

## Iron Oxide Contribution to the Modification of Natural Zeolite

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### *Príspevok oxidov železa k zmene prírodného zeolitu*

*Prírodný zeolit bol modifikovaný časticami oxidu železa pri vybraných teplotách s cieľom zvýšiť jeho sorpčné vlastnosti. Zmeny po modifikácii boli charakterizované adsorpčnými meraniami, metódami SEM, TEM analýzy a RTG difrakčnou metódou. Efekt častíc oxidu železa na zmeny štruktúrnych vlastností modifikovaného zeolitu sa skúmal na syntetizovaných časticách oxidu železa pripravených za rovnakých podmienok bez nosiča. Z výsledkov vyplynulo, že hodnoty štruktúrnych parametrov modifikovaných zeolitov ako špecifický povrch, celkový objem pórov, ktoré sú zodpovedné za sorpčné vlastnosti minerálov, sa zvýšili úmerne teplote použitej pri modifikácii zeolitu magnetickými časticami.*

**Key words:** nitrogen adsorption measurements, structural parameters, nanoparticles, SEM, TEM

### Introduction

Natural and synthetic zeolites with unique physical and chemical properties play an important role in many environmental applications. Their sorption behaviour with respect to heavy metals was studied for example by Álvarez-Ayuso et al. (2003). If the physical and chemical properties of natural zeolites are improved by a special modification process, the adequate supplies for environmental purposes can be obtained. Moreno et al. (2004) evaluated the natural Mexican zeolite as microfiltration membranes and described a manufacturing process of porous membranes. The sorption properties of Transcarpathian natural zeolites were studied by Korkuna et al. (2006), where the pores and channels changed after acid treatment. The magnetic particles were also used for coating the surface of synthetic zeolite (Oliveira et al., 2004) offering such a simple adsorption of contaminants followed by easy separation of adsorbent from medium in magnetic field.

The aim of this paper is to study the effect of iron oxide particles used in the modification of the surface of natural zeolite at selected temperatures 20 and 85 °C. The changes after the zeolite modification were characterized using nitrogen adsorption measurements, methods of scanning (SEM), transmission electron microscopy (TEM) and XRD analyses. The basic properties specifying the porous structure of investigated samples were determined. The synthesized iron oxide particles were prepared without zeolite to understand their contribution to the changes in surface and porous properties of modified zeolite.

### Experimental

#### Materials

Natural zeolite of grain size 0.045-0.09 mm from the locality Nižný Hrabovec was added into the solution of Fe ions prepared from FeSO<sub>4</sub>·7H<sub>2</sub>O and FeCl<sub>3</sub> salts (Fe<sup>2+</sup>/Fe<sup>3+</sup> = 0.5) by continuous stirring for 0.5 h in nitrogen atmosphere at selected temperatures 20 and 85 °C (Matík et al., 2004). The amount of zeolite was adjusted to obtain the zeolite/iron oxide ratio of 5:1. A solution of NH<sub>4</sub>OH was added drop wise to the suspension of zeolite and Fe ions to precipitate particles of iron oxides. The final product was filtrated and dried at temperature 70 °C. The iron oxide particles were also synthesized without zeolite under the same conditions.

#### Characterization

The porous properties of parent zeolite, samples of modified zeolite and of synthesized iron oxides were studied using nitrogen adsorption method realized on the ASAP 2400 (Micromeritics, USA) apparatus at 77K. Before measuring, the samples were heated at temperature 300 °C and degassed at 3 Pa. Specific surface area was calculated from the adsorption isotherms according to the BET method in the range of relative pressure 0.03-0.2 p/p<sub>0</sub> and the value of total pore volume was determined from the amount of adsorbed volume at relative pressure 0.98 p/p<sub>0</sub>. The micropore volume V<sub>micro</sub> was determined using

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the t-plot analysis. The pore size distribution of investigated samples was obtained from the desorption isotherms.

The crystalline structure of the parent zeolite and modified zeolite were studied by X-ray diffraction analyses using the Phillips X' Pert Pro diffractometer equipped with the CuK $\alpha$  radiation (40 kV, 40 mA) with the positional sensitive detector (X' Cellerator); the structure of synthesized iron oxides were examined by diffractometer Philips 1830. The obtained data were analysed using the Catalogue JCPDS (Joint Committee on Powder Diffraction Standards).

