

Hydrodesulfurization of sulfur-containing polyaromatic compounds in light gas oil using noble metal catalysts

Atsushi Ishihara^{*}, Franck Dumeignil, Jeayoung Lee,
Kouhei Mitsuhashi, Eika W. Qian, Toshiaki Kabe

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

Received 22 November 2004; received in revised form 12 April 2005; accepted 20 April 2005
Available online 13 June 2005

Abstract

We systematically monitored the hydrodesulfurization (HDS) activity of dibenzothiophene (DBT) and groups of substituted DBTs present in a SR-LGO over various noble metal catalysts (Ru, Rh, Ru-Rh, Pt, Pd and Pt-Pd) supported on alumina. The catalytic performances were compared to those obtained over a conventional CoMo catalyst. The Pd-based catalysts exhibited excellent HDS performances, especially for desulfurizing the refractory compounds. In particular, the 4,6-dimethyldibenzothiophene (4,6-DMDBT) HDS activity over the Pd or the Pd-Pt catalyst was equivalent to that over the CoMo catalyst. This was attributed to the exceptional hydrogenation (HYD) properties of the Pd-based catalysts, which enable desulfurization of the refractory compounds by considerably minimizing the effect of the steric hindrance due to their substituents. The synergetic effect observed on the bimetallic Pt-Pd system at low temperature for all the sulfur compounds was largely attenuated in the high temperature range, probably due to shifting of the HYD/dehydrogenation equilibrium to dehydrogenation. Despite a much lower metal loading (0.25 wt.%), the performances of the Rh catalyst were superior to those of the optimized 16 wt.% Ru catalyst. A synergetic effect was observed on the Ru-Rh catalyst, on which the DBT HDS activity was significantly enhanced compared to the activity of each corresponding monometallic catalyst.

Further, we recently showed that the use of SiO₂ or SiO₂-Al₂O₃ as a support allows higher optimal Rh contents, making the Rh-based HDS catalysts even more promising. In brief, we obtained encouraging results, which showed for instance that the excellent properties of the noble metal catalysts in model HDS reactions are still observed during the HDS treatment of real feeds.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Platinum; Palladium; Ruthenium; Rhodium; CoMo; Hydrodesulfurization; SR-LGO; DBT; 4-MDBT; 4,6-DMDBT; Substituted dibenzothiophenes

1. Introduction

The environmental regulations concerning the sulfur content in the diesel-engine fuels are becoming more and more severe. The maximum sulfur quantity will have to be decreased to 15 ppm in the US by 2006 [1], and to 10 ppm in EU by 2009 [2]. Japan plans to decrease the actual level of 50 ppm to 10 ppm by 2007 [3]. In order to achieve a sufficient HDS level, it is not only essential to develop new hydrodesulfurization (HDS) catalysts but also to elucidate

the HDS reaction mechanism [4]. In the literature, among a large number of attempts to propose new catalytic formulations, noble metal-based catalysts are attracting a particular attention due to their superior performances. For instance, it has been shown that non-supported ruthenium sulfides exhibit a remarkable activity in the thiophene HDS reaction [5–9]. In addition, supported Ru catalysts promoted by alkali exhibited HDS activities comparable to those of conventional CoMo/Al₂O₃ catalysts [10,11]. Further, rhodium, iridium and platinum or their combinations exhibited an HDS activity comparable to that of conventional CoMo/Al₂O₃ catalysts, or even better. Harris and Chianelli [12] found that, for very low metal loadings, carbon-supported

^{*} Corresponding author. Tel.: +81 42 388 7228; fax: +81 42 388 7228.
E-mail address: atsushii@cc.tuat.ac.jp (A. Ishihara).

rhodium and iridium sulfides exhibited activities higher than that of ruthenium; similar results were reported by Vissers et al. [13]. In addition, our group also reported that catalysts based on a rhodium carbonyl complex supported on alumina exhibited very interesting DBT HDS catalytic properties. Indeed, for rather low Rh loadings, the prepared catalysts exhibited a specific activity much higher than that of a conventional CoMo/Al₂O₃ catalyst [14]. We also showed that Pt-Pd/Al₂O₃ catalysts exhibited a DBT HDS activity comparable to that of conventional CoMo catalysts, with a significant promotion of the hydrogenation (HYD) properties [15]. Nevertheless, despite these interesting results in HDS of model molecules, the literature concerning the use of noble metals for treating light gas oils is rather scarce. Recently, Fujikawa et al. have reported that Pt-Pd/SiO₂-Al₂O₃ catalysts possess a high catalytic activity in the HYD of the aromatics present in diesel fuels [16,17], together with a high HDS activity [18].

In a previous work, we have analyzed the compounds present in a light gas oil using gas chromatography combined with mass spectroscopy (GC-MS) and gas chromatography atomic emission detection (GC-AED). We found 42 different kinds of alkyl-substituted benzothiophenes and 29 different kinds of alkyl-substituted dibenzothiophenes [19]. Among them, the methyl-substituted dibenzothiophenes, especially 4-methyl-benzothiophene (4-MDBT) and 4,6-DMDBT, were identified as being the sulfur compounds in light gas oils that are the most refractory to the direct desulfurization processes [20]. Thus, to achieve deep HDS of light gas oils, catalysts with superior performances are required in order to desulfurize these refractory compounds. In this sense, the results obtained for noble metals in HDS of model molecules are promising, so we aimed at using them for this purpose. We selected a set of noble metal-based catalysts that previously exhibited DBT HDS activities comparable to that of conventional CoMo catalysts, that is Pt and Pd as well as their binary combinations [15], and Ru and Rh as well as their binary combinations [10,11,14]. Their catalytic performances in the HDS of light gas oil were evaluated and subsequently compared to that of a conventional commercial CoMo system.

2. Experimental

2.1. Materials

The feedstock used was a straight run light gas oil (SR-LGO) containing 1.5 wt.% of total sulfur, which was obtained by direct distillation of an Arabian light crude oil. Some important properties of the SR-LGO are summarized in Table 1. Hydrogen used for pre-reducing and during the HDS experiments and the hydrogen sulfide mixed in hydrogen gas (H₂S: 4.95 vol.%) used for pre-sulfiding were obtained from Tohei Kagaku Co.

Table 1
Some properties of the SR-LGO

Sulfur (wt.%)	1.5
Carbon (wt.%)	85.2
Density (15 °C)	0.858
Nitrogen (ppm)	140
Hydrogen (wt.%)	12.7
Saturated fraction (wt.%) ^a	67.0
Aromatics (wt.%) ^a	
1 Ring	18.3
2 Rings	13.6
3 Rings	0.9
4 Rings	0.2
Distillation (°C)	
IBP	165
10 vol.%	274
20 vol.%	284
30 vol.%	293
50 vol.%	311
70 vol.%	336
80 vol.%	351
90 vol.%	371
EP	–

^a The saturated fraction and the multi-rings aromatic fractions were determined by HPLC.

2.2. Preparation of the catalysts

A reference CoMo catalyst supported on alumina was supplied by Nippon Ketjen Co. Ltd. (KF-707). The chemical composition and the BET surface areas of all the catalysts, of which the preparation procedures are described hereafter, are given in Table 2.

2.2.1. Pt- and Pd-alumina catalysts

The Pt- and Pd-supported alumina catalysts were prepared according to a conventional impregnation method [15]: a 20–80 mesh alumina was impregnated with an aqueous solution of H₂PtCl₆ or a mixed solution of H₂PtCl₆ and PdCl₂ with the desired quantities. The catalyst was then dried at 120 °C for 3 h and subsequently calcined in air at 430 °C for 20 h.

