COMPARISON OF SELECTIVITY OF Ni, Mo, AND Ni–Mo SULFIDE CATALYSTS IN PARALLEL HYDRODENITROGENATION AND HYDRODESULFURIZATION

Alexandra DRAHORÁDOVÁ and Miroslav ZDRAŽIL

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchdol

Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.

Selectivity of hydrodenitrogenation/hydrodesulfurization (HDN/HDS) using carbon supported Ni, Mo, and Ni–Mo sulfide catalysts was studied at a pressure of 2 MPa and over a temperature range of 280 – 350 °C. A commercial alumina supported Ni–Mo sample was also included as reference catalyst. Model compounds used were pyridine and thiophene. Selectivity (HDN/HDS) increased with decreasing temperature and decreased in the order Ni, Mo, Ni–Mo. Ni/C catalyst exhibited unusually high HDN/HDS selectivity at low temperature, where HDN of pyridine was faster than HDS of thiophene. Selectivity was interpreted as an intensive property of a catalyst characterizing quality of active surface. The combination of Ni and Mo sulfides in Ni–Mo catalyst resulted in a strong shift in HDN/HDS selectivity to the HDS side; the selectivity of Ni–Mo sample was very low and was not an average of the selectivities of Ni and Mo catalyst. This was interpreted as the evidence of the chemical synergism in the Ni–Mo sulfide system, because structure synergism cannot cause such selectivity changes accompanying combination of Ni and Mo sulfide into the mixed catalyst.

Under industrial hydroprocessing conditions over Ni–Mo or Co–Mo sulfide catalysts, hydrodenitrogenation (HDN) is more difficult that hydrodesulfurization (HDS)[1,2]. It has been suggested that this can partially be explained by the relative strength of carbon–nitrogen and carbon–sulfur bonds[1]. The first purpose of the present paper is to show that the low ratio of rates (HDN/HDS) is not a general phenomenon and that, with other catalysts and under proper conditions, HDN can be faster than HDS.

Selectivity of heterogeneous catalyst is determined by the relation between various parallel and consecutive reaction steps in the coupled reaction network of simultaneously catalyzed reactions. It is an intensive property of a catalyst (similarly as, e.g., activation energy) and can be used as a fingerprint probe of the nature of the active surface. It was found previously[3,4] that the well known synergism in activity between Co(Ni) and Mo(W) in two-component Co(Ni)–Mo(W) sulfide catalysts is systematically accompanied by a characteristic change in selectivity (hydrogenation/C–S

hydrogenolysis) in consecutive or parallel reactions. Selectivity of a two-component Co(Ni)–Mo(W) catalyst was not an average of selectivities of single-component Co(Ni) and Mo(W) catalysts, but was strongly shifted to the side of C–S hydrogenolysis. The second purpose of the present paper is to show that an analogous characteristic shift of selectivity also occurs in HDN/HDS selectivity in a parallel reaction network of simultaneous HDN and HDS reactions.

Simultaneous HDS of thiophene and HDN of pyridine were used as model reactions in the present work. It is well known that over two-component Ni–Mo catalyst, HDS of thiophene is faster than HDN of pyridine[5 – 9]. However, the reaction of this pair of reactants over single-component Mo catalyst has been studied much less[9] and no data are available for single-component Ni sulfide catalyst.

EXPERIMENTAL

Catalysts. The active carbon was commercial product (GA-1, Slovenské lučobné závody, Hnúšťa, Czechoslovakia) with BET surface area of 1 100 m^2 g^{-1}, pore volume 0.75 cm^3 g^{-1}, and volume of micropores 0.45 cm^3 g^{-1}. The particle size of it was 0.16 – 0.32 mm. It was washed with hot water and dried in vacuum rotary evaporator before impregnation.

