Novel hydrodesulfurization catalysts derived from a rhodium carbonyl complex

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Abstract

The first part of this work aimed at optimizing Rh based HDS catalysts by modification of the precursor nature as well as the selection of an adequate pre-activation method. Further, the combination of the Rh catalysts with Ru catalysts was also investigated. Although no obvious synergetic effect was observed, the combined Rh-Ru catalysts exhibited higher activities than the single metal-based ones. Among all the prepared catalysts, the RhCs/Al$_2$O$_3$ catalysts prepared from the rhodium carbonyl precursor with a ratio Rh/Cs $= 1$–2 exhibited the most interesting catalytic performance. The effect of the Rh loading on the activity of these catalysts was studied. An increase in activity was observed when the Rh loading increased up to 0.5 wt.% but further Rh addition did not lead to any noticeable effect on the catalytic performance. Whilst the prepared catalysts exhibited a gross activity inferior to that of a classical CoMo system, their specific activity calculated per mole of metal was considerably higher than the one obtained for the latter conventional system. Furthermore, the conversion of the 4 wt.% Rh catalyst was about twice as high as the one of a 4 wt.% Ru catalyst. Therefore, in order to elucidate the interesting catalytic properties of such Rh based catalysts, ^{35}S radioactive tracer DBT HDS experiments were performed. We found that for 4 wt.% Rh, k_{RE}, the H$_2$S release rate constant, was almost the same as the one obtained for the 4 wt.% Ru catalyst. However, S_0 was significantly higher on the Rh catalyst than on the Ru catalyst ($+70\%$). This indicated that the high activity was due to the formation of a great quantity of active sites (labile sulfur atoms).

1. Introduction

In big city areas the problem of the air pollution due to the diesel engine fumes has become more and more serious. Especially, the quantity of sulfur released in the atmosphere is pointed out as being an important cause of pollution. Therefore, a number of approaches aiming at improving the deep hydrodesulfurization (HDS) of light gas oils have been investigated through the development of new HDS catalysts together with thorough studies of the relevant reaction mechanism [1]. Among all the possible candidates for new efficient catalysts, solids consisting on ruthenium species deposited on high surface area supports exhibited several promising properties. Such catalysts were devel-oped by some research teams, which performed various attempts in order to obtain ruthenium catalysts competitive for the HDS reaction [2–5], hydrogenation (HYD) [6] and hydrodenitrogenation (HDN). On the other hand, whilst supported metal carbonyl complexes were found to be active for several catalytic reactions [7], e.g. hydrogenation of carbon monoxide [8], metathesis of olefin [9], etc. their HDS reactivities toward thiophenic molecules have been only scarcely investigated [10,11]. Indeed, we can find only a few examples of HDS of thiophenic molecules over catalysts derived from supported-Mo(CO)$_6$ and Ru$_3$(CO)$_{12}$ precursors. Maezawa et al. [12] reported that a Mo(CO)$_6$/Al$_2$O$_3$ catalyst with a low Mo loading was more active than a conventional MoO$_3$/Al$_2$O$_3$ catalyst for the thiophene HDS. However, the catalytic activity of the catalyst derived from supported Ru$_3$(CO)$_{12}$ was sometimes lower than that of the one derived from the supported RuCl$_3$ [13]. The effect of the support was investigated by Harvey and Matheson [14].

They studied the benzothiophene (BT) HDS reaction catalyzed by supported ruthenium sulfide species derived from $Ru_3(CO)_{12}$ and $RuCl_3$. The reactions were performed in a batch autoclave, and the relative efficiency of both catalysts was dependant on the reaction temperature and the nature of the support (alumina, zeolite). Our group have not only studied HDS of DBT over conventional molybdenum–alumina systems [15–17] but also over alumina-supported metal carbonyl complexes ($Mo(CO)_6$, $Cr(CO)_6$, $W(CO)_6$) [18], alumina-supported anionic ruthenium carbonyls [19,20], alumina and silica-alumina supported molybdenum and cobalt carbonyls [21], and alumina-supported ruthenium carbonyl-alkali metal hydroxides [22]. We have also studied the effect of the support on HDS activities of catalysts prepared from supported anionic molybdenum carbonyls [23] and of catalysts prepared from supported ruthenium carbonyl–cesium hydroxide systems [24]. The main results of these studies can be summarized as follows:

(1) The catalysts prepared by activation of metal carbonyls complexed with triethylamine (NEt_3) and ethanethiol (EtSH) (formation of anionic complexes containing metal-sulfur bonds) were active in HDS of DBT. Especially, a $Mo(CO)_6$–Net_3–EtSH/Al_2O_3 system activated by H_2 or H_2S exhibited a higher catalytic activity than a conventional molybdenum–alumina system.
(2) The HDS rate calculated per gram of molybdenum decreased in the following order: SiO_2–Al_2O_3 > TiO_2 > NaY zeolite > Al_2O_3 > SiO_2.
(3) When the amount of alkali metal hydroxides added to an alumina-supported ruthenium carbonyl system increased, the DBT conversion increased concomitantly before reaching a maximum value at M/Ru = 2 (M = Na or Cs). Such catalysts exhibited activities comparable to the one of a conventional Co-Mo/Al_2O_3 HDS catalyst.