2.2.2. Ru- and Rh-alumina catalysts

The Ru- and Rh-supported alumina catalysts were prepared by impregnation under Ar atmosphere. For example, in the preparation of the Rh/Al₂O₃ catalyst loaded with 0.25 wt.% Rh, 0.0112 g of Rh₆(CO)₁₆, 0.0107 g of CsOH·H₂O and 25 mL of CH₃OH were introduced into a 50 mL reactor. Next, after the mixture was stirred at room temperature for 1 h, 2.5337 g of Al₂O₃ (20–80 mesh) were added into the obtained solution, which was stirred again for 2 h. Finally, the solvent was removed under vacuum. The other catalysts (the 16 wt.% Ru/Al₂O₃ catalyst and the 16 wt.% Ru-0.25 wt.% Rh/Al₂O₃ catalyst) were prepared by a similar method. The detailed preparation procedure is described elsewhere [11,14].

Table 2
Chemical composition of the catalysts

Catalyst	Chemical composition (mmol/g Catalyst)						BET surface area (m ² /g Catalyst)
	Pt	Pd	Ru	Rh	Co	Mo	
Pt(3)	0.15						256
Pd(10)		0.94					231
Rh(0.25)				0.025			256
Ru(16)			1.58				158
Pt-Pd ^a	0.15	0.94					229
Ru-Rh ^b			1.58	0.025			158
CoMo					0.6	1.18	

^a Pt-Pd (3 wt.% Pt, 10 wt.% Pd).

^b Ru-Rh (16 wt.% Ru, 0.25 wt.% Rh).

2.3. HDS activity evaluation

The HDS experiments were carried out in a fixed-bed flow reactor (17 mm i.d. × 365 mm). First, 2.54 g (4 mL) of fresh catalyst were diluted in 8 mL of quartz sand and introduced into the reactor. Then, the catalyst was pre-sulfided in situ with a mixture of 4.95 vol.% H₂S/H₂ or pre-reduced in a 99.99% H₂ flow (the pretreatment procedure used for each catalyst is shown in Fig. 1). The HDS reactions were performed under the following conditions: temperature, 330–390 °C; total pressure, 3.0 MPa; LHSV, 4 h⁻¹; gas/oil ratio, 125 Nm³/m³. Samples were collected every 15 min from a gas–liquid separator; the products were analyzed using a gas chromatograph (GC-14A, Shimadzu Corp.) equipped with a flame photometric detector (FPD). The sulfur compounds in the SR-LGO were identified by comparison with the GC–AED (gas chromatograph equipped with an atomic emission detector) chart obtained for a light gas oil (Arabian light) that was extensively characterized in a previous work [21]. Fig. 2 represents the GC–AED chart of this Arabian light gas oil. In addition, the contents of DBT and substituted DBT compounds initially present in the SR-LGO are given in Table 3.

To simplify the presentation of the results, we classified the refractory sulfur compounds present in the SR-LGO into six groups: i.e., group 1: DBT; group 2: C1-dibenzothiophenes (C1-DBT); group 3: C2-dibenzothiophenes (C2-DBT); group 4: C3-dibenzothiophenes (C3-DBT); group 5: 4-MDBT (4-methyldibenzothiophene); and group 6: 4,6-DMDBT, where C1, C2 and C3 represent the number of methyl groups, i.e., 1, 2 and 3, respectively. Before analysis, polyaromatic sulfur compounds (PASC) were separated from the samples using a specific methodology based on successive high performance liquid chromatography (HPLC) separations described elsewhere [21]. Then, 2 μL of each PASC sample were analyzed by GC–AED. Quantitative analysis was performed using calibration curves previously plotted with DBT (for group 1), 4-MDBT (for groups 2 and 5) and 4,6-DMDBT (for groups 3, 4 and 6) solutions prepared with various dilution factors. For samples

with a high PASC concentration (for example, for the non-treated SR-LGO in Fig. 3), peak area was measured after subtraction of the drifted baseline from the point of inflexion at the beginning of the peak to the point of inflexion at the end of the peak. Conversion of each group of compounds was then calculated from the respective area decrease. Note that this conversion is a global conversion that also takes into account the formation of non-desulfurized hydrogenated products. Nevertheless, their presence could be hardly detected on the GC–AED charts, indicating that their formation was negligible. Then, the conversion calculated by this way can be assimilated to the HDS conversion.

As an example, Fig. 3 shows the GC–AED charts obtained for SR-LGO experiments performed at various temperatures over the reference CoMo catalyst. At 350 °C the peaks attributed to C2- to C6-BT (retention times inferior to ~17 min) almost completely disappeared; the area of the peak attributed to DBT at a retention time of about 16 min was considerably reduced. In contrast, peaks attributed to substituted DBTs were still clearly observable.

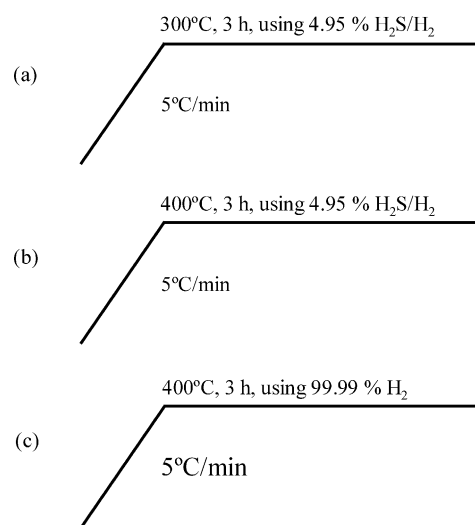


Fig. 1. Description of the in situ pretreatments used for each type of catalyst: (a) for Ru and Rh catalysts; (b) for the reference CoMo catalyst; (c) for Pt and Pd catalysts.

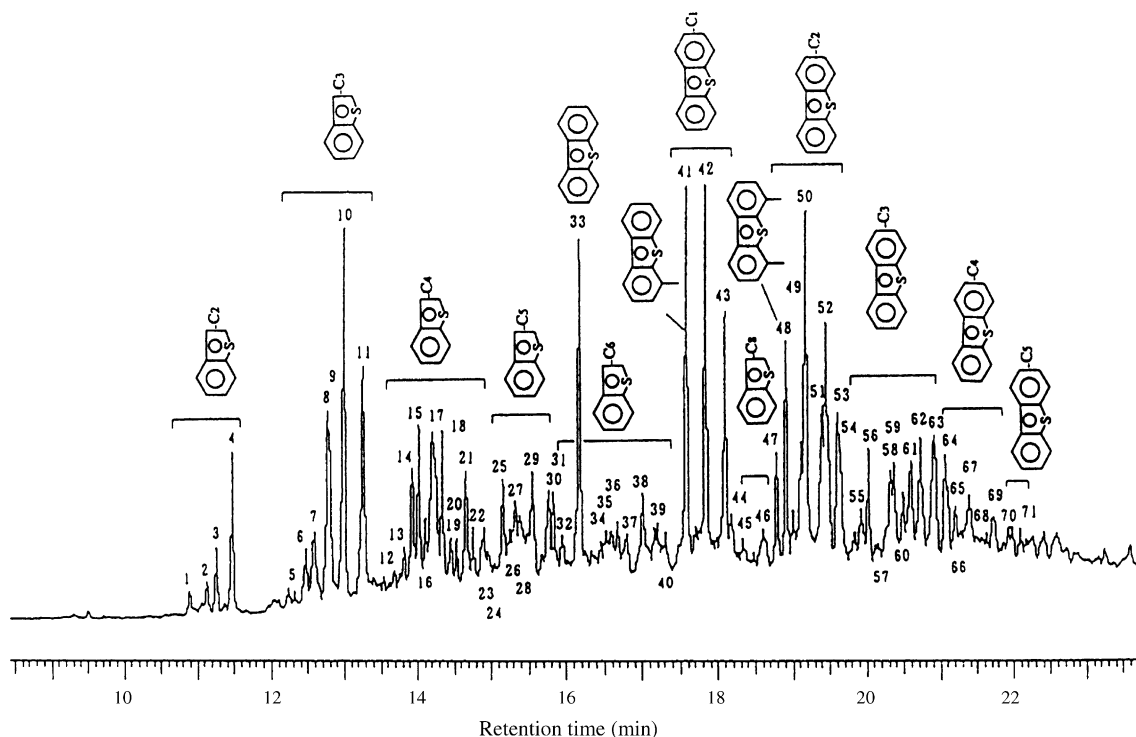


Fig. 2. Reference GC-AED chart of the polyaromatic sulfur compounds in a non-treated SR-LGO [21].