Active carbon supported Mo/C, Ni/C and Ni–Mo/C catalysts contained 0.83 (mmol Mo) g^{-1}, 0.83 (mmol Ni) g^{-1}, and (0.83 (mmol Mo) + 0.42 (mmol Ni)) g^{-1}, respectively. This corresponds to loading (in mass %) 12% MoO_3, 6% NiO, and (12% MoO_3 + 3% NiO), respectively. The catalysts were prepared by conventional sequential impregnation in rotary vacuum evaporator, using aqueous solutions of ammonium molybdate and nickel nitrate. The catalysts were not calcined.

The Mo/C sample: 5 g of the active carbon was mixed with the solution of 0.87 g of $(NH_4)_6Mo_7O_{24}$. 4 H_2O in 30 ml of water. The main part of water was removed in rotary evaporator at 80 °C in such a way that the solid was wet and no excess solution was present. This wet mass was heated for 1 h at 80 °C under atmospheric pressure and dried for 1 h at 100 °C under vacuum. The Ni/C sample: 5 g of the active carbon was mixed with the solution of 1.24 g of $Ni(NO_3)_2$. 6 H_2O in 10 ml of water. The slurry was heated 1 h at 80 °C and dried 1 h at 100 °C under vacuum. The sample Ni–Mo/C: 5.9 g of the Mo/C catalyst was mixed with the solution of 0.69 g of $Ni(NO_3)_2$. 6 H_2O in 10 ml of water and dried 1 h at 100 °C under vacuum.

The commercial Ni–Mo/alumina catalyst designated Shell 324 (17.7% MoO_3, 3.4% NiO) was used as the reference of activity and selectivity. The extrudates were crushed to particle size 0.16 – 0.32 mm.

Apparatus. The integral conversions were measured in flow reactor with fixed bed of catalyst and with all reactants in the gas phase. The reactor was made of a stainless-steel tube of 2 mm i.d. and the catalyst charge, W (0.01 – 1 g), was placed in it between two plugs of glass wool. The composition of the inlet and outlet streams of the reactor was analyzed using on line gas chromatograph.

The feed was prepared in a simple flow evaporator (not bubble saturator) filled by a mixture of liquid thiophene (FLUKA, purum) and pyridine (FLUKA, p.a.). The feed rates, $F(i)$, of hydrogen, thiophene (TH), and pyridine (PY) were 400, 0.09, and 0.08 mmol h^{-1}, respectively.

Analysis. The gas chromatographic analysis (FID detector) was carried out isothermally at 122 °C on a 2.5 glass column (3 mm i.d.) packed with 60/80 Carbopack B/4% Carbowax 20 M/0.8% KOH (Supelco). The products of the reaction of thiophene were C4-hydrocarbons (C4); other carbon containing products were negligible. The products of pyridine reaction were C5-hydrocarbons (C5), piperidine (PI), and 1-pentylamine (PA). The amount of PA was always much lower than that of PI. Products hydrogen sulfide and ammonia were not analyzed.

Procedure. The catalysts were presulfided in situ at atmospheric pressure with a H_2S/H_2 mixture (1 : 10) at 400 °C for 2 h. Integral conversions were measured at various values of space time W/F. The flow rate of the feed was the same in all experiments and space time was changed by variation of W. The run at each space time value was performed with a fresh catalyst charge.

Definition of conversions $x(i)$ in terms of initial and final number of moles, $n^0(i)$ and $n(i)$, respectively: overall conversion of thiophene: $x(TH) = (n^0(TH) - n(TH))/n^0(TH)$; hydrodesulfurization conversion of thiophene: $x(C4) = n(C4)/n^0(TH)$, (under our conditions $x(TH) = x(C4)$); overall conversion of pyridine: $x(PY) = (n^0(PY) - n(PY))/n^0(PY)$; and hydrodenitrogenation conversion of pyridine: $x(C5) = n(C5)/n^0(PY)$.

RESULTS AND DISCUSSION

Activity

The subject of the present paper is HDN/HDS selectivity. Activity data will not be presented in detail because they are not important for the conclusions. However, it is useful to mention the relative level of activity of the discussed catalysts.

