SURFACE PROPERTIES AND CATALYTIC BEHAVIOUR
IN THIOPHENE HYDRODESULFURIZATION
ON Mo- AND NiMo-MODIFIED HZSM-5 ZEOLITES

Alla A. SPOJAKINA and Nina G. KOSTOVA

Institute of Kinetics and Catalysis,
Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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

Zeolite HZSM-5 containing 1 wt.% Ni and 10 wt.% Mo has been investigated using IR spectroscopy and thiophene hydrodesulfurization (HDS). The IR spectra indicate the strong interaction of molybdenum and nickel with zeolite lattice, forming polymolybdates of different composition. The acidity of the samples is influenced by the composition and reduction treatment. The zeolite is found to exhibit shape selectivity during thiophene conversion.

Zeolite catalysts containing molybdenum are attractive for many reactions, including HDS[1 – 8]. The commercial hydrocracking catalysts contain sulfided Ni and Mo phase as the hydrogenation component and zeolites as the acidic component[2]. Zeolites, particularly faujasites are used as promoting additive to HDS catalysts[3]. The effect of faujasite modification on the stability and selectivity of Mo-containing catalysts in thiophene conversion has been studied[4]. Siliceous zeolites have been used in HDS reaction less frequently[5 – 8]. Givens et al.[5] examined hydrogenolysis of thiophene on RhZSM-5. HDS of diethylsulfide on zeolites containing transition metals has been studied by Davidova et al.[6]. The study of surface properties and thiophene HDS activity of a molybdenum-impregnated ZSM-5 zeolite was carried out by Lopez Agudo et al.[7]. Some physico-chemical properties of Mo-containing ZSM-5 zeolite have been reported[6 – 11].

We have reported on some comparative features of Mo-containing different zeolites in HDS reaction[9]. This paper presents more details on physico-chemical properties of Mo(Ni)-containing HZSM-5 samples and their catalytic behaviour in thiophene hydrogenolysis.

EXPERIMENTAL

HZSM (SiO_2/Al_2O_3 = 44) was used as the starting material. Nickel was impregnated on the zeolite using a nickel nitrate solution. Molybdenum-containing samples were prepared by impregnation with ammonium heptamolybdate solution. For the NiMo zeolite, nickel was introduced before molybdenum. The samples

contained 1 wt.% Ni and 10 wt.% Mo. Catalysts were dried at 378 K for 4 h and calcined 2 h at 623 K. The state of molybdenum in the catalysts was characterized by IR spectroscopy in the $400 - 1\,300$ cm^{-1} region, using pellets of zeolites pressed in KBr (SPECORD IR 75 spectrometer). IR spectra of powdered samples in the region of surface hydroxyl groups were measured at 300 K using a Perkin–Elmer 580B spectrophotometer provided with diffuse reflectance adapter[12]. The acidity of the samples was evaluated by means of pyridine chemisorption at 423 K on a sample treated beforehand with pyridine at 623 K and evacuated at the same temperature[13].

The conversion of thiophene was studied at 623 K using a fixed bed continuous flow microreactor at atmospheric pressure (WHSV 0.6 h^{-1}, partial pressure of thiophene 2.853 kPa). The products were analyzed by gas chromatography[14]. Prior to thiophene admission, the catalysts were heated in a flow of hydrogen from room temperature to 623 K for 1.5 h (40 ml/min). H$_2$S evolved from thiophene sulfided the catalysts. Catalyst activity was evaluated by thiophene conversion to hydrocarbons and H$_2$S.

RESULTS AND DISCUSSION

The IR spectra of HZSM-5, MoHZSM-5 and NiMoHZSM-5 are presented in Fig. 1. The intensities of structurally sensitive bands at 540, 790, and 1 220 cm^{-1} for HZSM-5 are maintained in the modified samples. These results correlate with the intensity of lines in the corresponding diffractograms of the samples. This indicates that the structure of the zeolite did not decompose in the course of modification.

