

# Synergetic effects of Pt and Ru added to Mo/Al<sub>2</sub>O<sub>3</sub> sulfide catalyst in simultaneous hydrodesulfurization of thiophene and hydrogenation of cyclohexene

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## Abstract

The effect of Pt and Ru (~0.6%) added to Mo/Al<sub>2</sub>O<sub>3</sub> sulfide catalyst on the simultaneous hydrodesulfurization (HDS) of thiophene and hydrogenation (HYD) of cyclohexene was studied. The addition of Pt and Ru significantly increased the HDS and HYD activities of the Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. The addition of Pt led to a weaker synergy in HDS, which was almost independent of the reaction temperature. The addition of Ru led to much stronger synergy in both reactions, which increased at higher reaction temperatures. The synergy in HDS over Ru-promoted catalyst occurred between 240 and 320 °C, approaching values of up to 6. The strong synergy in HYD (up to 4) appeared only at temperatures 300–330 °C and was accompanied by a more than twofold increase in the apparent activation energy. As the most probable explanation, a change in the quality of the sites participating in HYD was proposed. HYD mainly proceeds on separate Ru and Mo sulfides at lower temperatures and while on mixed Ru–Mo–S sites at above 300 °C. This change is ascribed to a partial release of Ru–Mo–S sites by desorption of thiophene or H<sub>2</sub>S at the higher temperatures, which compete for the adsorption and reaction with HYD.

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## 1. Introduction

Transition-metal sulfides of the second and third rows possess high activity in reactions such as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrogenation (HYD). It was demonstrated more than two decades ago that Ru sulfide is the most active in the HDS of dibenzothiophene [1]. Later, Ru sulfide, unsupported, deposited on different supports, or in combination with the Mo sulfide phase, has frequently been studied from the point of view of hydrorefining as a potential promoter [2–6]. Such an interest can be ascribed to its favorably high activity, a relatively good knowledge of its chemistry, and its lower price compared with other noble metals. Pt sulfide was another often studied sulfided noble metal, again supported as a sin-

gle phase [7,8] or as possible dopant for the conventional NiW/Al<sub>2</sub>O<sub>3</sub> catalyst [9].

Some transition-metal sulfides, in addition to their good HDS activity, also show a high capacity for hydrogenation. Hydrogenation is key reaction in hydrorefining because it is involved in the reaction scheme of many compounds. A relation between HDS and HYD catalyst functions is an important issue in connection with the deep HDS of FCC naphtha, where selective sulfur removal without the loss of olefinic components is desirable in order to keep the high octane number of gasoline [10,11]. On the other hand, the higher hydrogenation activity of the catalysts could be valuable in the production of diesel fuel, in which refractory sulfur compounds undergo direct HDS with difficulty and need to be hydrogenated before C–S bond cleavage [8–10].

It seems that the use of catalysts based on noble metals as such is practically excluded because of their exceptional price. Combination with a suitable conventional phase

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could mean a reasonable solution, provided that the resulting activity is much higher than that achieved with the single components, that is, when a significant synergetic effect takes place. Data from the literature show that modification of the conventional Mo or CoMo/Al<sub>2</sub>O<sub>3</sub> systems by small amounts of noble metals around 0.5 wt% led in some cases to synergetic effects in HDS and HYD [5,12]. Recently, the significant improvement of the activity of the HDS of benzothiophene and HYD of naphthalene was achieved by the deposition of Pt, Pd, and Ru on the presulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst [12].

In recent years we have systematically studied the catalytic properties of noble metal sulfides and the effect of their addition to a Mo/Al<sub>2</sub>O<sub>3</sub> catalyst, first with the Ir sulfide [13,14] and then with Pt, Pd, Ru, and Rh sulfides [15], on the activity in the simultaneous HDS of thiophene and HDN of pyridine. In accordance with the work of Meriño et al. [12], we showed that the synergetic effect of noble metals can be substantially strengthened by their deposition on the presulfided Mo/Al<sub>2</sub>O<sub>3</sub> instead of the oxidic catalyst [14,15]. This was ascribed to the higher dispersion of the Ir sulfide phase achieved on the sulfided Mo/Al<sub>2</sub>O<sub>3</sub> and to a possible protection of the Mo phase against partial reduction to MoO<sub>2</sub> in the presence of Ir [14]. In our preceding paper we showed that the addition of Rh, Ru, and Pd had the most significant effect on the HDS of thiophene, and the addition of Pt influenced more the HDN of pyridine. This led to the strong synergy in HDS over the Ru–Mo(S) system and in HDN over the Pt–Mo(S); the latter was probably due to the high capacity of Pt to hydrogenate pyridine [15]. This difference in catalytic behavior of the two groups of noble metals was in line with the experimental results obtained by other authors earlier and was explained by periodic trends observed in different hydrotreating reactions [1].

The aim of this work was to determine whether synergetic effect of noble metals added to the presulfided Mo/Al<sub>2</sub>O<sub>3</sub> also occurs in the hydrogenation reaction and compare it with the synergy achieved in the HDS. The noble metals studied were Pt and Ru, which were selected because of their high hydrogenation and HDS catalytic efficiency. The noble-metal-modified catalysts contained 9 wt% Mo and around 0.6 wt% Pt or Ru. Hydrogenation of cyclic olefins was chosen as a test reaction and cyclohexene as a model compound. The simultaneous HDS/HYD reaction was performed at the low sulfur level of 200 ppm in the feed. The catalytic properties of the samples promoted by Pt and Ru were compared with those of the conventional CoMo and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts.