The average crystallite size of iron oxide particles synthesized at temperatures 20 and 85 °C were estimated using Scherrer's formula. An information on the size, and the morphology of individual particles of investigated iron oxide samples was provided by analytical techniques as scanning microscopy (SEM). The detailed structure was analysed by the transmission electron microscopy (TEM) using the method of replicas.

## Results and discussion

### Nitrogen adsorption method

The total adsorption and desorption isotherms (Fig. 1) were obtained from the volume of adsorbed gas plotted against the relative pressure. The hysteresis loop confirms the occurring of mesopores in the pore structure of zeolite samples. The final, arising part of the total adsorption isotherm suggests the occurrence of macropores in the structure of zeolite.

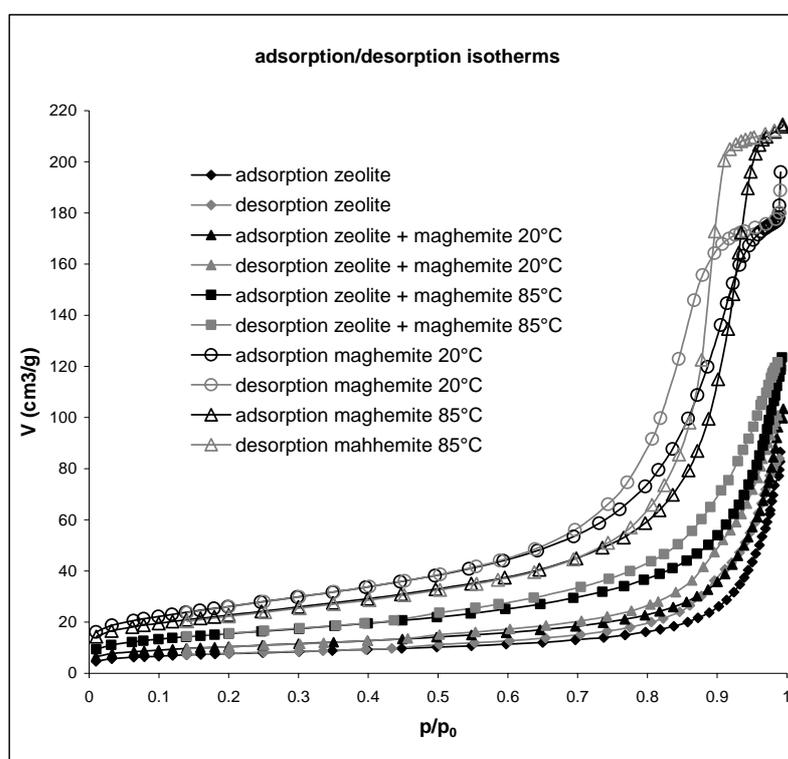


Fig. 1. Adsorption/desorption isotherms of zeolite, modified zeolites and synthesized iron oxide samples.

Obr. 1. Adsorpčné/desorpčné izotermie zeolitu, modifikovaných zeolitov a vzoriek syntetizovaného oxidu železa.

The contribution of small pores to the pore size distribution is not significant because the values of the micropore volume determined from the t-plot analysis were equal almost to zero. The BET surface area was calculated using the adsorption isotherm in the range of relative pressure from 0.03 to 0.2. The values of total pore volume and external surface were also determined and they are listed in Table 1. As follows from it, the specific surface area  $S_{\text{BET}}$  and the total pore volume  $V_a$  have increasing tendency and are depending on the temperature of zeolite modification. That should be explained by the formation of secondary pore structure during the precipitation of iron oxide particles. The adsorption and desorption isotherms of synthesized iron oxide samples really indicate strongly their mesoporous structure. Moreover, the hysteresis loop of iron oxide samples is according to the IUPAC report (Sing et al., 1985) typical for observation with aggregates. Thus it can be assumed that the particles of iron oxide were precipitated on the surface of zeolite forming aggregates. The other values characterizing the changes in pore structure of iron oxide particles synthesized at 20 and 85 °C are also included in Tab. 1.

