Structural and textural characterisation of NiMo catalysts supported on various zeolites

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Structural and textural properties of nickel-molybdenum catalysts supported on four various type of zeolites of different chemical composition and porous structure have been studied by the methods of IR, XRD and the low-temperature sorption of nitrogen. The catalysts have been obtained by the two-stage impregnation of the supports with the solutions of nickel and molybdenum salts by the method of incipient wetness. The catalysts have been shown to preserve the structure characteristic of the appropriate zeolite supports.

Keywords: Zeolites, NiMo catalysts, structural properties, surface area, porosity.

INTRODUCTION

The NiMo catalysts deposited on acidic supports represent typical catalysts used for catalytic hydrocracking. They are bifunctional of hydrogenating-dehydrogenating and acidic properties. The metallic centres in the hydrocracking catalysts increase the rate of hydrogenation reaction, while the Brønsted acidic centres activate the reaction of catalytic cracking. The hydrogenation reaction can be activated by noble metals (Pt, Pd) or group 6 transition metals (Mo, W) in combination with group 9 metals (Co) and group 10 metals (Ni). The NiMo supports most often used are amorphous or crystalline aluminosilicates (zeolites). Among different functions of supports in catalytic processes their most important role is to ensure proper dispersion and stabilisation of the active components over large surfaces. The support should also provide the lowest possible resistance to the reagent diffusing into the active centres thanks to its properly chosen porous structure. The most commonly applied methods of the NiMo phase deposition include the impregnation with water solutions of metal salts followed by calcination. The conditions of impregnation and calcination are adjusted so that the introduction of the metallic phase into the zeolite would cause minimum changes in its texture and acidity and to ensure the best possible dispersion of the NiMo phase[1, 2].

EXPERIMENTAL

Catalysts preparation

The catalysts supports were the commercially available synthetic zeolites: NaX produced by the Inowrocław Sodium Factory in, NaY and Ultrazet (UZ is a pentasil type zeolite) produced by the Institute of Industrial Chemistry in Warsaw and Na-mordenite (NaM) from Norton Company. At the first stage of preparation the zeolites were converted into the H-form active in cracking by subjecting them to a solution of ammonium nitrate (NH_4NO_3) at 90ºC for 2 hours, drying at 110ºC for 6 hours and then calcined at 450ºC for 18 hours. Nickel and molybdenum ions were deposited in two stages by the method of incipient wetness. The first stage was the impregnation with Mo ions with the use of water solution of ammonia heptamolybdate $(NH_4)_6Mo_7O_{24}$, while the second was the impregnation with the solution of nickel nitrate $Ni(NO_3)_2$.

After impregnation and calcination the samples were dried and calcined in the impregnation procedure were subjected to following physicochemical studies.

Elemental analysis

Elemental composition was determined by X-Ray Fluorescence (XRF) on a spectrometer Philips PW 2400, using the scintillation detector, proportional flow-through a detector (Ar/CH_4) and a proportional sealed detector (Xe). The samples were prepared by melting or pressing.

X-Ray diffraction study

X-Ray diffraction patterns of the samples studied were taken on a diffractometer TUR M-62 with CuKα (λ = 1,5418 Å) radiation, generated at the voltage 30 KV at the current of 25mA, transmitted through a nickel filter.

IR study

IR spectra were recorded on a Perkin-Elmer 180 spectrometer, in the range 4000 – 400 cm^{-1} with a resolution of 2 cm^{-1} for the samples in the form of a disc made of 1.5 mg of the sample with 30 mg of potassium bromide.

Surface area, pore size and pore volume determination

The surface area and the porous structure of the samples were determined by the method based on the low-temperature (-197ºC) sorption of nitrogen at the Micrometrics ASAP 2010 apparatus. On the basis of the equilibrium pressures recorded in the range 0.0 do 1.0 the adsorption-desorption isotherms were drawn. The surface area was calculated from the BET (Brunauer-Emmett-Teller) equation for the relative pressure (p/p_o) range 0.05 to 0.3. The mean pore radius and the mean pore volume were calculated and the pore volume distribution was established on the basis of the BJH (Barret-Joyner-Halenda) theory.

