Influence of activation and the HDS reaction on the structure of magnesium fluoride-supported Ru catalysts derived from ruthenium chloride hydrate

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The effect of activation conditions and the hydrodesulfurization (HDS) process on the structure of Ru/MgF_2 prepared from $RuCl_3{\cdot}nH_2O$ precursor catalysts was studied. During the first 6–7 h of the HDS process significant differences in activities were detected between samples pretreated in 50% H_2S/H_2 and in 50% H_2S/He. During this transient time, the Ru/MgF_2 catalyst pretreated in 50% H_2S/H_2 increased in activity while the activity of that pretreated in H_2S/He decreased. XRD, TPR and quantitative analysis of sulfur content revealed that directly after activation in H_2S/He crystalline ruthenium sulfide is the main component of the surface, whereas after activation in H_2S/H_2 both RuS_2 and metallic Ru are present on the surface. These differences decrease during the thiophene HDS process. Despite the different pretreatment conditions, the composition of the surface tends to "equilibrate", which results in similar activity after prolonged reaction time.

KEY WORDS: ruthenium sulfide; thiophene hydrodesulfurization; hydrodesulfurization activity; hydrotreating; magnesium fluoride.

1. Introduction

Hydrotreating catalysis refers to a number of catalytic processes that serve to hydrogenate different petroleum streams and remove heteroatoms (such as N, S and O) from organic compounds. The primary purpose of hydrodesulfurization (HDS) is to remove organic sulfur compounds from a feedstock prior its use as various fuels. Current commercial HDS catalysts contain a mixture of either nickel and molybdenum or cobalt and molybdenum as active-phase metals. The active phase is typically supported on a high-surface-area alumina. These catalysts are very efficient for reaching a desired level of desulfurization. Today, however, as petroleum feedstock supplies dwindle, the processing of "more dirty" feeds containing larger amounts of sulfur is increasing and, as a result, a new generation of transition metal sulfide-based catalysts are needed with higher activities, greater selectivities and better resistance to poisons. Pecoraro and Chianelli [1] reported that an unsupported ruthenium sulfide catalyst was 13 times more active in HDS of dibenzothiophene than molybdenum sulfide. Others have also identified ruthenium sulfide catalyst to be the most active HDS catalyst among the transition metal sulfides and with very high activity in many other hydrotreating reactions [2–5]. The properties of the RuS_2 catalyst are significantly affected by the support used. For example, RuS_2 is highly active in HDS when supported on carbon [6], while supported on Al_2O_3 [7] it has lower activity. Our earlier studies [8] have shown that the application of magnesium fluoride as a support for RuS_2 produces very active HDS catalysts. The catalysts prepared using $RuCl_3{\cdot}nH_2O$ as active-phase precursor were found to be more active than those obtained using $Ru_3(CO)_{12}$ [9].

In this study we present the synthesis and HDS properties of RuS_2 catalysts supported on MgF_2 derived from $RuCl_3{\cdot}nH_2O$ precursor. Thiophene is used as a model compound for the HDS reaction. The effect of the pretreatment on the structure of Ru/MgF_2 catalysts before and after exposure to reaction conditions was examined. Comparisons between the fresh and spent catalyst structure are necessary since the sulfide active phase is formed during the reaction.

2. Experimental

2.1. *Preparation of catalysts*

Magnesium fluoride was obtained by adding small portions of $MgCO_3{\cdot}3H_2O$ to an aqueous solution of hydrofluoric acid until neutralization, and acidifying it by introducing a few additional drops of the acid. The precipitate was then aged at room temperature for a few days under stirring, followed by calcination in 673 K. After calcination, MgF_2 was ground to obtain 0.2–0.5 mm mesh

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size. The support obtained in this way had a surface area of $38\,m^2/g$ and a well-developed pore structure. Some of the properties of magnesium fluoride, such as its hardness, resistance to calcination in oxygen and well-developed porous structure, make it a prospective catalytic support for transition metal oxides or metals [10].

Ruthenium catalysts were prepared by impregnation of the support with an alcoholic (methanol) solution of ruthenium chloride ($RuCl_3 \cdot nH_2O$). All the prepared catalysts contained 2.0 wt% ruthenium.