In addition, our group has developed an in situ method, which permits to investigate the behavior of the sulfur on working catalysts. As dibenzothiophene (DBT) is a key compound in the desulfurization of heavy feedstocks such as light oils, ^{35}S-labeled DBT ([^{35}S]DBT) HDS model reactions were performed under practical HDS conditions [25–28]. By recording the change in the unreacted [^{35}S]DBT and the formed [^{35}S]H_2S quantities, the behavior of the sulfur on the working catalyst could be monitored in situ.

In the present work, we studied Rh based catalysts because rather good activity results were previously obtained on Ru based catalysts [20]. It would be interesting to extend the study to other elements close to Ru in the periodic classification of the elements. The effects of the rhodium precursor, the catalyst activation method, the Cs and/or Ru addition on the DBT HDS catalytic activity were investigated. In the second part, the high intrinsic activity observed for low Rh loading was explained by using the above-described [^{35}S]DBT radioisotope tracer method.

2. Experimental

2.1. Materials

Commercially available $Ru_3(CO)_{12}$, ethanethiol (EtSH), triethyl amine (NEt_3), cesium hydroxide ($CsOH \cdot EH_2O$), tetrahydrofuran (THF), decalin and methanol (purity: 98%) (Kishida Chemicals) were used without further purification. Hexarhodium hexadecacarbonyl ($Rh_6(CO)_{16}$) was supplied from Aldrich Chem. Co. The gamma-alumina was supplied from Nippon Ketjen, and was crushed and screened to obtain 0.84–1.19 mm grains of catalyst carrier. Alumina was dried under vacuum at 350 °C for 4 h and stored under Ar atmosphere prior to use. Hydrogen, nitrogen (99.99%) and hydrogen sulfide in hydrogen mixed gas (H_2S 5.0%) were obtained from Tohei Chemicals. All scintillation solvents used for radioactivity measurements were supplied by Packard Japan.

2.2. Preparation of the catalysts

2.2.1. Rh/Al_2O_3 catalysts
A first series of alumina-supported rhodium catalysts was prepared with two different rhodium precursors with a rhodium loading fixed at 2 wt.%. The first precursor was prepared by complexation of $Rh_6(CO)_{16}$. 0.0176 g of $Rh_6(CO)_{16}$ was mixed with EtSH and NEt_3 (Rh:N:S = 2:1:1) into a 50 ml reactor before introduction of the solvent (10 ml of THF). After stirring the mixture at 70 °C for 1 h, the reactor was cooled down to room temperature. Then, 0.4900 g of Al_2O_3 was added into the obtained solution, which was stirred again during 2 h. The solvent was removed under vacuum. The second precursor was commercially available $RhCl_3$. The catalyst was prepared under argon atmosphere by the conventional impregnation method using water as the solvent.

2.2.2. RhCs/Al_2O_3 catalysts
An anionic rhodium carbonyl complex was prepared by reaction of $Rh_6(CO)_{16}$ with CsOH in methanol. Then, alumina was added into the prepared solution. After the mixture was stirred for 2 h, the solvent was removed under vacuum. The first series of catalysts was prepared with 2 wt.% Rh by varying the Cs/Rh molar ratio (Cs/Rh = 0, 1, 2 and 4). A second series was prepared with Cs/Rh = 1 by varying the Rh loading (0.0125, 0.25, 0.5, 1, 2, 4 and 8 wt.%). Due to their instability under the atmospheric conditions the catalysts were prepared and stored under an argon atmosphere.

2.2.3. RuCs(1)-Rh/Al_2O_3 and RhCs(1)-Ru/Al_2O_3 catalysts preparation (catalysts designation explained in the next paragraph)
These catalysts were prepared by successive impregnation with first a Me_1Cs solution and then a Me_2 solution. The (Ru + Rh)/Cs ratio was fixed at 1. In the first series Rh was chosen as Me_1, which loading was fixed at 0.25 wt.%, and

Ru (6, 12 and 16 wt.%) was chosen as Me_2. In the second series, Ru was chosen as Me_1, which loading was fixed at 16 wt.%, and Rh with a loading of 0.125, 0.25, 0.5 or 1 wt.% was chosen as Me_2. The MeCs solutions were prepared in the same way as the one described in Section 2.2.2. When Me_1 was Rh and Me_2 was Ru, the Rh catalyst was calcined at 400 °C during one night before subsequent Ru impregnation. No intermediate calcination was performed for the reverse case.