3. Results

3.1. Pd- and Pt-alumina catalysts

HDS of the SR-LGO was performed over Pd-, Pt-, and Pt-Pd-supported alumina catalysts. The results are shown in Figs. 4–6.

Table 3

Sulfur contents of dibenzothiophenes in the SR-LGO ('peak no.' refers to the number attributed to each peak in the reference GC-AED chart in Fig. 2)

Sulfur-containing compound	Sulfur content (wt.%)
Total sulfur	1.5
Dibenzothiophene	0.0186
C1-dibenzothiophenes	
Peak no. 41 (4-MDBT)	0.0230
Peak no. 42	0.0211
Peak no. 43	0.0152
C2-dibenzothiophenes	
Peak no. 47	0.0058
Peak no. 48 (4,6-DMDBT)	0.0126
Peak no. 49	0.0071
Peak no. 50	0.0242
Peak no. 51	0.0079
Peak no. 52	0.0182
Peak no. 54	0.0077
C3-Dibenzothiophenes	
Peak no. 56	0.0064
Peak no. 59	0.0056
Peak no. 62	0.0012

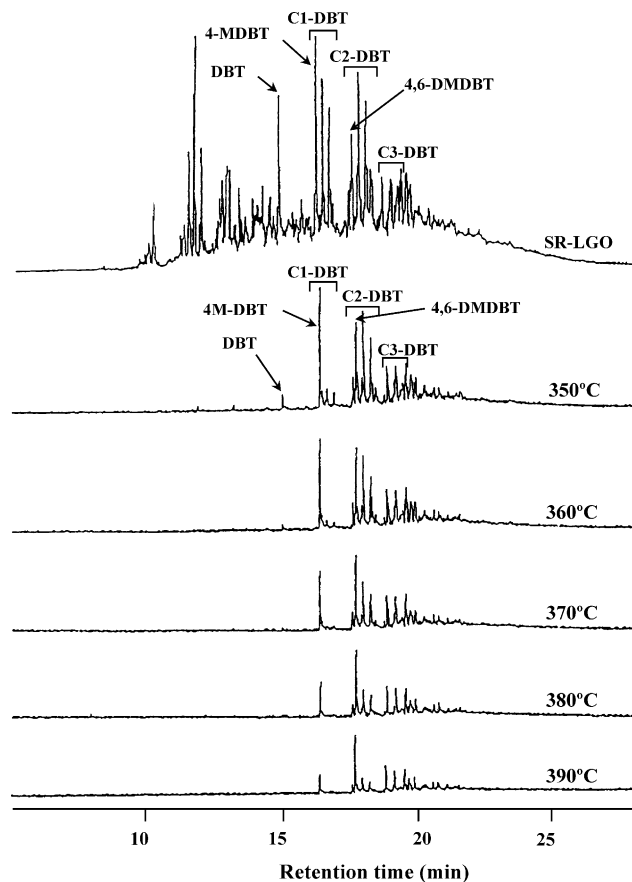


Fig. 3. GC-AED charts of the SR-LGO desulfurized over the CoMo catalyst at different temperatures.

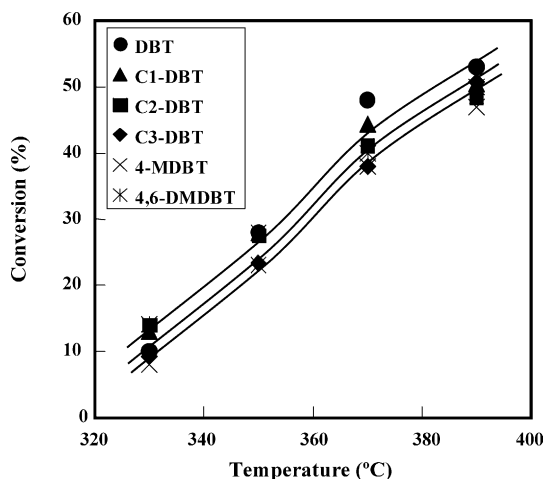


Fig. 4. Effect of temperature on the conversion of each group of sulfur compounds (over the 10 wt.% Pd catalyst).

As shown in Fig. 4, over the 10 wt.% Pd/Al₂O₃ catalyst the conversion of each group of sulfur compound increased with increasing reaction temperature. Contrary to the results obtained over all the other catalysts, the differences of reactivity among groups of sulfur compounds were not very pronounced, with a conversion almost equivalent for all the sulfur compounds.

Fig. 5 presents the conversion of each sulfur compound group over the 3 wt.% Pt/Al₂O₃ catalyst. Conversion increased with increasing reaction temperature but, unlike over the 10 wt.% Pd/Al₂O₃ catalyst, the reactivity difference between each group of sulfur compounds was this time clearly marked. Activity decreased in the order DBT > C1-DBT > C2-DBT > C3-DBT > 4,6-DMDBT ≥ 4-MDBT. Further, the conversion of each group of compounds was

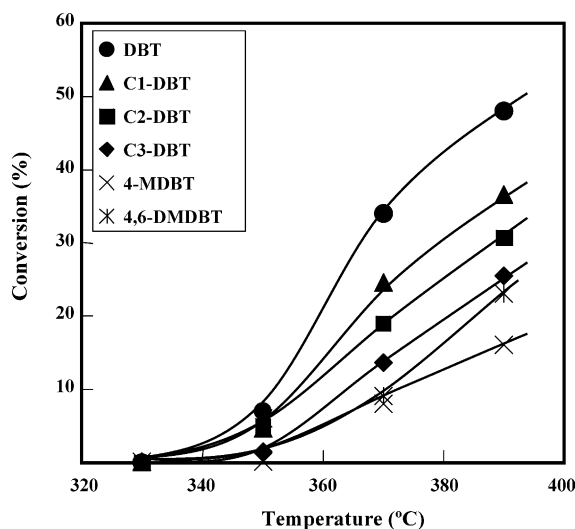


Fig. 5. Effect of temperature on the conversion of each group of sulfur compounds (over the 3 wt.% Pt catalyst).

