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Structural properties and HDS activity of NiMo catalysts supported on lanthana modified zeolite type X and Y

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Abstract

In the search for the active catalysts of hydrodesulfurization reaction, an attempt was made to use zeolites as supports. A series of NaLaX, Mo/NaLaX and NiMo/NaLaX as well as NaLaY, Mo/NaLaY and NiMo/NaLaY catalysts was prepared and their performance in this reaction was studied. It was shown that crystalline structure of the lanthana forms of the above zeolites only little collapsed after ion-exchange and impregnation with active Mo and NiMo components. The NiMo catalysts supported on the zeolites studied were found active in thiophene hydrodesulfurization. The catalysts with lanthana after the first step of ion exchange were the most active. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zeolites; NiMo catalysts; HDS; XRD; IR; DTA/TG

1. Introduction

The catalytic hydrocracking of hydrocarbons is an important process in the petroleum refining industry. Modern hydrocracking is carried out in one or two stage processes usually using bifunctional catalysts combining acidic and hydrogenation functions [1,2]. Such catalysts are nickel-promoted molybdenum ones [3]. Moreover, catalysts of this kind are also applied in hydrotreating processes, e.g. hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation and hydrodemetallization .These catalysts have been widely studied and important progress has been made in understanding their fundamental nature. The above refers to the hydrocracking and hydrorefining catalysts whose active components were supported on γ-Al_2O_3. As follows from the studies on the role of the support in the hydrocracking processes, the faujasite type zeolites make the supports of higher acidity and greater resistance to the contamination by nitrogen and sulphur compounds occurring in the petrochemical raw materials [4]. Moreover, NiMo(W) catalysts supported on zeolites are active in hydrodesulfurization of thiophene [5] and hydrodenitrogenation of organic compounds containing nitrogen [6]. It has also been shown that faujasite zeolites with Na^+ ions exchanged for cobalt or nickel cations are active in hydrodesulfurization of thiophene [7] and hydrogenolysis of *n*-butyloamine [8].

The paper presents results of the studies of hydrotreating catalysts based on X and Y zeolites as the supports. First of all we studied the behaviour of NiMo catalysts supported on these zeolites modified with La^{3+} cations introduced by the ion exchange. Rare earth exchanged faujasite zeolites have been evaluated as catalysts with high acidity and dehydrosulfurization activity [9]. In the present work a series of NaLaX, Mo/NaLaX and NiMo/NaLaX as well as

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NaLaY, Mo/NaLaY and NiMo/NaLaY catalysts has been prepared and investigated using X-ray diffraction, IR spectroscopy and thermal analysis. La^{3+} cations were introduced to the zeolite structure by the ion-exchange in three different concentrations. Finally, the HDS activity of the obtained NiMo catalyst samples was measured.

Table 1
Characteristics of the zeolite supports

Sample	Na^+ exchange for La^{3+}(%)	Sample	Na^+ exchange for La^{3+}(%)
NaX	0	NaY	0
NaLaX(1)	15	NaLaY(1)	14
NaLaX(2)	33	NaLaY(2)	45
NaLaX(3)	49	NaLaY(3)	63

2. Experimental

The starting materials for the preparation of the catalysts were NaX and NaY zeolites free of binders; the first one, characterised by the molar ratio of $SiO_2/Al_2O_3 = 2.48$, produced by Inowroclaw Soda Factory (Mątwy, Poland) and the other, characterised by the molar ratio $SiO_2/Al_2O_3 = 4.56$ produced by the Institute of Industrial Chemistry (Warsaw, Poland).

The lanthana forms of the zeolites were prepared by manifold exchange of sodium ions from the starting zeolites with La^{3+} cations, using 0.05 M nitrate solutions at pH near 5, at the room temperature and under continuous stirring for 2 h. After the ion exchange, samples were washed, dried at 120°C and calcined at 450°C.