RESULTS AND DISCUSSION

Table 1 presents the chemical composition of the supports and NiMo catalysts determined by the XRF method, expressed in terms of appropriate oxides. As we can see UZ zeolite is a high-silica material characterised by the SiO_2/Al_2O_3 ratio of 234, whereas NaX and NaY are low-

**Table 1.** The chemical composition of zeolite and the supported NiMo catalysts

Component	Composition (mass.%)							
	NaX	NiMo-X	NaY	NiMo-Y	NaM	NiMo-M	UZ	NiMo-UZ
Na_2O	16,1	9,9	11,3	6,25	7,21	2,6	–	–
Al_2O_3	25,0	23,5	16,5	21,0	10,2	9,44	0,67	0,58
SiO_2	37,6	35,4	49,6	43,3	68,8	62,9	92,1	76
NiO	–	4,06	–	4,38	–	4,04	–	4,57
MoO_3	–	8,71	–	9,79	–	8,93	–	6,37
SiO_2/Al_2O_3	2,56	2,56	5,11	3,51	11,47	11,39	234	223

silica zeolites with the SiO_2/Al_2O_3 ratio of 2,56 and 5,11 respectively and for NaM this ratio is 11,47.

A comparison of the X-ray diffraction patterns of the supports and supported NiMo catalysts are shown in fig. 1 – 4. A small decrease in the intensity of crystallographic reflexes characteristic of the crystalline structure of the zeolites is noted for the supported NiMo catalysts. The numerical values at the reflexes stand for the interplanar distances *d*. The X-ray diffraction patterns of the supported catalysts do not show new reflexes characteristic of the crystalline structure of the Mo and Ni species, corresponding to the interplanar distances d, that would indicate the formation of crystallites of these groups.

A small loss of crystallinity is probably related to the destruction of supports network during the thermal treatment of the catalyst. Only in the diffraction pattern of the catalyst supported on the UZ zeolite (Fig. 4) there appears a reflex corresponding to *d*=3.74, which is characteristic of the orthorhombic structure of MoO_3 [3].