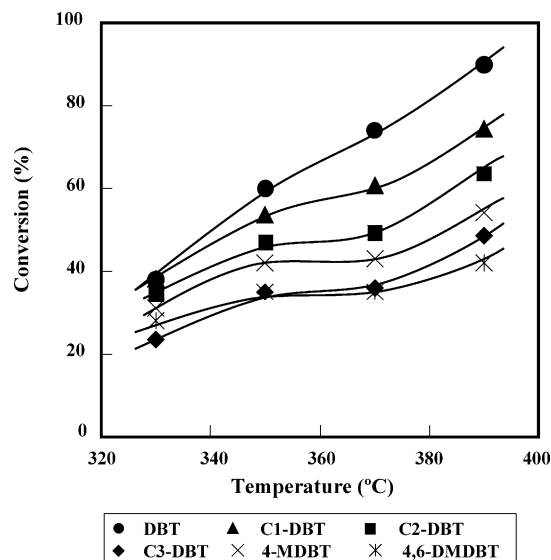


Fig. 6. Effect of temperature on the conversion of each group of sulfur compounds (over the 3 wt.% Pt-10 wt.% Pd catalyst).

lower than that observed over the 10 wt.% Pd/Al₂O₃ catalyst.

Then an experiment was performed with a bimetallic 3 wt.% Pt-10 wt.% Pd/Al₂O₃ catalyst (Fig. 6). A synergistic effect was observed at low temperatures, although no clear enhancement of the activity was observed at higher temperature when one compares this value to the activity that can be reasonably expected when summing the individual performance of each single metal catalyst. Further, for 390 °C, conversions of particularly refractory compounds (i.e., C3-DBT and 4,6-DMDBT) were even lower than over the single metal Pd/Al₂O₃ catalyst.

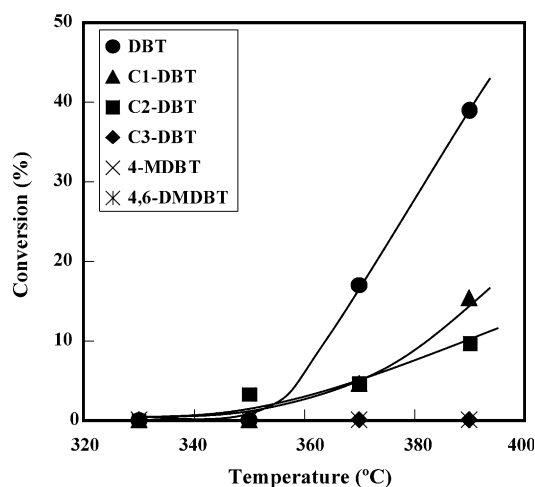


Fig. 7. Effect of temperature on the conversion of each group of sulfur compounds (over the 16 wt.% Ru catalyst).

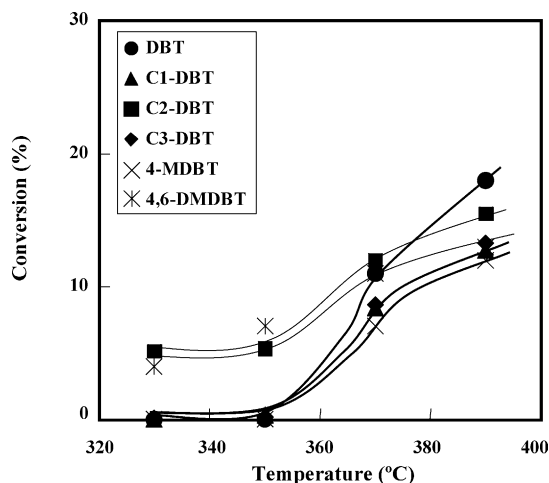


Fig. 8. Effect of temperature on the conversion of each group of sulfur compounds (over the 0.25 wt.% Rh catalyst).

3.2. Ru- and Rh-alumina catalysts

Fig. 7 shows the effect of temperature on conversion of each group of sulfur compounds over the 16 wt.% Ru/Al₂O₃ catalyst. While conversions of DBT, C1-DBT and C2-DBT increased with increasing reaction temperature, C3-DBT, 4-MDBT and 4,6-DMDBT were only slightly converted even at a temperature as high as 390 °C. The reactivity of the sulfur compounds decreased in the order: DBT > C1-DBT > C2-DBT ≫ C3-DBT, 4-MDBT, 4,6-DMDBT.

Fig. 8 shows the results obtained over the 0.25 wt.% Rh/Al₂O₃ catalyst. In contrast to the 16 wt.% Ru/Al₂O₃ catalyst, conversion of all the groups of sulfur compounds increased with increasing reaction temperature. In addition, except for DBT, the activity measured at 390 °C over the Rh/Al₂O₃ catalyst for all the groups was close to or higher than that over the Ru/Al₂O₃ catalyst. The DBT conversion over the

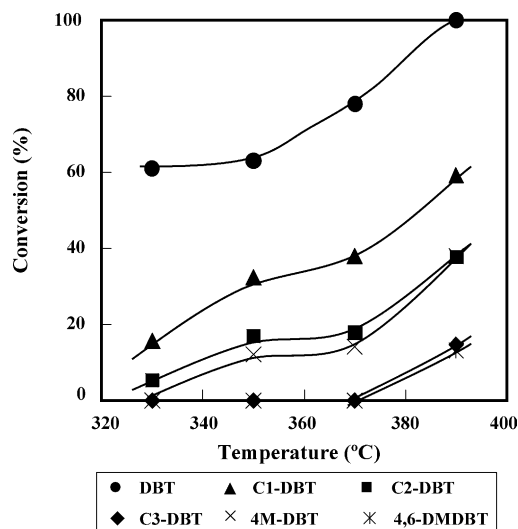


Fig. 9. Effect of temperature on the conversion of each group of sulfur compounds (over the 16 wt.% Ru-0.25 wt.% Rh catalyst).

Rh/Al₂O₃ catalyst was roughly divided by a factor of two when compared with that over the Ru/Al₂O₃ catalyst. Unlike over the Ru/Al₂O₃ catalyst, C3-DBT, 4-MDBT and 4,6-DMDBT were converted, even at a low temperature for the latter, indicating that the Rh/Al₂O₃ catalyst exhibits a superior ability to treat the particularly refractory compounds.

Further, Fig. 9 shows the results obtained over the 16 wt.% Ru-0.25 wt.% Rh/Al₂O₃ catalyst. Conversion of each group of sulfur compounds increased with increasing reaction temperature. Reactivity decreased in the order: DBT > C1-DBT > C2-DBT ≥ 4M-DBT > C3-DBT ≥ 4,6-DMDBT. In particular, the conversions of 4-MDBT and 4,6-DMDBT were significantly lower than those of C1-DBT and C2-DBT, respectively. This illustrates the fact that the substitution of the 4- and the 6- positions induces a strong steric hindrance, which is particularly negative for the HDS performances. DBT conversion was quite high. At 390 °C for instance, DBT conversion was about 1.5 times higher than the conversion that would be obtained by simply summing the conversions of the Ru/Al₂O₃ and the Rh/Al₂O₃ catalysts, suggesting that a synergetic effect was obtained. This result is different from that of a previous study carried out with a feed constituted of DBT dissolved in decalin, in which only a very limited synergetic effect occurred [14].

4. Discussion

4.1. Pt- and Pd-alumina catalysts

4.1.1. Monometallic Pd and Pt catalysts

The results showed that over the Pd catalyst activity was essentially identical for all the groups of sulfur compounds (Fig. 4). This was different from the observations over the Pt catalyst (Fig. 5) for which the activity of each group of sulfur compounds was markedly different. The following discussion will show that this difference is related to the superior HYD properties of the Pd catalyst.