The NiMo catalysts with nominal composition: NiO 4 wt.% and MoO_3 12 wt.% were prepared by step impregnation of lanthana exchanged zeolites using ammonium heptamolybdate (AHM) and nickel nitrate solutions. The obtained samples were dried at 120°C for 16 h and then calcined at temperature 450°C for 6 h.

The X-ray diffraction (XRD) patterns were obtained on a TUR-M62 diffractometer using Ni-filtered Cu K_α radiation ($\lambda = 1.5418$ Å). The IR spectra were taken within the range of 1800–400 cm^{-1} on a Perkin-Elmer 180 spectrometer using 1.5 mg of the sample mixed with 300 mg of KBr and pressed into transparent disc.

Thermal analysis was performed on an OD-102 apparatus (Hungary). Samples were heated to 1000°C in a ceramic crucible at a rate of 10°C/min in a nitrogen atmosphere.

The labelling of examined catalysts and degree of Na^+ exchange for La^{3+} cations are presented in Table 1.

All catalysts were tested in HDS of thiophene at the atmospheric pressure using a pulse reactor system directly coupled to gas chromatograph. The catalysts

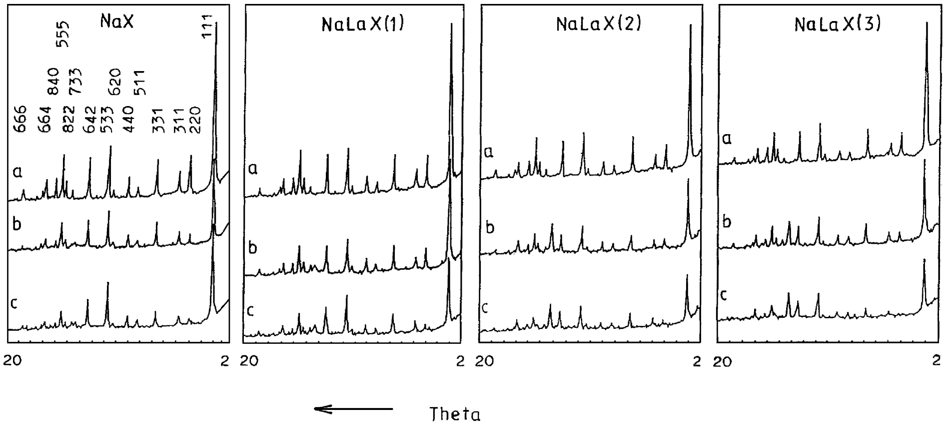


Fig. 1. X-ray diffraction patterns of zeolite NaX and lanthana exchange NaX zeolites NaLaX(1), NaLaX(2), NaLaX(3) - a; Mo supported on zeolites - b; NiMo supported on zeolites - c.

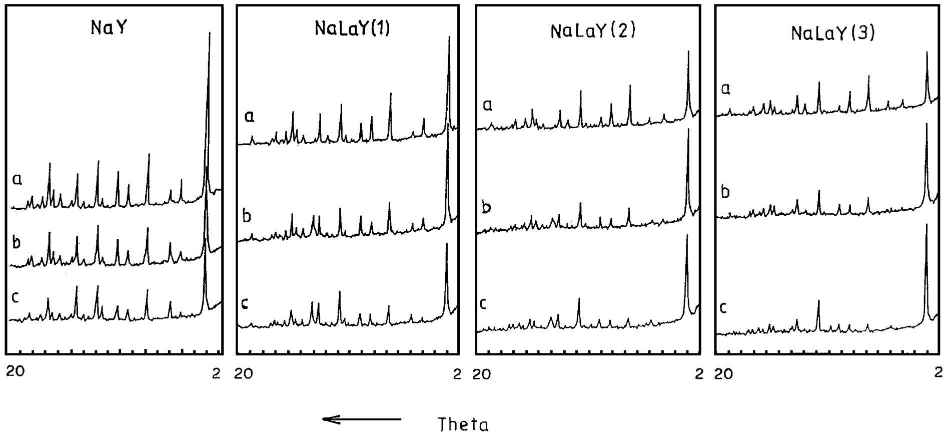


Fig. 2. X-ray diffraction patterns of zeolite NaY and lanthana exchange NaY zeolites NaLaY(1), NaLaY(2), NaLa(3) - a; Mo supported on zeolites - b; NiMo supported on zeolites - c

were activated at a temperature of 400°C in H_2 flow for 2 h. Sulphidation was performed at 400°C by 20 injections of CS_2, each 10 μl in the H_2 flow. HDS measurements were performed on the sulphided samples at 400°C by injecting 10 μl pulses of thiophene at every 15 min in the hydrogen flow.