## 2. Experimental

The preparation and characterization of the catalysts have been described in detail elsewhere [15]. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (CS-331, Süd-Chemie AG) and sulfided Mo/Al<sub>2</sub>O<sub>3</sub>, both of 0.16–0.32 mm particle size, were impregnated by solutions of Pt

Table 1  
Composition and surface area of catalysts

Catalyst	Composition (wt%)			Surface area (m <sup>2</sup> /g)
	Noble metal	Mo	S	
Mo/Al <sub>2</sub> O <sub>3</sub>	–	9.0	5.9	204
Pt/Al <sub>2</sub> O <sub>3</sub>	0.30	–	1.2	242
Ru/Al <sub>2</sub> O <sub>3</sub>	0.34	–	1.7	249
Pt–Mo(S)/Al <sub>2</sub> O <sub>3</sub>	0.52	9.0	7.2	221
Ru–Mo(S)/Al <sub>2</sub> O <sub>3</sub>	0.63	9.0	7.3	215

or Ru acetylacetonates in ethanol. The dried catalyst precursors were sulfided *ex situ* with 10% H<sub>2</sub>S in H<sub>2</sub> at 400 °C for 1 h. The catalysts were cooled to room temperature in H<sub>2</sub> and stored under argon. The promoted catalysts are further denoted by the symbols Pt–Mo(S) and Ru–Mo(S), where S means the preparation from the sulfided Mo/Al<sub>2</sub>O<sub>3</sub>. The actual contents of Mo, noble metals and sulfur in the catalysts, were determined with the inductively coupled plasma method (ICP). The surface areas of the sulfided catalysts were evaluated on a Flowsorb III Instrument (Micromeritics). The composition and surface areas of the prepared catalysts are listed in Table 1. The content of Mo was 9 wt%, and the amount of noble metals was between 0.3 and 0.6 wt%. The content of sulfur in the freshly sulfided catalysts corresponded to a S/Mo ratio of 2.0 for the Mo/Al<sub>2</sub>O<sub>3</sub> and to an average value of 2.3 for the promoted catalysts, indicating the complete sulfidation of the MoS<sub>2</sub> phase. The nominal surface area of the starting  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 255 m<sup>2</sup>/g. The deposition of the small amounts of noble metals had practically no effect on this value. The smaller decrease in the surface area to about 204–221 m<sup>2</sup>/g in the case of Mo/Al<sub>2</sub>O<sub>3</sub> and both promoted samples can be ascribed to the higher amount of the deposited Mo phase. The pulse H<sub>2</sub> adsorption on the catalysts containing noble metals was performed at 22 °C as described elsewhere [13]. The H<sub>2</sub> uptake on the Pt/Al<sub>2</sub>O<sub>3</sub>, Ru/Al<sub>2</sub>O<sub>3</sub>, and both promoted Pt–Mo(S) and Ru–Mo(S) catalysts was suppressed to zero after sulfidation, which shows that the noble metals were completely covered by sulfur and did not possess free Pt (or Ru) metallic sites. Two commercial catalysts, CoMo/Al<sub>2</sub>O<sub>3</sub> (Shell 344, 2.4 wt% Co, 9.2 wt% Mo) and NiMo/Al<sub>2</sub>O<sub>3</sub> (Shell 324, 2.8 wt% Ni, 11.8 wt% Mo), were included in this study for comparison. The surface areas of CoMo and NiMo catalysts were 178 and 157 m<sup>2</sup>/g, respectively.

The activity of the catalysts in simultaneous HDS of thiophene (TH) and HYD of cyclohexene (CHE) was evaluated in an integral flow microreactor with fixed bed of the catalyst at temperatures of 230–330 °C and an overall pressure of 2 MPa. The catalyst was placed in a stainless-steel reactor tube (i.d. 2 mm) between two layers of glass wool and was sulfided *in situ* with 10% H<sub>2</sub>S in H<sub>2</sub> (0.05 mol/h) at atmospheric pressure. The temperature was gradually raised to 400 °C at a rate of 6 °C/min and held at 400 °C for 1 h. Then the H<sub>2</sub>S was switched off and the catalyst was cooled to reaction temperature in a flow of H<sub>2</sub>. Then H<sub>2</sub> was replaced by means of a six-port valve with the feed containing

equimolar amounts of TH and CHE (200 ppm of each) in  $H_2$  (0.4 mol/h) at an overall pressure of 20 bar. The feed was generated in a pressure flow evaporator filled with a mixture of liquid reactants. Their concentrations in the gas phase were adjusted, in addition to the proper composition of the liquid, by the ratio of  $H_2$  flowing through the evaporator above the liquid and via the bypass regulated by a fine needle valve. The  $H_2$  flow and pressure in the reactor system were stabilized with a mass flow controller (Sierra Instruments, Inc.) and a back-pressure regulator (Tescom Corp.), respectively. The on-line analyses of the feed and reaction mixture were alternatively performed by an automatically operated sampling valve (VICI AG). The samples were taken every 15 min, and the analyses proceeded isothermally at 50 °C on a 4890D gas chromatograph (Agilent) equipped with a 30-m capillary DB-5 column (J&W Scientific) and a flame ionization detector. The composition of the reaction mixture was expressed by the conversions  $x_i = 1 - n_i/n_i^0$ , where  $i$  is TH or CHE, and  $x_j = n_j/n_i^0$ , where  $j$  is butane (BU) or cyclohexane (CA);  $n$  and  $n^0$  are the numbers of moles in the reactor effluent and the feed, respectively.

The steady state was usually achieved after 2–3 h on stream. The majority of  $x_{i,j}$  varied in the range 0.25–0.80. The space time  $W/F_i$  was changed by the amount of the catalyst  $W$  ( $5\text{--}70 \times 10^{-6}$  kg) while the flow rates  $F_i$  of TH and CHE were kept constant (each  $8 \times 10^{-5}$  mol<sub>*i*</sub>/h). Samples, differing greatly in the HDS and HYD activities, were tested several times with different catalyst amounts. This was necessary for the evaluation of the activity in a broad range of reaction temperatures. Blank tests with the empty reactor gave the values  $x_{TH} = x_{C_4} < 0.03$  and  $x_{CHE} = x_{CA} < 0.01$  for temperatures of 300–330 °C and 20 bar, showing that the effect of the reactor material on both reactions was small. The values  $x_{i,j}$  evaluated during catalytic tests were corrected by the values given above. At reaction temperatures of 280 °C and less, the contribution of the reactor material was almost zero and was neglected. Both reactions were described by pseudo-first-order rate constants for thiophene HDS ( $k_{TH}$ ) and cyclohexene HYD ( $k_{CHE}$ ). They were calculated as follows and expressed in mol<sub>*i*</sub>/(h kg<sub>cat</sub>):

$$k_i = -(F_i/W) \ln(1 - x_i). \quad (1)$$

The selectivity of butane formation during HDS was defined by  $100 n_{BU} / \sum n_{C_4}$ , where  $\sum n_{C_4}$  is the overall number of the moles of  $C_4$  hydrocarbons. The HDS/HYD selectivity was defined by the ratio of the rate constants  $k_{TH}/k_{CHE}$ .