Some new bands at $880 - 950$ cm^{-1} and $610 - 650$ cm^{-1} in the IR spectra of Mo-containing samples can result from interaction of the supported Mo species with the zeolite
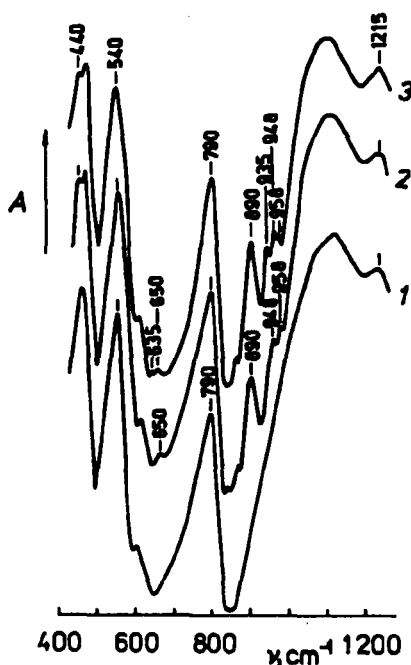

FIG. 1
IR spectra of the samples calcined at 623 K.
1 HZSM-5; 2 MoHZSM-5; 3 NiMoHZSM-5

framework or on the other hand between the components introduced. The bands are characteristic of polymolybdate structures analogous to aluminium heteropolymolybdate (bands at 440, 650, 890, and 948 cm^{-1}), nickel heteropolymolybdate[15] (bands at 635, 875, and 930 cm^{-1}) and molybdosilicic heteropoly acid[16] (bands at 860, 958). These data agree with our earlier results[4].

Two hydroxyl bands at 3 740 and 3 610 cm^{-1}, present in the spectra of the HZSM-5 zeolite (Fig. 2, curve *1*), characterize acidic –Si–OH and –Si–OH–Al– groups. The band at 3 610 cm^{-1} is related to the sites of strong acidity and that at 3 740 cm^{-1} reflects a relatively weak acidity[17]. The intensity of the band at 3 610 cm^{-1} was taken as a measure of the Brønsted acidic sites concentration[18]. In the spectrum of MoHZSM-5 the band at 3 740 cm^{-1} disappears and the band at 3 610 cm^{-1} shows slight intensity decrease. An appreciable shift of the band at 3 610 cm^{-1} to the higher frequencies is observed. Ezzamarty et al.[19] have shown that the band at 3 665 cm^{-1} along with 3 610 cm^{-1} in MoHY is connected with the extraframework aluminium. In our case, the above mentioned frequence shift could be assigned to this form of aluminium as the result of the interaction of molybdenum with zeolite framework, followed by alumi-
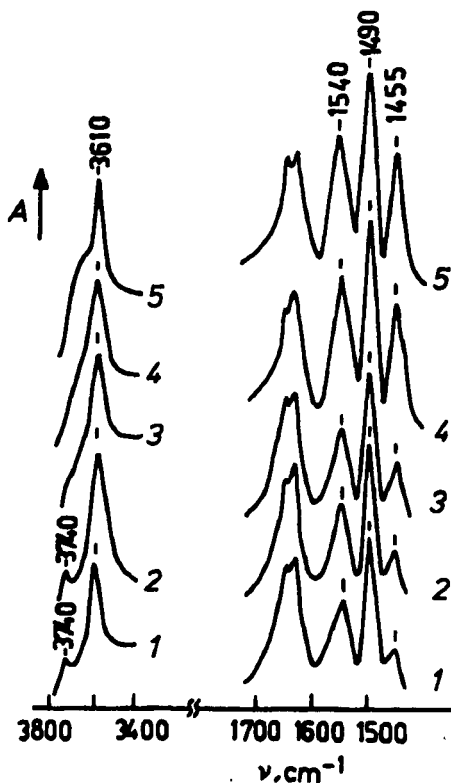

Fig. 2
IR spectra of OH groups (3 800 – 3 400 cm^{-1}) and of pyridine (1 700 – 1 400 cm^{-1}) adsorbed on samples calcined at 623 K. *1* HZSM-5; *2* NiHZSM-5; *3* MoHZSM-5; *4* NiMoHZSM-5; *5* NiMoHZSM-5 (reduced)

nium extraction. The latter seems to take part in the formation of the aluminium hete-ropolymolybdate (Fig. 1, curve 2). Introduction of nickel in HZSM-5 increases the intensity of the band at 3 610 cm^{-1} (Fig. 2). The intensity of the bands at 3 740 and 3 610 cm^{-1} in the spectra of NiMoHZSM-5 decreases. The band at 3 610 cm^{-1} is less intense in comparison with that for NiHZSM-5. This could indicate an interaction of a part of nickel with molybdenum. Characteristic bands of nickel heteropolymolybdate in the spectra of NiMoHZSM-5 sample confirm this assumption (Fig. 1).