Two different *in situ* presulfidation procedures were applied: (i) 50% H_2S/H_2, denoted 5SH; and (ii) 50% H_2S/He, denoted 5SHe.

All procedures were performed at 623 K for 2 h before reaction. The composition of the pretreating gases was chosen based on the results of earlier experiments [9].

2.2. Surface area and pore volume measurements

The low-temperature adsorption of nitrogen was performed using a Micromeritics ASAP 2010 instrument. Specific surface area was determined using the BET method and pore size distribution was established on the basis of the BJH method, using a desorption isotherm.

2.3. HDS activity

Thiophene was introduced into the reactor by bubbling a stream of pure hydrogen at a rate of $30\,cm^3/min$ (STP) through a thiophene saturator, maintained in an ice bath at 273 K. The reaction was conducted using a single-pass microreactor at atmospheric pressure and at 673 K. The concentration of thiophene in the feed stream was maintained at approximately 6.0×10^{-5}–$8.0 \times 10^{-5}\,mmol/cm^3$ by adjusting the H_2 flow rate through the saturator. The gas mixtures were analyzed by on-line gas chromatography. A 50 mg sample of the catalyst with a grain size of 0.5–0.25 mm was used for the tests.

The HDS rate of thiophene (per min) is given by:

$$\mathrm{HDS}_{\mathrm{rate}} = \frac{VC_{\mathrm{T}}\chi}{n}$$

where V is the total flow rate of the feed (cm^3/min), C_T the concentration of thiophene in the feed ($mmol/cm^3$), χ the fractional conversion and n the amount of ruthenium in the sample (mmol). The main products of the reaction were butane and butenes [9].

The catalysts after reaction were denoted 5SH-R and 5SHe-R.

2.4. TPR experiments

Temperature-programmed reduction (TPR) was performed using a Micromeritics ChemiSorb 2705 instrument. A 10% H_2 with the balance Ar mixture at a flow rate of $30\,cm^3/min$ and temperature ramp of 10 K/min was used for the TPR experiments. The gas-phase reduction products were cold-trapped at ~200 K (n-propanol/solid CO_2 mixture). All TPR profiles presented were recalculated for equal weight of the sample.

2.5. XRD experiments

X-ray diffraction (XRD) studies were performed with a Philips PW1050 instrument equipped with a CuKα source and Ni filter in the range $2\theta = 3$–$152°$.

2.6. Sulfur content

The sulfur concentration was determined by the ICP-AES method using the analytical line at 181.978 nm.

3. Results and discussion

3.1. HDS activity

The HDS activity of presulfided catalysts was tested at 673 K for 8 h using thiophene as a model compound. Figure 1(a) presents the effect of sulfidation conditions on the activity in the HDS process. The catalyst pretreated in 50% H_2S/H_2 (5SH) revealed a steady increase of activity with time on stream, reaching a plateau after approximately 6 h of reaction. On the contrary, the catalyst pretreated in 50% H_2S/He (5SHe) despite a high initial activity systematically deactivated, finally reaching a steady state after 7 h of reaction at a level slightly lower than that of the 5SH sample. Magnesium fluoride after activation under the latter conditions did not reveal any activity in the HDS reaction. Figure 1(b) compares the activities of ruthenium catalysts supported on magnesium fluoride and other, traditionally used materials (alumina and silica). The activity of the samples supported on MgF_2 was found to be much higher than that of the other two systems. The activity of the Ru/Al_2O_3 catalyst was ~50% lower, while the Ru/SiO_2 sample was drastically less active.

