both activity and selectivity increased with use of sodium sulfide, the conversion of DBT was less than that with NaOH. It is suggested that the catalytic activity in HDS did not increase since these compounds can not react with Ru₃(CO)₁₂ to give Na[HRu₃(CO)₁₁].

When an alkali metal was changed in the alumina-supported Ru₃(CO)₁₂-alkali metal hydroxide system, as shown in **Table 3**, the conversion of DBT increased in the order Li<Na<K<Rb<Cs, which seems to be related to the ion radius of the alkali metal. When the rate of HDS of DBT was plotted against the reciprocal of the ion radius of the alkali metal shown in **Fig. 1**, it markedly increased for large ions such as Cs and Rb, indicating that ion radius would affect the catalytic activity. As shown in **Fig. 2**, the conversion of DBT and the selectivity for BP increased with an increase in a M/Ru molar ratio (M=Na or Cs). Both values for Cs were greater than those for

Table 1 Hydrodesulfurization of Dibenzothiophene Catalyzed by Alumina-supported Ruthenium Catalysts^{a)}

Run	Catalyst	Conv. of DBT [%]	Conv. of DBT to BP [%]	Conv. of DBT to CHB [%]	Selectivity for BP [%]
1	Ru ₃ (CO) ₁₂ /Al ₂ O ₃	44	38	6	86
2	Ru(acac) ₃ /Al ₂ O ₃ ^{b)}	35	30	5	87
3	RuCl ₃ /Al ₂ O ₃ ^{c)}	29	23	6	80
4	Ru ₃ (CO) ₁₂ -3NaOH/Al ₂ O ₃	71	67	4	95
5	Ru(acac) ₃ -NaOH/Al ₂ O ₃	43	40	3	93
6	RuCl ₃ /Al ₂ O ₃ +NaOH ^{d)}	15	14	1	95
7	Ru ₃ (CO) ₁₂ /Al ₂ O ₃ +3NaOH ^{e)}	43	40	3	94
8	3NaOH/Al ₂ O ₃ +Ru ₃ (CO) ₁₂ ^{f)}	32	30	2	94

a) Reaction temp. 300°C, pressure 50 kg/cm², WHSV 16.5 h⁻¹, cat. 0.5 g, H₂ 18 l/h, Amount of Ru₃(CO)₁₂ 0.13 mmol; Presulfided by H₂S in H₂ at 300°C (H₂S 3%). b) acac=acetylacetonate. c) Presulfided by H₂S in H₂ at 400°C (H₂S 3%). d) Initially RuCl₃ was supported on Al₂O₃ and then NaOH was added at Ru/Na=1. e) Initially Ru₃(CO)₁₂ was supported on Al₂O₃ and then NaOH was added at Ru/Na=1. f) Initially NaOH was supported on Al₂O₃ and then Ru₃(CO)₁₂ was added at Ru/Na=1.

Table 2 Hydrodesulfurization of Dibenzothiophene Catalyzed by Alumina Supported Ruthenium Carbonyl-Alkali Metal Compound Systems^{a)}

Run	Catalyst	Conv. of DBT [%]	Conv. of DBT to BP [%]	Conv. of DBT to CHB [%]	Selectivity for BP [%]
9	$\text{Ru}_3(\text{CO})_{12}\text{-3NaI}/\text{Al}_2\text{O}_3$	16	14	2	87
10	$\text{Ru}_3(\text{CO})_{12}\text{-3NaHCO}_3/\text{Al}_2\text{O}_3$	37	35	2	95
11	$\text{Ru}_3(\text{CO})_{12}\text{-3NaC}_2\text{H}_3\text{O}_2/\text{Al}_2\text{O}_3$	49	47	2	96
12	$\text{Ru}_3(\text{CO})_{12}\text{-3NaHSO}_3/\text{Al}_2\text{O}_3$	40	37	3	93
13	$\text{Ru}_3(\text{CO})_{12}\text{-3Na}_2\text{S}/\text{Al}_2\text{O}_3$	60	59	1	99

a) Reaction temp. 300°C, pressure 50 kg/cm², WHSV 16.5 h⁻¹, cat. 0.5 g, H₂ 18 l/h; concentration of DBT 1.0 wt%. Presulfided by H₂S in H₂ at 300°C (H₂S 3%).