It is now well admitted that aromatic sulfur molecules are desulfurized through two different reaction pathways, as shown in Fig. 10, in the cases of DBT and 4,6-DMDBT. The first main route is the hydrogenation route (HYD) followed by desulfurization and the second route is the direct desulfurization (DDS). In general, differences of reactivity observed between DBT and 4,6-DMDBT can be discussed in terms of preferential reaction pathways. Indeed, as a general tendency DBT is relatively easily desulfurized through the DDS route while 4,6-DMDBT desulfurization mainly occurs via the HYD route due to steric hindrance generated by the methyl groups [22,23], which inhibits the η^1 adsorption (by the sulfur atom) [24]. Thus, 4,6-DMDBT must have at least one aromatic ring pre-hydrogenated to lower steric hindrance and subsequently enable HDS. This means that the HDS of 4,6-DMDBT is facilitated over catalysts with high HYD properties allowing the

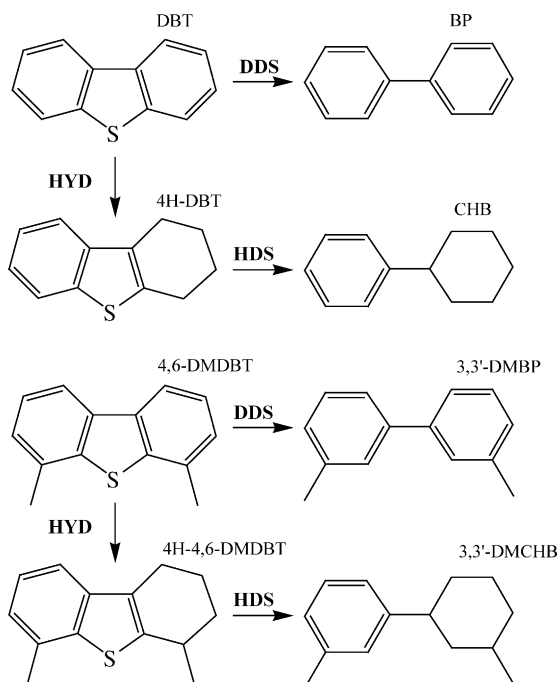


Fig. 10. Simplified reaction pathways for DBT and 4,6-DMDBT HDS.

π -adsorption of benzenic rings and their further conversion into hexyl rings. This is why, over conventional CoMo catalysts, high 3,3'-DMCHB selectivities ($\sim 5 \pm 10\%$) are observed in 4,6-DMDBT HDS, contrary to DBT HDS for which BP is largely predominant as the main product ($\sim 85 \pm 10\%$). Generally speaking, this is after HYD, i.e., after lowering the more or less strong steric hindrance modulated by the nature, number and location of the substituents on the aromatic rings of sulfur compounds that the catalysts can effectively express their desulfurization activity. Over conventional catalysts a reactivity order of $\text{DBT} > 4\text{-MDBT} > 4,6\text{-DMDBT}$ is generally observed [25]. Indeed, the approach of the sulfur atom to the active sites is particularly obstructed when substituents are in positions 4- and 6- in DBTs, making 4-MDBT and 4,6-DMDBT compounds particularly refractory to the conventional HDS processes among the substituted DBTs.

On the other hand, it was previously shown that Pd catalysts exhibit HYD properties superior to that of Pt catalysts. Indeed, DBT HDS experiments at 260 °C showed that, at *iso*-conversion, the CHB selectivity was about eight times higher over the Pd catalyst (2 wt.% Pt/Al₂O₃: DBT conversion = 54.8%, CHB selectivity = 11.2%; 10 wt.% Pd/Al₂O₃: DBT conversion = 53.8%, CHB selectivity = 88.8%) [26]. Further, the 10 wt.% Pd/Al₂O₃ catalyst was roughly 2.5 times more active in phenanthrene HYD than the 2 wt.% Pt/Al₂O₃ catalyst, with respective activities of 40.0×10^{-4} mol/h g Catalyst and 15.4×10^{-4} mol/h g Catalyst at 280 °C, illustrating the superior HYD properties of the Pd catalyst [15].

Then, the differences observed in the present study between the Pt and the Pd catalyst can be attributed to the

particularly high HYD properties of the Pd catalyst. These high HYD properties allow the material to equally enable the desulfurization of all the substituted DBT compounds present in the SR-LGO, whatever their refractory character, by remarkably removing the steric hindrance due to their substituents, irrespective of their number, location or complexity. Thus, over the Pd catalyst, HDS conversions of the substituted DBTs are equivalent to that of DBT, which is not a common result when compared to other types of HDS catalytic formulations.

4.1.2. Bimetallic Pd-Pt catalyst

For low reaction temperatures, combining Pd and Pt (Fig. 6) led to a synergetic effect, in good agreement with a previous study on HDS of DBT performed at 260 °C [26]. However, increasing the temperature did not give further sufficient increase in conversion, especially for the sulfur compounds supposedly particularly difficult to desulfurize (4,6-DMDBT and C3-DBT). For these compounds, at high temperature, the activity over the bimetallic catalyst was even lower than that over the Pd catalyst, suggesting that the combined effect of Pd and Pt might not be so favorable at higher temperatures. As discussed above (cf. Section 4.1.1), in addition to good intrinsic desulfurization properties themselves, good HYD properties are crucial for achieving high desulfurization rates especially for the so-called refractory compounds. In the meantime, it is well known that a temperature increase is accompanied with shifting of the equilibrium hydrogenation/dehydrogenation in favor of dehydrogenation, in good agreement with the above discussion. Further, note that there is also a possibility that some Pd active species were covered by Pt species, decreasing the activity for high temperatures.

4.2. Ru- and Rh-alumina catalysts

4.2.1. Monometallic Ru and Rh catalysts

The difference of catalytic behavior between the Ru- and the Rh-alumina catalysts is very interesting. Indeed, despite the number of Rh moles in Rh/Al₂O₃ being 63 times lower than the number of Ru moles in the Ru/Al₂O₃ catalyst (Table 2), the catalytic performances were globally in favor of the former (Figs. 7 and 8). This is in good agreement with the results of a previous study in which we showed that Rh/Al₂O₃ catalysts exhibit activities comparable to that of Ru/Al₂O₃ catalysts, but for significantly lower metal loadings [14]. Further, we previously characterized Rh- and Ru-based catalysts using a [³⁵S]DBT HDS radiotracer method described elsewhere [27]; we found that for a 4 wt.% Rh/Al₂O₃ catalyst with a DBT conversion of ca. 54% at 300 °C, the ratio S_0/S_{total} representing the ratio between the experimentally determined number of labile sulfur atoms to the total number of sulfur atoms (if the catalyst were fully sulfided into Rh₂S₃), was equivalent to ca. 65%. In contrast, for a 4 wt.% Ru/Al₂O₃ catalyst, S_0/S_{total} (supposing a theoretical complete sulfided state for RuS₂) was only ca.

29% with a DBT conversion of ca. 26%. Further, k_{RE} , the H_2S release rate calculated by the [^{35}S]DBT HDS method, was almost equal for both catalysts, with a value of $3.62 \times 10^{-2} \text{ min}^{-1}$ for the Rh-based one and of $3.70 \times 10^{-2} \text{ min}^{-1}$ for the Ru-based one. Then, the higher conversion observed over the Rh catalyst for the same metal loading was attributed to the creation of a larger amount of labile sulfur atoms, i.e., a larger amount of active sites [14]. Unfortunately, for problems of radioactivity detection limits, S_0 and k_{RE} for very low Rh loadings (e.g. 0.25 wt.%) could not be easily determined by the radiotracer method. However, we could obtain reliable results for a 2 wt.% Rh/ Al_2O_3 catalyst; S_0/S_{total} and k_{RE} were as high as ca. 96% and $4.32 \times 10^{-2} \text{ min}^{-1}$, respectively [14]. This illustrates the excellent intrinsic properties of the Rh catalysts for low metal loadings. Then, rather high global activities are observed for low metal loadings, in contrast with the Ru/ Al_2O_3 catalysts with poorer intrinsic properties that require high Ru amounts to exhibit a satisfactory global activity [28]. However, as a drawback, over alumina an increase in Rh loading leads to a decrease in the excellent intrinsic properties of the Rh-based catalysts observed for very low metal loadings; as a consequence, the global activity becomes stable at a rather constant value for Rh loadings higher than ca. 0.5 wt.% [14].