3.2. Surface area and pore volume of the Ru/MgF_2 catalysts

Figure 2(a) presents the adsorption isotherm of the MgF_2 support. According to the IUPAC classification [11], they are type IV isotherms and the hysteresis loops are H1 type. For both catalysts, 5SH and 5SHe, the adsorption isotherms (not presented in the figure) were almost the same as those observed for the support, which was also reflected in the unchanged surface area of the samples after impregnation with active phase. Figure 2(b) shows the pore volume distribution as a function of pore radius. Magnesium fluoride is characterized by the pore size changing within a narrow range, with a maximum radius of 95 Å. The H1 type of hysteresis loop indicates the narrow necks of the pores. The total pore

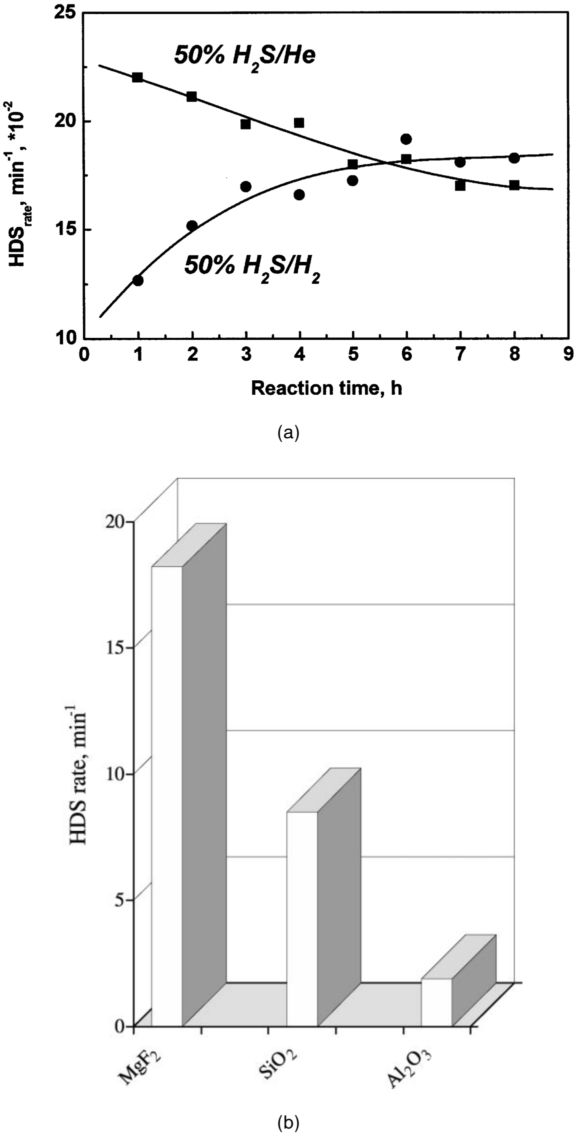

Figure 1. (a) Effect of presulfiding by H_2S on the HDS of thiophene over Ru/MgF_2 catalysts at 673 K. (b) HDS activity of ruthenium catalysts supported on different support materials. Catalysts were activated in 50% H_2S/He. Conversion presented after 6 h in stream.

volume and average pore radius of 5SH and 5SHe before reaction are somewhat smaller compared to MgF_2 (figure 2(b), table 1). This indicates the location of sulfide on the inner walls of mesopores. After the HDS reaction the surface area of the 5SHe-R catalyst does not change. On the other hand, the 5SH-R sample reveals a decrease in surface area which is correlated with the decrease of average pore size.

3.3. Sulfur content

Table 2 presents the results of the sulfur analysis of the catalysts pretreated in H_2S. Activation under 5SHe conditions results in significant sulfidation—the sulfur content is much higher than the stoichiometric ratio S/Ru = 2. After activation under 5SH conditions a much lower S/Ru ratio is obtained (1.2). Analysis of spent catalysts indicated a 50–60% decrease in sulfur content for both types of pretreated catalysts compared to the fresh samples. This may result from the gradual