Pyridine adsorption on the oxide forms of the samples demonstrates the effect of Ni and Mo on the HZSM-5 acidity. The parent HZSM-5 (curve 1) possesses both Brønsted (BPy^{+} at 1 540 cm^{-1}) and Lewis acid sites (LPy at 1 455 cm^{-1}) (Fig. 2). The Ni-modi-fied sample (curve 2) shows increasing intensity of the band at 1 540 cm^{-1}. Molybde-num (curve 3) slightly increases both Brønsted and Lewis acidity. The spectrum of NiMoHZSM-5 (curve 4) after pyridine adsorption shows growing bands due to Brønsted and Lewis acidity as well as the band 1 490 cm^{-1} due to BPy + LPy.

The calcined NiMoHZSM-5 sample was also investigated after hydrogen reduction at 623 K (curve 5). The reduction increases mainly Brønsted acidity (the band at 1 540 cm^{-1}), likely as a consequence of the reduction of a part of nickel resulting in new acidic sites[19]. Growing band at 3 610 cm^{-1} in the OH groups region of the spectrum of reduced NiMoHZSM-5 sample (Fig. 2, curve 5) agrees with this result. As regards Lewis acid sites, the 1 455 cm^{-1} band shows increased intensity.

The study of thiophene hydrogenolysis provides data on the influence of composition of modified samples on the activity and selectivity of Mo- and NiMoHZSM-5 zeolites
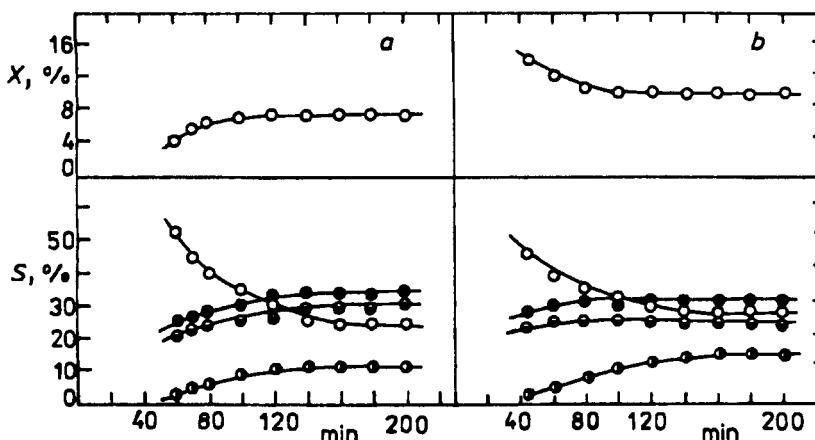

FIG. 3

Hydrodesulfurization of thiophene over a MoHZSM-5 and b NiMoHZSM-5 catalysts. X (%) stands for the conversion of thiophene and S (%) represents selectivity to butane (O), C_2 (●) and C_3 (◉) hydrocarbons, and to aromatics (◐)

in HDS. NiHZSM-5 samples showed no measurable activity at 623 K and its promoting effect is less expressed in comparison with traditional $NiMo/Al_2O_3$ catalyst at the same content of the components. But Ni affects the conversion change with process time (Fig. 3).

The secondary reactions are responsible for the important part of reaction products. In comparison with thiophene HDS on Mo-modified faujasites[4,9], the shape selectivity of HZSM-5 zeolite changes significantly the product composition. No butenes are detectable in the reaction products (Fig. 3). Only $C_2 - C_3$ hydrocarbons, butane and aromatics are observed on HZSM-5 supported samples. The H_2S evolved from the reacted thiophene interacts with the catalyst components and stabilizes conversion of thiophene (see X values). A relatively stable composition of reaction products is observed at the steady state conversion of thiophene. Amount of H_2S in the reaction mixture equals to C-products when the steady state conversion is reached. Absence of butenes in the reaction products is explained by their participance in secondary reactions, such as hydrogenation to butane, hydrogenolysis to lower hydrocarbons and aromatization. The main aromatic was benzene. Only traces of C_7 and C_8 aromatics were detected. Echigoya and Fujitani[20] observed decrease in the aromatics formed from olefins and alkanes over HZSM-5 zeolites at growing SiO_2/Al_2O_3 ratio. In contrast to our results, no aromatics in the reaction products of thiophene HDS were observed by Lopez Agudo et al.[7] who used HZSM-5 with SiO_2/Al_2O_3 = 200 to prepare MoHZSM-5 samples. The ratio SiO_2/Al_2O_3 in ZSM-5 seems to be important for aromatization. Introduction of nickel increases the yield of butane and aromatics hydrocarbons in comparison with that for MoHZSM-5 sample (Fig. 3) at the similar conversions. The specific properties of ZSM-5 zeolite and its modification by nickel and molybdenum lead to multifunctional behaviour of the investigated samples in the thiophene conversion.

