EFFECT OF NICKEL AND PHOSPHORUS IN HYDRODESULFURIZATION OF THIOPHENE AND HYDRODENITROGENATION OF PYRIDINE OVER ALUMINA-SUPPORTED MOLYBDENUM CATALYSTS

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The effect of nickel and phosphorus on activity of alumina-supported molybdenum catalysts in simultaneous hydrodesulfurization (HDS) of thiophene and hydrodenitrogenation (HDN) of pyridine was studied. The introduction of nickel into molybdenum-containing catalysts promotes strongly HDS of the alumina-supported nickel-molybdenum catalyst while the increase in HDN activity is less pronounced. The synergistic effect in pyridine HDN is explained as the consequence of synergism in HDS. The weak promoting effect of phosphorus was observed for NiMo/Al₂O₃ catalyst containing 1 wt. % of phosphorus. Above this concentration, both HDS and HDN activities decrease again. HDS activity of P-modified NiMo/Al₂O₃ samples was similar to that of the commercial NiMo/Al₂O₃ Shell catalyst. However, the HDN selectivity in pyridine reaction was higher for commercial catalyst which is explained by exceptionally higher dispersion of nickel on this catalyst.

The large content of organic sulfur and nitrogen compounds present in petroleum crudes must be reduced before transformation to liquid fuels. The key reactions are both catalytic hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) proceeding as a part of this process. In connection with processing of heavier fractions the ways leading to higher activity and selectivity of catalysts are intensively studied, i.e. promoters addition or modification of molybdenum catalysts with different agents such as phosphorus compounds.

Up to now it is not quite clear whether Co or Ni (being the effective promoters in HDS) play also the same role in HDN. The literature data¹ regarding the promoting effect in HDN are scarce and contradictory. The synergism between Ni and Mo in alumina-supported catalysts was found in HDN of tetrahydroquinoline² and in some cases with real feedstock^{3,4}. On the other hand, in pyridine HDN the Mo/Al₂O₃ catalyst was more efficient than the NiMo/Al₂O₃ sample⁵ and in HDN of heavy vacuum gas oil the activity of NiMo/Al₂O₃ catalyst corresponds to the sum of the activities of Ni and Mo catalysts⁶. The mechanism of synergism in HDN

seems to be different from that observed in HDS. Perot et al², observing the promoting effect in propylcyclohexane formation in HDN of tetrahydroquinoline (THQ) under presence of H_2S , explained the synergism by kinetic reasons: it can occur only when hydrogenation of THQ to decahydroquinoline (DHQ) as intermediate is the rate limiting step. This situation occurs in the presence of H_2S which affects positively the C—N bond scission in DHQ and negatively the hydrogenation of THQ to DHQ. All these results of previous authors suggest that the matter of synergism in HDN seems to be less general than in HDS, being probably more sensitive to the experimental conditions used¹.

The positive effect of phosphorus on HDS reaction over alumina-supported molybdenum catalysts is mostly explained by preventing the formation of catalytically inactive metal aluminates⁷⁻⁹, by increasing the strength and heat stability of the alumina support¹⁰. Also, the promoting effect of P is expressed by increased dispersion of the active phase^{11,12} and by suppression of the coke formation¹³. The HDS activity improvement after phosphorus addition has been usually observed to vary between 20-50% (refs^{14,15}). The effect of phosphorus on HDN activity for alumina-supported Mo, NiMo and CoMo catalysts varied between 10-50% compared to the activity of catalysts without phosphorus^{6,15-20}. The widely accepted opinion regarding the role of phosphorus in alumina-supported molybdenum catalysts is that phosphorus does not alter the nature of the active sites but it rather affects their number and distribution being optimal at definite phosphorus concentration²¹⁻²³. The promoting effect of phosphorus on the catalytic activity of alumina-supported catalysts can be explained by the strong interaction of phosphate with the alumina support with the formation of surface AlPO₄²⁴.

In contrast to alumina-supported catalysts, the HDS activity of the carbon-supported catalysts is strongly reduced by phosphorus whereas the HDN activity increases or decreases in dependence on the type of the transition metal used¹⁹. The nature of the poisoning effect of P is due to the adsorption of PH₃ on the anion vacanciones²⁴ and the formation of inactive metalphosphides or metalfosphosulfides^{19,20}.

