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New supported ruthenium catalyst for hydrodesulfurization reaction

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Abstract

The effect of the kind of ruthenium precursor $\{Ru_3(CO)_{12}$ or $RuCl_3{\cdot}nH_2O\}$ and the activation conditions on the performance of Ru/MgF_2 preparations in thiophene hydrodesulfurization has been studied. The highest activity, higher than that of the commercially available system $CoMo/Al_2O_3$, was revealed by the Ru/MgF_2 catalyst sulfided in the 50% H_2S/He atmosphere. According to the results of TPR study, this preparation was characterized by exceptionally high content of RuS_2, which seems to be responsible for its high activity. As follows from the product distribution of thiophene HDS, the activation in the H_2S/He atmosphere mainly leads to the formation of saturated products (butane), while the activation in the atmosphere of H_2S/H_2, to the formation of unsaturated products (butene-1, *cis*- and *trans*-butene-2). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thiophene HDS; Ruthenium catalysts; Ru/alumina; Ru/silica; Ru/magnesium fluoride

1. Introduction

Sulfur removal from petroleum derivatives is a very important industrial process. Tomorrow's gasoline must have a much lower heteroatom content than that is allowed even today. Many investigations of the hydrotreatment of petroleum based feedstocks show that the current commercial catalysts based on molybdenum sulfide doped with Ni or Co do not have sufficient activity to meet today's refinery requirements determined by the environmental standards [1]. To attain compliance in the future, new hydrotreatment catalysts are necessary for the hydrodesulfurization (HDS) of feedstocks.

In the last two decades, other transition metal sulfides have been investigated. For example, Pecoraro and Chianelli [2] reported that unsupported ruthenium sulfide catalyst exhibited an activity for HDS of dibenzothiophene 13 times higher than that of molybdenum sulfide. Ruthenium sulfide catalyst was found to be the most active HDS catalyst among the transition metal sulfides and exhibited very high activity in many other hydrotreating reactions [3–6]. The properties of the RuS_2 catalyst was found to be in a significant degree modified by the support used. For instance, RuS_2 is highly active in HDS when supported on carbon [7] or MgF_2 [8], while supported on Al_2O_3 [9] it reveals lower activity.

In this study we presented the preparation of RuS_2 supported over MgF_2 and HDS properties of these new catalysts using thiophene conversion as a model reaction and to compare their performance with those for a typical commercial $CoMo/Al_2O_3$ catalyst. The effect of the H_2S treatment on the activity of Ru/MgF_2 catalyst in HDS was examined. The properties of the active phase were characterized by the temperature

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programmed reduction (TPR) after sulfiding in various atmospheres.

2. Experimental

2.1. Catalysts preparation

Magnesium fluoride was obtained in the reaction of magnesium carbonate with 20% water solution of hydrofluoric acid. After drying at 70°C the support was calcined at 400°C for 4 h.

The support obtained in this way had the surface area equal to 37.7 m^2/g and a well-pronounced pore structure.

Ruthenium catalysts were prepared by the conventional impregnation of the support with the alcoholic solution of ruthenium dodecacarbonyl $\{Ru_3(CO)_{12}\}$ and ruthenium chloride $\{RuCl_3 \cdot nH_2O\}$. The catalyst contains 1.6 wt.% of ruthenium. For the sake of comparison the catalysts containing the same amount of Ru supported on γ-Al_2O_3 (160 m^2/g) and SiO_2 (360 m^2/g) were also prepared.

2.2. Catalyst presulfidization

Three different in situ presulfidation procedures were applied, with H_2S at two different concentrations and in one case with He instead of H_2, at the flow rate of ca. 20 cm^3/min, for each of them different catalyst notation was used:

1. 10% H_2S/H_2 — 1SH
2. 50% H_2S/H_2 — 5SH
3. 50% H_2S/He — 5SHe

All procedures were performed at 350°C for 1 h before reaction. Presulfidization conditions and symbols of the catalysts are presented in Table 1.