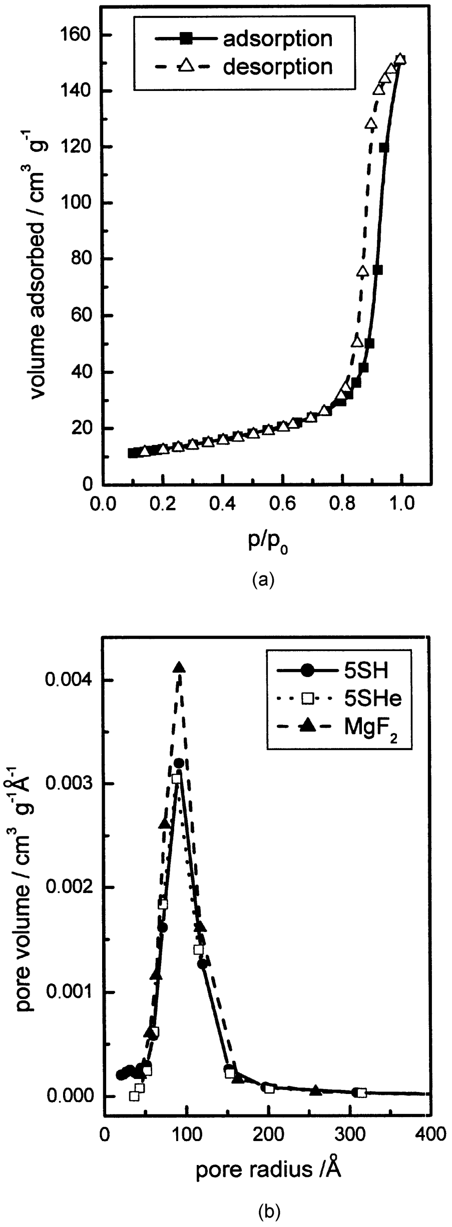

Figure 2. (a) Nitrogen adsorption–desorption isotherms on MgF_2 and (b) pore distribution on MgF_2 and on 5SH and 5SHe catalysts.

Table 1

BET surface area, total pore volume and average pore radius of MgF_2 and the Ru/MgF_2 catalysts

Sample	Surface area (m^2/g)	Total pore volume (m^3/g)	Average pore radius (Å)
MgF_2	38	0.22	95
5SH	39	0.19	86
5SHe	38	0.18	80
5SH-R	30	0.19	118
5SHe-R	38	0.19	99

Table 2
Sulfur content in the Ru/MgF_2 catalysts after sulfidation and after reaction

Activation	S (wt%)	S/Ru mole ratio
5SH	1.01	1.2
5SH-R	0.41	0.5
5SHe	3.55	4.1
5SHe-R	1.65	1.9

desulfurization of the catalysts by hydrogen present in the stream.

3.4. *XRD experiments*

Figure 3 presents XRD patterns of the samples after activation under different conditions as well as the spent catalysts (after 8 h of reaction). The intense signal at 32° detected for the 5SHe sample indicates the presence of RuS_2 phase [12,13]. The same signal was not detected for the 5SH sample; however, the presence of amorphous RuS_2 cannot be excluded. At the same time metallic ruthenium phase was detected, based on the appearance of the peak at 38.3° and distinct baseline elevation at around 42° [13,14].

After the HDS process the intense signal originating from crystalline RuS_2 decreases significantly for the 5SHe-R sample, which indicates partial desulfurization of the surface. This is confirmed by the sulfur content analysis. On the other hand, a RuS_2 peak appears for the spent 5SH-R sample simultaneously with the disappearance of the metallic ruthenium peak.

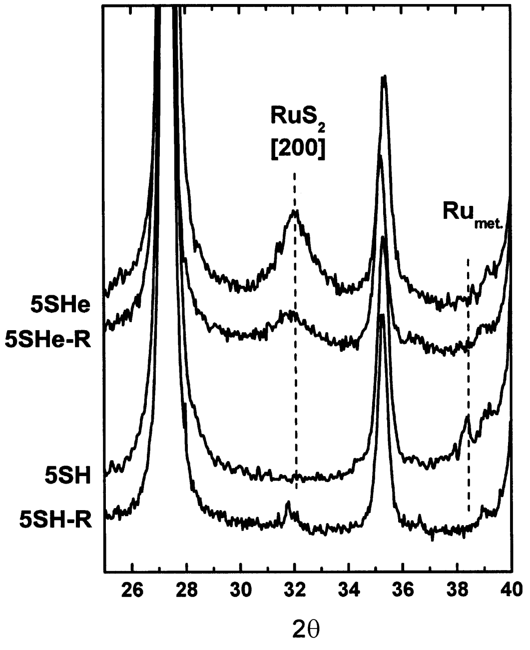

Figure 3. XRD spectra of Ru/MgF_2 catalysts presulfided under various conditions and after reaction.