The aim of the present work was to check the presence and if any, the magnitude of the promoting effect of nickel together with the effect of phosphorus addition into alumina-supported nickel-molybdenum catalysts, both with main emphasis on HDN reaction of pyridine proceeding simultaneously in the presence of thiophene HDS.

EXPERIMENTAL

Catalysts

The nickel and molybdenum catalysts were prepared by impregnation of γ -alumina of BET

Hydrodesulfurization of Thiophene

surface area 240 m² g⁻¹ with aqueous solutions of nickel nitrate and ammonium heptamolybdate, respectively. The impregnated samples were dried at 120°C for 4 h and calcined at 450°C for 3 h. The catalysts contained 2.4 wt. % of nickel and 10 wt. % of molybdenum, respectively. The nickel-molybdenum catalysts were prepared by co-impregnation of the same support with ammonium heptamolybdate and nickel nitrate solutions under absence or presence of phosphoric acid followed by the same drying and calcination as in the case of nickel and molybdenum catalysts. In these samples, the content of nickel and molybdenum was kept constant (2.4 and 10 wt. %, respectively), while the content of phosphorus varied from 0 to 5 wt. %. All catalysts were crushed and sieved to the particle size of 0.16-0.30 mm. The commercial NiMo catalyst Shell 324 of the same particle size was used for comparison (2.7 wt. % of nickel, 11.8 wt. % of molybdenum and 2.7 wt. % of phosphorus).

Diffuse Reflectance Spectroscopy

The state of molybdenum and nickel in the oxide form of the calcined catalysts was investigated by diffuse reflectance spectroscopy (DRS). The diffuse reflectance spectra were recorded on a Beckman 5270 spectrophotometer in the 2 200-200 nm range. The barium sulfate pellet was used as the reflectance white standard.

Activity Measurements

The catalytic activity of catalysts in HDS of thiophene in the absence of pyridine was studied at 400°C and atmospheric pressure and WHSV of $2 h^{-1}$ employing a continuous flow reactor system connected with a gas chromatograph. Thiophene was admitted to the reactor after pieliminary heating of the samples to the reaction temperature of 400°C in a flow of hydrogen for 1.5 h. The partial pressure of thiophene in the hydrogen-thiophene mixture was 6 kPa. The sulfiding agent was hydrogen sulfide liberated during thiophene hydrogenolysis. The steady state conversion was achieved after 1.5-2 h.

The HDS activity of catalysts in the absence of pyridine was evaluated on the basis of thiophene conversion to C_4 hydrocarbons (x_{TH}) . The products were analysed by thermal conductivity detector with hydrogen as eluent. Two successively connected columns were used to separate the products of thiophene conversion. One of them (2 m) packed with Carbowax (10 wt. %) on Chromosorb W was used at 110°C for separation of the uncoverted thiophene from other products. The other one (8 m) was filled with 20 wt. % $\beta\beta'$ -oxidipropionitrile on Chromosorb P and separated n-butane, 1-butene, *trans*-2-butene, *cis*-2-butene and hydrogen sulfide at room temperature

The activity of catalysts in simultaneous HDS and HDN reactions of thiophene and pyridine was measured in a high-pressure flow apparatus with fixed bed²⁵. The sample was in situ sulfided by a mixture of H_2S/H_2 (1:10) at 400°C and atmospheric pressure for 1 h. After sulfidation, the temperature was adjusted at 280°C and the feed containing thiophene ($p_{TH} = 0.65 \text{ kPa}$) and pyridine ($p_{PY} = 1 \text{ kPa}$) in hydrogen was introduced at 2 kPa of total pressure. The flow rate of the feed was 0.4 mol h^{-1} . The steady state conversions were achieved after 3-4 h on stream.

Hydrocarbons C_4 were the only products of thiophene HDS in the presence of pyridine. The intermediate tetrahydrothiophene was not detected and the reaction was described by Eq. (1). The HDS activity of each sample in the presence of pyridine was characterized by thiophene conversions (x_{TH}) determined at a fixed space time value W/F = 1.1 g h mmol⁻¹.

