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Simultaneous Hydrodenitrogenation of Pyridine and Hydrodesulfurization of Thiophene over Carbon-Supported Platinum Metal Sulfides

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The activity and selectivity in parallel hydrodenitrogenation and hydrodesulfurization of carbon-supported sulfides of Ru, Rh, Pd, Ir, and Pt were evaluated using the simultaneous reaction of pyridine and thiophene at 280°C and under 2 MPa. The properties of these sulfides were also compared with the behavior of commercial Ni–Mo/alumina and Co–Mo/alumina Shell catalysts. The carbon-supported sulfides of platinum metals were better hydrodesulfurization catalysts and much better hydrodenitrogenation catalysts than the commercial bimetallic systems. The HDN/HDS selectivity of the Rh, Ru, and Pd catalysts was similar to the selectivity of Co–Mo and Ni–Mo systems but the Ir and Pt catalysts were extremely selective for hydrodenitrogenation. The results suggest that the use of active carbon as the support contributed to the exceptional hydrodenitrogenation properties of the sulfides of platinum metals.

INTRODUCTION

Research on sulfide catalysts for hydrorefining has concentrated above all on the hydrodesulfurization (HDS) function. However, the hydrodenitrogenation (HDN) reaction currently receives increasing attention in the literature. It is the key reaction in the hydrorefining of feedstocks for the cracking and hydrocracking processes.

Previous research on HDN has concentrated mainly on the kinetics and mechanism of the reaction over the conventional Co–Mo and Ni–Mo systems (e.g., Refs. (*1–3*)). The experience with other sulfide catalysts is limited. The catalytic properties of the industrial Co–Mo–S/Al_2O_3, Ni–Mo–S/Al_2O_3, and Ni–W–S/Al_2O_3 catalysts are well described in the literature. The Ni–Mo and Ni–W systems possess better HDN activity and better HDN/HDS selectivity than the Co–Mo combination (*4–6*). However, the following two questions remain open.

First, it seems that the highest activity limits are not as well established for HDN as for HDS. The HDS activity of the conventional Co–Mo and Ni–Mo systems is not much below the highest activity attainable with any other catalyst. Some platinum metal group sulfides have been reported to be even more active but their activity still falls into the same rank as that of the Co–Mo and Ni–Mo catalysts (for a review see Ref. (*5*)).

The data on HDN are scarce but they suggest that the platinum metal group sulfides belong to the most active catalysts. Ru sulfide supported on zeolite or alumina exhibited HDN activity comparable with that of the Ni–Mo/Al_2O_3 BASF M8-21 catalyst (*7*). The addition of Ru to the Co–Mo sulfide catalyst substantially increased its HDN activity (*8*). A recent paper (*9*) on the periodic trends in HDN activity of transition metal sulfides reported that platinum metal group sulfides were the most active; however, the work did not include a comparison with the conventional bimetallic systems. The other very active HDN catalyst seems to be Re sulfide (*9, 10*).

The second open question concerns the HDN/HDS selectivity. The difference in this respect between the Co–Mo and Ni–

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Mo systems is small. The available data on catalysts containing other transition metals suggest that the HDN/HDS selectivity can generally vary in a much broader range. Ruthenium sulfide exhibited a remarkable preference for nitrogen over sulfur removal and was more selective for HDN than the conventional hydrorefining catalysts (*7*). The mixed Cr–Mo sulfide catalyst was extremely selective toward HDN and provided an HDN-to-HDS activity ratio 10 times higher than that of the Ni–Mo system (*11*). These results invite further research on the selective HDN catalysts.

The purpose of the present work was to obtain more information on the attainable limits of HDN activity and HDN/HDS selectivity. The sulfides of the platinum metals were selected as catalysts because the literature suggests that these sulfides have exceptional properties for HDN. The sulfides were supported on active carbon and the catalytic activities were measured using a mixture of pyridine and thiophene in the gas phase in a flow reactor under 2 MPa pressure.