A comparison of the diffraction patterns of particular zeolites and the corresponding to them NiMo catalysts
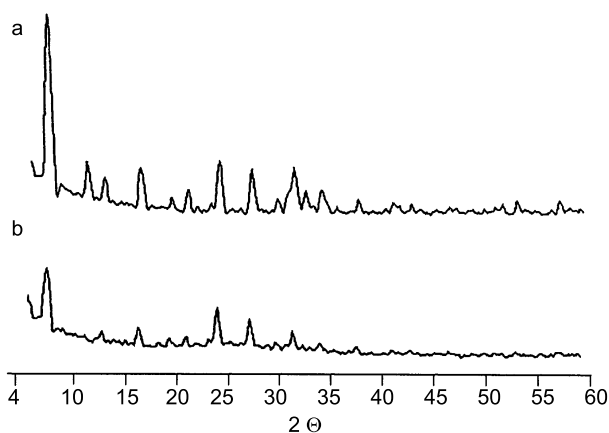
Figure 1. The XRD patterns of the blank NaX (a) and NiMo-X catalyst (b)
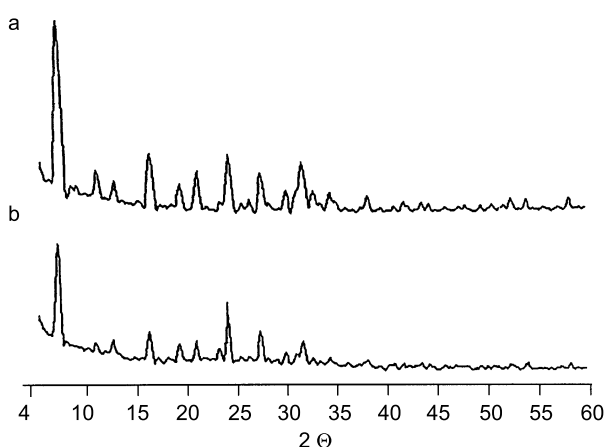
Figure 2. The XRD patterns of the blank NaY (a) and NiMo-Y catalyst (b)
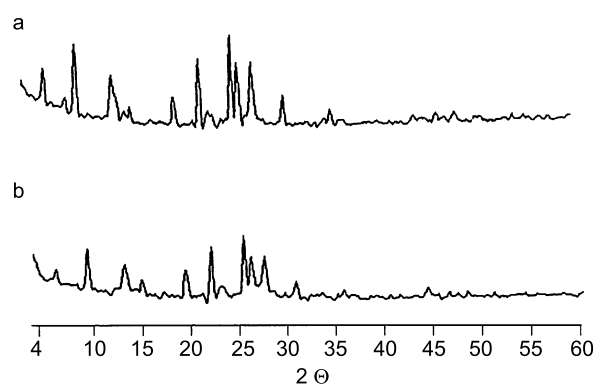
Figure 3. The XRD patterns of the blank NaM (a) and NiMo-M catalyst (b)
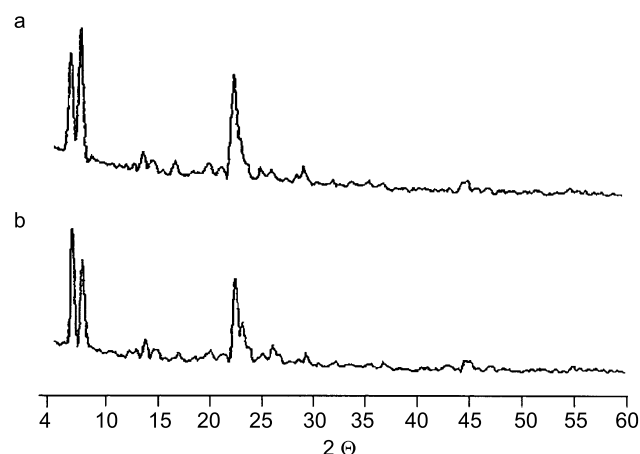
Figure 4. The XRD patterns of the blank UZ (a) and NiMo-UZcatalyst (b)

has shown that after the catalysts deposition the zeolites preserved their characteristic crystalline structure and the process of impregnation with the solutions of nickel and molybdenum salts and subsequent calcination at 450°C caused only insignificant changes in the crystalline structure.

The analysis of the IR spectra of the zeolites and the catalysts in the range from 1400 cm^{-1} to 450 cm^{-1} (Fig. 5 – 8) which covers the bands assigned to the vibrations in the $Al(Si)O_4$ tetrahedra does not reveal significant shifts of the characteristic bands in the IR spectra of the catalysts that could indicate the framework destruction[4].

The IR bands assigned to the structure-sensitive vibrations appearing in the NaX zeolite spectrum at 1005 cm^{-1}, in the NaY zeolite spectrum at 1027 cm^{-1}, in the UZ spectrum at 1097 cm^{-1} and in the NaM spectrum at 1060 cm^{-1}, are shifted as a result of molybdenum deposition by 2 to 5 cm^{-1} and their intensity does not change. The IR spectra of the catalysts NiMo-X and NiMo-Y taken after the deposition of molybdenum show new bands at 1400 cm^{-1}, and after the deposition of nickel also new bands at 1385 cm^{-1}, assigned to the asymmetric vibrations support-metal.

In the spectra of the other catalysts these bands are very weak. Zeolite supports of X and Y zeolite and NaM possess a broad IR band (not presented) in the range 3200 do 3800 cm^{-1} related to the presence of hydroxyl groups on the support surface,. In the spectra of the corresponding catalysts these bands are broadened and their intensity decreases, which is explained by the formation of the surface NiMo species[5-7].

A comparison of the positions and intensities of the absorption bands in the IR spectra show that the changes in these parameters are small and the structure of the catalysts remains very close to that of the relevant supports. This conclusion is consistent with the earlier conclusions following from the X-ray study implying that the procedure of the two-stage impregnation and subsequent calcination do not change much the structural properties of the supports.