Tab. 1. Structural characteristics of zeolite and iron oxide samples.

Tab. 1. Štruktúrne parametre zeolitových vzoriek a vzoriek oxidu železa.

Sample	SBET [m <sup>2</sup> /g]	V <sub>a</sub> [cm <sup>3</sup> /g]	V <sub>micro</sub> [cm <sup>3</sup> /g]	St [m <sup>2</sup> /g]
zeolite	27.5	0.108	0.003	20.7
zeolite + iron oxide 20 °C	37.2	0.136	0.003	29.8
zeolite + iron oxide 85 °C	55.5	0.174	0.003	47.1
iron oxide 20 °C	93.8	0.274	0.003	85.4
iron oxide 85 °C	81.2	0.331	0.004	70.4

The distribution of adsorbed volume on the zeolite samples was estimated by the BJH method from the desorption isotherms. Fig. 2 shows the dependence of the volume density distribution on the average pore diameter of the natural zeolite and its modified samples. The curve for the sample modified at 20 °C indicates an increase in the volume of mesopores, but the zeolite modification at temperature 85 °C brought a formation more pores, especially in the range from 3.7-30 nm. Thus the effect of zeolite modification on the secondary pore formation is more expressive at the modification of zeolite at temperature 85 °C.

The pore size distribution of synthesized iron oxide particles (Fig. 3) shows the maximum at 18 nm for the iron oxide prepared at 85 °C and the maximum between 12 and 14 nm for the sample prepared at 20 °C. It should be assumed that the pores at the sample prepared at 20 °C are smaller due to the smaller sizes of particles. An indirect evidence of that is given by the value of BET surface area (Tab. 1).

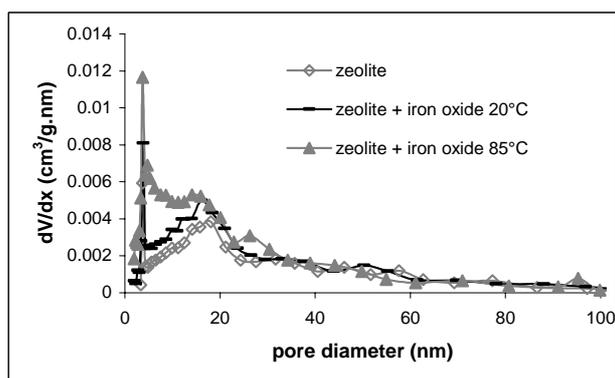


Fig. 2. Plot of differential pore volume in dependence on the average pore diameter for zeolites

Obr. 2. Grafická závislosť diferenciálneho objemu na veľkosti pórov pre zeolity

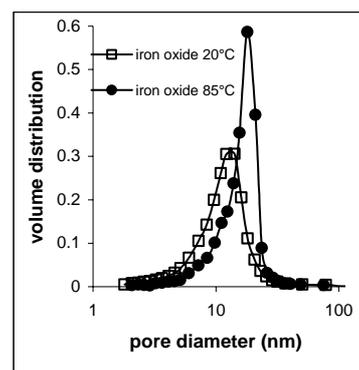


Fig. 3. Pore size distribution of iron oxide samples

Obr. 3. Distribúcia pórov vzoriek oxidu železa

### X-ray diffraction, SEM, TEM analysis

The XRD analyses revealed a very complicated structure of the natural parent zeolite used, consisting of clinoptilolite (more than 80 %), but also of a high silica content (Fig. 4). The phase analyse of modified zeolite at 85 °C confirmed the inherence of the precipitated iron oxide on the zeolite surface (Fig. 5). The high reflections have decreased but the crystal structure of zeolite is still retained.

The XRD pattern of both iron oxide samples showed a more crystalline structure (Figs. 6-7). Two expressive peaks appeared in the sample of iron oxide 85 °C. The phase analyse of iron oxides synthesized at both selected temperatures showed diffraction peaks coincident for maghemite and magnetite reflections. The mean dimension of crystallites composing the fine powder iron oxide samples was calculated from Scherer's formula and the values 17.2 nm for iron oxide synthesized at 20 °C and 19.1 nm for the sample prepared at 85 °C were obtained.