EXPERIMENTAL

The catalysts were prepared by the impregnation of active carbon (GA-1, Slovenské lučobné závody, Czechoslovakia; BET surface, 960 m^2/g; particle size, 0.2–0.3 mm) by $RuCl_3 \cdot H_2O$, $RhCl_3 \cdot 3H_2O$, $PdCl_2$, $(NH_4)_2IrCl_6$, and H_2PtCl_6. The loading was 0.83 mmol of metal (Me) per gram of catalyst and corresponded to the typical content of Mo in commercial catalysts (12 wt% MoO_3, i.e., 0.83 mmol Mo/g). The content of metals in wt% was: Ru 8.3, Rh 8.5, Pd 8.8, Ir 15.9, and Pt 16.2. The slurry of the support with the solution of the metal compound was dried under vacuum in a rotary evaporator at 50°C. The catalysts were not calcined.

The commercial catalysts, $Ni–Mo/Al_2O_3$ Shell 324 and $Co–Mo/Al_2O_3$ Shell 344, contained 0.46 mmol Ni/g and 1.23 mmol Mo/g (i.e., 1.69 mmol Me/g) and 0.40 mmol Co and 0.96 mmol Mo/g (i.e., 1.36 mmol Me/g), respectively. They were crushed to a particle size of 0.2–0.3 mm and were *ex situ* presulfided by a 1 : 10 H_2S/H_2 mixture for 2 h at 400°C.

The catalytic activity was measured in a flow apparatus with a fixed bed of catalyst and with all the reactants in the gas phase. The reactor was made of a stainless-steel tube of 2 mm i.d. and the catalyst charge (0.01–0.3 g) was placed in it between two plugs of glass wool. The composition of the inlet and outlet streams of the reactor was determined using on-line gas chromatography.

The reaction mixture fed into the reactor contained 450 molar ppm of pyridine and 350 molar ppm of thiophene in hydrogen; the hydrogen flow was 0.4 mol/h. This feed was prepared in a simple flow evaporator filled by a mixture of liquid pyridine and thiophene.

The gas chromatographic analysis (FID detector) was carried out isothermally at 122°C on a 2.5-m glass column (i.d. 3 mm) packed with 60/80 Carbopack B/4% Carbowax 20 *M*/0.8% KOH (Supelco). The following acronyms will be used: C_4 hydrocarbons (C4), C_5 hydrocarbons (C5), thiophene (TH), pentylamine (PA), piperidine (PI), pyridine (PY), and tetrahydrothiophene (THT). The composition of the reaction mixture was expressed in terms of molar fractions $a(i) = n(i)/n^0(\mathrm{TH})$, where i is TH or C4, and $a(j) = n(j)/n^0(\mathrm{PY})$, where j is PY, PA, PI, or C5; n and n^0 are the final and initial number of moles, respectively.

The catalyst charge in the reactor was sulfided by the $H_2S : H_2$ mixture (1 : 10) under atmospheric pressure. The temperature was increased to 400°C during 30 min and held at 400°C for 1 h. This relatively short *in situ* sulfidation was assumed to be quite sufficient for the carbon-supported samples, but was rather short for the oxidic form of the alumina-supported catalysts. In order to complete the run with the alumina-supported catalysts in 1 day, these samples were charged into the reactor in the *ex situ* presulfided form. It was verified that the

two-step sulfidation of commercial samples (2 h *ex situ* and 1 h *in situ*) gives the same activity as one-step *in situ* sulfidation for 3 h at 400°C.

The sulfiding mixture was exchanged for hydrogen and the temperature was decreased to 280°C. The hydrogen under atmospheric pressure was exchanged for the reaction mixture at 2.0 MPa and the steady-state concentrations of the products were reached after 3–6 h. The run at each space time value (W/F) was performed with a fresh catalyst charge; W is the amount of mmol Me in the catalyst charge and F is the feed rate of thiophene (F(TH)) or pyridine (F(PY)) in mmol/h. The monometallic catalysts were thus compared with the bimetallic commercial samples using the activity normalized to millimoles of the active metal Me.

RESULTS

Preliminary experiments under 2 MPa pressure and at temperatures in the range 210–340°C have shown that some of the sulfides of the platinum metal group were much more active than the commercial Ni–Mo and Co–Mo catalysts. The relatively low temperature of 280°C was chosen for the measurement because a higher temperature would require the use of too small charges of the most active catalysts.