Thiophene
$$\xrightarrow{H_2} C_4$$
 Hydrocarbons + H₂S (1)

The HDN of pyridine in the presence of thiophene proceeds via piperidine to C_5 hydrocarbons and ammonia according reaction scheme proposed by McIlvried²⁶. N-Pentylamine was not detected in the reaction products over NiMo catalysts and only a small amount of it was formed on Mo catalyst. The reaction scheme was described by Eq. (2):

Pyridine
$$\xrightarrow{H_2}$$
 Piperidine $\xrightarrow{H_2}$ C₅ Hydrocarbons + NH₃ (2)

The catalysts were characterized by the overall conversion of pyridine (x_{PY}) and by the conversion to C_5 hydrocarbons (x_{C5}) , both at the space time W/F = 0.7 g h mmol⁻¹. The value of x_{C5} was used as measure of HDN activity. The HDN selectivity was characterized graphically by the position of the curves $x_{C5} = f(x_{PY})$ in the graph with coordinates x_{C5} and x_{PY} . It holds $x_{C5} = x_{PY}$ for all values of x_{PY} for the theoretically most selective catalyst. On the other hand, the lowest possible selectivity means that ammonia is formed only after hydrogenation of all pyridine to saturated amines.

RESULTS

The Effect of Nickel on HDS and HDN Catalytic Activities

Table I presents the results of the catalytic activity measurements in thiophene HDS and pyridine HDN proceeding simultaneously. The Ni/Al₂O₃ sample displayed no activity in both reactions. The catalyst containing molybdenum alone possesses a low HDS activity and a relatively high activity in pyridine hydrogenation. x_{PY} , but its HDN activity expressed by the value of x_{CS} is relatively low.

The introduction of nickel into the molybdenum-containing sample strongly promotes the activities of $NiMo/Al_2O_3$ sample in both reactions (Table I). The effect of nickel is much more pronounced with respect to the HDS activity which becomes three times higher than the activity of the Mo/Al_2O_3 sample. The overall conversion of pyridine does not increase significantly after Ni addition, while the conversion in C₅ hydrocarbons increases nearly twofold suggesting also the appearance of synergistic effect in HDN.

TABLE I

Activity of Ni/Al_2O_3 , Mo/Al_2O_3 and $NiMo/Al_2O_3$ catalysts in simultaneous HDS and HDN reaction of thiophene and pyridine at 280°C and pressure 2 MPa

Catalyata	HDS Reaction	HDN Reaction		
	x _{TH}	x _{PY}	x _{C5}	
Ni/Al ₂ O ₃	0.00	0.00	0.00	
Mo/Al_2O_3	0.22	0.42	0 ·0 4	
$NiMo/Al_2O_3$	0.66	0.48	0.07	
Mo/Al ₂ O ₃ NiMo/Al ₂ O ₃	0·22 0·66	0·42 0·48	0∙04 0∙07	

The Effect of Phosphorus on HDS and HDN Catalytic Activities

Figure 1 shows the change in conversion of thiophene to C_4 products, versus the P content in the catalyst samples at WHSV of $2 h^{-1}$ in the absence of pyridine. A weak maximum of thiophene conversion is observed at 1 wt. % P in the samples. The conversion of thiophene decreases with the increase of phosphorus concentration.

The addition of 1 wt. % of phosphorus to the catalyst enhaces x_{TH} , x_{PY} and x_{C5} (Table II). At higher phosphorus concentration in the catalysts (from 2 to 5 wt. %) the activities decrease uniformly. The alumina-supported NiMo samples, containing less than 3 wt. % P, display HDS activity comparable to that of the commerical

TABLE II

Activity of P-modified NiMo/Al₂O₃ catalysts in simultaneous HDS and HDN reactions of thiophene and pyridine at 280°C and pressure 2 MPa

Catalusta	P Content	HDS Reaction	HDN Reaction	
Catalysis	wt. %		x _{PY}	x _{C5}
NiMo/Al ₂ O ₃	0.00	0.66	0.48	0.07
1PNiMo/Al ₂ O ₂	1.00	0.73	0.55	0.08
2PNiMo/Al ₂ O	2.00	0.63	0.45	0.06
3PNiMo/Al ₂ O	3.00	0.38	0.35	0.03
5PNiMo/Al,O	5.00	0.48	0.34	0.04
Commercial cat	2.70	0.69	0.42	0.12



FIG. 1

Effect of phosphorus on the HDS activity of $PNiMo/Al_2O_3$ catalysts in absence of pyridine at WHSV of $2 h^{-1}$ and $400^{\circ}C$

catalyst. Similarly, the hydrogenation activity is very close to that of the commercial catalyst for most of the prepared by us samples. However, the HDN activity of $PNiMo/Al_2O_3$ catalysts is distinctly lower than that of the commercial catalyst.