### 3. Results and discussion

#### 3.1. Model reactions

The activity of the majority of the catalysts was tested in the range of reaction temperatures of 250–300 °C. The preliminary experiments showed that some catalysts could not

practically be tested at the higher or lower temperatures, because their activity was too high (HDS over CoMo, NiMo) or too low (HDS over Pt/Al<sub>2</sub>O<sub>3</sub>). However, all of the catalysts could be compared at the temperature of 280 °C. The Ru-based catalysts were studied in the broader range of 230–330 °C, because of the unusual activity feature of the Ru–Mo(S) sample. The activity of all of the catalysts was stable during catalytic tests. The Ru–Mo(S) catalyst did not display any observable loss of its activity after 13 h on stream. This agrees with our earlier experience obtained with these catalysts in the simultaneous HDS/HDN [15].

Tetrahydrothiophene as the intermediate of HDS of thiophene was present in the reaction products only in small amounts of 1–2% over the majority of the catalysts. Higher amounts (3–5%) were found over the monometallic Mo and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts at reaction temperatures of 280 °C and less. The main reaction products of HDS were H<sub>2</sub>S and C<sub>4</sub> hydrocarbons (C<sub>4</sub>), with butane (BU) and 2-butenes as major components. The HDS followed the first-order reaction with respect to thiophene, in agreement with our earlier results.

Cyclohexene was hydrogenated to cyclohexane over all catalysts without the formation of other products. This shows that isomerization or splitting does not occur on the alumina-supported noble metal systems, as on alumina-supported NiMo catalysts [16]. The order of the reaction with respect to cyclohexene was mostly assumed in the literature to be 1 [6,17] or was found experimentally to be between 0 and 1 [16]. In the present work, the fit of experimental data on the HYD of cyclohexene over the Mo/Al<sub>2</sub>O<sub>3</sub> and RuMo(S) catalysts is shown in Fig. 1, where  $-\ln(1 - x_{CHE})$  is plotted versus  $W/F$ . The points corresponding to the Ru–Mo(S) catalyst gave a straight line, confirming first-order behavior. The fit of the data obtained with the Mo/Al<sub>2</sub>O<sub>3</sub> catalyst was a little worse, suggesting that some deviation from the first-order behavior could not be excluded. Nevertheless, to describe both simultaneous reactions in the same simple way, we decided to use the first-order description for the HYD of cyclohexene.

#### 3.2. Activity and HDS/HYD selectivity

Table 2 summarizes the activity and HDS/HYD selectivity of all of the catalysts evaluated at a reaction temperature of 280 °C. The Mo/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited almost

Table 2  
Activity and HDS/HYD selectivity of catalysts in simultaneous HDS of thiophene and HYD of cyclohexene at 280 °C and 2 MPa

Catalyst	$k_{TH}$ (mol/(h kg <sub>cat</sub> ))	$k_{CHE}$ (mol/(h kg <sub>cat</sub> ))	$k_{TH}/k_{CHE}$
Mo/Al <sub>2</sub> O <sub>3</sub>	3.0	2.5	1.20
Pt/Al <sub>2</sub> O <sub>3</sub>	0.24	14.2	0.02
Ru/Al <sub>2</sub> O <sub>3</sub>	0.41	3.0	0.14
Pt–Mo(S)/Al <sub>2</sub> O <sub>3</sub>	7.9	9.7	0.81
Ru–Mo(S)/Al <sub>2</sub> O <sub>3</sub>	9.4	8.6	1.09
CoMo/Al <sub>2</sub> O <sub>3</sub>	26.9	7.7	3.49
NiMo/Al <sub>2</sub> O <sub>3</sub>	48.4	46.9	1.03

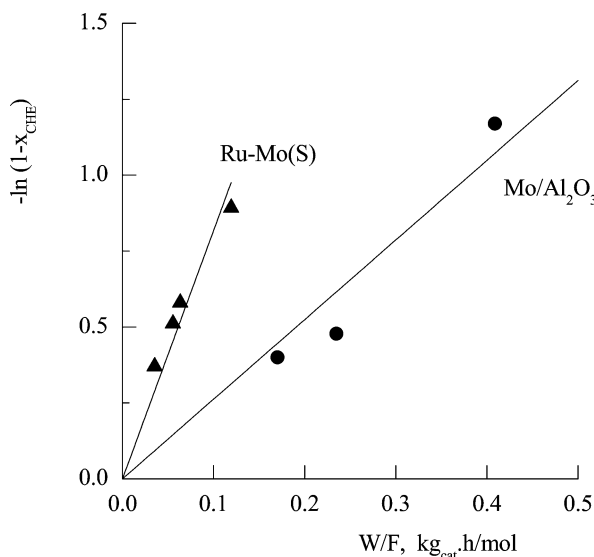


Fig. 1. Plot of  $-\ln(1-x_{\text{CHE}})$  versus  $W/F$  for HYD of cyclohexene at 280 °C over Ru–Mo(S) (▲) and Mo/Al<sub>2</sub>O<sub>3</sub> (●).

the same HDS and HYD activities. The monometallic Pt and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts generally showed much lower HDS and higher HYD activity compared with the Mo/Al<sub>2</sub>O<sub>3</sub>. Pt/Al<sub>2</sub>O<sub>3</sub> showed the highest HYD by far and, at the same time, the lowest HDS. A much higher HYD activity of the Pt/Al<sub>2</sub>O<sub>3</sub> in comparison with the Ru/Al<sub>2</sub>O<sub>3</sub> was previously observed in hydrogenation reactions of different aromatic compounds [18]. This result observed by us in the reaction of cyclohexene therefore agrees well with this trend.

The deposition of about half a percent of Pt and Ru onto the sulfided Mo/Al<sub>2</sub>O<sub>3</sub> led to an improvement of the activity by factors of 3–4. In the case of HDS, the activities of both bimetallic systems highly exceeded the activities of their single components. This also holds for the HYD over the Ru–Mo(S) system. However, the HYD activity of the Pt–Mo(S) combination was between the activities of the Pt/Al<sub>2</sub>O<sub>3</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. The HDS activities of the noble-metal-promoted catalysts did not achieve those of the conventional CoMo and NiMo catalysts. In HYD, they were slightly above the activity of the CoMo catalyst and below the activity of the NiMo catalyst. The activity differences between the two groups of promoted catalysts can probably be explained by much higher amounts of Co and Ni promoters than noble metals.