C_4 hydrocarbons were the only products of the HDS of thiophene under the conditions used. The intermediate tetrahydrothiophene was not detected at the sensitivity of our GC analysis (the limit of sensitivity was about $a(i) = 0.01$) and, therefore, the course of the reaction can be described as

$$\text{thiophene} \xrightarrow{H_2} C_4 \text{ hydrocarbons} + H_2S. \quad (1)$$

The primary data were the integral dependences of a(TH) on the space time W/F in the range of a(TH) 0.9–0.1. The curves followed the first-order kinetics given by

$$a(\text{TH}) = \exp[-k(\text{TH})W/F(\text{TH})], \quad (2)$$

where k(TH) is the rate constant [mmol h^{-1} (mmol Me)$^{-1}$]. The rate constants were evaluated by nonlinear regression of the data and are summarized in Table 1. They were used as the measure of the HDS activity of the catalysts.

Piperidine and 1-pentylamine were detected as intermediates of HDN of pyridine under the conditions used and the reaction can be described by Eq. (3). The hydrogenation of pyridine to piperidine,

$$\text{pyridine} \xrightarrow{H_2} \text{piperidine} \xrightarrow{H_2} \text{1-pentylamine} \xrightarrow{H_2} \text{C5 hydrocarbons} + NH_3, \quad (3)$$

is generally a reversible reaction (*1, 12*). However, the equilibrium is shifted entirely to the side of piperidine at the low temperature and high pressure of our measurements, and the first step in Eq. (3) can be taken as irreversible. *N*-Pentylpiperidine, which was found as an intermediate during the reaction in the absence of sulfur (*2*), was not detected in our case. These features of the HDN of pyridine agree with the results on the conventional bimetallic catalysts reported in the literature (e.g., (*1, 13*)).

Typical examples of the primary data on pyridine HDN are the results obtained (shown in Fig. 1) with the Pt/C and Ru/C catalysts. The dependences of $a(j)$ vs W/F for all other catalysts followed the same pattern.

The amount of 1-pentylamine was always much lower (a(PA) < 0.1) than that of piperidine, the molar fraction of which reached the value of 0.4 in some cases. In this situation, the overall HDN reaction was described by the simplified reaction scheme of the two consecutive irreversible steps

$$\text{pyridine} \xrightarrow{H_2} \text{saturated amines} \quad (4)$$

$$\text{saturated amines} \xrightarrow{H_2} \text{C5 hydrocarbons} + NH_3. \quad (5)$$

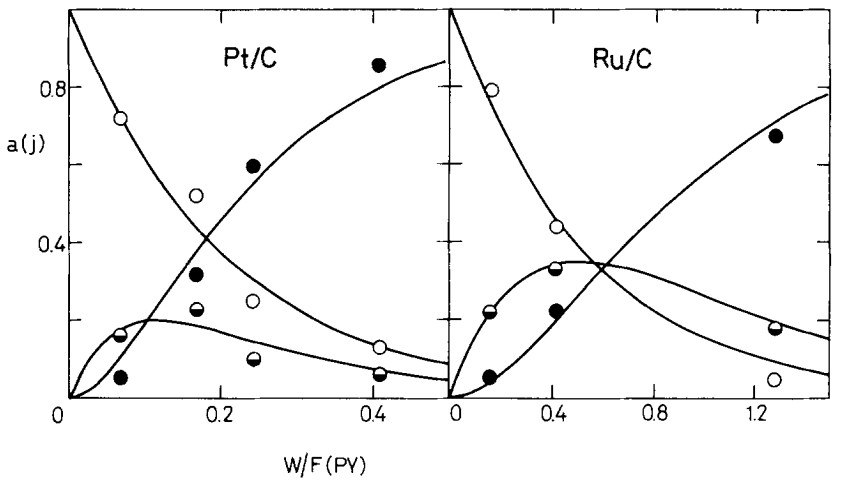

FIG. 1. Hydrodenitrogenation of pyridine in the presence of thiophene at 280°C and under 2 MPa pressure. (○) Pyridine, (◒) piperidine + pentylamine, (●) C_5-hydrocarbons. The curves were calculated using the constants from Table 1; the units of W/F(PY) are [mmol Me h (mmol PY)$^{-1}$].