Table 2 presents the surface area SBET calculated for the range of relative pressures from p/p_o 0.05 to 0.3), mean pore volume and mean pore radius measured at each stage of the preparation procedure.

Table 2. Surface area, pore volume and pore size of the support and the supported NiMo catalysts

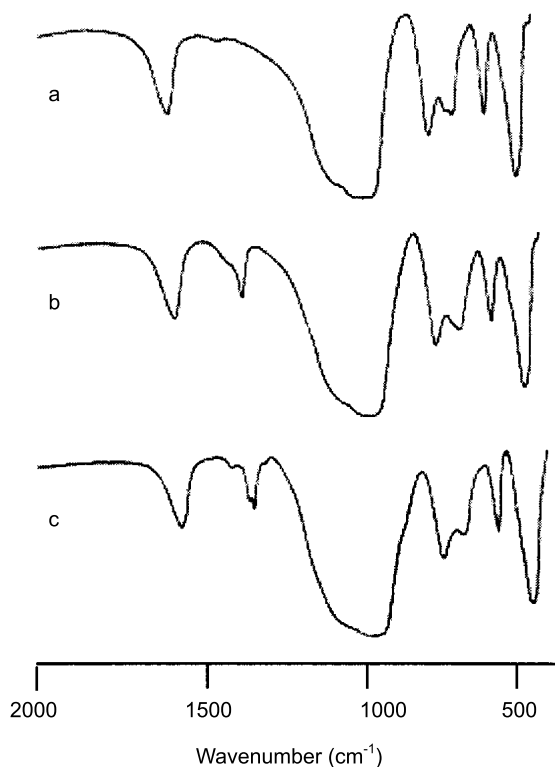| Sample	Surface area (m²/g)	Average pore volume (cm³/g)	Average pore size (Å)
NaX	708	0,34	19
Mo-X	567	0,28	20
NiMo-X	400	0,25	22
NaY	739	0,35	9
Mo-Y	618	0,30	10
NiMo-Y	416	0,25	12
NaM	229	0,11	19
Mo-M	257	0,13	20
NiMo-M	170	0,08	20
UZ	275	0,14	20
Mo-UZ	265	0,13	19
NiMo-UZ	263	0,14	21

Figure 5. The IR spectra of NaX (a), Ni-X (b) and NiMo-X (c) samples
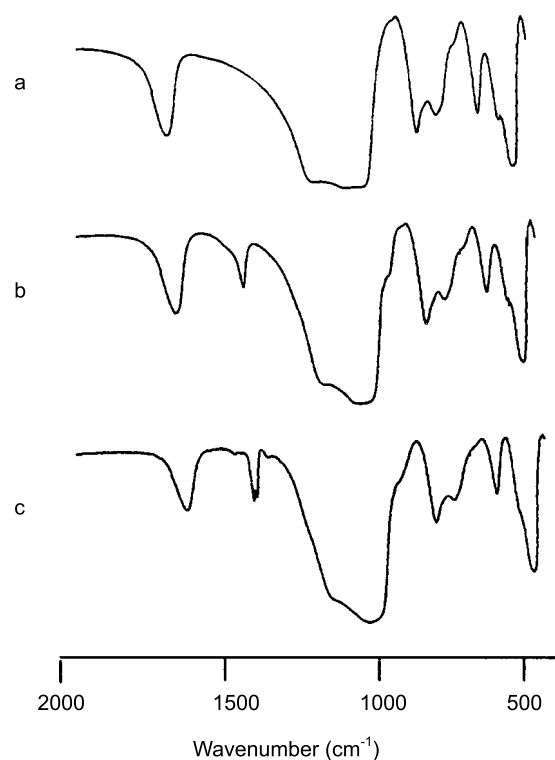