4.2.2. Bimetallic Ru-Rh catalyst

The results obtained when using a bimetallic Ru-Rh system to desulfurize the SR-LGO were slightly different from those obtained in the DBT HDS model reaction. Indeed, while in the DBT HDS model reaction we found that a bimetallic Ru-Rh catalyst gave only a little higher DBT conversion rate (feed = DBT in decalin) than the one that would be obtained by adding the conversion of the corresponding single metal catalysts [14], in the case of the SR-LGO, the DBT HDS activity was remarkably enhanced when using the bimetallic system (Fig. 9), revealing a synergetic effect between Rh and Ru. In contrast, no synergetic effect on HDS of the substituted DBTs in the SR-LGO was obtained. In the next discussion, we will show that the difference in synergetic effect between DBT and substituted DBTs might be related with the origin of the relatively low activity of the monometallic Ru-based catalyst (Fig. 7).

In a previous paper, we showed that the pore volume of the 16 wt.% Ru/ Al_2O_3 catalyst ($0.358 \text{ cm}^3 \text{ g}^{-1}$) was significantly lower than that of the alumina support ($0.647 \text{ cm}^3 \text{ g}^{-1}$) from which it was derived [11], due to combined impregnation of large quantities of Ru and Cs, this latter having a very large ionic radius. Further, even in the case of catalysts with pores of a supposedly reasonable size (40–50 nm) it has been suggested that the pore size/shape can be responsible for significant differences in catalytic HDS activity between DBT and 4,6-DMDBT. This was attributed in part to an increase in the cross section of 4,6-DMDBT of about 15% due to the presence of methyl groups

[29]. This suggests then that in the case of unfavorable morphology of the pores, the approach of the substituted DBTs to the Ru active sites might be more hindered than that of DBT. Further, this phenomenon is amplified due to competitive adsorption between the polyaromatic sulfur compounds to be treated and the other various molecules such as olefins that are present in the SR-LGO, all the more so if these molecules are confined in a limited space (lower pore volume) in which a great quantity of big Cs atoms are gathered, further sterically hindering the molecules' approach to the Ru catalytic sites. Furthermore, as discussed above, contrary to DBT which is 'easily' desulfurized through a DDS pathway, the desulfurization of (refractory) substituted DBTs requires two steps: HYD of an aromatic ring, which has the effect to lower steric hindrance, and then desulfurization itself. That is to say, two adsorptions are needed; therefore, HDS of refractory substituted DBTs might be even more sensitive to catalyst morphological modifications than HDS of DBT, which needs only one step to be efficiently desulfurized. In brief, the modified morphology of the catalyst induced by the presence of great quantities of Cs atoms explains the results of Fig. 7 for the Ru-based catalyst.

In the case of the Ru-Rh catalyst, the limitation related to the lowered pore volume is still present. Further, each of the monometallic catalysts gave almost no DBT HDS activity under 350 °C (Figs. 7 and 8). In contrast, DBT conversion over the Ru-Rh catalyst was about 60% at 330 °C (Fig. 9). While DBT conversion over the Ru-Rh catalyst did not significantly vary when increasing temperature to 350 °C with a value sensibly equal to 60%, an increase was observed for further increase in temperature with a conversion of ca. 80% at 370 °C and 100% at 390 °C. This suggests that the DBT HDS conversion profile over the Ru-Rh catalyst is due to the contribution of the aforementioned two desulfurization pathways. First, good DBT HDS activity at low temperature reflects good HYD performances of the bimetallic system. Even if good HYD performances are not particularly required to obtain good performances in the specific case of DBT HDS, the hydrogenation of one aromatic ring of DBT has supposedly a beneficial effect on DBT HDS activity. Indeed, in a DBT molecule, one of the two unpaired electron doublets on the sulfur atom is monopolized by aromaticity on the central thiophenic ring. Thus, HYD of one adjacent aromatic ring will make the central ring loose its aromatic character and the S atom will then have its two electron doublets available. As a consequence, the DBT adsorption on active sites will be facilitated. Further, as mentioned above, a temperature increase shifts the hydrogenation/dehydrogenation equilibrium to dehydrogenation. Therefore, the beneficial effect of HYD on HDS is progressively lost when temperature increases. In contrast, the DDS function of catalysts is enhanced when temperature increases and an 'S'-shaped conversion profile is usually obtained when plotting conversion of conventional catalysts (e.g. CoMo-based

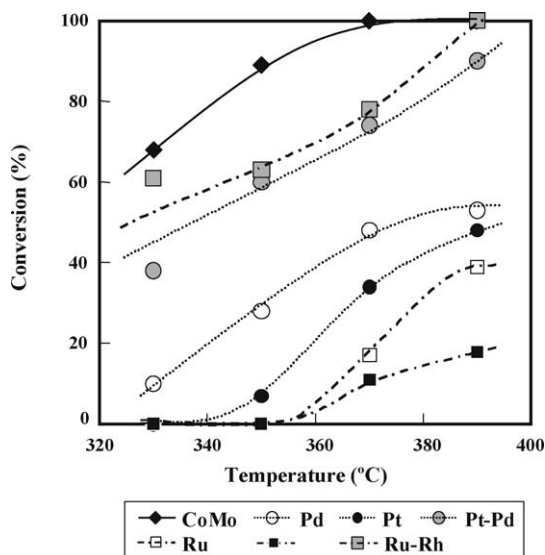


Fig. 11. Effect of temperature on the DBT conversion over each catalyst.

catalysts) as a function of temperature. In brief, upon temperature variation the efficiency of the two desulfurization pathways evolves in an opposite manner, which gives the profile of DBT HDS activity as a function of temperature in Fig. 9. In contrast, due to morphological constraints, the substituted DBTs can only very partially benefit from the enhanced HYD effect and only a very limited synergetic effect is obtained.

4.3. Global comparison

We compared the performances of all the catalysts including a commercial CoMo catalyst for three model compounds: DBT (Fig. 11); 4-MDBT (Fig. 12); and 4,6-DMDBT (Fig. 13).

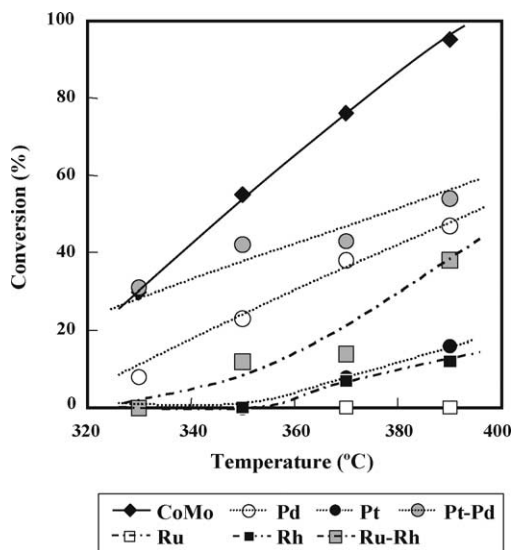


Fig. 12. Effect of temperature on the 4-MDBT conversion over each catalyst.