The experimental data were fitted by Eqs. (6)–(8), derived for the two irreversible consecutive first-order reactions,

$$a(\mathrm{PY}) = \exp[-k(\mathrm{PY})\,W/F(\mathrm{PY})] \quad (6)$$

$$a(\mathrm{SA}) = \frac{k(\mathrm{PY})}{k(\mathrm{C5}) - k(\mathrm{PY})} (\exp[-k(\mathrm{PY})W/F(\mathrm{PY})] - \exp[-k(\mathrm{C5})\,W/F(\mathrm{PY})]) \quad (7)$$

$$a(\mathrm{C5}) = 1 - \frac{k(\mathrm{C5})}{k(\mathrm{C5}) - k(\mathrm{PY})} \exp[-k(\mathrm{PY})\,W/F(\mathrm{PY})] + \frac{k(\mathrm{PY})}{k(\mathrm{C5}) - k(\mathrm{PY})} \exp[-k(\mathrm{C5})\,W/F(\mathrm{PY})], \quad (8)$$

where SA stands for saturated amines, k(PY) [mmol h^{-1} (mmol Me)$^{-1}$] is the rate constant of the step represented by Eq. (4) and k(C5) [mmol h^{-1} (mmol Me)$^{-1}$] is the rate constant of the step represented by Eq. (5), and a(SA) = a(PI) + a(PA). The rate constants k(PY) and k(C5) were obtained by nonlinear regression and are summarized in Table 1.

The definition of the activity of the catalyst for HDN of pyridine, A(HDN), is not straightforward. The transformation of pyridine to the hydrocarbons and ammonia is a two-step process and neither k(PY) nor k(C5) alone defines the activity. The degree of HDN depends on both these constants in the rather complicated manner described by Eq. (8). We have used the reciprocal value of W/F(PY) at which a(C5) = 0.5 is achieved as the measure of the HDN activity, A(HDN). Its values were read out from the curves a(C5) = $f(W/F(\mathrm{PY}))$ calculated using the constants k(PY) and k(C5), and are presented in Table 1.

The selectivities of the catalysts for the formation of saturated amines during HDN of pyridine, S(SA), can be conveniently compared by plotting a(SA) vs (1 − a(PY)), as shown in Fig. 2. The selectivity was defined as the area under the curve a(SA) = $f(1 - a(\mathrm{PY}))$ and was given by the integral

$$S(\mathrm{SA}) = \int_1^0 a(\mathrm{SA})\, da(\mathrm{PY}). \quad (9)$$

The value of the selectivity S(SA) defined in such a way can vary between 0 and 0.5. No saturated amines are desorbed to the gas phase during the HDN of pyridine over the catalyst with S(SA) = 0; the composition of the reaction mixture changes along the x-axis in Fig. 2. On the other hand, the composition of the reaction mixture over

TABLE 1

Kinetic Parameters of the Parallel HDN of Pyridine and HDS of Thiophene at 280°C and under 2 MPa Pressure

Catalyst	Activity[a]				Selectivity[b]	
	HDS	HDN				
	k(TH)	k(PY)	k(C5)	A(HDN)	S(SA)	S(HDN/HDS)
Ir/C	3.5	9.9	19.9	8.1	0.17	0.74
Pt/C	1.9	4.9	14.1	4.6	0.13	0.76
Rh/C	5.4	3.0	2.9	1.7	0.25	0.06
Ru/C	2.7	1.8	2.0	1.2	0.24	0.10
Pd/C	1.1	1.6	1.4	0.8	0.26	0.24
$NiMo/Al_2O_3$	0.6	0.5	0.5	0.4	0.23	0.12
$CoMo/Al_2O_3$	0.5	0.4	0.1	0.1	0.38	0.05

[a] The units of the rate constants $k(i)$ and A(HDN) are [mmol h^{-1} (mmol Me)$^{-1}$].
[b] The parameters S(SA) and S(HDN/HDS) are dimensionless.

the catalysts with S(SA) = 0.5 changes along the diagonal in Fig. 2; all pyridine disappears from the gas phase before any ammonia is desorbed. The values of S(SA) for all catalysts measured were calculated using Eqs. (9), (6), and (7) and the constants k(PY) and k(C5) and are presented in Table 1.