3. Results and discussion

Table 1 presents characterisation of the supports including the degree of Na^+ ions exchanged into La^{3+}. The introduction of La^{3+} cations, which in water solution occur as large volume hexaaqua ions $[La(H_2O)_6]^{3+}$, into the crystal structure of zeolites may lead to a partial collapse of zeolite structure. The effects can be observed on diffraction patterns (Figs. 1 and 2).

The diffraction patterns of both zeolites show that with the increasing ion-exchange the intensity of individual reflexes decreases. The intensity of reflexes decreases much more for the zeolites NaLaY(2) and NaLaY(3), than for NaLaX(2) and NaLaX(3) and this effect is clearly related to a high degree of ion-exchange in these two Y type zeolites. The introduction of La^{3+} ions also results in an increase in the thermal stability of the Y type zeolites (Fig. 3); however, it does not affect significantly the thermal stability of the X type zeolites (Fig. 4).

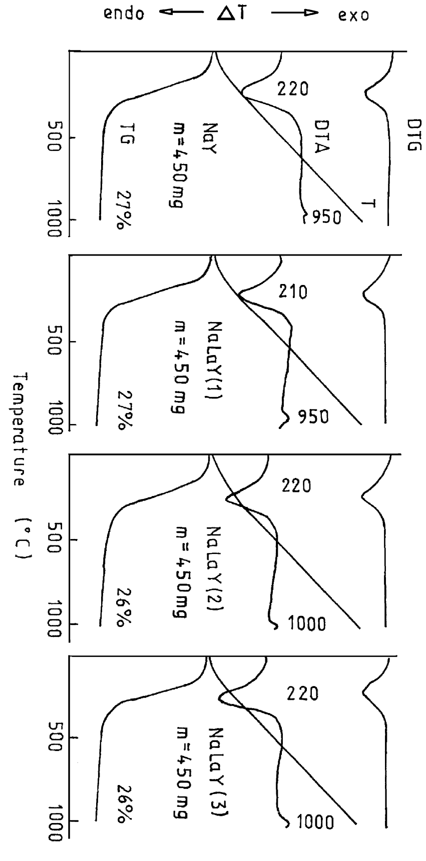


Fig. 3. Thermal analysis of zeolite NaY, NaLaY(1), NaLaY(2) and NaLaY(3).