The deactivation of hydrotreating catalyst is mostly caused by coking. The high ratio of partial pressure of hydrogen to partial pressure of organic compounds in the feed used in our experiments was unfavourable for coking. In agreement with it, the activity of the catalysts was relatively stable. Activity data presented are based on steady state conversions attained after 4 h on stream; the activity decline in another 4 h was negligible.

In Table I, hydrodenitrogenation activity $A(HDN)$, mmol h^{-1} g_{cat}^{-1}, is shown, which was defined as space velocity $F(PY)/W$ at which $x(C5)$ was 50%; values relative to the reference Shell catalyst are given. The sulfided catalyst Ir/C studied in the previous paper[8] is also included in Table I because the selectivity of this catalyst is also discussed below. The reproducibility of the values of $A(HDN)$ in the Table I was better than 20%.

TABLE I
Relative hydrodenitrogenation activity $A(HDN)$ of sulfided catalysts at 280 °C and 2 MPa

Catalyst	$A(HDN)^a$
Mo/C	1.7
Ni/C	0.3
Ni–Mo/C	5.0
Ir/C[b]	9.9
Ni–Mo/Al$_2$O$_3$ (Shell 324)	1.0

[a] Dimensionless values relative to the reference catalyst Shell 324. [b] The catalyst studied in previous work[8], the metal content was 0.83 mmol g_{cat}^{-1}.

Evaluation of Selectivity

The selectivity of catalysts measured in the present work was integral selectivity. It was evaluated by plotting conversions in diagrams $x(PY) = f(x(TH))$ and $x(C5) = f(x(TH))$. The position of the curve in the first type of diagram characterizes the selectivity of the catalyst in the pair of reactions: (i) overall removal of pyridine and (ii) HDS of thiophene. The second type of conversion diagram characterizes the selectivity of the catalyst in the pair of reactions: (i) HDN of pyridine and (ii) HDS of thiophene.

The conversion data are plotted in Figs 1, 2, and 4. The curves for various catalysts do not intersect each other. So, the discussed relative order of the selectivity of the catalysts is independent of the level of conversion.

However, the selectivity (HDN/HDS), evaluated by the position of the curve in conversion diagram, depends on three types of variables: (i) transition model sulfide or combination of them, (ii) type of carrier, metal loading, preparation and activation procedure, and (iii) kinetic variables: composition of the feed and temperature. The main purpose of the present work was to study the effect of metal sulfide (variable (i)) at fixed kinetic variables (variable (iii)). The results on the temperature dependence of the selectivity of Ni/C catalyst were also obtained.

In general, variables (ii) strongly influence activity, because this strongly depends on dispersion and surface area of active sulfides. However, selectivity depends much less than activity on the extensive parameters such as surface area and dispersion of active phase, because it is determined by relative activities of the catalyst to various reactions in the reaction network. Our previous experience with various Ni–Mo samples in parallel HDN and HDS, and also with other types of selectivities in hydrorefining catalysis, coincides with this rule. It is believed that the relative order of selectivity of the catalysts observed in the present work is independent of carrier, metal loading and preparation and activation procedure.

The reproducibility of the selectivity measurement was very good. This is documented by the data for Ni–Mo catalyst shown in Fig. 4. Each of the nine points for Ni–Mo catalyst was obtained on the fresh catalyst charge. Also the change of the selectivity with deactivation of the catalyst was negligible.

High Selectivity of Ni/C Catalyst to HDN

The selectivity data obtained on Ni–Mo and Mo catalyst were in full agreement with published results on simultaneous HDS of thiophene and HDN of pyridine[5–9] and can be summarized as follows:

a) over Ni–Mo catalyst, HDN is much slower then HDS;

b) HDN/HDS selectivity of Mo catalyst is higher than that of Ni–Mo catalyst;

c) HDN/HDS selectivities of Mo and Ni–Mo catalyst increase with decreasing temperature; over Ni–Mo catalyst HDN remains slower than HDS even at a low tempe-

rature of about 280 °C; over Mo catalyst HDN and HDS conversions become comparable at that low temperature.