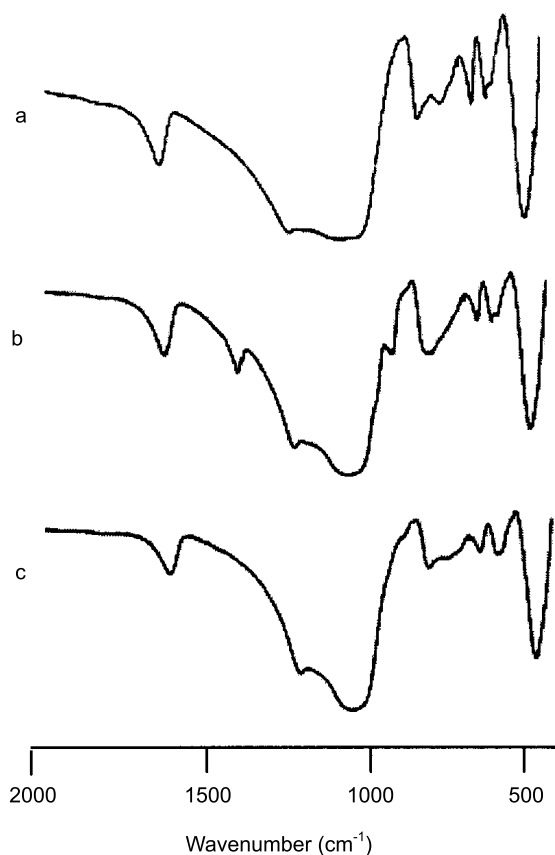**Figure 6.** The IR spectra of NaY (a), Ni-Y (b) and NiMo-Y (c) samples

Figure 7. The IR spectra of NaM (a), Ni-M (b) and NiMo-M (c) samples

The NaX and NaY zeolites have greater mean pore volume and about three times greater surface area than the UZ and NaM ones. After impregnation with Ni and Mo ions the surface area of NaX and NaY zeolites decreases more than 40%. This means that part of cages
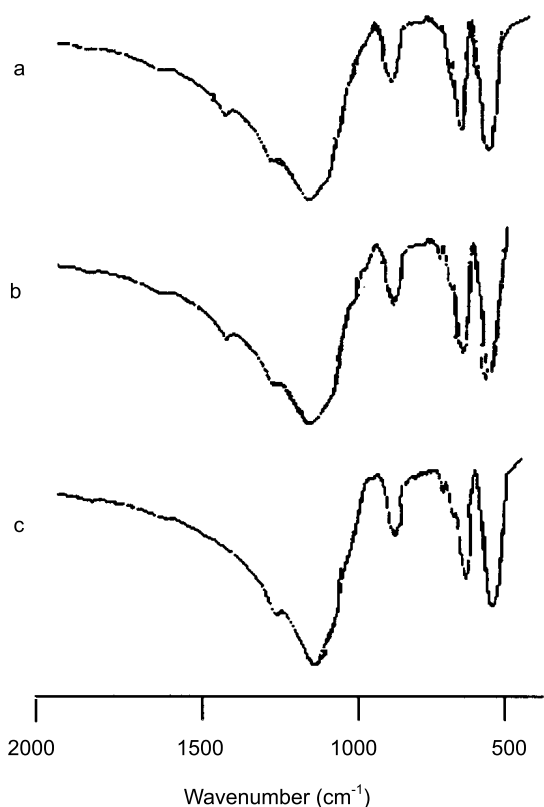
Figure 8. The IR spectra of UZ (a), Ni-UZ (b) and NiMo-
UZ (c) samples

becomes inaccessible to nitrogen on adsorption, probably
due to zeolite windows blocking. The surface area of UZ
remains almost unchanged after the impregnation with
the NiMo phase, while the parameter of NaM after im-
pregnation decreases by about 25%. A decrease in the
surface area does not ensue significant changes in the pore
openings volume.

Figs. 9 – 12 present the isotherms of nitrogen adsorp-
tion and desorption on the initial zeolites and the NiMo
catalysts. The shapes of the adsorption isotherms deter-
mined for NaX, NaY and the NaM zeolite are type I
according to the IUPAC classification[8], an almost hori-
zontal adsorption curve is characteristic of the ideally
microporous structure. The curve obtained for UZ is clas-
sified as type I/II according to the same classification.
However, this type of the curve indicates the micro- and
mesoporous structure of the material.