2.3. HDS activity

Thiophene was introduced into the reactor by bubbling a stream of pure hydrogen at the rate of 30 cm^3/min (STP) through a thiophene saturator, maintained in an ice bath at 0°C. The reaction was conducted using a single-pass microreactor in the atmospheric pressure at 400°C. The concentration of thiophene in the feed stream was maintained at approximately 2.5×10^{-4} mol/l by adjusting the H_2 flow rate through the saturator. The gas mixtures were analyzed by on-line gas chromatography. 50 mg of catalyst with a grain size range 0.5–0.25 mm was used for tests. The rate of HDS of thiophene is given by HDS rate $= FXC/W$ where F is the total flow rate of feed; X the fractional conversion; C the concentration of thiophene in the feed and W the catalyst weight.

2.4. TPR experiments

The temperature programmed reduction experiments were carried out with an ASAP ChemiSorb 2705 (Micromeritics). A 50–100 mg catalyst was re-

Table 1
Presulfidization conditions and sample symbols

Symbol	Precursor	Activation			
		Oxidized at 400°C/2 h	10% H_2S/H_2 at 350°C/1 h	50% H_2S/H_2 at 350°C/1 h	50% H_2S/He at 350°C/1 h
Cl-1SH	$RuCl_3 \cdot nH_2O$		+		
Cl-5SH				+	
Cl-5SHe					+
Cl-O1SH		+	+		
Cl-O5SH		+		+	
Cl-O5SHe		+			+
CO-1SH	$Ru_3(CO)_{12}$		+		
CO-5SH				+	
CO-5SHe					+
CO-O1SH		+	+		
CO-O5SH		+		+	
CO-O5SHe		+			+

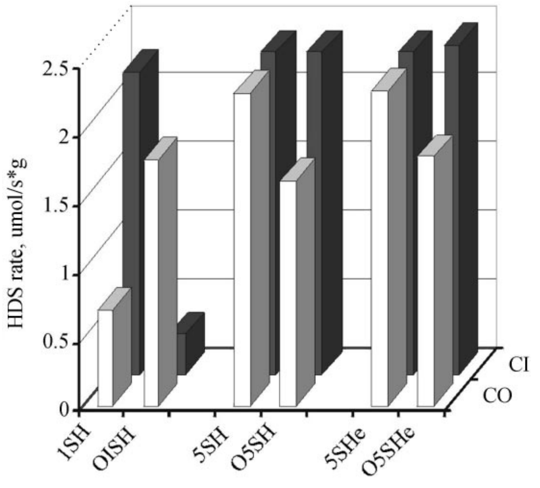

Fig. 1. Effect of presulfiding by hydrogen sulfide on the HDS of thiophene over Ru/MgF_2 catalysts at 400°C.

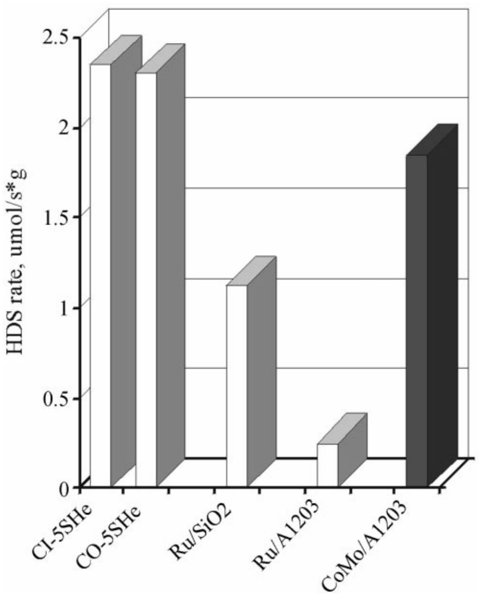

Fig. 2. Comparision of HDS activity over Ru/MgF_2, Ru/SiO_2, Ru/Al_2O_3 and commercial $CoMo/Al_2O_3$ catalysts. Activation for Ru/Al_2O_3 and Ru/SiO_2: 50% H_2S/He; for $CoMo/Al_2O_3$: 10% H_2S/H_2.

duced in a mixture of 10 vol.% H_2 in Ar at a total flow rate of 30 cm^3/min (STP) and at 10°C/min heating rate up to a final temperature of 850°C.