Table 3 Hydrodesulfurization of Dibenzothiophene Catalyzed by Alumina-supported Ruthenium Carbonyl-Alkali Metal Hydroxide Systems^{a)}

Run	Catalyst	Conv. of DBT [%]	Conv. of DBT to BP [%]	Conv. of DBT to CHB [%]	Selectivity for BP [%]
14	$\text{Ru}_3(\text{CO})_{12}\text{-3LiOH}/\text{Al}_2\text{O}_3$	61	57	4	93
15	$\text{Ru}_3(\text{CO})_{12}\text{-3KOH}/\text{Al}_2\text{O}_3$	76	73	3	96
16	$\text{Ru}_3(\text{CO})_{12}\text{-3RbOH}/\text{Al}_2\text{O}_3$	82	79	3	96
17	$\text{Ru}_3(\text{CO})_{12}\text{-3CsOH}/\text{Al}_2\text{O}_3$	95	93	2	98

a) Reaction temp. 300°C, pressure 50 kg/cm², WHSV 16.5 h⁻¹, cat. 0.5 g, H₂ 18 l/h; concentration of DBT 1.0 wt%. Presulfided by H₂S in H₂ at 300°C (H₂S 3%) for 3 h.

$\text{Ru}_3(\text{CO})_{12}\text{-3MOH}/\text{Al}_2\text{O}_3$ (M=Li, Na, K, Rb or Cs), 300°C; 50 kg/cm²; H₂ 18 l/h; WHSV, 16.5 h⁻¹; initial concentration of DBT in xylene, 1.0 wt%; catalyst, 0.5 g; Ru 8 wt%.

Fig. 1 Rate of HDS vs. 1/(Ion radius)

Conversion of DBT: ○ Cs, △ Na.

Selectivity for BP: ● Cs, ▲ Na.

$\text{Ru}_3(\text{CO})_{12}\text{-nMOH}/\text{Al}_2\text{O}_3$ (M=Na or Cs), 300°C; 50 kg/cm²; H₂ 18 l/h; WHSV, 16.5 h⁻¹; initial concentration of DBT in xylene, 1.0 wt%; catalyst, 0.5 g; Ru 8 wt%.

Fig. 2 Effect of M/Ru Ratio on the Conversion of DBT and Selectivity for BP

Na in every M/Ru value. Further, the former showed that the maximum at M/Ru=2 which was greater than the amount of alkali metal hydroxide needed to form $\text{M}[\text{HRu}_3(\text{CO})_{11}]$ (M/Ru=1), suggesting that excess of alkali metals were consumed by alumina. Further addition of alkali metals decreased the conversion, probably because such large amount of alkali metal would shield active ruthenium species.

To compare the activities between catalysts derived from $\text{Ru}_3(\text{CO})_{12}\text{-6CsOH}/\text{Al}_2\text{O}_3$ and a commercial Co-Mo/ Al_2O_3 , HDS of DBT were performed under the following conditions: 200-260°C; 50 kg/cm²; H₂ 18 l/h; WHSV, 70 h⁻¹; initial

concentration of DBT, 1.0 wt% in decalin; catalyst, 0.2 g. The results are shown in Fig. 3. Although the conversion of DBT over the ruthenium catalyst was slightly less than that over Co-Mo/ Al_2O_3 , HDS rate of DBT per the supported amount of transition metal of the former was greater than that of the latter.