2.2.4. Catalysts denomination

The catalysts were named as follows: the chemical symbols of the impregnated metals were written in the same order as the impregnation order, separated by a '-'. When the impregnation of two metals was simultaneous, their symbols were directly linked (without intercalation of a '-'). When the catalyst contained Cs, the ratio of the *total amount of metal* divided by the amount of Cs was indicated in parentheses after 'Cs'. The Ru and the Rh loadings (wt.%) were indicated before the symbol of the respective metal. For example, $0.25RhCs(1)-8Ru/Al_2O_3$ means a catalyst prepared by successive impregnation of the active metals. Rh and Cs are impregnated before the Ru impregnation. This catalyst contains 0.25 wt.% of Rh and 8 wt.% of Ru with a (Rh + Ru)/Cs molar ratio equal to 1. A catalyst named $8RuCs(1)-0.25Rh/Al_2O_3$ would be the same catalyst except that the impregnation order of the active metals is reversed. Indeed, in this case Ru impregnation is performed before the simultaneous Rh and Cs impregnation.

2.3. Apparatus and procedures

2.3.1. Characterization of the catalysts

The amount of Rh loaded was measured by X-ray fluorescence (Shimadzu Co. Ltd., Rayny EDX-800). The surface area, pore volume and pore distribution were measured by a BET apparatus (Coulter Co., SA3100). After outgassing the sample at 300 °C for 30 min, the measurement was performed using a 10-point pre-programmed BET method. The pore distribution was obtained using the BJH method [30]. The results are shown in Table 1. The specific surface area of the RhCs catalysts was $255 \pm 6 \, m^2 \, g^{-1}$ and their pore volume was $0.72 \pm 0.02 \, cc \, g^{-1}$. In addition, the mean pore

diameter of all the catalysts was $8.3 \pm 0.2 \, nm$. If we take into account the 2% measurement error induced by the device, the observed differences can be considered negligible. Therefore, the textural parameters were not parameters that can explain the variations of DBT HDS activity among the different catalysts.

Powder X-ray diffraction (XRD) spectra were recorded on a Rigaku RINT 2000 apparatus using a Cu Kα radiation ($\lambda = 0.15405 \, nm$). The Debye–Scherrer equation was used to estimate the mean size of the Rh particles deposited on Al_2O_3.

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 set in the microscope. The pictures were recorded with a magnification of 175,000–255,000.

2.3.2. HDS activity measurement

The HDS experiments were carried out in a fixed-bed flow reactor (8 mm i.d. × 300 mm). The catalysts were presulfided with a mixture of 5 vol.% H_2S/H_2 or prereduced in a 99.9% H_2 flow. After the pretreatment, the reactor was cooled down to room temperature and then pressurized with hydrogen. Then, a decalin solution of DBT was fed into the reactor by a high-pressure liquid pump (Kyowa Seimitsu KHD-16). The DBT HDS reactions were carried out under the following conditions: H_2 flow rate $= 12.5 \, l \, h^{-1}$; WHSV $= 28 \, h^{-1}$; 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 a FID detector (Shimadzu-17A, Shimadzu Co. Ltd.) and a commercial capillary column (DB-1).

2.3.3. [^{35}S]DBT radioisotope tracer method

The [^{35}S]DBT HDS reactions were carried out under the following conditions: 1 g of catalyst, H_2 flow $= 25 \, l \, h^{-1}$, 300 °C. A typical operation procedure can be described as follows:

1. A decalin solution of 1 wt.% [^{32}S]DBT was pumped into the reactor until the conversion became constant (after about 2 h).
2. Then, the [^{32}S]DBT decalin solution was replaced by that of 1 wt.% [^{35}S]DBT (7000 dpm g^{-1}). The reaction with [^{35}S]DBT was performed until the amount of [^{35}S]H_2S released from the reactor became constant (after about 4 h).
3. The reactant solution was then replaced again by a 1 wt.% [^{32}S]DBT solution and the reaction was pursued until the radioactivity of released [^{35}S]H_2S could be no more detected (after about 4 h).

The radioactivities of the unreacted [^{35}S]DBT in the liquid product and the quantity of [^{35}S]H_2S released in the gas phase were measured by a liquid scintillation counter

Table 1
BET surface area and pore volume of the RhCs catalysts

Sample	Rh loading[a] (wt.%)	Surface area ($m^2 \, g^{-1}$)	Pore volume ($cc \, g^{-1}$)
0 (Alumina)	–	256	0.738
0.5Rh(BPS)[b]	0.56	253	0.723
1.0Rh(BPS)	1.20	259	0.735
2.0Rh(BPS)	2.08	254	0.722
2.0Rh(APS)[c]	2.08	249	0.702

Mean pore diameter was $8.3 \pm 0.2 \, nm$ for all the catalysts.
[a] The amount of loaded Rh was measured by XRF.
[b] BPS means "before presulfidation".
[c] APS means "after presulfidation".

(Beckman, LS-6500) after addition of an appropriate scintillator solution.

3. Results and discussion

3.1. Optimization of the DBT HDS activity of the Rh based catalysts

The selected strategy was to optimize first the DBT HDS catalytic performance of the Rh based catalysts. The formulation of the catalysts was modified (addition of a cocatalyst, etc.) and optimal experimental conditions (pretreatment, etc.) were determined. Then, radioactive tracer experiments were performed on a series of catalysts that exhibited interesting catalytic properties.