The data in Table 2 show that the HDS/HYD selectivity of the catalysts greatly depends on the kind of active phase. The CoMo catalyst showed markedly the highest selectivity value in favor of HDS. This result corresponds well to recent observations of other authors in the case of reactions of thiophene and cyclohexene [5,19] or 1-hexene [3], or reactions of benzothiophene and naphthalene [12,20] and shows that Co in combination with Mo has a much greater effect on HDS than on HYD. On the other hand, the monometallic noble metal sulfide catalysts represented the opposite extreme because their HYD activity strongly exceeded the HDS ac-

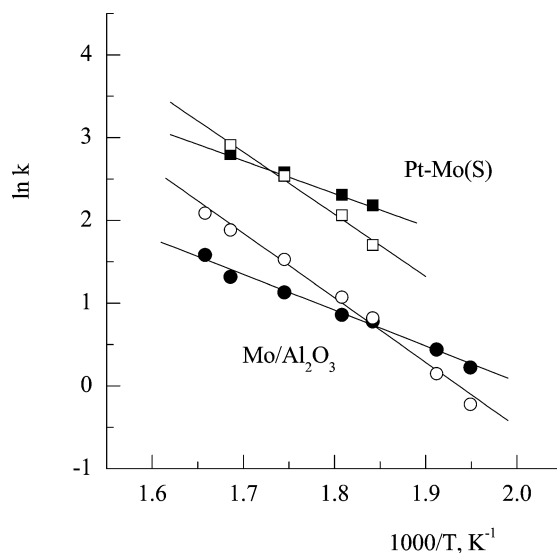


Fig. 2. Dependence of  $\ln k$  versus  $1/T$  for HDS of thiophene and HYD of cyclohexene over Pt–Mo(S) (□,■) and Mo/Al<sub>2</sub>O<sub>3</sub> (○,●). HDS (open points), HYD (full points).

tivity. In general, the data in Table 2 show that the addition of small amounts of Ru and Pt decreased the HDS/HYD selectivity in comparison with Mo/Al<sub>2</sub>O<sub>3</sub>. This effect was smaller over the Ru–Mo(S) catalyst, in agreement with the fact that the Ru addition improves both HDS and HYD well [2,5]. The selectivity of the Pt–Mo(S) sample was substantially lower than the selectivity of the Ru–Mo(S), which we explain by the much higher HYD activity of the Pt/Al<sub>2</sub>O<sub>3</sub> compared with the Ru/Al<sub>2</sub>O<sub>3</sub>. Both catalysts promoted by noble metals therefore have enhanced hydrogenation efficiency, resulting in lower HDS/HYD selectivity. The selectivity of the Ru–Mo(S) was similar to that of the conventional NiMo catalyst.

### 3.3. Effect of reaction temperature on activity

Fig. 2 shows temperature dependences of the logarithms of the rate constants corresponding to HDS and HYD over the Mo/Al<sub>2</sub>O<sub>3</sub> and Pt–Mo(S) catalysts. A specific character of these dependences allows us to draw two conclusions. First, the slopes of the plots corresponding to HDS were substantially higher than those corresponding to HYD. This shows that the apparent activation energies of HDS ( $E_a^{\text{HDS}}$ ) were higher than the apparent activation energies of HYD ( $E_a^{\text{HYD}}$ ). The consequence of this is that the hydrogenation was prevailing at the lower reaction temperatures, and the HDS was predominant at the higher temperatures. Another interesting aspect is that the slopes corresponding to Pt–Mo(S) were almost the same as those for the Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. The  $E_a$  of both reactions therefore remained unchanged after the addition of Pt to the Mo/Al<sub>2</sub>O<sub>3</sub>.

Fig. 3 shows analogous dependences for the Mo/Al<sub>2</sub>O<sub>3</sub> and Ru–Mo(S) catalysts. The temperature dependence of  $\ln k_{\text{TH}}$  for the Ru–Mo(S) catalyst showed a good linearity over the whole range of the reaction temperatures, 230–



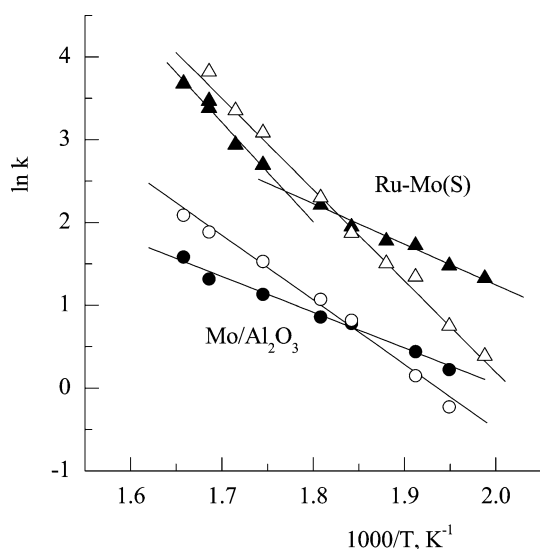


Fig. 3. Dependence of  $\ln k$  versus  $1/T$  for HDS of thiophene and HYD of cyclohexene over Ru–Mo(S) ( $\Delta$ ,  $\blacktriangle$ ) and Mo/Al<sub>2</sub>O<sub>3</sub> ( $\circ$ ,  $\bullet$ ). HDS (open points), HYD (full points).

330 °C. In contrast to this, the analogous plot of  $\ln k_{\text{CHE}}$  followed a trend that was almost parallel to that for Mo/Al<sub>2</sub>O<sub>3</sub> up to about 280 °C and then significantly deviated upward. The experimental points in the 300–330 °C range gave another linear fit with the substantially greater slope. Such a course clearly shows that  $E_a^{\text{HYD}}$  significantly changed at temperatures near 300 °C. This behavior is clearly unusual and evokes a question about its origin. Taking into account that hydrogenation reactions are exothermic, one can argue that the observed effect could be ascribed to catalyst overheating, leading to a much higher increase in HYD activity. However, we consider such a possibility improbable, for the following reasons. A sudden increase in the catalyst temperature should also have an impact on the simultaneously proceeding HDS, in a parallel increase in the HDS activity. However, such a change was not observed. Second, the values of the rate constants  $k_{\text{CHE}}$  over the Ru–Mo(S) catalyst at 300–330 °C were between 15 and 40 mol/(h kg<sub>cat</sub>), still lower than  $k_{\text{CHE}}$  for the more active NiMo catalyst (Table 2), which itself did not show any unusual activity features. Moreover, the feed contained only 200 ppm of cyclohexene, in addition to thiophene, diluted by H<sub>2</sub>. Such a composition rather supports a good transfer of the reaction heat from the catalyst instead of its accumulation. We therefore conclude that the effect observed on the Ru–Mo(S) catalyst cannot be ascribed to side thermal effects.