3. 2. The Effects of the Addition of Cesium Hydroxide on the Hydrodesulfurization Reactivities of Alumina-supported Ruthenium Catalysts

When $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{acac})_3$ and RuCl_3 were treated with CsOH and then supported on

Conversion of DBT: ○ Ru-Cs/Al, △ Co-Mo/Al.
Rate of DBT HDS: ● Ru-Cs/Al, ▲ Co-Mo/Al.
Ru₃(CO)₁₂-6CsOH/Al₂O₃ (Ru, 8 wt%); Co-Mo/Al₂O₃ (Mo, 8 wt%, Co/Mo=0.58); 50 kg/cm²; H₂ 18 l/h; WHSV, 70 h⁻¹; initial concentration of DBT in decalin, 1.0 wt%; catalyst, 0.2 g.

Fig. 3 Effect of Temperature on the Conversion of DBT and the Rate of DBT HDS

alumina, catalytic activity and selectivity for BP remarkably increased for all of the catalysts. This meant that to obtain the high activity and selectivity, it may be important to prepare alkali metal salts of ruthenium compounds at the initial stage. Activity for the same amount of cesium increased in the order RuCl₃-CsOH/Al₂O₃ < Ru(acac)₃-CsOH/Al₂O₃ < Ru₃(CO)₁₂-3CsOH/Al₂O₃. As shown in Fig. 2 and Table 4, the conversion of DBT reached maximum at Cs/Ru=2, that is, where the selectivity for BP was higher than 99%, in Ru₃(CO)₁₂-6CsOH/Al₂O₃.

In order to investigate why the activity and selectivity had increased with the addition of alkali metals, characterization of the catalysts was conducted by means of the measurements of FTIR spectra of catalyst precursors, the amount of NO chemisorption and XPS spectra of the catalysts,

a) Ru₃(CO)₁₂/Al₂O₃; b) Ru₃(CO)₁₂-3CsOH/Al₂O₃; c) Ru₃(CO)₁₂-6CsOH/Al₂O₃; d) Ru₃(CO)₁₂-9CsOH/Al₂O₃.

Fig. 4 FTIR Spectra of Ru₃(CO)₁₂-nCsOH/Al₂O₃

before and after use for HDS.

3. 2. 1. FTIR Spectra of the Catalyst Precursors

The results from the FTIR spectra of the catalyst precursors are shown in Fig. 4. Ru₃(CO)₁₂ supported on alumina showed three peaks at 1998 (s), 2020 (vs) and 2058 (vs) cm⁻¹. Because Ru₃(CO)₁₂ without alumina showed almost same peaks, Ru₃(CO)₁₂ was just located on alumina surface in the Ru₃(CO)₁₂/Al₂O₃ system. When Ru₃(CO)₁₂ was treated with 3 fold of CsOH in methanol, all of Ru₃(CO)₁₂ was converted to Cs[HRu₃(CO)₁₁].

Table 4 Hydrosulfurization of Dibenzothiophene Catalyzed by Ru₃(CO)₁₂-nCsOH/Al₂O₃ Systems and Characterization of the Catalysts by Means of XPS

Run	Activation condition	HDS of DBT ^{a)}		XPS Measurement ^{b)}			
		Conv. of DBT [%]	Selectivity for BP [%]	S 2p [eV]	Ru 3p _{3/2} [eV]	Ru 3p/Al ^o	S/Ru 3p ^o
18	RuCl ₃ /Al ₂ O ₃	29	80	162.8	461.8	0.041	0.52
19	RuCl ₃ -CsOH/Al ₂ O ₃	62	90	162.4	461.6	0.040	2.50
20	Ru(acac) ₃ /Al ₂ O ₃	35	87	162.8	462.2	0.026	0.97
21	Ru(acac) ₃ -CsOH/Al ₂ O ₃	74	98	161.0	462.1	0.037	2.49
22	Ru ₃ (CO) ₁₂ /Al ₂ O ₃	44	86	162.5	462.1	0.025	0.45
23	Ru ₃ (CO) ₁₂ -3CsOH/Al ₂ O ₃	95	98	161.4	461.9	0.027	2.93
24	Ru ₃ (CO) ₁₂ -6CsOH/Al ₂ O ₃	100	99	160.5	462.2	0.016	7.19
25	Ru ₃ (CO) ₁₂ -9CsOH/Al ₂ O ₃	73	100	161.3	461.3	0.027	1.18