The adsorption-desorption isotherms for all the exam-
ined initial zeolite samples show a hysteresis loop, which
are of type H4 according to the IUPAC classification, and
indicates aggregates of platy particles with slit-shaped
pores in the micropore range. After the deposition of the
NiMo phase and after subsequent stages of calcination the
width of the hysteresis loop changes, which suggests the
formation between the aggregates meopores in X and Y
zeolites. In the case of the NiMo-UZ and the NiMo-M
catalysts the widths are similar to initial zeolites

The mean pore radius and mean pore volume (Table 2)
have been calculated according to the BJH theory from
the desorption branches of the isotherms. The pore distri-
bution according to their size is presented in Figs. 13 –
16. For all the catalysts the distribution of pore volume
is relatively narrow. In the catalysts supported on X and
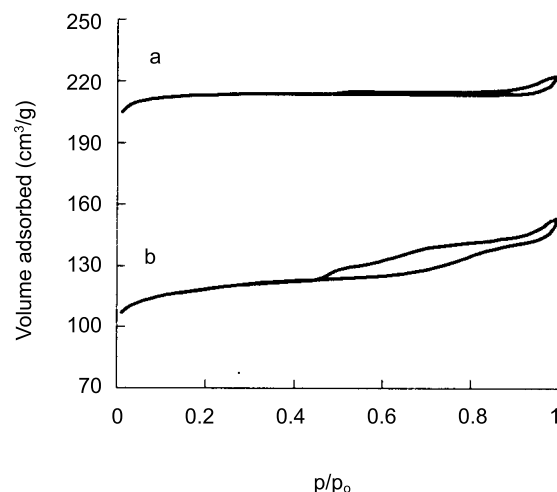Y zeolites the dominant ones are the pores of 48 Å in

Figure 9. Nitrogen sorption isotherms for the NaX zeolite
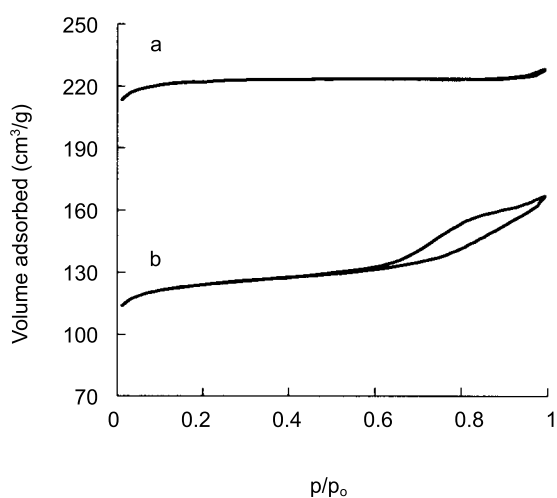(a) and the NiMo-X catalyst (b)

Figure 10. Nitrogen sorption isotherms for the NaY zeolite (a)
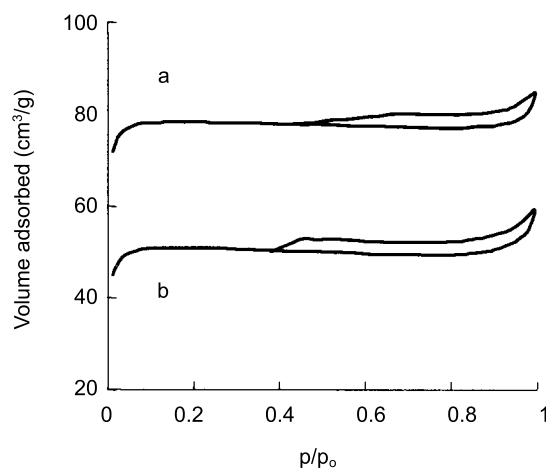and the NiMo-Y catalyst (b)

Figure 11. Nitrogen sorption isotherms of the NaM zeolite (a)
and the NiMo-M catalyst (b)

diameter, in those supported on UZ and mordenite the
dominant ones are channels of 38 and 45 Å, respectively.
In the NiMo-X and NiMo-Y catalysts there are also
mezopores of diameters from the range 50 – 100 Å. It
means, that pores (openings) with such a width can be
formed only between the particles of the samples.