The values  $E_a^{\text{HDS}}$  and  $E_a^{\text{HYD}}$  evaluated from Arrhenius plots are summarized for all catalysts in Table 3. These data show that the  $E_a^{\text{HDS}}$  values were almost always higher than  $E_a^{\text{HYD}}$ , with the lone exception of the Ru–Mo(S) catalyst in the range of 300–330 °C. This result is in a fairly good agreement with the results obtained by other authors. The higher values of  $E_a^{\text{HDS}}$  for HDS of thiophene and lower  $E_a^{\text{HYD}}$  for HYD of 1-hexene were found over the CoMo/Al<sub>2</sub>O<sub>3</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts earlier [3]. Low values of 21–25 kJ/mol were also reported for the HYD of cyclohexene over monometallic Pt [21,22], which are close to the values for the sulfided Pt and Ru/Al<sub>2</sub>O<sub>3</sub> observed in the present work. On the other hand, the higher values of  $E_a^{\text{HYD}}$  around 157–193 kJ/mol were reported for the HYD of cyclohexene in the absence of thiophene over NiMo catalysts, performed at temperatures of 310–350 °C and 50 bar of pressure [16]. The values  $E_a^{\text{HDS}}$  in Table 3 evaluated by us for the conventional catalysts are well in the range of 65–114 kJ/mol reported in the literature [2,3,23–25].

The values  $E_a^{\text{HDS}}$  for the Mo/Al<sub>2</sub>O<sub>3</sub> and Pt–Mo(S) catalysts were found to be 65 and 63 kJ/mol, respectively, that is, within the limits of experimental error (Table 3). The same situation obviously occurred in the HYD of cyclohexene, where  $E_a^{\text{HYD}}$  values of 36 and 33 kJ/mol were found for Mo/Al<sub>2</sub>O<sub>3</sub> and Pt–Mo(S), respectively. Such an agreement clearly shows that the addition of Pt to Mo/Al<sub>2</sub>O<sub>3</sub> did not change the apparent activation energy of either reaction. On the contrary, the addition of Ru to Mo/Al<sub>2</sub>O<sub>3</sub> significantly changed  $E_a^{\text{HDS}}$ , which approached a value of 92 kJ/mol. The effect of Ru addition on HYD of cyclohexene performed at lower reaction temperatures was similar to the effect of Pt; the  $E_a^{\text{HYD}}$  was again practically the same as that for Mo/Al<sub>2</sub>O<sub>3</sub> (Table 3). A significant increase in  $E_a^{\text{HYD}}$  to 100 kJ/mol occurred when the reaction temperatures exceeded 300 °C. The value of 100 kJ/mol is highest among those evaluated for HYD in this work, but still within the limits found for the same reaction over the conventional NiMo catalysts used by us (67 kJ/mol) and other authors (157–193 kJ/mol) [16].

To the best of our knowledge, a similar change of the apparent activation energy of the HYD of cyclohexene over sulfide catalysts has not yet been reported in the literature. Changes in the apparent activation energy have recently been observed in HDS of thiophene over a conventional CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst performed at temperatures of 177–512 °C by Leliveld et al. [25]. An approximately twofold increase of the apparent activation energy of HDS at reaction

Table 3  
Apparent activation energies of HDS of thiophene and HYD of cyclohexene

Reaction	$E_a$ (kJ/mol)						
	Mo/Al <sub>2</sub> O <sub>3</sub>	Pt/Al <sub>2</sub> O <sub>3</sub>	Ru/Al <sub>2</sub> O <sub>3</sub>	Pt–Mo(S)/Al <sub>2</sub> O <sub>3</sub>	Ru–Mo(S)/Al <sub>2</sub> O <sub>3</sub>	CoMo/Al <sub>2</sub> O <sub>3</sub>	NiMo/Al <sub>2</sub> O <sub>3</sub>
HDS	65	44	72	63	92	76	108
HYD	36	16	17	33	41, <sup>a</sup> 100 <sup>b</sup>	53	67

<sup>a</sup> For temperature range 230–280 °C.

<sup>b</sup> For temperature range 300–330 °C.

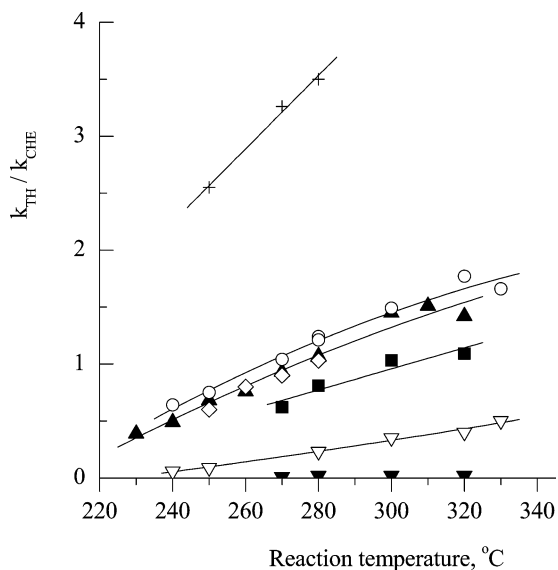


Fig. 4. Selectivity HDS/HYD as a function of reaction temperature. CoMo/Al<sub>2</sub>O<sub>3</sub> (+), Mo/Al<sub>2</sub>O<sub>3</sub> (O), NiMo/Al<sub>2</sub>O<sub>3</sub> (◇), Ru–Mo(S) (▲), Pt–Mo(S) (■), Ru/Al<sub>2</sub>O<sub>3</sub> (▽) and Pt/Al<sub>2</sub>O<sub>3</sub> (▼).

temperatures above 400 °C was explained by the participation of the second type of the active site. It was proposed that the sulfur vacancies on the Co atom were the active sites at temperatures below 400 °C, and the bridging sulfur vacancies between the Co and Mo atoms with the higher activation energy were active at temperatures above 400 °C. This shows that the number and quality of the active sites in sulfide catalysts are not constant and can be strongly affected by the reaction conditions used. In our case, the HYD reaction was studied over a broad range of temperatures (230–330 °C) and in the presence of thiophene and H<sub>2</sub>S, originating from thiophene decomposition, both strongly competing in adsorption and the reaction. We believe that both factors were decisive for the appearance of the catalytic effect observed over the Ru–Mo(S) catalyst.