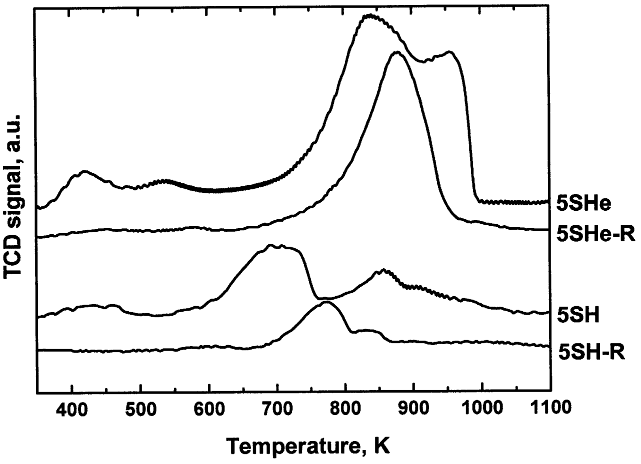

Figure 4. TPR patterns of presulfided Ru/MgF_2 catalysts before and after the HDS reaction.

3.5. *TPR experiments*

TPR experiments were performed for both pretreated and spent samples (figure 4). A characteristic feature of the TPR curves recorded for the preparations activated with 50% H_2S/He condition is a broad and very intense peak in the range 700–950 K assigned to the reduction of RuS_2. The high intensity of the TPR peaks for the catalysts sulfided in the H_2S/He atmosphere indicates a high degree of ruthenium sulfidation. Such an effect was also observed by De Los Reyes *et al.* [15] for Ru/Al_2O_3 catalysts. The preparations sulfided in a hydrogen-free atmosphere (15% H_2S/N_2) were characterized by an S/Ru ratio two times higher than those activated in a 15% H_2S/H_2 atmosphere. Similar results were reported for Ru/Y-type zeolite catalysts [16].

The TPR spectra of the samples sulfided in the H_2S/H_2 atmosphere, similar to those activated in the H_2S/He mixture, revealed signals assigned to RuS_2, although much less intense. In the case of these samples, a peak in the range 400–700 K also appeared, assigned to nonstoichiometric sulfur species [17].

In the case of the spent catalysts, the areas under the peaks related to RuS_2 reduction in the TPR profile decrease twofold for both pretreatment conditions. Such a decrease of the peak area results either from the decrease of RuS_2 content (5SHe) or removal of nonstoichiometric sulfur of the catalyst surface (5SH).

4. Summary

We have found that the pretreatment conditions have a significant effect on the structure and transient behavior of Ru/MgF_2 catalysts in the HDS process. The initial low activity of the 5SH samples compared to the activity recorded for the 5SHe catalyst was related to the small amount of RuS_2 formed (as shown by TPR experiments) as well as its amorphous structure. The presence of hydrogen in the pretreatment gas resulted in the reduction of ruthenium to the metallic state. This form of ruthenium is more difficult to sulfide. The presence of metallic ruthenium after sulfidation in the presence of molecular hydrogen was also reported by others [15,18].

During time on stream in the HDS reaction the 5SH catalyst gradually increased in activity and finally reached a steady state after 7 h of reaction. Since the XRD analysis of spent catalyst revealed the presence of crystalline RuS_2, we attribute the increase of activity to the formation of crystalline ruthenium sulfide during the reaction.

The 5SHe catalyst reveals very high initial activity. This catalyst contained a large amount of sulfur directly after the activation process (three times higher than 5SH), mainly in the form of RuS_2. However, during the transient stage of the reaction the activity of this catalyst decreased gradually and stabilized to a similar level to the 5SH sample. Analysis of spent catalysts revealed a distinct decrease of the amount of sulfur as well as RuS_2 compared to the fresh sample.

Based on the results obtained it is evident that the formation of an active sulfide phase occurs during the catalytic process and crystalline RuS_2 is most probably the active phase. This is why different pretreated samples have eventually a similar activity after reaching a steady state.

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