3.1.1. Selection of the rhodium precursor

In the case of Ru/Al$_2$O$_3$ catalysts, we have reported [20] that the effect of the precursor on the activity of the final catalyst is important. Indeed, we have found that the ruthenium carbonyl gives better catalytic results than the ruthenium chloride. Fig. 1 shows the effect of the rhodium precursor on the DBT conversion and the BP selectivity of Rh catalysts presulfided with a mixture of 5 vol.% H$_2$S in H$_2$ at 300 °C during 3 h. The DBT conversion of the 2Rh/Al$_2$O$_3$ catalyst derived from either rhodium carbonyl or rhodium chloride was quite high and increased with the temperature. The 2Rh/Al$_2$O$_3$ catalyst derived from the rhodium carbonyl precursor exhibited a higher activity than that derived from the rhodium chloride precursor. It is likely that some chloride residues remaining on the latter catalyst surface were responsible for a negative effect on the HDS activity. The BP selectivity of both catalysts was similar, with values above 90% irrespective of the temperature.

In brief, the rhodium carbonyl based precursor gave better results than the rhodium chloride one, and the former was therefore selected as the precursor for further catalysts synthesis.
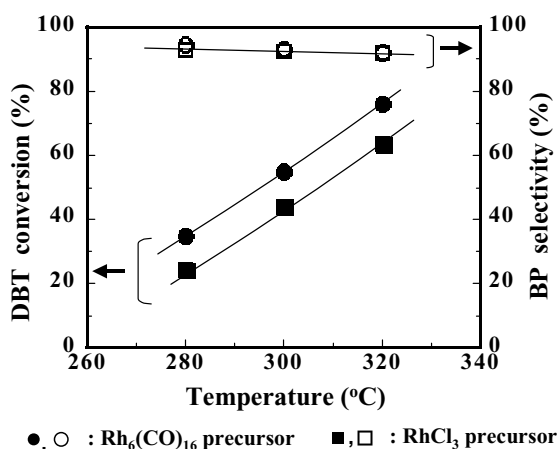

Fig. 1. Effect of the temperature on DBT conversion and BP selectivity (Rh 2 wt.%).
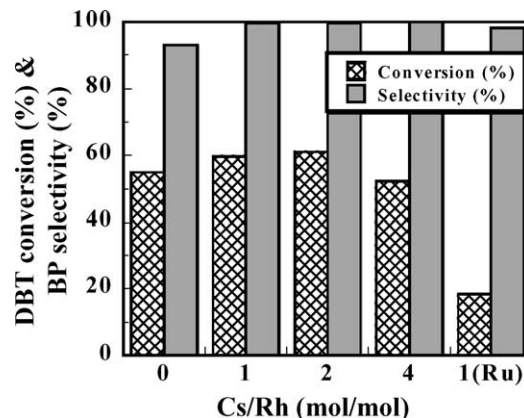

Fig. 2. Effect of Cs addition on BP selectivity and DBT conversion (metal 2 wt.%; 300 °C).

3.1.2. Effect of cesium addition on the Rh/Al$_2$O$_3$ catalysts

We found in a previous study that the Cs addition on Ru/Al$_2$O$_3$ catalysts leads to a drastic increase in activity [20]. Therefore, we investigated the effect of Cs addition on Rh catalysts derived from the rhodium carbonyl precursor.

Fig. 2 shows the effect of the Cs addition on the HDS activity and the BP selectivity of the 2Rh/Al$_2$O$_3$ catalyst derived from the rhodium carbonyl complex. In comparison with the result obtained previously for a 2RuCs(1)/Al$_2$O$_3$ catalyst [20], surprisingly the RhCs(1)/Al$_2$O$_3$ catalyst HDS activity was about three times as high as the RuCs(1)/Al$_2$O$_3$ catalyst. This means that the intrinsic activity of rhodium was significantly higher than that of ruthenium. In the case of a RuCs/Al$_2$O$_3$ series, it was found that the synthesized RuCs complex was destroyed during the impregnation through the reaction of the cesium species with the alumina surface hydroxyl groups [20]. Therefore, the quite bad performance observed for Ru/Cs = 1 was attributed to the fact that the RuCs direct interaction was not preserved after impregnation. Nevertheless, when the Ru/Cs ratio was increased, a part of the impregnated complexes remained intact because all the alumina OH surface groups were already neutralized by the Cs excess in the system. In this case, a drastic increase in activity was observed. In the case of the RhCs catalysts, as we can see in Fig. 2, the change in the Rh/Cs ratio had only a very limited influence on the activity, suggesting that the RhCs complex is more stable than the RuCs complex and might not be easily destroyed upon impregnation. Therefore, an excess of Cs atoms in the system is not needed to neutralize the alumina surface, because the complex structure is likely to be preserved after impregnation. It is also remarkable to note that the BP selectivity reached almost 100%, indicating that the direct HDS pathway (DDS) was promoted by cesium addition on a Rh based catalyst.