The difficulties in the definition of the HDN activity of a catalyst also cause problems with the definition of the HDN/HDS selectivity of a catalyst, S(HDN/HDS). This selectivity cannot be evaluated by the ratios of the constants $k(i)$ in Table 1. We have defined the selectivity as the value of a(C5) at a(TH) = 0.5; it can vary in the range 0–1. The values of S(HDN/HDS) were read out from the curves a(TH) = $f(W/F$(TH)) and a(C5) = $f(W/F$(PY)) calculated using Eqs. (2) and (8) and the constants k(TH), k(PY), and k(C5), and are presented in Table 1. It should be stressed that F(TH) = 0.78 F(PY) in our measurements (see Experimental).

DISCUSSION

Hydrodesulfurization Activity

Two previous papers compared the activity of carbon-supported platinum metals group sulfides in HDS of thiophene under atmospheric pressure and in the absence of nitrogen compounds. Vissers *et al.* (*14*) reported the following order of activity at 400°C: Ir > Rh > Ru > Pt > Pd. Ledoux *et al.* (*15*) found the activity trend at 280°C to be: Rh > Ir ⩾ Ru > Pd > Pt. Our data in Table 1 were obtained under other condi-

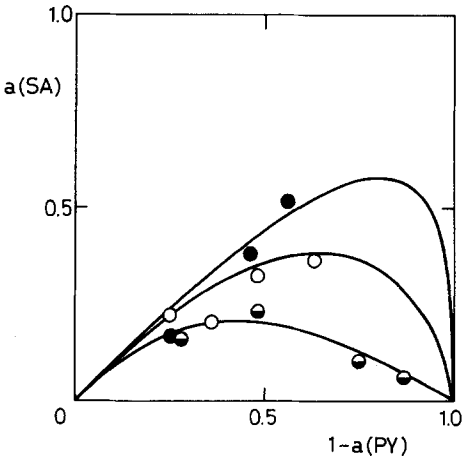

FIG. 2. Integral curves of the composition of the reaction mixture during HDN of pyridine used for the definition of the selectivity S(SA). (●) (Co–Mo/Al_2O_3, (○) Pd/C, (◒) Pt/C. The curves were calculated using Eqs. (6) and (7) and the constants from Table 1.

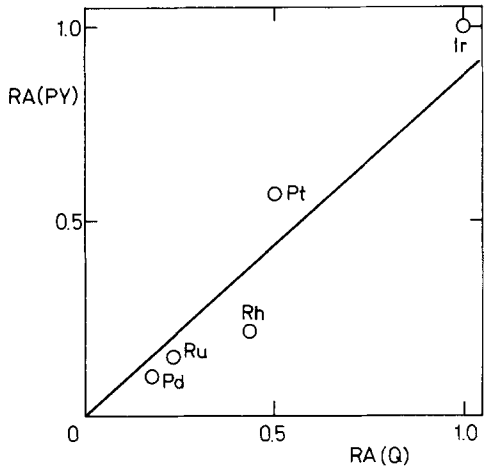

FIG. 3. Comparison of the relative activity (RA) of the carbon-supported sulfides in HDN of pyridine (PY) and quinoline (Q). RA(Q) is the relative first-order rate constant calculated using data from Ref. (*9*); RA(PY) is the relative *A*(HDN) calculated from data from Table 1.

tions, namely under elevated pressure and in the presence of the nitrogen compounds. Notwithstanding this, they exhibit similar features: the highest activities were shown by Ir and Rh sulfides, the activity of Ru sulfide was of medium range, and the activities of Pd and Pt sulfides were the lowest. This comparison of our data with the results of other papers (*14, 15*) suggests that the presence of nitrogen compounds does not influence significantly the relative hydrodesulfurization activities of sulfides of the platinum metals.

According to the previous literature, platinum metal sulfides are the only catalysts having HDS activity comparable to the activity of the bimetallic, synergistic Co–Mo and Ni–Mo sulfide systems (for a review, see Ref. (*5*)). However, in our experiments, the activities of the sulfides of Ir and Rh not only were comparable to the activities of the Co–Mo and Ni–Mo samples, but also were higher by almost one order of magnitude. Our explanation for this is based on an assumed lower sensitivity to the presence of basic nitrogen compounds of the catalysts supported on neutral active carbon compared with the catalysts supported on acidic alumina. The strong retardation of HDS on the conventional alumina-supported catalysts by nitrogen compounds is well known (*16*).