The analysis of the volume of the adsorbed nitrogen
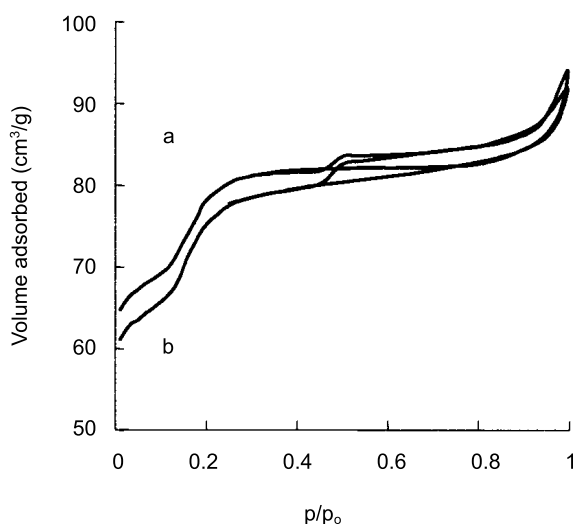calculated at the relative pressure of $p/p_o=0,2$, when a

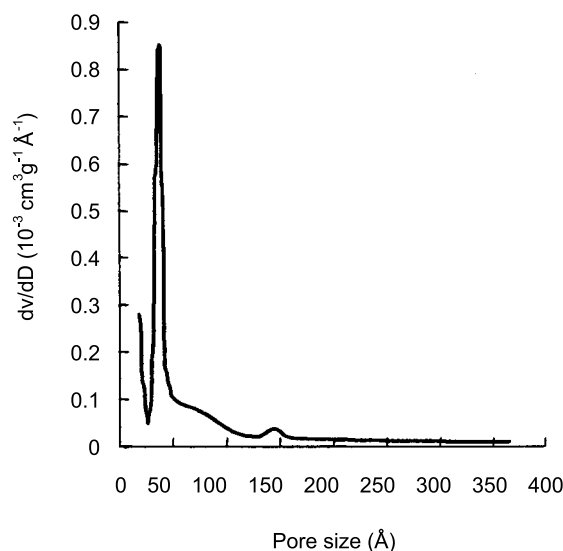**Figure 12.** Nitrogen sorption isotherms of the UZ zeolite (a) and the NiMo-UZ catalyst (b)

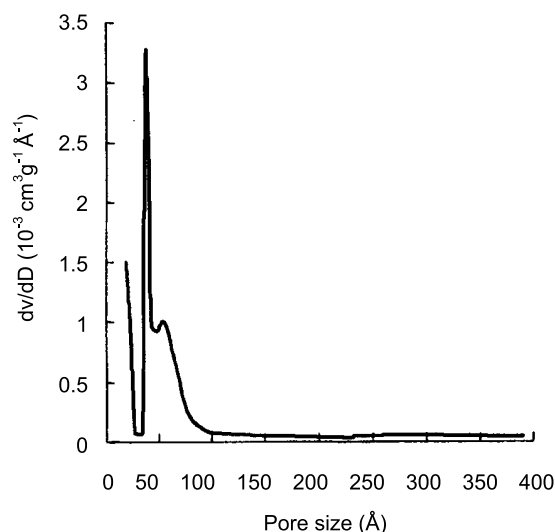**Figure 15.** The pore volume distributions of the catalysts