The data obtained on the Ni catalyst are plotted in Fig. 1. It is seen that the effect of temperature was the same as discussed above for Mo and Ni–Mo catalysts: HDN/HDS selectivity increased with decreasing temperature. This seems to be caused by competitive adsorption, rather than by a higher activation energy of the surface HDS reaction as compared with the surface HDN reaction. The overall HDS rate of thiophene is strongly inhibited by competitive adsorption of pyridine[5 – 7,10,11]. This adsorption and inhibition increases with decreasing temperature[7]. Full kinetic analysis with one catalyst is needed to verify this hypothesis explaining the change of selectivity with temperature. However, the present work concentrated on the comparison of different catalysts and the data do not allow more detailed analysis of the problem.

The nickel sulfide catalyst was very selective to HDN at low temperature (280 °C), as shown in Fig. 1. Pyridine was much more reactive than thiophene at that conditions; at an HDS conversion x(TH) of 25% the overall conversion of pyridine x(PY) was 80% and the HDN conversion x(C5) was 50%. Very high HDN/HDS selectivity was previously also found for sulfided Pt/C and Ir/C catalysts[8]; the data of that paper on Ir/C sample are replotted in Fig. 2 for comparison (selectivity of the Pt/C sample was similar to that of the Ir/C catalyst). It is seen from Figs 1 and 2 that Ni/C sample was even more selective to HDN than the Ir/C catalyst. Figure 2 also shows that the HDN/HDS selectivity of the reference alumina supported Ni–Mo catalyst was low, in agreement with the literature[5 – 9]. It is concluded that among sulfide catalysts reported in the literature up to now, Ni/C catalyst exhibits the highest HDN/HDS selectivity. This is an important result even though the activity of Ni catalyst was relatively low (Table I).
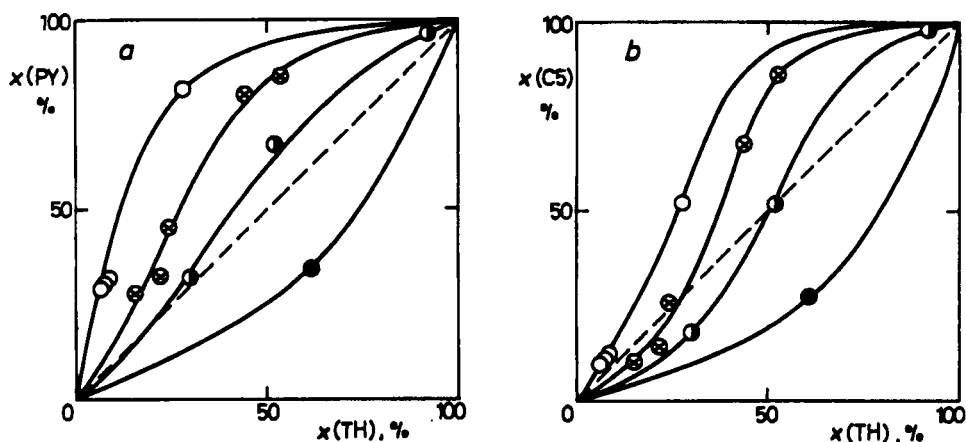

Fig. 1

Selectivity in parallel hydrodenitrogenation of pyridine (a) and hydrodesulfurization of thiophene (b) over Ni/C catalyst at a pressure of 2 MPa; O 280 °C; ⊗ 300 °C; ◑ 320 °C; ● 350 °C

We suggest that even higher HDN/HDS selectivity can be achieved. It is well known that HDS of thiophene and HDN of pyridine are inhibited[11 - 13] and promoted[11,14] by addition of hydrogen sulfide to the feed, respectively. High HDN/HDS selectivity observed over Ni/C catalyst at low temperature should be shifted to even higher values by addition of hydrogen sulfide to the feed; the HDS activity should decrease while the HDN activity should increase.