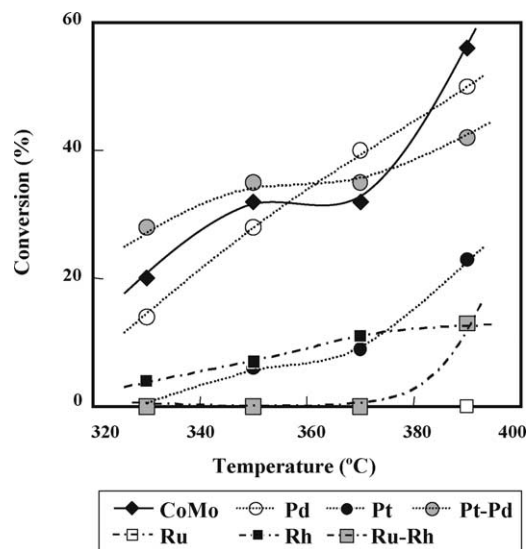


Fig. 13. Effect of temperature on the 4,6-DMDBT conversion over each catalyst.

4.3.1. DBT HDS activity

As DBT does not have any substituent, the DBT HDS activity can be considered as a measure that is mainly representative of the catalyst desulfurization properties, contrary to the other substituted compounds for which good HYD properties are essential to enable the desulfurization functionality of the catalysts. Indeed, as mentioned above for substituted DBTs, pre-HYD allows one to decrease the steric hindrance generated by the substituents on the aromatic rings, which is responsible for hindering S adsorption on the desulfurization catalytic sites. In Fig. 11, the DBT reactivity order is $\text{CoMo} > \text{Ru-Rh} \geq \text{Pt-Pd} > \text{Pd} > \text{Pt} > \text{Ru} > \text{Rh}$. This indicates that the classical CoMo formulation is better for 'pure' desulfurization compared to the noble metal-based catalysts.

4.3.2. 4-MDBT HDS activity

The 4-MDBT HDS activity order is $\text{CoMo} > \text{Pt-Pd} > \text{Pd} > \text{Ru-Rh} > \text{Pt} \approx \text{Rh} \gg \text{Ru}$ (Fig. 12). The presence of the methyl substituent in '4' position on one benzyl ring plays an important role on the HDS activity; better HDS performances are expected in the case of hydrogenating catalysts, which explains why the order is different from that observed for DBT HDS. Indeed, the Pd catalyst and the Pt-Pd catalyst exhibit this time the best performances, just after the CoMo catalyst. As mentioned above, Pd exhibits remarkable HYD properties that seem to be sufficient to make negligible the hindering effect of the methyl group(s) on the catalytic desulfurization performances. Then, the full intrinsic desulfurization potential of the Pd-containing catalysts is enabled by remarkably getting rid of the limitation usually observed on conventional catalysts, which is related to the efficiency/speed of the necessary pre-hydrogenation step. Further, at the low temperature of 330 °C, the activity of the Pt-Pd catalyst is equivalent to that

of the CoMo catalyst. This is also related to the superior HYD properties of the Pt-Pd catalyst especially at low temperatures, which will be briefly discussed in Section 4.3.3 in the case of 4,6-DMDBT HDS.

4.3.3. 4,6-DMDBT HDS activity

To desulfurize 4,6-DMDBT, which has one methyl group on each aromatic ring in positions that generate the most important steric hindrance effect (positions '4' and '6'), particularly enhanced HYD performances are crucial. For this reason, this compound is among the compounds that are the most difficult to desulfurize and that remain in relatively high quantities in the classically HDS-treated feeds, being an obstacle for the achievement of ultra-deep HDS. In 4,6-DMDBT HDS, the exceptional HYD capabilities of the Pd-containing catalysts are a great advantage. The activity order becomes $\text{CoMo} \approx \text{Pd} \approx \text{Pt-Pd} > \text{Pt} > \text{Rh} > \text{Ru-Rh} \gg \text{Ru}$ (Fig. 13). At low temperature, the Pt-Pd catalyst exhibits even better performances than the CoMo catalyst. This is in good agreement with the results of a previous study in which we compared the performances of NiMo and Pt-Pd catalysts in phenanthrene (PHE) HYD [30]. Indeed, we found that the NiMo catalyst was significantly less active than the Pt-Pd catalyst in PHE HYD for low temperatures, while the performances of both catalysts at intermediate temperatures were equivalent and further decreased in the same way when temperature increased. It is well known that NiMo catalysts exhibit globally better HYD capabilities than CoMo catalysts. Then, the above results [30] implicitly suggest that the Pt-Pd catalysts HYD performances at low temperatures are quite superior to those of CoMo catalysts.

4.4. Influence of the nitrogen-containing compounds

It is well known that nitrogen compounds have a detrimental influence on HDS performances due to catalyst poisoning. In a previous study [31] we showed that the retarding effect of acridine during HDS of the SR-LGO over a CoMo/Al₂O₃ catalyst decreased in the order DBT > 4-MDBT > 4,6-DMDBT. Addition of 0.1 wt.% of acridine (1000 ppm) to the SR-LGO led to a significant decrease in HDS reaction rate of ca. 25% at a temperature of 345 °C. Further, we studied the concomitant effect of the addition of acridine and DBT on the PHE HYD over the Pt-Pd catalyst [30]. In this study, we also monitored the effect of acridine addition on DBT HDS conversion. While addition of 0.01 wt.% of acridine (100 ppm) to the feed had only a very limited influence on DBT conversion, addition of 0.05 wt.% of acridine (500 ppm) led to a drastic decrease in DBT HDS conversion (DBT conversion was roughly divided by a factor 2 at 240 °C). Further, while PHE conversion changed only very slightly upon addition of 0.01 wt.% of acridine (100 ppm) in the feed, it decreased from ca. 95% in the absence of acridine to ca. 75% upon addition of 0.1 wt.% of acridine (1000 ppm); however, a reasonable PHE conversion (of ca. 90%) could be recovered after subsequently

removing acridine from the feed. Thus, these results show that the presence of rather high concentrations of acridine has a detrimental effect on the HYD properties of the Pt-Pd catalyst, which might be particularly detrimental for the HDS conversion of substituted DBTs. Nevertheless, considering that the SR-LGO used in the present study contains only 140 ppm of nitrogen (Table 1), the poisoning effect of nitrogen compounds might be supposedly relatively limited for the Pt-Pd catalyst. For the moment, we have no data concerning the retarding effect of nitrogen compounds on the Ru-Rh catalyst.

Further investigation of the comparative effect of nitrogen-containing compounds on the activity of the series of catalysts presented in this paper is needed. Nevertheless, in the present paper all the experiments were performed with the same SR-LGO, i.e., with the same quantity of nitrogen compounds of the same nature. Therefore, the results can be directly compared, even if, for instance, the influence of the time on stream on the activity of each catalyst seems worth further studying.