a) Reaction temp. 300°C, pressure 50 kg/cm², WHSV 16.5 h⁻¹, cat. 0.50 g, H₂ 18 l/h; concentration of DBT 1.0 wt%. Presulfided by H₂S in H₂ (H₂S 3%). b) XPS spectra were measured for samples used in HDS of DBT. Before the measurement, the samples were sputtered by Ar⁺ ion for 10 min. Every binding energy was referenced to Oxygen O 1s 532.0 eV. c) Ratio of peak areas between Al 2p, S 2p, and Ru 3p_{3/2}.

Table 5 Characterization of Alumina-supported Ruthenium Catalysts by Means of NO Chemisorption and XPS

Run	Catalyst	NO Chemisorption ^{a)}		Before HDS ^{c)}			
		Irreversible [$\times 10^2 \mu\text{mol/g-cat}$]	Dispersion ^{b)} [%]	S 2p [eV]	Ru 3p _{3/2} [eV]	Ru 3p/Al ^{d)}	S/Ru 3p ^{d)}
26	RuCl ₃ /Al ₂ O ₃	1.4	18	162.8	462.1	0.027	2.31
27	RuCl ₃ -CsOH/Al ₂ O ₃	0.2	3	162.0	462.0	0.070	1.57
28	Ru(acac) ₃ /Al ₂ O ₃	1.3	16	162.5	461.9	0.035	1.51
29	Ru(acac) ₃ -CsOH/Al ₂ O ₃	1.0	13	162.0	462.2	0.041	2.68
30	Ru ₃ (CO) ₁₂ /Al ₂ O ₃	1.3	16	162.8	462.0	0.026	0.83
31	Ru ₃ (CO) ₁₂ -3CsOH/Al ₂ O ₃	1.8	23	162.0	462.0	0.027	3.30
32	Ru ₃ (CO) ₁₂ -6CsOH/Al ₂ O ₃	9.1	115	162.1	462.3	0.015	7.33
33	Ru ₃ (CO) ₁₂ -9CsOH/Al ₂ O ₃	8.8	111	162.0	462.0	0.025	3.04

a) Amounts of NO chemisorption was measured at 25°C. b) Calculated as 100% at NO/Ru=1 mol/mol. In this calculation, the amount of ruthenium is $7.9 \times 10^2 \mu\text{mol/g-cat}$. c) XPS spectra were measured for samples used in NO adsorption. Before the measurement, the samples were sputtered by Ar⁺ ion for 10 min. Every binding energy was referenced to Oxygen O 1s 532.0 eV. d) Ratio of peak areas between Al 2p, S 2p, and Ru 3p_{3/2}.

After Cs[HRu₃(CO)₁₁] was supported on alumina, however, three peaks at 2000 (s), 2030 (vs) and 2062 (s) cm⁻¹ were observed, indicating that Cs[HRu₃(CO)₁₁] had reacted with acid sites on alumina to reproduce Ru₃(CO)₁₂ on alumina. The result shows that the location of cesium close to ruthenium species is intrinsic to increase the activity, even when Ru₃(CO)₁₂ is reproduced. When Ru₃(CO)₁₂ was treated with 6 fold of CsOH in methanol and was supported on alumina, Ru₃(CO)₁₂ was not reproduced and anionic species were maintained on alumina, since peaks with wavenumbers lower than those of Ru₃(CO)₁₂ were observed. The result shows that the maintenance of the anionic species on alumina as well as the location of cesium close to ruthenium species is also essential to increase the activity. When Ru₃(CO)₁₂ was treated with 9 fold of CsOH in methanol and was supported on alumina, anionic species were also maintained as shown in Fig. 4d. It seems, however, that the trinuclear anionic [HRu₃(CO)₁₁]⁻ can not be maintained on alumina, probably because the amount of CsOH added was too much to maintain the structure. Although it is not clear whether or not the trinuclear structure is needed to obtain the high catalytic activity, the addition of excess amount of cesium would shield the active ruthenium species and decrease the activity.