The common opinion in the literature related to hydrotreating is that HDS of thiophene is generally much easier than HDN of pyridine (see the literature cited above). However, the conclusion of the present work is that the relative reactivity of thiophene and pyridine is not so unambiguous and that it strongly depends on the transition metal sulfide and the temperature. HDS is much easier than HDN in one situation, namely at high temperature and using Ni–Mo/alumina catalyst (or even better, using Co–Mo/alumina catalyst which is known to be more selective to HDS in parallel HDN and HDS than Ni–Mo system (e.g. refs[8,15]). However, HDS is more difficult than HDN at other conditions, namely at low temperature, and using Ni/C catalyst and addition of hydrogen sulfide to the feed.

Synergistic Shift in HDN/HDS Selectivity

Synergism in activity of two-component sulfides Co–Mo, Ni–Mo, Co–W, and Ni–W is systematically accompanied by a shift of hydrogenation/C–S hydrogenolysis selectivity, (HYD/CSH), to the hydrogenolysis side as compared with single-component catalysts. This general conclusion was derived from analysis of formation of intermediates
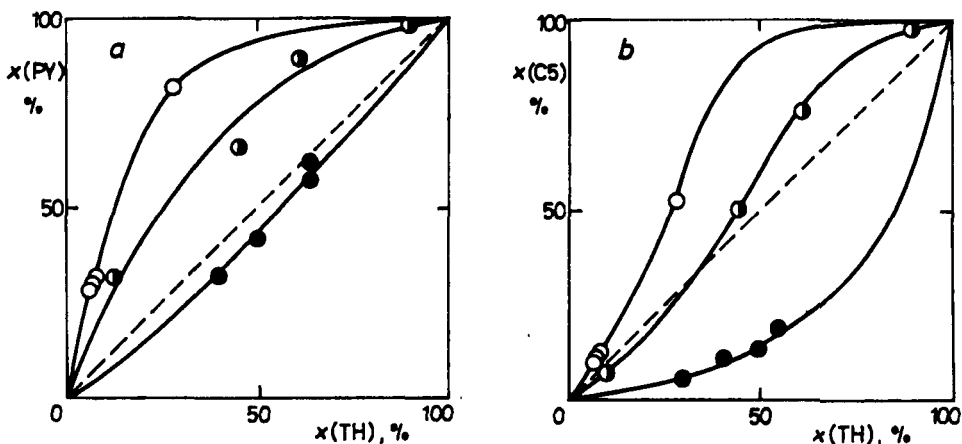

FIG. 2
Selectivity in parallel hydrodenitrogenation of pyridine (*a*) and hydrodesulfurization of thiophene (*b*) at 280 °C and 2 MPa. Present work: O Ni/C; ● Ni–Mo/Al$_2$O$_3$ Shell 324; replotted from previous work[8] ◑ Ir/C

in HDS of aromatic sulfur heterocycles (selectivity in a consecutive reaction scheme which contains hydrogenation and hydrogenolysis steps) and of relative reactivities of olefins and sulfur heterocycles (selectivity in parallel reactions)[3,4].

The phenomenon is illustrated by formation of intermediate dihydrobenzothiophene (DHBT) in hydrodesulfurization of benzothiophene (BT), as shown in Fig. 3; DHBT is formed by hydrogenation and decomposed by C–S hydrogenolysis. The selectivity HYD/CSH of a two-component synergistic catalyst was not an average of selectivities of corresponding single-component sulfides, but was much smaller. This will be refered as SYnergistic Shift in SElectivity, SYSSE. Over two-component catalysts not exhibiting synergism in activity, such as Ni–V, Ni–Cr, or Ni–Mn, SYSSE was not observed[16]; the selectivity of two-component catalyst was an average of selectivities of corresponding single-component catalysts.