Hydrodenitrogenation Activity

The data in Table 1 on HDN activity, *A*(HDN), can be compared with the results of a recent study of quinoline HDN over carbon-supported transition metal sulfides (*9*). The approximate agreement between both series of data is shown in Fig. 3. It can be generalized that the sulfides of the third-row platinum metals are better HDN catalysts than the sulfides of the second-row platinum metals.

All our model catalysts were much better HDN catalysts than the commercial samples which are considered to belong to the best industrial products. The difference between Ir/C and Pt/C catalysts on the one hand and the Ni–Mo/Al_2O_3 catalyst on the other hand is especially remarkable. Such large differences have not previously been reported in the literature. It seems therefore that active carbon is an especially suitable carrier for sulfides of platinum metals intended for HDN.

It was suggested that Ru and Rh are promoters of the HDN activity of the Ni–Mo and Co–Mo catalysts (*8, 17*); however, the activity of the Ru and Rh catalysts alone was not measured. Our data suggest that the increased activity of the Ru–Co–Mo, Ru–Ni–Mo, and Rh–Co–Mo catalysts in the above-mentioned papers was caused by the high activity of Ru and Rh alone and not by the promotional interaction between Ru or Rh with Ni–Mo or Co–Mo systems.

Selectivity to Saturated Intermediates

The formation of the saturated nitrogen-containing intermediates on various catalysts has not been compared in the previous literature. The data on *S*(SA) in Table 1 show that some of the catalysts differed in this respect.

The data on the Co–Mo and Ni–Mo catalysts give additional insight into the known different performances of these systems.

The rate constant k(PY) was similar for both catalysts and thus their different activities originated predominantly from the differences in the constant k(C5). The value of k(C5) was higher for the Ni–Mo combination and this catalyst produced lower amounts of saturated intermediates. It is interesting that a similar phenomenon was observed also in the HDS of benzothiophene; the Ni–Mo combination produced less intermediate dihydrobenzothiophene in comparison to the Co–Mo catalyst (*5*).

The sulfides of the third-row platinum metals formed distinctly lower quantities of saturated intermediates and were more active than the sulfides of the second-row platinum metals. Thus, an approximately inverse relation between the A(HDN) and the S(SA) can be observed both on the commercial and on the model catalysts.

The differences between the catalysts in the constant k(C5) were larger than the differences in the constant k(PY) and the ability of the catalysts to decompose the intermediate saturated amines seems to be the key factor determining the overall HDN activity. The chemical nature of this hydrogenolytic step is not quite clear at the present time. It was reported that its rate is not sensitive to the partial pressure of hydrogen under high pressure and that it is controlled by the ratio of hydrogen sulfide and hydrogen (for a recent discussion, see Ref. (*13*)).

HDN/HDS Selectivity

The Ni–Mo/Al_2O_3 catalyst possessed better HDN/HDS selectivity than the Co–Mo/Al_2O_3 sample. This finding is in full agreement with the literature (for a review, see Ref. (*5*)) and confirms the correctness of our method of measurement and the evaluation of the data.

The selectivity of the sulfides of the second-row platinum metals was not much different from that of the commercial samples. As for the Ru sulfide, this result does not agree with previous work (*7*) which reported the selectivity of the Ru sulfide supported on Y-zeolite to be much higher than the selectivity of the conventional catalysts. However, the different support and conditions must be considered.

The sulfides of the third-row platinum metals, Ir and Pt, exhibited quite exceptional HDN selectivity. No data on the selectivity of these sulfides are available in the literature. Our result shows that the HDN/HDS selectivity can vary with the type of catalyst in a rather broad range.

The recent data on the Cr–Mo system (*11*) suggest that very high selectivities can also be achieved on catalysts based on non-platinum metals. However, the high selectivity is obtained on these metals at relatively low activity level and further research is required to improve the activity of the selective HDN catalysts of unconventional composition not containing platinum metals.

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