3. 2. 2. NO Chemisorption of the Catalysts

It can be considered that the amount of NO chemisorption is proportional to that of coordinatively unsaturated sites on a catalyst. The amount of NO chemisorption was measured because the amount of coordinatively unsaturated sites on a catalyst often relates to the catalytic activity. No irreversible chemisorption of NO was observed on CsOH/Al₂O₃. As shown in Table 5, the addition of CsOH to RuCl₃/Al₂O₃ and Ru(acac)₃/Al₂O₃ did not increase the amount of NO chemisorption. Especially, in the former

catalyst, CsOH seems to obstruct the coordinatively unsaturated sites on the catalyst, at least at the presulfidation step. On the contrary, the use of CsOH for the alumina-supported ruthenium carbonyl increased the amount of NO chemisorption. It is assumed that the dispersion of ruthenium species may increase with an increase in Cs/Ru ratio, because the anionic ruthenium complex may have interaction with acid sites to be anchored to alumina at the presulfidation step. As shown in FTIR measurement, the anionic ruthenium carbonyls were maintained on alumina only in Ru₃(CO)₁₂-6CsOH/Al₂O₃ and Ru₃(CO)₁₂-9CsOH/Al₂O₃ systems. In these systems, the dispersion exceeded 100%, indicating that there may be dinitrosyl species where two molecules of NO are adsorbed on one ruthenium atom. Further, it is also suggested that there may be stable ruthenium sulfide because dinitrosyl species were often observed for metal sulfide^{20b), 23), 24)}. In order to confirm the presence of ruthenium sulfide, XP spectra of the catalysts were measured before and after HDS.

3. 2. 3. XPS Measurement of the Catalysts before and after HDS Reaction

XP spectra were measured for the catalysts before and after HDS reaction and the results are shown in Tables 4 and 5, respectively. The catalysts before HDS were the samples used for NO chemisorption. The S 2p and Ru 3p_{3/2} XP spectra from the alumina-supported ruthenium used for HDS showed peaks in the ranges 160.5-162.8 eV and 461.3-462.2 eV, respectively. These results suggest that ruthenium species for every catalyst are between ruthenium metal (461.0 eV) and RuS₂ (462.7 eV). The binding energies of Ru 3p_{3/2} for the Ru₃(CO)₁₂-6CsOH/Al₂O₃ system before and after HDS were highest among examined catalysts, while those for some catalysts were not affected by the addition of alkali metal. This shows that ruthenium species for the Ru₃(CO)₁₂-6CsOH/

Al_2O_3 system may be close to RuS_2 , rather than ruthenium metal. Further, the binding energies of S 2p decreased with alkali metal for both catalysts before and after HDS, indicating that the sulfur atom in the catalysts with alkali metal would have higher electron density than that without alkali metal. The values of Ru 3p/Al and S/Ru 3p were obtained from the peak areas of XP spectra. Although the values of Ru 3p/Al for alumina-supported RuCl_3 and $\text{Ru}(\text{acac})_3$ catalysts were higher than those for alumina-supported $\text{Ru}_3(\text{CO})_{12}$, the catalytic activities for the former catalysts were lower than those for the latter, indicating that the dispersion of the former ruthenium species were not as high as that of the latter while the bulk of the ruthenium species for the former catalysts existed with higher concentration. Most important phenomenon was observed with the S/Ru 3p ratio values. When cesium existed in the catalysts, the values of S/Ru 3p remarkably increased, as shown in Table 4, for the catalysts after HDS, indicating that the presence of cesium could stabilize ruthenium sulfide to accommodate sulfur on the catalyst surface. These values of S/Ru 3p were plotted against the conversions of DBT shown in Fig. 5. Figure 5 shows the tendency of the conversion of DBT increasing with increase in the S/Ru 3p ratio. The result suggests that the catalytic activity increases when ruthenium sulfide is stabilized in the presence of cesium. Further, it seems that the presence of alkali metal strengthen the bond of ruthenium and sulfur to stabilize ruthenium sulfide, where the carbon-sulfur bond scission may proceed more easily than ruthenium species sulfided less and close to low valent ruthenium metal.