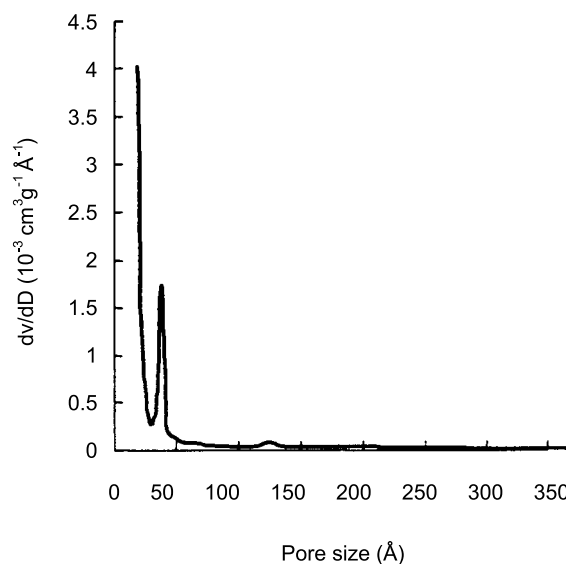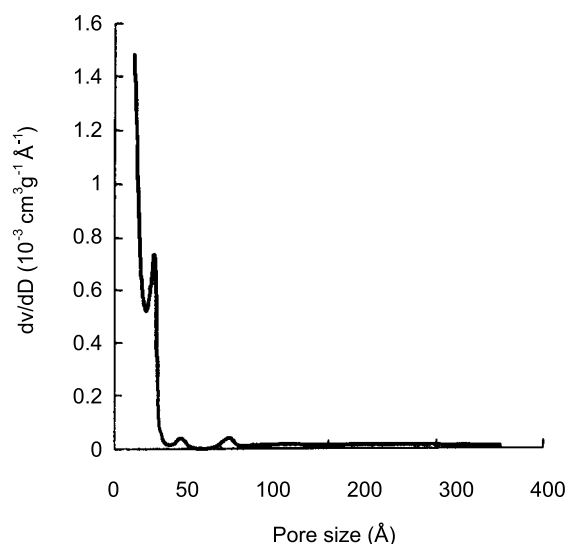**Figure 13.** The pore volume distributions of the catalysts

Figure 16. The pore volume distributions of the catalysts

monolayer of nitrogen is adsorbed on the pore walls, reveals that the volume significantly decreases for the supported catalysts relative to the value for supports only. This result suggests that the metal ions introduced occupy the intergrain pores (openings) in the zeolites and block the access to the channels and cages in the supports. However, for the NiMo-UZ and UZ samples the pore volume is almost the same.

The analysis of above described changes in the zeolites after impregnation provides the information that the metal ions deposit mainly on the external zeolite surfaces.

CONCLUSIONS

The NiMo catalysts supported on X, Y, mordenite and UZ zeolites using a two-stage impregnation method with the solutions of the Ni and Mo salts preserve the crystalline structure of supports. The above conclusion follows from the X-ray diffraction study and the analysis of the IR spectra in the range covering the zeolite framework vibrations recorded for the initial supports and the catalysts supported on them. The porous structure parameters

Figure 14. The pore volume distributions of the catalysts

undergo changes indicating that the ions of the metals introduced are deposited in the intergrain cavities in the zeolites and block the accessibility of some part of the channels and cages of the supports.

LITERATURE CITED

(1) Ward J. W.: Stud. Surf. Sci. and Catal., **1983**, 16, 587.

(2) Valyon J., Meszaros A. K.: Zeolites; Facts, Figures, Future, Elseviere, Amsterdam, **1989**, 1015.

(3) Ali M. A., Tatsumi T., Masuda T.: Appl. Catal.A, **2002**, 233, 77.

(4) Ciciszwili G. W.: Zeolity naturalne, **2000**, 60, 193.

(5) Beck L., Haw J. H.: J. Phys. Chem., **1995**, 99, 1076.

(6) de Menorval L. C., Buckermann L. C., Figures W.: J. Phys. Chem., **1996**, 100, 465.

(7) Su B., Norberg V.: Zeolites, **1997**, 19, 65.

(8) IUPAC Reporting Physisorption Data, Pure Appl. Chem., **1985**, 57, 603.