An analogous SYSSE phenomenon was observed in the present work in the case of HDN/HDS selectivity. As shown in Fig. 4, the selectivity of Ni–Mo catalyst was not an average of the selectivities of Ni and Mo catalysts, but was strongly shifted to the HDS side. The synergistic shift in HYD/CSH and HDN/HDS selectivities is connected with the higher magnitude of synergism in C–S hydrogenolysis activity as compared with hydrogenation and C–N hydrogenolytic activities.

Importance of Selectivity Measurements for the Theory of Synergism

The alternative concepts of "electronic promotion (synergism)" and of "structural promotion (synergism)" are still discussed as for theory of synergism in sulfide catalysis (recently, for instance ref.[18]). The SYSSE observed in the present work can serve as an additional argument that "electronic promotion" is more important than "structural promotion". If the surface of a Ni–Mo catalyst were a simple sum of surfaces of Ni
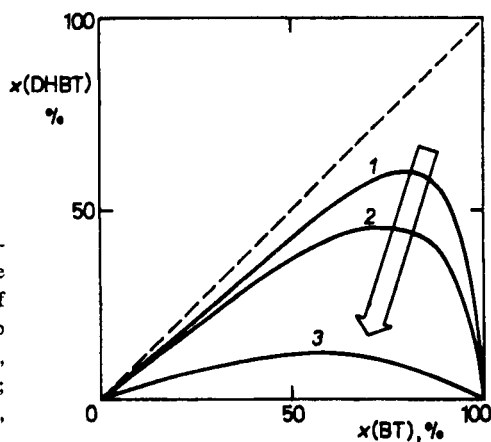

FIG. 3
Synergistic shift in hydrogenation/C–S hydrogenolysis selectivity of formation of intermediate dihydrobenzothiophene (DHBT) in HDS of benzothiophene (BT), (schematically according to data in refs[16,17]). x(BT) overall conversion of BT, x(DHBT) conversion of BT to DHBT, *1* Mo or W; *2* Co or Ni; *3* Co–Mo or Ni–Mo or Co–W or Ni–W, arrow shows synergistic shift in selectivity

and Mo sulfides without any chemical interaction, that is in the case when none or only structural synergism occurs, the selectivity curve for Ni–Mo catalyst in Fig. 4 should be between the curves for the Ni and Mo catalysts.

We suggest that selectivity measurement can be very useful in evaluation of the degree of utilization of Co(Ni) and Mo(W) in the formation of a synergic structure (e.g. "Co–Mo–S phase" or the point of contact between crystals of Co and Mo sulfides). In a set of catalysts with the same overall composition, the catalyst with the best utilization of components exhibits highest SYSSE, that is, the selectivity curve of two-component catalyst is in the extreme position. Poor utilization of components (caused, for instance, by inproper preparation of the catalyst) is indicated by the shift of the selectivity curve from the extreme position on the HDS side toward the selectivity curves of single components; the magnitude of SYSSE is decreased. The measurement of selectivity can also be easily used to test the occurence of electronic (chemical) synergism in other than classical pairs of sulfides, Co–Mo, Ni–Mo, Co–W, and Ni–W. The important point is that selectivity measurements provide information on synergism independently of extensive factors such as surface area of catalyst.

CONCLUSIONS

1) Sulfided Ni/C catalyst exhibited very high HDN/HDS selectivity and seems to be the most selective catalyst to HDN among catalysts reported up to now. At low temperature over this catalyst, HDN of pyridine is faster than HDS of thiophene.