Diffuse Reflectance Spectra

Figure 2 shows the diffuse reflectance spectra of the calcined alumina-supported nickel-molybdenum catalysts with and without a phosphorus promoter and the spectra of a commercial catalyst in the 800-200 nm interval.

A strong absorption band is observed in the UV-Visible range of the electronic spectra at around 260 nm, which is due to the charge-transfer: $O^2 \rightarrow Mo^{6+}$ (ref.²⁷).

The bands with weakly expressed maxima at about 660 and 740 nm in the UV--Visible range and at 1 140 and 1 230 nm in the NIR range (which are not reflected in the figure) indicate the presence of Ni²⁺ ions in octahedral coordination²⁸⁻³¹. The weak shoulder at about 410 nm on the background of the charge-transfer band of $O^{2-} \rightarrow Mo^{6+}$ also confirms the presence of Ni(Oh). The splitting of the band at 660 and 745 nm in the spectra of nickel-molybdenum catalysts due to the incorporation of MoO_4^{2-} ions in the coordination sphere of the Ni²⁺ ions confirms the formation of polymolybdenum compounds of nickel³⁰.

A broad band is observed in the region 640-570 nm in the spectra of the samples without and with low content of phosphorus (1-2 wt. % P). This band can be associated with Ni²⁺ doublet t₃ in a tetrahedral coordination on the basis of data from the literature³¹. Upon increasing the P concentration the intensity of this





Diffuse reflectance spectra of the calcined catalysts: a $NiMo/Al_2O_3$; b 1 PNiMo/ $/Al_2O_3$; c 2 PNiMo $/Al_2O_3$; d 3 PNiMo/ $/Al_2O_3$; e 5 PNiMo $/Al_2O_3$ and f commercial catalyst

1039

band decreases. Similar results have been obtained for the $PNiMo/Al_2O_3$ catalysts^{2,14} and they can be explained by the inhibiting effect of phosphorus on the spinel formation. On the other hand, the intensity of the bands at 740 and 660 nm of the octahedrally coordinated Ni²⁺ increases when the P content increases. Consequently, in the samples with greater P content a higher amount of the polymolybdenum compounds of nickel has been formed.

DISCUSSION

It is known from the literature³²⁻³⁵ that the nitrogen-containing compounds can inhibit the hydroprocessing strongly by competitive adsorption on acid sites. On the other hand, the acidity of alumina-supported nickel-molybdenum catalysts increases with their sulfidation³⁶. This probably brings to a decrease in the poisoning effect of pyridine on the thiophene HDS. The change in the HDS activity of both $NiMo/Al_2O_3$ and Mo/Al_2O_3 samples (Table II) demonstrates distinctly a synergistic effect, which is well known in the literature. The data in Table I evidence that irrespective of the competitive adsorption of thiophene and pyridine on the catalytic surface, the HDN activity, x_{c5} , of NiMo/Al₂O₃ sample, which is associated with breaking of the C-N bond on the acid sites of the catalyst surface^{6,37-39} significantly increases. This fact can be explained by a greater acidity of the NiMo catalyst (than Mo sample) as a result of both preliminary sulfidation and participation of thiophene and H₂S formed during thiophene hydrogenolysis⁴⁰. It should be noted that in the case of simultaneously proceeding HDS and HDN reactions, the synergism in HDN seems to be induced by the synergism in the HDS reaction, producing H_2S which enhances the catalyst acidity required for hydrogenolysis of the C-N bond. This is probably the reason for the difference between our data and those of Ledoux⁵. They found no promoting effect of nickel on the catalyst activity in the case of pyridine hydrodenitrogenation.