### 3.4. Effect of reaction temperature on HDS/HYD selectivity

A comparison of the HDS/HYD selectivities of all the catalysts as a function of reaction temperature is shown in Fig. 4. The data show that the HDS/HYD selectivity is significantly temperature dependent. The  $k_{\text{TH}}/k_{\text{CHE}}$  ratios increase for all of the catalysts with increasing reaction temperature, which is given by the higher apparent activation energies of HDS compared with HYD (Table 3). The HDS activity of some catalysts, such as Mo/Al<sub>2</sub>O<sub>3</sub>, Ru–Mo(S) and NiMo, prevails at temperatures above 300 °C but greatly diminishes below 250 °C, where HYD becomes dominant. CoMo and both monometallic Pt/Al<sub>2</sub>O<sub>3</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts keep their own specific selectivity features over a broad range of reaction temperatures, the former in high HDS and the two latter in high HYD.

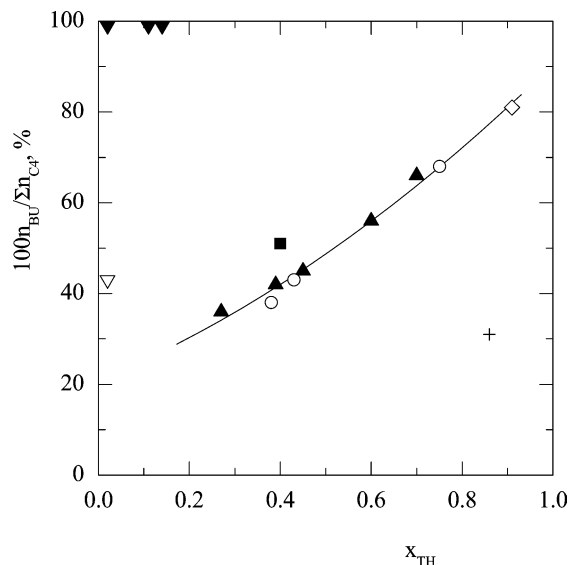


Fig. 5. Selectivity of butane formation in HDS of thiophene at 280 °C as a function of thiophene conversion. Notation of catalysts as in Fig. 4.

### 3.5. Selectivity for butane formation

The percentage of butane in C<sub>4</sub> hydrocarbons formed during HDS, that is, the selectivity of butane formation, is compared as a function of  $x_{\text{TH}}$  for all of the catalysts in Fig. 5. The content of butane was almost the same over the Mo/Al<sub>2</sub>O<sub>3</sub> and Ru–Mo(S) catalysts and increased at the higher thiophene conversions. The CoMo catalyst gave much less butane than the other ones, suggesting its lower hydrogenation activity. On the other hand, the monometallic noble metal sulfides, especially Pt/Al<sub>2</sub>O<sub>3</sub>, produced much more butane even at very low  $x_{\text{TH}}$ .

Some selectivity features common to Figs. 4 and 5 suggest a parallelism between the hydrogenation activities of the catalysts in the two reactions. Such a correlation is shown in Fig. 6, where the conversions of cyclohexene to cyclohexane are plotted versus the conversions of thiophene to butane. The data for Mo/Al<sub>2</sub>O<sub>3</sub> and all of the promoted catalysts fall more or less into one curve, clearly confirming this hypothesis. The experimental points obtained for Pt/Al<sub>2</sub>O<sub>3</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> were out of this correlation, because their too low HDS activities were the limiting factor, in contrast to the other catalysts (Table 2).

### 3.6. Synergetic effect of Pt and Ru

The magnitude of the synergetic effect (SE) was expressed by the ratio of the rate constants over the promoted catalyst ( $k_{\text{prom}}$ ) and the sum of the rate constants over Mo and noble-metal catalysts (Me = Pt or Ru), according to

$$\text{SE} = k_{\text{prom}} / (k_{\text{Mo}} + k_{\text{Me}}). \quad (2)$$

The monometallic Pt/Al<sub>2</sub>O<sub>3</sub> catalyst showed the lowest HDS activity. A deposition of 0.5% Pt on the Mo/Al<sub>2</sub>O<sub>3</sub> led to a

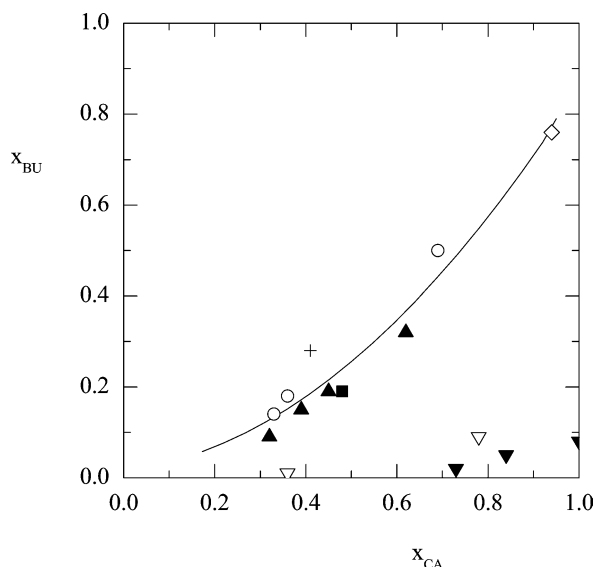


Fig. 6. Correlation between conversion of cyclohexene to cyclohexane and thiophene to butane for reaction at 280 °C. Notation of catalysts as in Fig. 4.

significant increase in the HDS activity and to a weaker synergy slightly above 2. This value was almost independent of the reaction temperature (Fig. 7). On the other hand, the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited by far the highest HYD activity, which exceeded that of the original Mo/Al<sub>2</sub>O<sub>3</sub> catalyst (Table 2). The activity of the bimetallic Pt–Mo(S) combination was between the values for Pt/Al<sub>2</sub>O<sub>3</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, and the synergy in the HYD of cyclohexene did not occur. The Ru/Al<sub>2</sub>O<sub>3</sub> catalyst was also of rather low HDS activity. The addition of about 0.6% Ru to the Mo/Al<sub>2</sub>O<sub>3</sub> led to a synergy between 2 and 3 at reaction temperatures of 280 °C and lower (Fig. 7). This is close to the values obtained with the Pt–Mo(S) system. However, the SE values rose significantly to about 6 at the higher temperatures. Such behavior differs greatly from that observed over the Pt–Mo(S) and shows that the synergetic effect of Ru was strongly temperature dependent. A similar situation also exists for the HYD of cyclohexene. Almost no synergy was observed at the lower reaction temperatures, whereas above 300 °C it became apparent and increased to about 4. These results demonstrate the different behaviors of Pt–Mo(S) and Ru–Mo(S) systems in HDS and HYD reactions.