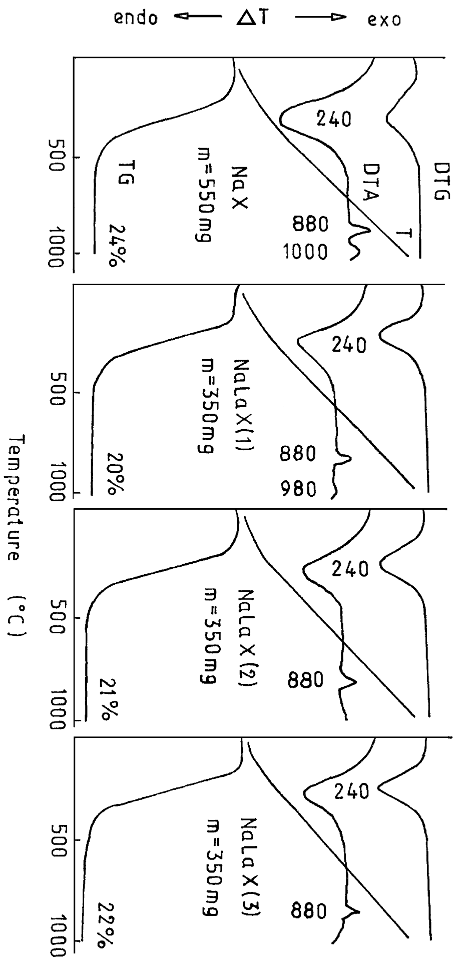


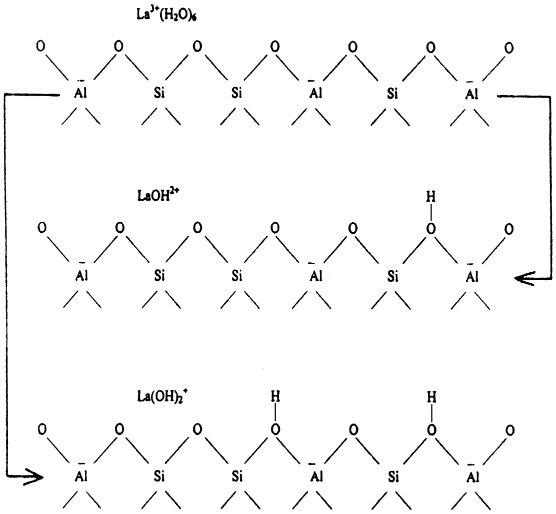
Fig. 4. Thermal analysis of zeolite NaX, NaLaX(1), NaLaX(2) and NaLaX(3).

Significant structural changes were observed as a result of impregnation of the lanthanide forms of the zeolites type X and Y with a water solution of ammonium heptamolybdate. In the solution used for impregnation the following equilibrium is reached: according to scheme (1);

$$(\mathrm{Mo_7O_{24}})^{6-} + 4\mathrm{HOH} \Leftrightarrow 7(\mathrm{MoO_4})^{2-} + 8\mathrm{H^+} \qquad (1)$$

and it can be shifted by changing pH of the solution. In heptamolybdate anions, the molybdenum ions are in octahedral coordination and seven octahedra are joined by corners. In molybdate anions the molybdenum ions are arranged in tetrahedral coordination. In the neutral solution used for the impregnation,the equilibrium is shifted almost totally to the right so that the molybdate ions $(\mathrm{MoO_4})^{2-}$ can enter through the 12-membered windows of the zeolite of the diameter 7.5 Å into the zeolite supercage of the volume of ca. 1000 Å^3.

Already on drying of the preparation, the equilibrium described by scheme (1) is shifted to the right and the molybdate ions interact with hydroxyl groups from the zeolite [10]. On such support there are hydroxyl groups bonded to aluminium and silica atoms and those bonded to the atoms of the lanthanide introduced as shown below. Upon dehydroxylation taking place at about 500°C (Figs. 3 and 4) the lattice hydroxyl groups and those bonded to the cations disappear and the lattice defects of the type of Lewis acid centres and three-coordinated silica species are formed.



Thus, molybdate ions enter into the zeolite supercage and cause a destruction of the zeolite crystal lattice, which is evidenced on the diffraction patterns (b) shown in Figs. 1 and 2. A further destruction of the zeolite lattice is caused by the entrance of the hydrated $\mathrm{Ni^{2+}}$ ions into the supercage, which is evidenced on the diffraction patterns (c) in Figs. 1 and 2. It should be underlined, if the molybdate and nickel ions were localised only on the zeolite surface, the zeolite lattice structure would be unaffected. In our case the $\mathrm{MoO_4}^{2-}$ ions as well as $\mathrm{Ni^{2+}}$ cations are introduced to supercage of examined zeolites and caused destruction of some building elements, e.g. hexagonal prisms of zeolite structure. Moreover in