The sample of iron oxide synthesized at 85 °C was observed also by transmission electron microscope (TEM) using the method of electron diffraction. The six crystallographic planes corresponding only to maghemite  $\gamma\text{-Fe}_2\text{O}_3$  were confirmed (Fig. 8). The lattice parameter of crystalline structure  $a = 0.83574$  nm calculated from the Rietveld analyse corresponds to maghemite. The average particle size of maghemite 85 °C found out from the TEM images was 28 nm, confirming its nanostructure character. The images obtained from SEM indicate their tendency to form aggregates (Fig. 9), what should support the result shown by the adsorption method.

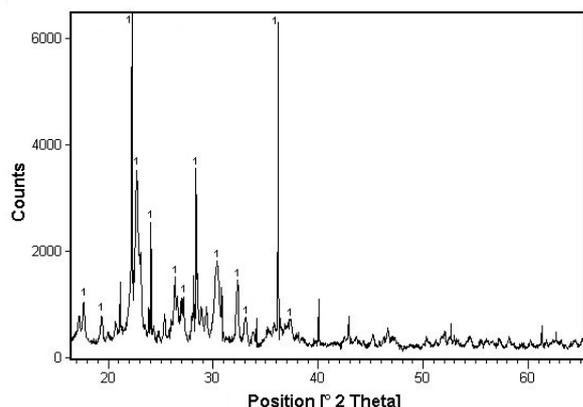


Fig. 4. XRD of parent zeolite.  
Obr. 4. RTG záznam pôvodného zeolitu.

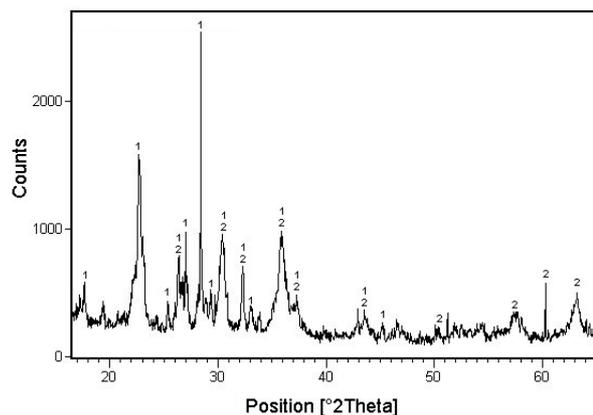


Fig. 5. XRD of zeolite modified at 85 °C (1-clinoptilolite, 2-iron oxide)  
Obr. 5. RTG záznam zeolitu modifikovaného pri 85 °C (1-klinoptilolit, 2-oxid železa)

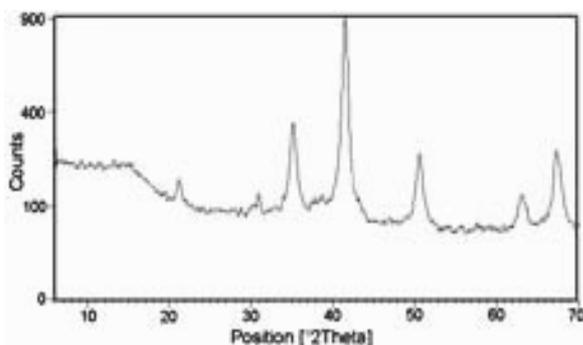


Fig. 6. XRD of iron oxide synthesized at 20 °C  
Obr. 6. RTG záznam oxidu železa syntetizovaného pri 20 °C

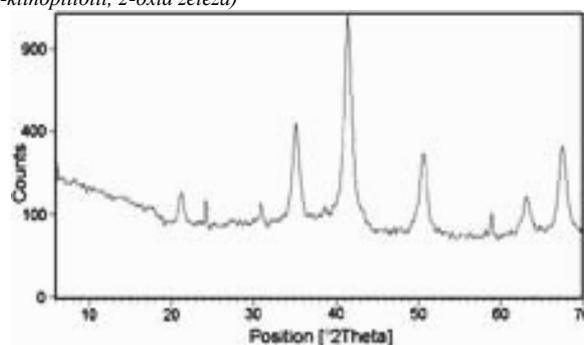


Fig. 7. XRD of iron oxide synthesized at 85 °C  
Obr. 7. RTG záznam oxidu železa syntetizovaného pri 85 °C