It has been reported that when alumina-supported ruthenium chloride was presulfided by $\text{H}_2\text{S}/\text{H}_2$, H_2S and $\text{H}_2\text{S}/\text{N}_2$, the treated catalysts revealed 1.8, 3.6 and 4.2 of S/Ru in XPS measurement, respectively⁷⁾. The latter two catalysts were sulfurized completely and showed catalytic activity in HDS of thiophene higher than the former one, which was not sulfurized completely. In this case, the value of S/Ru in XPS was also much greater than the stoichiometric value of ruthenium disulfide, 2. In the present study, when alumina-supported ruthenium chloride was presulfided by $\text{H}_2\text{S}/\text{H}_2$, the treated catalyst revealed 2.31 of S/Ru in XPS measurement, as shown in Table 5. Further, in cesium promoted $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ systems, both catalysts, before and after HDS, showed the maximum value of S/Ru 3p at Cs/Ru=2, which was also much larger than the stoichiometric value of ruthenium disulfide, 2. It

Fig. 5 Plots of S/Ru Ratio in XPS vs. Conversion of DBT

can be suggested that in this catalyst system, not only ruthenium species are sulfurized completely, but also a significant amount of sulfur formed by the HDS reaction may be accommodated on the catalyst and coat ruthenium atoms, because HDS of DBT is much more rapid than the formation of hydrogen sulfide by the reaction of surface sulfur with hydrogen. The coating of the ruthenium atoms by large amounts of sulfur may result in higher value of S/Ru 3p and lower value of Ru 3p/Al. The further addition of cesium decreased S/Ru 3p ratio, however, indicating that excess of CsOH would prevent the formation of ruthenium sulfide by shielding the coordinatively unsaturated sites on ruthenium species. Although the formation of cesium sulfide can be also considered, the amount of sulfur accommodated on a catalyst as cesium sulfide may not be significant, since the value of S/Ru 3p at Cs/Ru=3 was lower than that at Cs/Ru=2.

3. 3. Effects of the Conditions of Activation on Hydrodesulfurization Using Catalyst Derived from $\text{Ru}_3(\text{CO})_{12}$ -6CsOH/ Al_2O_3

It has been reported that method to activate the catalyst precursor largely affects HDS activity⁷⁾. The authors investigated the effects of the conditions of activation on the activity by using $\text{Ru}_3(\text{CO})_{12}$ -6CsOH/ Al_2O_3 and measured XPS spectra of the catalysts used for HDS. The results are shown in Table 6. When the $\text{Ru}_3(\text{CO})_{12}$ -6CsOH/ Al_2O_3 system was activated with H_2S in H_2 (H_2S 50%), the conversion of DBT was 98%, similar to that in Run 24, where H_2S in H_2 (H_2S 3%) was used. It seems that the concentration of H_2S does not affect the activity. When H_2S in N_2 (H_2S 50%) and H_2S 100% were used instead of H_2S in H_2 , the conversions of DBT slightly decreased to 89 and 82%, respectively, compared with that in Run 24. When N_2 and H_2 were used, the conversions de-

Table 6 Hydrodesulfurization of Dibenzothiophene Catalyzed by $\text{Ru}_3(\text{CO})_{12}$ -6CsOH/ Al_2O_3 Systems and Characterization of the Catalysts by Means of XPS