Therefore, unlike the RuCs based catalysts that requires an excess of Cs to obtain enhanced catalytic performances, the RhCs catalysts are activated even for a low Cs content. Thus, catalysts hereafter were prepared by loading a RhCs
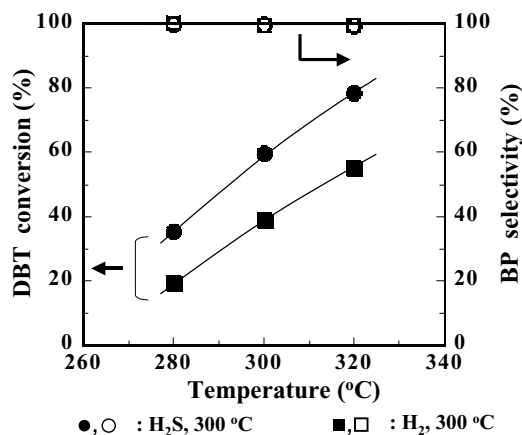
Fig. 3. Effect of the catalyst pretreatment on DBT conversion and BP selectivity (Rh 2 wt.%).

complex with Rh/Cs = 1, which was synthesized by the reaction of Cs hydroxide with Rh carbonyl.

3.1.3. Effect of the catalyst pretreatment

The effect of the pre-reduction on the RhCs(1)/Al$_2$O$_3$ catalysts activity and selectivity was studied. The results are compared with the one obtained for the catalyst activated by conventional pre-sulfiding (Fig. 3). The HDS activity observed after the pre-reduction treatment was lower than the one obtained after the pre-sulfiding treatment. The BP selectivity was not dependant on the pretreatment method, with a value of about 100% in both cases (DDS pathway).

3.1.4. Effect of the Rh loading

The HDS activities of RhCs(1)/Al$_2$O$_3$ catalysts were investigated at different temperatures for various Rh loadings. The results are presented in Fig. 4. These catalysts exhibited very high HDS activities even for low Rh contents (for example, a catalyst loaded with only 0.25 wt.% Rh exhibited a DBT conversion of about 40% at 300 °C). The activity increased linearly up to 0.5 wt.% Rh before stabilizing with further Rh addition. This phenomenon is different from the one classically observed over other noble metals (Pd,
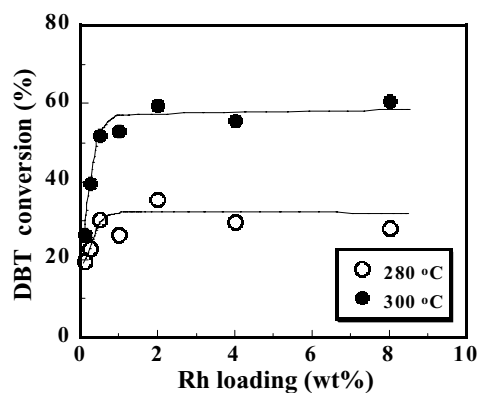

Fig. 4. Effect of the Rh loading on DBT conversion (Rh/Cs = 1).

Pt) for which the activity increases even for higher metal loading. To check the role of the particle size, we recorded the XRD spectra of Rh/Al$_2$O$_3$ catalysts containing 0.5, 1 and 4 wt.% Rh. The mean particle size was estimated by the Debye–Scherrer's equation [31] applied to the Rh(1 1 1) ($d = 0.22$ nm) reflection. Before measurement, the catalysts were presulfided with a mixture of 5 vol.% H$_2$S/H$_2$ and then prereduced in pure hydrogen at 300 °C for 3 h in order to obtain a surface state as close as possible to the one that is supposedly obtained under the reaction conditions. Neither the 0.5 wt.% Rh/Al$_2$O$_3$ catalyst nor the 1 wt.% Rh/Al$_2$O$_3$ showed diffraction peak due to Rh species, but a small peak attributed to metallic Rh species was detected in the case of the 4Rh/Al$_2$O$_3$ catalyst at $2\theta = 41.0°$ (1 1 1). For the latter sample the mean particle size was found to be about 10 nm. Brenner et al. [32] reported that the size of the Rh particles present on Rh/Al$_2$O$_3$ catalysts drastically increased upon presulfiding treatment or after HDS even for catalysts containing low Rh loading (0.1 or 0.5 wt.%). For example, the mean particle size observed for a catalyst containing 0.5 wt.% Rh was about 2 nm before sulfidation and increased up to 7 nm after sulfidation. In any case, the activity of Rh sulfides was comparable to the one of sulfided commercial Co(Ni)-Mo catalysts. The activity per gram of metal was much higher on the former than on the latter. The same authors attempted to correlate the particle size with the activity. They found that the DBT HDS activity of the 0.5 wt.% Rh catalyst (with 9.1 nm Rh particles) was higher than that of catalysts containing smaller Rh particles (5.4 nm). Nevertheless, their study also showed that the DBT HDS activity did not increase by loading large contents of Rh (up to 10 wt.% Rh). Therefore, the relationship between the HDS activity and the Rh metal particle size is still a matter of debates. In addition, It is well known that γ-alumina possess both Lewis and Brönsted acid sites on their surface. It is very likely that the Rh carbonyl complexes are selectively adsorbed on the Lewis acid sites of the γ-alumina support. When all the Lewis acid sites are covered with Rh carbonyl complexes, the Rh carbonyl complexes introduced in excess cannot be chemically anchored to the support and are not stabilized on the Lewis acid sites. Therefore, the Lewis acid sites covered with Rh carbonyl complexes become the nucleation point for the aggregation of Rh particles. Actually, we found the presence of Rh particles larger than 20 nm by XRD and TEM (photographs not presented here) on the 4Rh/Al$_2$O$_3$ catalyst. For lower Rh loading, the presence of such big particles was not evidenced. In brief, a high Rh loading led to an increase in the mean Rh particle size, which may not be favorable for further DBT HDS activity increase as observed in Fig. 4.