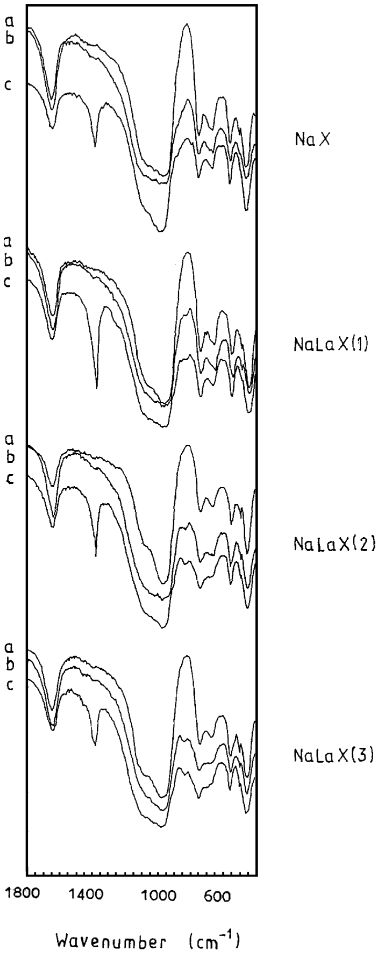


Fig. 5. Infrared spectra of zeolite NaX NaLaX(1), NaLaX(2), NaLaX(3) - a; Mo supported on zeolites - b; NiMo supported on zeolites - c.

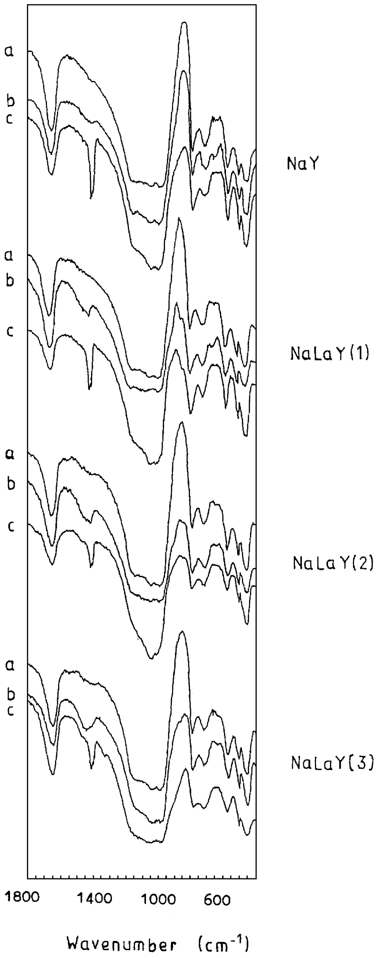


Fig. 6. Infrared spectra of zeolites NaY, NaLaY(1), NaLaY(2) and NaLaY(3) - a; Mo supported on zeolites - b; NiMo supported on zeolites - c.

the diffractogram patterns (Figs. 1 and 2) of Mo and NiMo forms of NaLaX(1)–(3) and NaLaY(1) and (2) samples, new reflections located at theta 14.2–14.4° are also observed, which can probably be due to the formation of segregated Mo oxide phases. The occurrence of changes in the zeolite lattice structure is also indicated by the analysis of IR spectra presented in Figs. 5 and 6.

The spectra shows bands assigned to the vibrations in the [SiO_4]and [AlO_4] tetrahedra (450–460, 665–720 and 950–1250 cm^{-1}) and to the vibrations between the tetrahedra (560–575, 745–790 and 1050–1150 cm^{-1}) [11]. With the increasing degree of ionic exchange in NaX zeolite (Fig. 5), the intensity of the band at 665–675 cm^{-1} significantly decreases. This band is assigned to symmetric stretching vibrations in the tetrahedra so that this decrease testifies to a destruction of the smallest elements of the zeolite crystal structure. The IR spectra of NaY zeolite and its modification (Fig. 6) show a significant decrease in the intensity of the band at 710–720 cm^{-1}, corresponding to the vibrations in the tetrahedra, and the bands at 785 and 790 in the spectra of the samples containing lanthanide in the two highest concentrations. The decrease of the intensity of these bands testifies to a par-