3. Results and discussion

Fig. 1 shows a comparison of HDS activities of Ru/MgF_2 preparations obtained from different precursors, i.e. $Ru_3(CO)_{12}$ (denoted as carbonyl series) and $RuCl_3 \cdot nH_2O$ (denoted as chloride series). Sulfidation was performed for dried or preliminary calcined preparations (Table 1).

The kind of ruthenium precursor as well as the composition of the sulfidation atmosphere was established to have a significant effect on the catalysts activity. In general, the preparations obtained on the basis of ruthenium chloride were more active than those based on ruthenium dodecacarbonyl. Moreover, the activity of the former was high, irrespective of the composition of the sulfidation atmosphere, whereas the activity of the carbonyl series preparations was higher after the sulfidation in the atmosphere of a higher concentration of H_2S (5SH and 5SHe), than in a mixture of 10% H_2S/H_2.

At the next stage the influence of the preliminary calcination of the preparations on their HDS activity was checked. It was found not to have significant effect on the activity of the chlorine series preparations, except for the one sulfided in the 10% H_2S/H_2 atmosphere, for which a drastic decrease in activity was noted. For the carbonyl series preparations sulfided in the atmosphere of 5SH or 5SHe, preliminary calcination resulted in a decrease in their activity; however, the activity of the preparation sulfided in the atmosphere of 10% H_2S/H_2 increased.

Moreover, the HDS activity of Ru/MgF_2 preparations was compared with that of the analogous systems containing ruthenium supported on Al_2O_3 and SiO_2 as well as the activity of the conventionally used catalyst. As follows from the results shown in Fig. 2, the Ru/MgF_2 (5SHe) preparations from both the chloride and carbonyl series were much more active than Ru/SiO_2 or Ru/Al_2O_3 and also more active than the catalyst $CoMo/Al_2O_3$ used in the industry.

The composition of the reaction products was determined for Ru/MgF_2 preparations activated in different conditions. The results are shown in Fig. 3. The activation in the H_2S/H_2 atmosphere (1SH and 5SH) led to the formation of unsaturated products mainly (butene-1, *cis*- and *trans*-butene-2) for both series of preparations studied. After activation in the

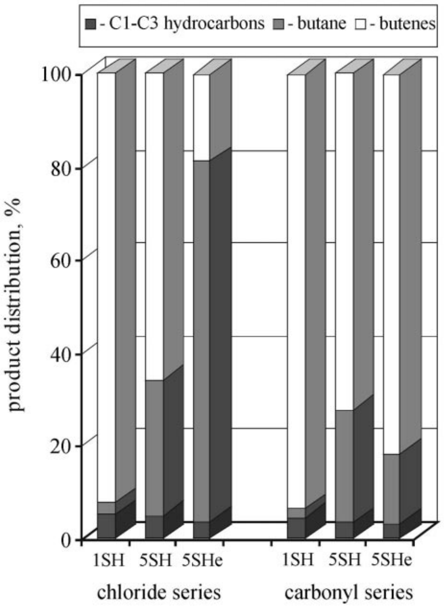

Fig. 3. Product distribution of thiophene HDS over Ru/MgF_2 catalysts.