3.1.5. Effect of ruthenium addition on the 0.25RhCs(1)/Al$_2$O$_3$ catalyst

The effect of the ruthenium addition on the HDS activity was checked. The prepared catalysts were derived from the 0.25RhCs(1)/Al$_2$O$_3$ catalyst on which 6, 12 and 16 wt.% of Ru were impregnated. The results are
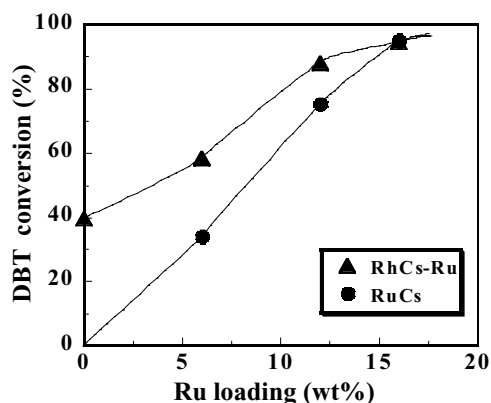
Fig. 5. Effect of Ru addition on the 0.25RhCs(1)/Al$_2$O$_3$ catalyst conversion (300 °C).

shown in Fig. 5 in which the activities previously obtained for RuCs(1)/Al$_2$O$_3$ catalysts [29] containing 6, 12 and 16 wt.% Ru are also shown for comparison. When 6 wt.% Ru was added to the 0.25RhCs(1)/Al$_2$O$_3$ catalyst (i.e. 0.25RhCs(1)-6Ru/Al$_2$O$_3$), the DBT conversion increased from 40 to 58%. Nevertheless, this value was lower than the sum of the activities obtained separately for the 0.25RhCs(1)/Al$_2$O$_3$ catalyst and the 6RuCs(1)/Al$_2$O$_3$ catalyst, meaning that no combination effect of Rh and Ru was obtained. Moreover, with further increase in the Ru loading, the DBT conversion on 0.25RhCs(1)Ru/Al$_2$O$_3$ became close to that on the corresponding RuCs(1)/Al$_2$O$_3$ catalyst. The 0.25RhCs(1)-16Ru/Al$_2$O$_3$ catalyst showed the same activity as the 16RuCs(1)/Al$_2$O$_3$ catalyst. This indicated that the highly active rhodium species were progressively covered by ruthenium species and that all the Rh catalytic sites were recovered when 16 wt.% Ru were added, which means that the supported Rh species could not contributed to the activity.

3.1.6. Effect of the impregnation order modification on the RuRhCs catalysts

The preparation method was therefore modified in order to avoid covering the Rh active species with the Ru species; ruthenium was loaded prior to rhodium. Fig. 6 shows the effect of the rhodium addition on the HDS activity of 16RuCs(1)/Al$_2$O$_3$. The HDS activity plot exhibited a volcano-type curve with a maximum near 0.25 wt.% Rh. The 16RuCs(1)-0.25Rh/Al$_2$O$_3$ catalyst exhibited a conversion of about 95% at 280 °C, whilst the catalyst prepared in the reverse order, i.e. 0.25RhCs(1)-16Ru/Al$_2$O$_3$ exhibited the same value at a reaction temperature 20 °C higher (Fig. 5). We deduced that the highly active rhodium species on the catalysts prepared by previous loading of Ru were present on the top surface of the solids and therefore efficiently participated in the reaction. Moreover, the 16RuCs(1)-0.25Rh/Al$_2$O$_3$ catalyst showed higher activity than the 0.25RhCs(1)-16Ru/Al$_2$O$_3$ catalyst but a simple calculation showed that the activity of the former was almost the same as the one that would be obtained if we assume the

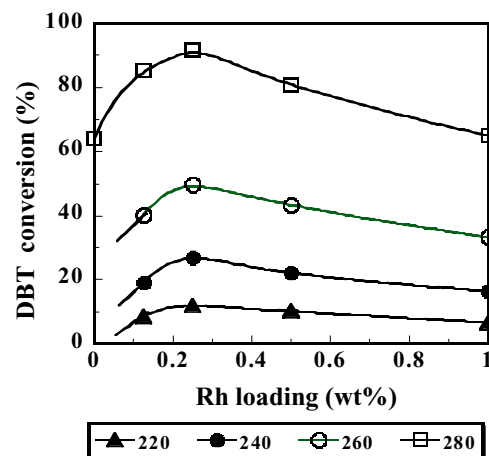mean value of the 0.25RhCs(1) and the 16RuCs(1)/Al$_2$O$_3$ catalysts activities. In addition, the apparent activation energy of the DBT HDS reaction over the RuCs-Rh catalysts was calculated. No significant difference was obtained when the Ru loading increased, with a value of $25 \pm 2\,\mathrm{kcal\,mol^{-1}}$ regardless of the catalyst.