REFERENCES

1. Whyte T. E., Dalla Betta R.: Catal. Rev.-Sci. Eng. *24*, 567 (1982).
2. Miller J. T.: U.S. 4 812 224 (1989); Chem Abstr. *111*, 42 700 (1989).
3. Chukin G. D., Sidelkovskaya V. G., Surin S. A., Kvashonkin V. J.: Kinet. Katal. *31*, 503 (1990).
4. Spojakina A. A., Kostova N. G., Damyanova S., Shopov D. M. in: *Proc. Int. Symp. Zeolite Catal., Siofok 1985*; Acta Phys. Chem. *31*, 591 (1985).
5. Givens K. E., Dillard J. G.: J. Catal. *86*, 108 (1984).
6. Davidova N., Kovacheva P., Shopov D. in: *Proc. 7th Int. Conf. Zeolites, Tokyo 1986; New Developments in Zeolite Science and Technology* (Y. Murakami, A. Iijima and J. W. Ward, Eds), p. 811. Kodansha Tokyo, Elsevier, Amsterdam 1986.

7. Lopez Agudo A., Benites A., Fierro J. L. G., Palacios J. M., Neiza J., Cid R.: J. Chem. Soc., Faraday Trans. *88*, 385 (1992).

8. Balkrishnan I., Rao B. S., Hedge S. G., Kotasthane A. N., Kulkari S. B., Ratnaswamy P.: J. Mol. Catal. *17*, 261 (1982).

9. Spojakina A. A., Kostova N. G. in: *Recent Research Reports of 8th Int. Conf.* (J. C. Jansen, L. Moscou and M. F. M. Post, Eds), p. 379. Akzo Chemicals, Amsterdam 1989.

10. Valyon J., Meszaros-Kirs A. in: *Zeolites: Facts, Figures, Future* (P. A. Jacobs and R. A. van Santen, Eds), Vol. 49, Part B, p. 1025. Elsevier, Amsterdam 1989.

11. Den Ouden C. J. J., Wielers A. F. H., Kuipers H. P. C. E., Vaarkamp M., Mackay M., Post M. F. M.: Ref.[10], p. 825.

12. Kazansky V. B., Kustov L. M., Borovkov V. Yu.: Zeolites *3*, 77 (1983).

13. Take J., Ueda T., Yoneda Y.: Bull. Soc. Chim. Jpn. *51*, 1581 (1978).

14. Petrov L., Vladov Ch., Shopov D. in: *Proc. 4th Int. Symp., Varna 1979; Heterogeneous Catalysis* (D. Shopov, A. Andreev, A. Palazov and L. Petrov, Eds), Part 2, p. 303.

15. Kazanskii L. P., Olgin-Kiniones S., Ivanov-Emin B. N., Filipenko L.: Koord. Khim. *4*, 1676 (1978).

16. Buckley R. I., Clarck R. J. H.: Coord. Chem. Rev. *65*, 167 (1985).

17. Jacobs P. A., Martines J. A., Weitkamp J., Beyer H.: Faraday Discuss. Chem. Soc. *72*, 353 (1981).

18. Bezouchanova Cv., Dimitrov Chr., Lechert H., Nenova V., Krusteva M. in: *Proc. 6th Int. Symp., Sofia 1987; Heterogeneous Catalysts* (D. Shopov, A. Andreev, A. Palazov and L. Petrov, Eds), Part 2, p. 216.

19. Ezzamarty A., Catherine E., Cornet D., Hemidy J. F., Janin A., Lavalley J. C., Leglise J., Meriaudeau: Ref.[10], p. 1025.

20. Echigoya E., Fujitani T. in: *Proc. 9th Int. Congr. Catal., Calgary 1988; Theory to Practice* (H. J. Phillips and M. Ternan, Eds), Vol. 1, p. 332.