Run	Activation condition	HDS of DBT ^{a)}		XPS Measurement ^{g)}			
		Conv. of DBT [%]	Selectivity for BP [%]	S 2p [eV]	Ru 3p _{3/2} [eV]	Ru 3p/ $\text{Al}^{\text{h)}$	S: Ru 3p ^{h)}
34	H_2S in H_2 (H_2S 50%) ^{b)}	98	100	—	—	—	—
35	H_2S in N_2 (H_2S 50%) ^{c)}	89	100	160.7	462.3	0.014	6.11
36	H_2S (100%) ^{d)}	82	100	161.1	462.3	0.015	4.87
37	H_2 ^{e)}	51	99	160.0	462.0	0.023	1.98
38	N_2 ^{f)}	47	100	159.8	461.8	0.026	3.18

a) Reaction temp. 300°C, pressure 50 kg/cm², WHSV 16.5 h⁻¹, cat. 0.50 g, H_2 18 l/h; concentration of DBT 1.0 wt%.
b) Presulfided by H_2S in H_2 (H_2S 50%). c) Presulfided by H_2S in N_2 (H_2S 50%). d) Treated with H_2S (100%) stream.
e) Treated with H_2 stream. f) Treated with N_2 stream. g) XPS spectra were measured for samples used in HDS of DBT. Before the measurement, the samples were sputtered by Ar^+ ion for 10 min. Every binding energy was referenced to Oxygen O 1s 532.0 eV. h) Ratio of peak areas between Al 2p, S 2p, and Ru 3p_{3/2}.

creased remarkably. In XPS measurement of these catalysts, S/Ru3p ratios also decreased in comparison with that in Run 24. It is likely that the catalyst precursor can not be sulfurized in the absence of H_2S to release carbon monoxide ligands. In contrast, in the presence of H_2S , it is suggested that anionic ruthenium carbonyls such as $[\text{HRu}_3(\text{CO})_{11}]^-$ etc. in $\text{Ru}_3(\text{CO})_{12}$ -6CsOH/ Al_2O_3 would react with H_2S to release carbon monoxide ligands easily and form the ruthenium-sulfur bonds at the preparation of the catalyst. In this process, H_2S adsorbed on ruthenium would oxidize Ru(0) species to the oxidation state close to Ru(IV) for RuS_2 with the release of hydrogen molecule. In the presence of alkali metals, the ruthenium-sulfur bonds formed may become stable to keep active ruthenium sulfide even under hydrogen pressure.

4. Concluding Remarks

Although HDS of thiophenes using ruthenium sulfide catalysts were reported, the effects of addition of alkali metals in those catalysts on the HDS reactions were not well-known. Göbölös *et al.* compared the activities in HDS of thiophene catalyzed by ruthenium catalysts supported on NaY, KY, HY and Na_2S -doped KY zeolites¹⁰⁾. The activity decreased in the order Na_2S -doped $\text{KY} > \text{KY} > \text{NaY} > \text{HY}$ and the Na_2S -doped KY showed activity three times higher than that of KY. The order of the activity was explained by the strength of Brønsted acids. They concluded that the addition of Na_2S neutralized the Brønsted acidity of zeolite to increase the activity, as a result. The effects of kind and amount of alkali metal, however, were not examined, and the activity was rather low in comparison with a commercial one⁷⁾ because the amount of ruthenium loaded on a support was too low, 2 wt%. Further, there was no reference to the effect of alkali metal on the

Scheme 1 Mechanism of Hydrodesulfurization Catalyzed by Alumina-supported Ruthenium-Alkali Metal Systems

stabilization of ruthenium sulfide.