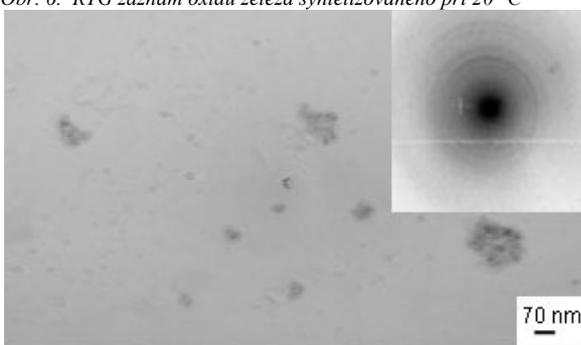


Fig. 8. TEM image of maghemite particles and their electron diffraction pattern  
Obr. 8. TEM obrázok maghemitových častíc a ich elektrónový difraktogram

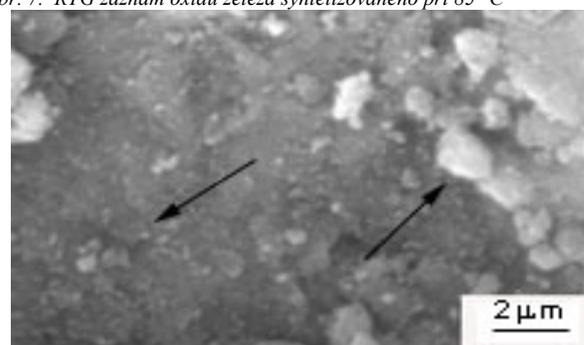


Fig. 9. SEM image of maghemite aggregates and fine particles  
Obr. 9. SEM obrázok agregátov maghemitu a jeho jemných častíc

## Conclusion

The changes after zeolite modification have been studied with the aim to obtain an enhancement of surface and pore properties of modified samples. The natural zeolite was modified by iron oxide particles precipitated at selected temperatures 20 and 85 °C on the bearing zeolite and the changes were identified using the nitrogen adsorption method, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and the XRD analyses. It follows from the results (Table 1) of adsorption measurements that the values of BET surface area and the total pore volume increased in dependence on the temperature of iron oxide preparation. The highest values were obtained for the sample of zeolite modified at 85 °C. The hysteresis loop of modified zeolite samples indicates occurring of mesopores and their final part

of macropores. The calculation of the volume of micropores brought values equal almost to zero. Following the pore size distribution curve, an increase in the total pore volume can be explained by the secondary mesopore structure formation.

To understand the influence of iron oxides on the structural properties of zeolite samples, the samples of iron oxide synthesized without the bearing zeolite were prepared and studied. The hysteresis loop of iron oxide (Fig. 1) confirms its mesopores structure, typical for observation with aggregates. The crystallite size of both samples of iron oxide were calculated according to the Scherer's formula, and the values 17.2 nm for the iron oxide 20 °C and 19.1 nm for the iron oxide 85 °C were found. The decrease of crystallite size resulted in an increase of  $S_{\text{BET}}$ .

It can be assumed that the particles of iron oxide precipitated on the surface of zeolite, forming aggregates. The tendency of iron oxide particles to form aggregates can be observed on the images obtained from SEM (Fig. 9).

Analysing the TEM (Fig. 8) electron diffraction pattern, it was shown that the crystallographic planes of iron oxide are typical for maghemite mineral.

Moreover, using of iron oxide particles as modifiers of properties of natural zeolite yields a composite material with higher magnetic susceptibility (Matik et al, 2004), which offers an easy separation process by means of an applied magnetic field.

The influence of temperature of zeolite modification by magnetic particles on the specific surface area has an increasing tendency and seems to be very interesting. What is the relation between the surface of synthesized iron oxides and those of composite materials modified by synthesized oxides? To find the answers on these questions should be the aim of the further study.

Summarizing all the results it can be concluded that the process of modification of the natural zeolite at temperature 85 °C by maghemite particles enhanced all properties responsible for better sorption purposes.

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