3.2. Behavior of the sulfur on the sulfided RhCs(1)/Al$_2$O$_3$ catalysts

As described above, no synergetic effect was obtained between Rh and Ru. Therefore, we did not further investigate these catalysts by the radioactive tracer method, but we focused on the RhCs catalysts. This system is interesting because, whilst the activity of the RhCs catalysts was inferior to that of a conventional CoMo catalyst, the specific activity per metal atom was much higher than that of the CoMo catalyst (Fig. 7).

Therefore, [^{35}S]DBT HDS reactions were performed to investigate the behavior of the sulfur on RhCs(1)/Al$_2$O$_3$ catalysts at 300 °C and 5 MPa. Initially, a decalin solution of
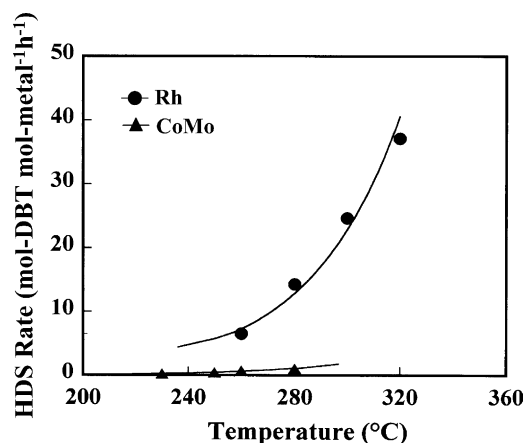

Fig. 6. Effect of the Rh loading on RuCs-Rh catalysts activities.

Fig. 7. 0.25RhCs(1)/Al$_2$O$_3$ catalyst and CoMo/Al$_2$O$_3$ (CoMo: 5 wt.% CoO, 16 wt.% MoO$_3$) catalyst specific conversions (per mole of metal).

1 wt.% [^{32}S]DBT was pumped into the reactor until the conversion of DBT became constant. Then, the [^{32}S]DBT solution was replaced with a 1 wt.% [^{35}S]DBT solution and the reaction was pursued until the amount of [^{35}S]H$_2$S formed became constant. After the [^{35}S]DBT introduction, the radioactivity of the unreacted [^{35}S]DBT in the liquid phase increased and approached a steady state quasi-immediately. However, it took about 75 min to achieve a steady state in the radioactivity of the produced [^{35}S]H$_2$S. This result indicated that the sulfur taken from the DBT molecules is not directly released as hydrogen sulfide but is temporarily accommodated on the catalysts, which is consistent with the results obtained for Al$_2$O$_3$-supported molybdenum catalysts [25,26]. Then, in the last part of the experiment, the [^{35}S]DBT solution was replaced with the initial [^{32}S]DBT one. The amount of labile sulfur on each catalyst (S_0), which is likely to represent the amount of the active sites, was calculated from the total radioactivity of the released [^{35}S]H$_2$S [25,26] as it is represented by the shaded area 'A' in Fig. 8.

In order to discuss the [^{35}S]H$_2$S release process more accurately, the [^{35}S]H$_2$S release rate constant was calculated. As reported previously [27], the [^{35}S]H$_2$S release in the range of area 'A' shown in Fig. 7 can be described as a first-order reaction. This permitted us to determine k_{RE}, the [^{35}S]H$_2$S release rate constant. The values of S_0 and k_{RE} are shown in Table 2. For comparison, some results previously obtained for RuCs(1)/Al$_2$O$_3$ catalysts are also shown [29]. The S_0/S_{total} ratio represents the percentage of S atoms effectively participating in the HDS reaction. When the Rh loading was increased from 2 to 8 wt.%, S_0 increased from 8.96 to 17.1 mg g-cat^{-1} whilst the HDS activity almost did not change. In the same time, both the k_{RE} value, which indicates the relative ease of migration of sulfur from the catalyst, and the S_0/S_{total} value decreased. When examining results obtained for a 4 wt.% Rh catalyst and a 4 wt.% Ru catalyst, we can see that the activity of the former is twice the activity of the latter. The higher activity of the 4RhCs(1)/Al$_2$O$_3$ catalyst was due to the fact that whilst k_{RE} was almost the

Table 2
Kinetic parameters on RhCs(1)/A1$_2$0$_3$ and RuCs(1)/A1$_2$0$_3$ catalysts

Catalysts (wt.%)	Conversion (%)	S_O (mg/g-cat.)	$k_{RE} \times 10^{-2}$ (min^{-1})	S_0/S_{total} (%)
Rh				
2	46.7	8.96	4.32	95.9
4	53.8	12.2	3.62	64.9
8	52.7	17.1	2.43	45.8
Ru				
4	25.8	7.25	3.70	28.6
8	59.7	12.9	3.11	25.4