The results obtained in this work concerning the reaction of thiophene and cyclohexene complement well our recent results obtained over the same catalysts in the simultaneous reaction of thiophene and pyridine [15]. First, both studies show that the Ru–Mo(S) combination is more efficient than the Pt–Mo(S) from the point of view of HDS of thiophene. The synergetic effect in HDS was much higher over Ru–Mo(S) combination, regardless of the presence of cyclohexene or pyridine in the feed. Because of the temperature dependence of the synergy, the HDS activity of the Ru–Mo(S) system evaluated in this work was about 2.5 times higher than that of the Pt–Mo(S) catalyst at 320 °C. The second aspect is that the synergy in HDS over the Ru–Mo(S)

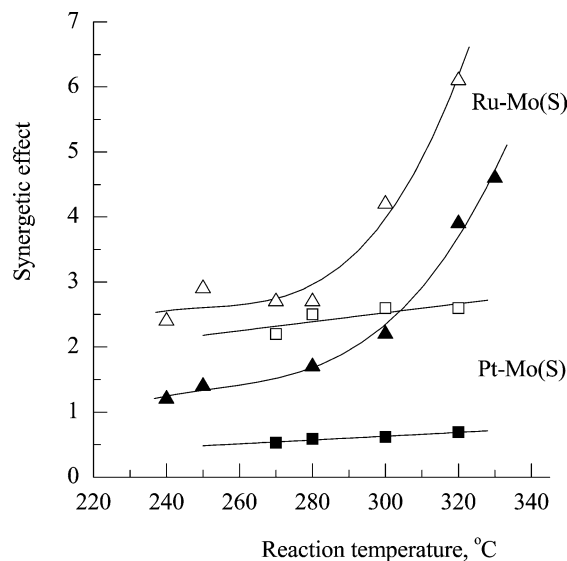


Fig. 7. Synergetic effect in HDS of thiophene and HYD of cyclohexene as a function of reaction temperature over Ru–Mo(S) ( $\Delta$ ,  $\blacktriangle$ ) and Pt–Mo(S) ( $\square$ ,  $\blacksquare$ ). HDS (open points), HYD (full points).

catalyst was always stronger than in simultaneously proceeding HYD. This was observed in HYD of cyclohexene in this work and recently in the reaction of pyridine [15]. However, in contrast to expectation, the high activity and synergy of the Pt–Mo(S) system in pyridine transformation were not observed in the reaction of cyclohexene. Although the monometallic Pt/Al<sub>2</sub>O<sub>3</sub> showed by far the highest HYD activity, the catalyst promoted by Pt did not show any synergetic behavior. We ascribe this result to different catalytic sites required for HYD of aromatics and cyclic olefins, as recently proposed [26].

The most striking finding in this work is the change in the  $E_a^{\text{HYD}}$  of HYD of cyclohexene over the Ru–Mo(S) catalyst, for which we propose the following explanation. A change in the apparent activation energy could reflect a change in the quality of catalytically active sites participating in the reaction, as recently observed in HDS over Mo and CoMo catalysts by Leliveld et al. [25]. In our case, this could mean the formation of some kind of surface species created from the sulfided noble metal and Mo atoms, a structure analogous to the so-called CoMoS phase. Such a model, explaining a strong synergetic effect in conventional HDS catalysts, is at present most widely accepted [27]. An assumption of the existence of mixed Ru–Mo–S sites could explain the differences observed in the course of the two simultaneous reactions. In HDS of thiophene over the Ru–Mo(S), the value of  $E_a^{\text{HDS}}$  was markedly higher than that corresponding to the nonpromoted Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. Then it can be assumed that HDS over the Ru–Mo(S) catalyst proceeds on sites different from those present on Mo/Al<sub>2</sub>O<sub>3</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts, that is, on mixed Ru–Mo–S sites, in a range of temperatures as broad as 230–330 °C.

In contrast to this, the HYD of cyclohexene proceeds over the Ru–Mo(S) catalyst with an  $E_a^{\text{HYD}}$  almost the same as that

over Mo/Al<sub>2</sub>O<sub>3</sub> up to 280 °C. We therefore conclude that under these conditions the HYD proceeds on the Mo and Ru sulfides more or less separately. The rapid increase in  $k_{\text{CHE}}$  at temperatures above 300 °C was observed only over the promoted catalyst and not on the Ru/Al<sub>2</sub>O<sub>3</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. This confirms that catalytic sites responsible for high HYD activity necessarily include both Mo and Ru. The HYD activity of the Ru–Mo(S) system at the higher reaction temperatures can therefore be mainly ascribed to the strong synergetic effect of Ru, which was accompanied by a more than twofold increase in  $E_{\text{a}}^{\text{HYD}}$ . We ascribe the increase in the rate of HYD to a partial release of mixed Ru–Mo–S sites by the desorption of thiophene or H<sub>2</sub>S, originating from thiophene decomposition, which allows competitive adsorption and cyclohexene reaction. A significant decrease in the surface coverage of the NiMo and CoMo catalysts by desorption of thiophene at temperatures over 280 and 317 °C, respectively, has already been documented [28,29]. At the same time, H<sub>2</sub>S is known to strongly inhibit HYD of cyclohexene over NiMo catalysts [16]. We assume an analogy between the noble-metal-promoted Mo and the conventional catalysts and suppose that the same phenomena also occur on the catalysts prepared in this work. An assumption that HYD and HDS could proceed on the same catalytic sites seems to contradict some earlier studies performed on the conventional catalysts. However, this question is still unanswered [10,25]. Moreover, more recent studies propose that interconversion between HDS and HYD sites is possible [11, and references therein].