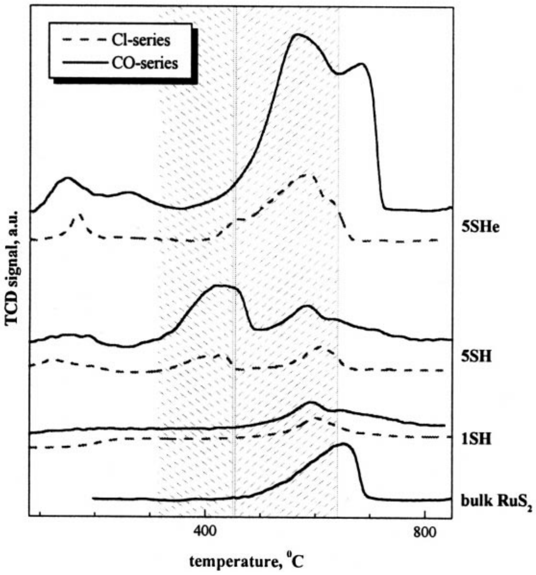

Fig. 4. TPR patterns of sulfided Ru/MgF_2 catalysts presulfided in various conditions.

10% H_2S/H_2 mixture, the reaction products revealed a certain amount of butadiene (2–4%). When the activation was carried out in the H_2S/He atmosphere, for the chloride series catalysts the main reaction product was butane (∼77%) while for the carbonyl series catalysts, unsaturated hydrocarbons (∼82%).

From the composition of the HDS reaction products some information on the reaction mechanism can be inferred. The presence of butadiene proves that the reaction involves direct hydrogenolysis of thiophene. The presence of butane suggests the involvement of tetrahydrothiophene (THT) as an intermediate. According to Kuo and Tatarchuk [10,11] the latter mechanism is favored in the presence of bulk RuS_2. Indeed, the Ru/MgF_2 preparation obtained from ruthenium chloride and activated in the 50% H_2S/He atmosphere, for which the main reaction product was butane, was characterised by a large content of RuS_2, which was confirmed by the TPR results shown in Fig. 4. A characteristic feature of TPR curves recorded for the preparations activated in the 50% H_2S/He atmosphere, in particular for the chloride preparation, is a broad and very intense signal in the range 500–700°C assigned to the reduction of RuS_2. High intensity of the TPR peaks for the catalysts sulfided in the H_2S/He atmosphere proves a high degree of ruthenium sulfiding. This phenomenon was also observed by De Los Reyes et al. [12] for Ru/Al_2O_3 catalysts. The preparations sulfided in the hydrogen-free atmosphere (15% H_2S/N_2) were characterized by a twice higher S/Ru ratio than those activated in the 15% H_2S/H_2 atmosphere. Similar results for the catalysts Ru/Y-type zeolite were reported in Ref. [13].

The TPR spectra of the preparations sulfided in the H_2S/H_2 atmosphere (1SH and 5SH), similarly as those of the preparations activated in a H_2S/He mixture, revealed signals assigned to RuS_2 but with much lower intensity. A higher concentration of H_2S (50% H_2S/H_2) led to the appearance of an additional signal in the range 350–500°C, assigned to nonstoichiometric sulfur species [14].

4. Summary

Ruthenium supported on MgF_2 has been found to be an excellent catalyst of thiophene hydrodesulfurization, much better than the commercially available $CoMo/Al_2O_3$ catalyst. The studies have shown that the preparations obtained on the basis of $RuCl_3{\cdot}nH_2O$ have much better catalytic properties than those based on $Ru_3(CO)_{12}$. A very important factor determining the activity as well as selectivity of the preparations has been the composition of the sulfiding atmosphere. Also a higher concentration of H_2S has been established to improve the properties of the catalysts. The sulfidation in a H_2S/He mixture has significantly increased the catalysts activity, however, at the expense of their selectivity (a large amount of saturated hydrocarbons formed). The catalysts activated in a H_2S/H_2 mixture show a lower activity, but only a small amount of saturated hydrocarbons is detected in the reaction products. It seems that RuS_2seems to be responsible for the high activity of the catalysts sulfided in a mixture of H_2S/He.

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