S_{total} is defined as the amount of sulfur that would be accommodated assuming a total sulfidation into Rh$_2$S$_3$ or RuS.

same as the one obtained for the 4RuCs(1)/Al$_2$O$_3$ catalyst, S_0 exhibited about twice the value obtained for the latter. Further, for a lower Rh loading, k_{RE} exhibited a quite high value (4.32 × 10^{-2} min^{-1} for 2 wt.% Rh). That explains why the activity per metal atom of Rh based catalysts with low Rh loadings is higher than the one of CoMo catalysts. Indeed, the latter ones exhibit usually a k_{RE} value of ∼3 × 10^{-2} min^{-1} at 300 °C. Therefore, for low Rh loadings, the observed good intrinsic performance can be explained at least in part by a good H$_2$S release turnover. Moreover, unlike the CoMo catalysts, almost all the sulfur present on the surface of the 2 wt.% Rh catalyst is of a labile type (96% for the latter and 20–40% for the former [33]). This indicates that a large part of the active phase participates efficiently in the HDS reaction on the catalysts with low Rh loadings.

Nevertheless, whilst the HDS activity of Ru based catalysts increased with increasing Ru content up to 16 wt.% [29], the HDS activity of RhCs based catalysts reached a maximum at 0.5 wt.% Rh and then stabilized. The radioisotope experiments results clarified the fact that whilst the amount of S_0 increased when the Rh loading increased, at the same time the sulfur mobility (k_{RE}) decreased proportionally to the increase in S_0, leading to almost no change in activity. The Rh particle size (deduced by the XRD pattern and the TEM measurements) might be considered as a factor influencing k_{RE}. Anyway, the fact that under certain conditions (low Rh loading) the intrinsic HDS activity of Rh is higher (due to an easier H$_2$S desorption) than that of a conventional CoMo catalyst is very interesting. Therefore, further research work will aim at keeping these interesting properties for higher Rh loadings, by modification of the carrier and/or modification of the preparation method, for example, in order to obtain catalysts with better HDS activities.

4. Conclusion

The first part of this work aimed at the optimization of the DBT HDS properties of Rh based catalysts. The use of a Rh carbonyl-based precursor gave better results than that of the classical Rh chloride precursor. Therefore, the former was selected for further catalysts synthesis. The use of a
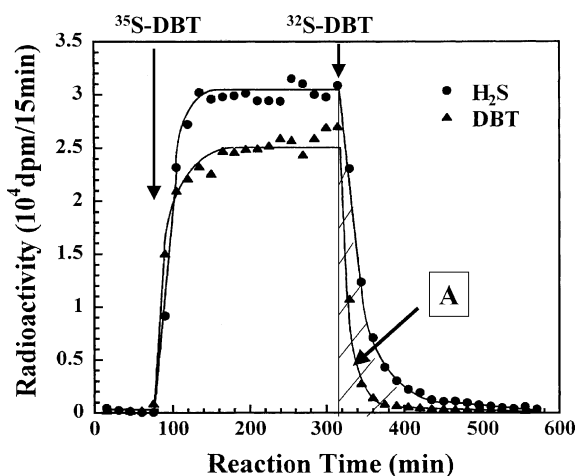

Fig. 8. Changes in radioactivities with reaction time.

RhCs complex derived from cesium hydroxide and Rh carbonyl resulted in an increase in DBT HDS activity. This increase in activity was accompanied with a remarkable increase in BP selectivity that reached almost 100%, indicating that the DBT HDS reaction over the RhCs system was mainly governed by a DDS (direct desulfurization) mechanism. Moreover, the addition of Ru as a co-catalyst was also investigated but optimization of the RuRhCs system did not produce any synergetic effect of Ru and Rh. Indeed, even in the best case the activity of the obtained catalyst was equal to the sum of the corresponding RuCs and RhCs catalysts.

In the second part of the work, as it was found that the intrinsic DBT HDS catalytic activity of a RhCs catalyst with a low Rh loading was much higher than that of a classical CoMo catalyst, we studied the former system by using the $[^{35}S]$DBT HDS radioactive tracer method. We found that, for 4 wt.% Rh, k_{RE}, the H_2S release rate constant and S_0, the number of labile sulfur, were almost the same as the one obtained for the 4 wt.% Ru catalyst. However, S_0 (assumed to be a representative of the number of the actives sites present on the catalysts) was significantly higher on the Rh catalyst than on the Ru catalyst (+70%). Therefore, the high intrinsic activity was due to the formation of a large quantity of labile sulfur atoms, i.e. a large quantity of active sites.

In brief, the intrinsic activity of a RhCs system containing a low Rh loading is higher than that of a classical CoMo catalyst, but an increase in the Rh loading tends to eliminate this interesting property. We are now making efforts to find a RhCs catalyst that can keep high k_{RE} values even for high Rh loadings.

Acknowledgements

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