5. Conclusions

- The results showed that the noble metal catalytic formulations that previously exhibited high performances in HDS of model molecules are also similarly efficient for the HDS of SR-LGO.
- The HDS performances over the Pd-containing catalysts were particularly interesting for compounds that are refractory to the HDS processes over conventional catalysts. This was explained by the exceptional HYD properties of the Pd-based catalysts. Indeed, the HDS mechanism of substituted aromatic sulfur compounds involves a pre-HYD step prior to desulfurization itself, which is necessary to release the steric hindrance due to the substituents, contrary to the non-sterically hindered compounds that are straightforwardly desulfurized via a DDS pathway. Thus, for classical catalytic formulations (e.g. CoMo) even with excellent DBT HDS properties, HYD efficiency becomes a neck for HDS in the case of substituted DBTs. In this case, the usual HDS efficiency order of DBT > 4-MDBT > 4,6-DMDBT is observed. In contrast, the HYD properties of Pd were supposedly high enough to hydrogenate a large number of aromatic rings in the SR-LGO, including aromatic rings of the compounds to desulfurize, and thus to entirely get rid of the HYD limitation usually affecting HDS performances for refractory compounds. Indeed, contrary to all the other tested catalysts, the HDS conversion over the Pd catalyst was almost identical for all the sulfur compounds in the SR-LGO.
- The Ru-Rh catalyst exhibited a synergetic effect for the DBT HDS in the SR-LGO. Unfortunately, this synergetic effect was not seen on the other sulfur compounds, supposedly due to inadequate morphology of the catalyst

porosity, together with the presence of a large amount of big Cs atoms in the vicinity of the active sites, which block off the adsorption on the active sites to a certain extent, especially in the case of sterically hindered molecules.

- The Rh-based catalyst gave good HDS properties, despite a very low metal loading (0.25%). We recently showed that the optimal Rh metal loading can be increased by using silica [32] or silica-alumina as a carrier [33]. The DBT HDS performances of a 0.5 wt.% Rh/Al₂O₃-SiO₂ catalyst were slightly better than those of a conventional CoMo/Al₂O₃ catalyst. Further, the 0.5 wt.% Rh/Al₂O₃-SiO₂ catalyst exhibited exceptionally high 4,6-DMDBT HDS performances, with a conversion at 240 °C about seven times higher than over the CoMo catalyst (ca. 67% versus ca. 10%) [32]. Such results confirmed that HDS catalysts derived from Rh complexes are promising. Thus, further SR-LGO HDS experiments have to be performed to check the activity of Rh/SiO₂-Al₂O₃ and Rh/SiO₂ catalysts with higher metal loadings.

References

- [1] EPA, control of air pollution from new motor vehicles: heavy-duty engine and vehicle standards and highway diesel fuel sulfur control requirements, Federal Register, vol. 66, 2001, p. 5101.
- [2] Directive of the European Parliament and of the Council on the Quality of Petrol and Diesel Fuels, Brussels, COM (2001) 241 final.
- [3] Central Environment Council, Future Policy for Motor Vehicles Exhaust Emissions Reduction (7th Report), Japanese Ministry of the Environment, 29 July 2003.
- [4] T. Kabe, A. Ishihara, W. Qian, *Hydrodesulfurization and Hydrodenitrogenation*, Kodansha Scientific, Wiley-VCH, Tokyo, New York, Berlin, 1999.
- [5] T.A. Pecoraro, R.R. Chianelli, *J. Catal.* 67 (1981) 430.
- [6] M. Lacroix, N. Boutarfa, C. Guillard, M. Vrinat, M. Breyse, *J. Catal.* 120 (1989) 473.
- [7] M. Vrinat, M. Lacroix, M. Breyse, L. Mosoni, M. Roubin, *Catal. Lett.* 3 (1989) 405.
- [8] A. Raje, S.-J. Liaw, B.H. Davis, *Appl. Catal. A: Gen.* 150 (1997) 297.
- [9] A. Raje, S.-J. Liaw, B.H. Davis, *Appl. Catal. A: Gen.* 150 (1997) 319.
- [10] A. Ishihara, M. Nomura, N. Takahama, K. Hamaguchi, T. Kabe, *Sekiyu Gakkaishi* 39 (3) (1996) 211–221.
- [11] A. Ishihara, J. Lee, F. Dumeignil, R. Higashi, A. Wang, W. Qian, T. Kabe, *J. Catal.* 217 (2003) 59.
- [12] S. Harris, R.R. Chianelli, *J. Catal.* 86 (1984) 400.
- [13] J.P.R. Vissers, C.K. Groot, E.M. Van Oers, V.H.J. de Beer, R. Prins, *Bull. Soc. Chim. Belg.* 93 (1984) 813.
- [14] J. Lee, A. Ishihara, F. Dumeignil, K. Miyazaki, Y. Oomori, E.W. Qian, T. Kabe, *J. Mol. Catal. A: Chem.* 209 (2004) 155.
- [15] W. Qian, Y. Yoda, Y. Hirai, A. Ishihara, T. Kabe, *Appl. Catal. A: Gen.* 184 (1999) 81.
- [16] T. Fujikawa, K. Idei, T. Ebihara, H. Mizuguchi, K. Usui, *Appl. Catal. A: Gen.* 192 (2000) 253.
- [17] T. Fujikawa, K. Tsuji, H. Mizuguchi, H. Godo, K. Idei, K. Usui, *Catal. Lett.* 63 (1999) 27.
- [18] T. Fujikawa, K. Idei, O. Katsuyoshi, H. Mizuguchi, K. Usui, *Appl. Catal. A: Gen.* 205 (2001) 71.
- [19] T. Kabe, A. Ishihara, H. Tajima, *Ind. Eng. Chem. Res.* 31 (6) (1992) 1577.
- [20] A. Ishihara, H. Tajima, T. Kabe, *Chem. Lett.* (1992) 669.
- [21] T. Kabe, A. Ishihara, Q. Zhang, H. Tsutsui, H. Tajima, *Sekiyu Gakkaishi* 36 (1993) 467.
- [22] M. Houalla, N.K. Nag, A.V. Sapre, D.H. Broderick, B.C. Gates, *AIChE J.* 24 (1978) 1015.
- [23] M. Houalla, D.H. Broderic, A.V. Sapre, N.K. Kag, V.H.J. de Beer, B.C. Gates, H. Kwart, *J. Catal.* 61 (1980) 523.
- [24] S. Cristol, J.-F. Paul, E. Payen, D. Bougeard, F. Hutschka, S. Clément, *J. Catal.* 224 (2004) 138.
- [25] T. Kabe, A. Ishihara, Q. Zhang, *Appl. Catal. A: Gen.* 97 (1993) L1–L9.
- [26] T. Kabe, W. Qian, Y. Hirai, L. Li, A. Ishihara, *J. Catal.* 190 (2000) 191.
- [27] F. Dumeignil, J.-F. Paul, E.W. Qian, A. Ishihara, E. Payen, T. Kabe, *Res. Chem. Int.* 29 (6) (2003) 589.
- [28] A. Ishihara, H. Godo, R. Kanamori, W. Qian, T. Kabe, *Appl. Catal. A: Gen.* 182 (1999) 345.
- [29] F. Dumeignil, K. Sato, M. Imamura, N. Matsubayashi, E. Payen, H. Shimada, *Appl. Catal. A: Gen.* 287 (1) (2005) 135.
- [30] A. Ishihara, J. Lee, F. Dumeignil, M. Takashi, E.W. Qian, T. Kabe, *Energy Fuels* 17 (5) (2003) 1338.
- [31] T. Kabe, K. Akamatsu, A. Ishihara, S. Otsuki, M. Godo, Q. Zhang, W. Qian, *Ind. Eng. Chem.* 36 (1997) 5146.
- [32] A. Ishihara, J. Lee, F. Dumeignil, E. W. Qian, T. Kabe, *Proceedings of the 10th Asian Pacific Confederation of Chemical Engineering (APChE) Congress*, On-line Number 135, 1G-08, 2004.
- [33] J. Lee, A. Ishihara, F. Dumeignil, E.W. Qian, T. Kabe, *J. Mol. Catal. A: Chem.* 213 (2) (2004) 207.