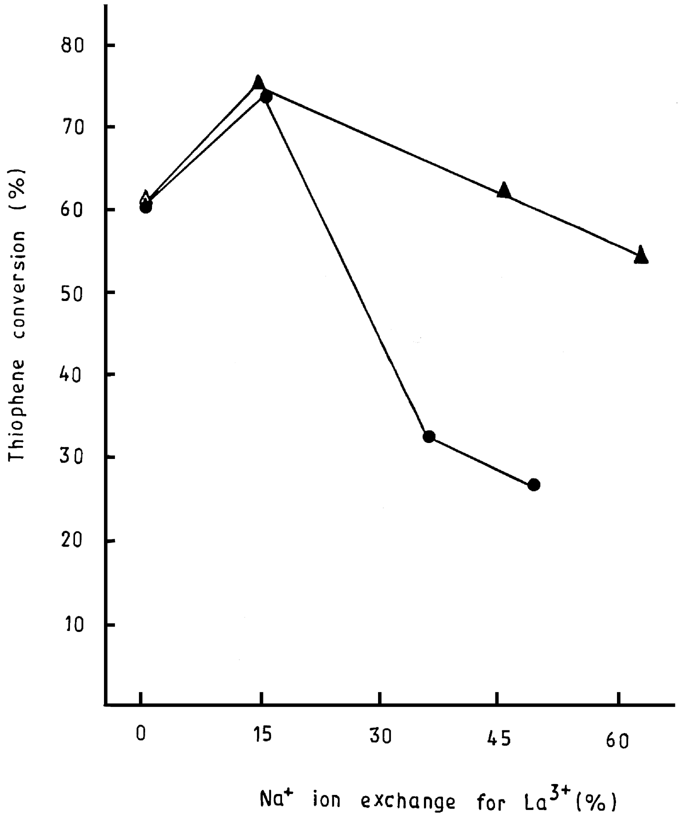


Fig. 7. Thiophene hydrodesulfurization on NiMo/NaLaX (ù) and NiMo/LaY (▲) catalysts as a function of ion-exchange degree.

tial destruction of larger elements of the zeolite crystal structure. This evidence leads to a conclusion that partial destruction of the zeolite crystal lattice takes place as a result of both Na^+ ions exchanged by the hydrated La^{3+} cations and the introduction of molybdate ions and nickel hydrated cations into the zeolite supercages.

The catalytic study concerned hydrodesulfurization (HDS) of thiophene. The initial NiMo catalysts supported on non-modified X and Y type zeolites were characterised by a similar and relatively high catalytic activity, reaching HDS conversion of thiophene about 60% (Fig. 7). The modification of zeolites with lanthanide cations resulted in a relatively significant increase in the catalysts activity in thiophene HDS. The use of NiMo/NaLaX(1) and NiMo/NaLaY(1) catalysts brought an increase of thiophene conversion to about 75%. A further increase in the Na^+ ion exchange for La^{3+} leads to a decrease in the HDS catalytic activity. This decrease is much higher for NiMo/NaLaX(2) and NiMo/NaLaX(3) than for NiMo/NaLaY(2) and NiMo/NaLaY(3) catalysts, despite the fact that in the latter the zeolite crystal lattice destruction is relatively higher when compared to zeolite type X. According to the above experimental evidence, the HDS activity of NiMo catalysts supported on the Y type zeolites is higher than that of those supported on the X type zeolite.

4. Conclusions

X-ray diffraction patterns and infrared spectra showed that the crystalline structure of lanthana forms of zeolites type X and Y is only little collapsed after ion-exchange and impregnation procedures.

La^{3+} modified NiMo catalysts showed higher HDS activity relative to that of the non-modified samples. Zeolites characterised by a higher SiO_2/Al_2O_3 ratio are more active. HDS activity strongly depends on the degree of the ion-exchange. The highest activity show the samples after the first step of Na^+ ion exchange with La^{3+} (15% of Na^+ exchange); samples of higher degree of ion-exchange are characterised by a lower HDS activity.

The results of the study show that zeolite modifications with a respectively low amount of La^{3+} cations lead to a considerable increase of HDS activity of the catalysts examined.

Further Reading

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