Alternatively, it cannot be excluded that the synergetic effect observed over noble-metal-promoted catalysts could also be ascribed, perhaps partly, to the hydrogen spillover between the noble metal and Mo sulfides. In principle, MoS<sub>2</sub> and noble-metal sulfides are known to readily activate hydrogen, and the spillover can originate from both noble metal and MoS<sub>2</sub> phase. An argument in favor of possible hydrogen spillover is a relatively low content of noble metals in modified catalysts, decreasing the probability of formation of some kind of mixed sites. It is possible to speculate that in the case of Ru–Mo(S), the adsorbed thiophene (or H<sub>2</sub>S) blocks the sites for possible migration of activated hydrogen at lower reaction temperatures. The hydrogen remains available only in the vicinity of the adsorbed cyclohexene molecule, and HYD can proceed only separately on Mo and noble-metal sites. Thiophene or H<sub>2</sub>S desorbing at higher temperatures allows a much easier hydrogen transfer between noble-metal and Mo sites, accelerating in this way the HYD reaction.

The results obtained in this work show that the synergetic effects over the Mo/Al<sub>2</sub>O<sub>3</sub> catalyst promoted by noble metals are possible to achieve in both HYD and HDS. In contrast to HDS of thiophene, the synergy in HYD of cyclohexene is weaker, and its occurrence is much more sensitive to the kind of noble metal and the reaction conditions used.

## 4. Conclusions

Modification of the MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst by Pt and Ru sulfides improved its activities in model reactions of thiophene and cyclohexene. However, the two noble metals differ substantially in their effects. The addition of Pt resulted in a weaker synergy in HDS, being almost the same for reaction temperatures between 270 and 320 °C. On the other hand, the addition of Ru led to much stronger synergy in HDS, which increased at the higher reaction temperatures to a value of 6. At 320 °C, the HDS activity of the Ru–Mo(S) system was about 2.5 times higher than that of the Pt–Mo(S) catalyst. Over the Ru–Mo(S) catalyst, the strong synergy in HYD appeared only at higher temperatures of 300–330 °C and was accompanied by a more than twofold increase of the apparent activation energy. It seems most likely that HYD proceeds on separate Ru and Mo sulfide phases at the lower reaction temperatures and on the mixed Ru–Mo–S sites at temperatures above 300 °C. This could be due to a partial desorption of thiophene (or H<sub>2</sub>S) from the Ru–Mo–S sites at around 300 °C, which in turn become available for the competitive adsorption and reaction of cyclohexene. In contrast to the Ru–Mo(S) catalyst, a modification of the Mo/Al<sub>2</sub>O<sub>3</sub> catalyst by Pt did not affect the activation energies either in HDS or in HYD. This indicates that the quality of sulfided Pt and Mo sites does not change during these reactions and suggests that the mixed sites are not obviously formed. The synergetic effect of noble metals is possible to achieve in both HDS and HYD reactions, although the latter is more limited by the type of noble metal and reaction conditions.

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## References

- [1] R.R. Chianelli, Catal. Rev.-Sci. Eng. 26 (3–4) (1984) 361.
- [2] P.C.H. Mitchell, C.E. Scott, Bull. Soc. Chim. Belg. 93 (8–9) (1984) 619.
- [3] Y.J. Kuo, B.J. Tatarchuk, J. Catal. 112 (1988) 229.
- [4] M. Lacroix, N. Boutarfa, C. Guillard, M. Vrinat, M. Breyse, J. Catal. 120 (1989) 473.
- [5] F.S. Xiao, Q. Xin, X.X. Guo, Appl. Catal. A 95 (1993) 21.
- [6] J. Quartararo, S. Mignard, S. Kasztelan, J. Catal. 192 (2000) 307.
- [7] M. Sugioka, F. Sado, T. Kurosaka, X. Wang, Catal. Today 45 (1998) 327.
- [8] H.R. Reinhoudt, R. Troost, S. van Schalkwijk, A.D. van Langeveld, S.T. Sie, J.A.R. van Veen, J.A. Moulijn, Fuel Process. Technol. 61 (1999) 117.
- [9] M. Breyse, G.D. Mariadassou, S. Pessayre, Ch. Geantet, M. Vrinat, G. Pérot, M. Lemaire, Catal. Today 84 (2003) 129.
- [10] Ch. Song, Catal. Today 86 (2003) 211.
- [11] S. Brunet, D. Mey, G. Pérot, Ch. Bouchy, F. Diehl, Appl. Catal. A 278 (2005) 143.



- [12] L.I. Meriño, A. Centeno, S.A. Giraldo, *Appl. Catal. A* 197 (2000) 61.
- [13] J. Cinibulk, Z. Vít, *Appl. Catal. A* 180 (1999) 15.
- [14] J. Cinibulk, D. Gulková, Y. Yoshimura, Z. Vít, *Appl. Catal. A* 255 (2003) 321.
- [15] Z. Vít, J. Cinibulk, D. Gulková, *Appl. Catal. A* 272 (2004) 99.
- [16] L. Qu, R. Prins, *J. Catal.* 207 (2002) 286.
- [17] S.G. de León, P. Grange, B. Delmon, *Appl. Catal. A* 107 (1993) 101.
- [18] M. Koussathana, D. Vamvouka, H. Economou, X. Verykios, *Appl. Catal. A* 77 (1991) 283.
- [19] C.I. Cabello, M. Muñoz, E. Payen, H.J. Thomas, *Catal. Lett.* 92 (2004) 69.
- [20] E. Hillerová, M. Zdražil, *Collect. Czech. Chem. Commun.* 54 (1989) 2648.
- [21] S.M. Davis, G.A. Somorjai, *J. Catal.* 65 (1980) 78.
- [22] D.E. Gardin, X. Su, P.S. Cremer, G.A. Somorjai, *J. Catal.* 158 (1996) 193.
- [23] M. Vrinat, *Appl. Catal. A* 6 (1983) 137.
- [24] M. Ziyad, M. Rouimi, J.L. Portefaix, *Appl. Catal. A* 183 (1999) 93.
- [25] R.G. Leliveld, A.J. van Dillen, J.W. Geus, D.C. Koningsberger, *J. Catal.* 175 (1998) 108.
- [26] L. Qu, R. Prins, *Appl. Catal. A* 250 (2003) 105.
- [27] H. Topsøe, B.S. Clausen, F.E. Massoth, in: J.R. Anderson, M. Boudart (Eds.), *Hydrotreating Catalysis, Catalysis-Science and Technology*, vol. 11, Springer, Berlin, 1996.
- [28] E.J.M. Hensen, M.J. Vissenberg, V.H.J. de Beer, J.A.R. van Veen, R.A. van Santen, *J. Catal.* 163 (1996) 429.
- [29] A. Borgna, E.J.M. Hensen, J.A.R. van Veen, J.W. Niemantsverdriet, *J. Catal.* 221 (2004) 541.