2) Selectivity (HDN/HDS) of two-component Ni–Mo catalyst was much lower than the selectivities of single-component sulfides Ni and Mo. This synergistic shift of
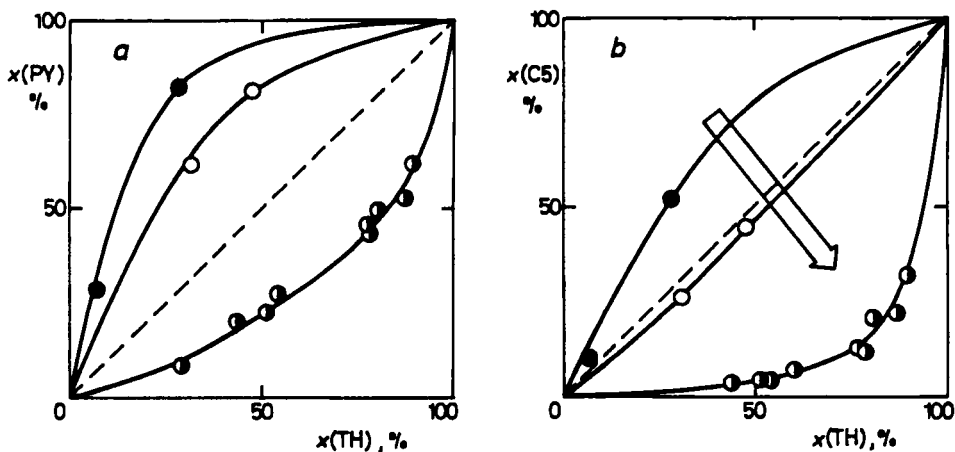

FIG. 4

Shift of HDN (*a*) and HDS (*b*) selectivity accompanying combination of sulfides in the synergistic pair Ni–Mo (280 °C, 2 MPa), ● Ni/C; ○ Mo/C; ◑ Ni–Mo/C; arrow shows synergistic shift in selectivity

selectivity is an additional argument for chemical (electronic) synergism in the Ni–Mo sulfide catalyst system.

REFERENCES

1. Katzer J. R., Sivasubramanian R.: Catal. Rev.-Sci. Eng. *20*, 155 (1979).
2. Ho T. C.: Catal. Rev.-Sci. Eng. *30*, 117 (1988).
3. Zdražil M., Kraus M. in: *Studies in Surface Science and Catalysis, Catalytic Hydrogenation* (L. Červený, Ed.), Vol. 27, p. 257. Elsevier, Amsterdam 1986.
4. Zdražil M.: Catal. Today *3*, 269 (1988).
5. Satterfield C. N., Modell M., Mayer J. F.: AIChE J. *21*, 1100 (1975).
6. Satterfield C. N., Modell M., Wilkens J. A.: Ind. Eng. Chem., Process Des. Dev. *19*, 154 (1980).
7. LaVopa V., Satterfield C. N.: J. Catal. *110*, 375 (1988).
8. Vít Z., Zdražil M.: J. Catal. *119*, 1 (1989).
9. Vít Z.: Catal. Lett. *13*, 131 (1992).
10. Massoth F. E., Miciukiewicz J.: J. Catal. *101*, 505 (1986).
11. Girgis M. J., Gates B. C.: Ind. Eng. Chem. Res. *30*, 2021 (1991).
12. Vrinat M.: Appl. Catal. *6*, 137 (1983).
13. Van Parijs I. A., Froment G. F.: Ind. Eng. Chem., Prod. Res. Dev. *25*, 431 (1986).
14. Hanlon R. T.: J. Energy, Fuels *1*, 424 (1987).
15. Kellet T. F., Sartor A. F., Trevino C. A.: Hydrocarbon Process. *59*(5), 139 (1980).
16. Koloušek V., Zdražil M. in: *Proc. VIth Int. Symp. Heter. Catal. Sofia 1987* (D. Shopov, A. Andreev, A. Palazov and L. Petrov, Eds), Vol. 1, p. 491. Bulgarian Academy of Sciences, Sofia 1987.
17. Peter R., Zdražil M.: Collect. Czech. Chem. Commun. *51*, 327 (1986).
18. Chianelli R. R., Daage M. in: *Studies in Surface Science and Catalysis, Hydrotreating Catalysts* (M. L. Occelli and R. G. Anthony, Eds), Vol. 50, p. 1. Elsevier, Amsterdam 1989.

Translated by the author (M. Z.).