In alumina-supported ruthenium catalysts, the HDS activity was often rather low^{4)~7)}, in comparison with that of commercial catalysts, probably because sulfidation of ruthenium species is incomplete and RuS_2 on alumina is unstable in hydrogen atmosphere. It has also been reported that the catalyst derived from supported $\text{Ru}_3(\text{CO})_{12}$ showed the lower activity for HDS of thiophene in atmospheric pressure of hydrogen than that derived from supported RuCl_3 ^{4), 6), 7)}. In contrast, the authors reported that in pressurized flow system, the catalysts derived from alumina-supported ruthenium carbonyls showed activity in HDS of DBT higher than those from alumina-supported RuCl_3 and $\text{Ru}(\text{acac})_3$ ²⁰⁾. Alumina-supported ruthenium carbonyls gave the active species, which shows the high activity for HDS under high pressure, more easily, at the presulfidation step, than alumina-supported RuCl_3 ²⁰⁾. In the present paper, however, it has been clarified that the modification of $\text{Ru}_3(\text{CO})_{12}$ with alkali

metal hydroxides improved the activity and selectivity of the catalyst obtained. Ruthenium species on the catalyst, in the presence of alkali metal, existed in the oxidation state close to RuS_2 rather than ruthenium metal. The mechanism of reaction is illustrated in Scheme I. It is suggested that RuS_2 which could be stabilized on alumina with alkali metal, even in pressurized hydrogen, would reveal activity comparable to that of $\text{Co-Mo/Al}_2\text{O}_3$.

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要 旨

担持金属カルボニル錯体を用いたジベンゾチオフェンの水素化脱硫反応（第 5 報）アルミナ担持
ルテニウムカルボニル-アルカリ金属水酸化物系より調製した水素化脱硫触媒

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硫化したアルミナ担持ルテニウム触媒を用いたジベンゾチオフェン (DBT) の水素化脱硫反応において, アルカリ金属水酸化物の触媒活性および生成物選択性に及ぼす影響を検討した。アルミナ担持ルテニウムカルボニルから得られる触媒へ水酸化ナトリウムを加えると, DBT の転化率は 41% から 71% に著しく向上した。この触媒系では, ルテニウムカルボニルが予め水酸化ナトリウムと反応し, ルテニウムのヒドリド錯体 $\text{Na}[\text{HRu}_3(\text{CO})_{11}]$ が生成した後, アルミナ上に担持することが高活性を得るために重要であることが分かった。 RuCl_3 , $\text{Ru}(\text{acac})_3$ (acac=アセチルアセトナート) および $\text{Ru}_3(\text{CO})_{12}$ を水酸化セシウムと反応させアルミナに担持させた時, 活性は $\text{RuCl}_3\text{-CsOH}/\text{Al}_2\text{O}_3 < \text{Ru}(\text{acac})_3\text{-CsOH}/\text{Al}_2\text{O}_3 < \text{Ru}_3(\text{CO})_{12}\text{-3CsOH}/\text{Al}_2\text{O}_3$ の順に増加した。アルミナ担持ルテニウムカル

ボニル系触媒において, アルカリ金属水酸化物の添加量を増加させた時, DBT の転化率は向上し, $\text{M}/\text{Ru}=2$ ($\text{M}=\text{Na}$ あるいは Cs) の時最大値を示した。さらに, アルカリ金属を添加すると活性は低下した。 $\text{Ru}_3(\text{CO})_{12}\text{-}n\text{CsOH}/\text{Al}_2\text{O}_3$ 系触媒において, ビフェニルが選択的に生成した。これらの現象を説明するために, NO の化学吸着および X 線光電子 (XP) スペクトルを脱硫反応前と後の触媒について測定した。 $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ へのセシウムの添加は NO の化学吸着量を増加させた。このことは, 触媒には硫化後もまだ多くの配位不飽和サイトがあることを示した。XP スペクトルより, 適当量のセシウムを加えると水素加圧下でさえアルミナ上に硫化ルテニウムが安定に存在することが分かった。 $\text{Ru}_3(\text{CO})_{12}\text{-6CsOH}/\text{Al}_2\text{O}_3$ より得られる触媒は, $\text{Co-Mo}/\text{Al}_2\text{O}_3$ に匹敵する触媒活性を示した。

Keywords

Hydrodesulfurization, Dibenzothiophene, Ruthenium carbonyl, Alkali metal hydroxide, Catalyst preparation, Pressurized flow system