This behaviour seems to be contradictory to our earlier observation, regarding carbon-supported CoMo catalysts, where the strong promoting effect of cobalt was observed only in thiophene HDS. No such effect appeared in the parallelly proceeding HDN¹. This difference can be explained by the different nature of the support.

The addition of a second promoter (phosphorus) to the samples has no substantial effect on the hydrodesulfurization of thiophene either in the presence (Table II) or in the absence (Fig. 1) of pyridine. The increase in the HDS activity, x_{TH} , at 1 wt. % P is negligible, which is in agreement with our previous results^{22,22} as well as with literature data²³.

Since phosphorus does not influence essentially the increase in HDS activity, we can obviously expect no substantial increase in the HDN activity, x_{C5} , and in the pyridine conversion, x_{PY} , of the 1PNiMo/Al₂O₃ sample in comparison to the activity

of the NiMo/Al₂O₃ without phosphorus (Table II). Similarly to the HDS activity, the HDN activity drops down at higher phosphorus concentrations.

From Table II it is seen that HDS and pyridine hydrogenation activities of our catalysts containing up to 2% of phosphorus are quite comparable with the commercial catalyst. However, HDN activity of commercial catalyst was distinctly higher. In order to get insight in this matter the data on conversion C₅ were plotted against pyridine conversion, x_{PY} , in Fig. 3.

In our previous experience with various catalysts, the integral conversion data follow the pseudo first-order kinetics²⁶. In this situation, the position of the curve $x_{C5} = f(x_{PY})$ in the Fig. 3 is determined only by the ratio k_{C5}/k_{PY} , as shown by Eq. (3), where k_{PY} , k_{C5} are the pseudo first-order rate constants of the first and second step in the Eq. (2), respectively.

$$x_{C5} = x_{PY} - \left[k_{PY}(k_{C5} - k_{PY})\right] \left[1 - x_{PY} - (1 - x_{PY}) k_{C5}/k_{PY}\right]$$
(3)

Figure 3 shows several curves calculated for different k_{C5}/k_{PY} ratios. The plotting of our experimental data into the diagram in Fig. 3 allows the discussion of the k_{PY}/k_{C5} ratio of our catalysts.

It is seen in Fig. 3 that experimental points for all our P-modified NiMo catalysts fit to one and those for the commercial catalyst fit to the another curve. It follows that the HDN selectivity toward C₅ hydrocarbons formation was the same for all NiMo catalysts prepared despite of different phosphorus content. At the same time, this selectivity was distinctly higher for the commercial catalyst. Data for the commercial catalyst correspond approximately to the curve calculated for the ratio $k_{PY}/k_{C5} = 0.8$. On the other hand, the data for the P-modified catalysts correspond to the curve with ratio $k_{PY}/k_{C5} = 3$. The set of our catalysts prepared by co-impregnation possessed therefore rather good hydrogenation activity but their hydrogenolytic efficiency was low.



Fig. 3

Effect of pyridine conversion, x_{PY} , on the HDN activity, x_{C5} , for PNiMo/Al₂O₃ (O) and commercial (\bullet) catalysts in presence of thiophene at 280°C and pressure 2 MPa. The numbers of curves correspond to the ratio k_{PY}/k_{C5} for which the dependence was calculated according Eq. (3). The dotted line stands for limiting case, when $k_{PY}/k_{C5} \rightarrow 0$

Collect. Czech. Chem. Commun. (Vol. 57) (1992)

1040

The markedly higher HDN activity and therefore higher HDN selectivity of the commercial NiMo catalyst can be most likely attributed to an optimum acidity of the sample under the conditions chosen. This acidity is supposed to ensure a larger amount of active sites responsible for the breaking of the C—N bond. In view of the mutual effect of the metal and the acid sites⁶ it can be expected that the splitting of the C—N bond should be associated with the presence of nickel of a higher dispersity in the commercial catalyst under the reaction conditions. The shift of the band (from 580-750 nm to 800 nm) and of the charge-transfer band of $O^{2-} \rightarrow Mo^{6+}$ to a higher wavelength (from 260 to 315 nm in the spectra of calcined samples are connected with the presence of high-dispersity polymolybdenum compounds of nickel (Fig. 2).

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