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

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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 SiO_2 or SiO_2-Al_2O_3 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.
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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/Al_2O_3 catalysts [10,11]. Further, rhodium, iridium and platinum or their combinations exhibited an HDS activity comparable to that of conventional CoMo/Al_2O_3 catalysts, or even better. Harris and Chianelli [12] found that, for very low metal loadings, carbon-supported

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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 $CoMo/Al_2O_3$ catalyst [14]. We also showed that $Pt-Pd/Al_2O_3$ 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 $Pt-Pd/SiO_2-Al_2O_3$ 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 (H_2S: 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 H_2PtCl_6 or a mixed solution of H_2PtCl_6 and $PdCl_2$ 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/Al_2O_3 catalyst loaded with 0.25 wt.% Rh, 0.0112 g of $Rh_6(CO)_{16}$, 0.0107 g of $CsOH \cdot H_2O$ and 25 mL of CH_3OH were introduced into a 50 mL reactor. Next, after the mixture was stirred at room temperature for 1 h, 2.5337 g of Al_2O_3 (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/Al_2O_3 catalyst and the 16 wt.% Ru-0.25 wt.% Rh/Al_2O_3 catalyst) were prepared by a similar method. The detailed preparation procedure is described elsewhere [11,14].