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X-RAY PHOTOELECTRON SPECTROSCOPIC STUDIES OF A IODINE DOPED NATURAL ZEOLITE OF CLINOPTILOLITE TYPE AND ITS THERMALLY DEGRADATED PRODUCTS

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Abstract

An iodine containing natural zeolitic material of the clinoptilolite type heated to different temperatures was investigated by means of X-ray photoelectron spectroscopy and thermal analysis methods. At room temperature the iodine was found to be present, depending on the preparation conditions, in the form of iodide or iodide combined with elementary iodine. After heating to 200°C, only iodide was observed which persists in the product in a small amount also after heating to 900°C.

Keywords: clinoptilolite, iodide, iodine, natural zeolitic material, thermal analysis, XPS

Introduction

Many new products have been prepared recently by sorption of different organic and inorganic molecules or ions in the natural clinoptilolite [1–3]. The chemical composition of these zeolites can be expressed by the simple formula $M_{m/n}[m(AlO_2)\cdot n(SiO_2)]\cdot qH_2O$ or by Meier's formula [4]:

$$M_xM'_yN_z[T_mT'_n..O_{2(m+n+..)-\varepsilon}(OH)_{2\varepsilon}](OH)_{br}(aq)_p\cdot qQ$$

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where $\varepsilon=0, 1, 2, 3...$, M and M' are exchangeable and non-exchangeable cations respectively, N are non-metallic cations (generally removable on heating), (aq) chemically bonded water (or other ligands) and Q sorbate molecules, which need not be only water. Main group elements are among the T and T' atoms.

The present investigations of zeolitic products doped with iodine are carried out as a continuation of a study of properties and possibilities of utilization [1] of a natural zeolitic material of clinoptilolite type from the East Slovakian deposit. The iodine may be present in the zeolite in different oxidation states. One of the reasons is that the studied natural zeolitic material contains Fe(III) ions [5, 6]. Literature data [7] show that these ions are capable of oxidizing iodide to elementary iodine. The distribution of the different iodine oxidation states depends essentially on the extent of thermal degradation of the iodine-doped zeolitic products. In the present work we used X-ray photoelectron spectroscopy (XPS) for identification of the different iodine forms present in the iodine-doped zeolite and in the products of its thermal degradation.

Experimental

Materials and methods of preparation

The natural zeolitic material of the clinoptilolite type studied (CT) came from the East Slovakian deposit in Nižny Hrabovec. This natural zeolitic material contains, on the average 57.2% [5, 6] of the zeolitic material clinoptilolite.

For preparation of the iodine containing zeolitic products we used the CT material after thermal activation at a temperature of 100–110°C for 1 h. By treating the zeolite with aqueous potassium iodide solution, under different experimental conditions [8, 9], we prepared several products containing different amounts of iodine and iodides, respectively. The iodine-containing zeolitic products are hereafter denoted CT1KI (content of iodine 4.2 wt%) and CT2KI (content of iodine 6.5 wt%).

The potassium iodide and other chemicals were of analytical purity (Lachema Brno).

Instrumentation

The TG, DTG and DTA measurements were performed up to 900°C in air with a Derivatograph MOM OD 102 (Paulik-Paulik-Erdey, Budapest). The conditions used were: weight of sample 100 mg, sensitivities; TG 50 mg, heating rate 9 deg·min^{-1}; reference material Al_2O_3.

The X-ray photoelectron spectroscopic measurements were carried out in laboratories in Catania and Prague. Some of the results obtained in the Prague laboratory have been published in our previous paper [8] in which the electrical conductivity of these iodine zeolitic products is discussed.

In Catania the XPS measurements were performed with a LHX1 Leybold spectrometer using unmonochromatized AlK$_\alpha$ radiation (1486.6 eV). The source was operated at 14 kV and 20 mA. The vacuum in the analyzer chamber was better than 10^{-6} Pa. The energy scale of the spectrometer was calibrated using the Cu 2p3/2 and Au 4f7/2 signals at 932.7 eV and 84.0 eV, respectively. Under these conditions, the binding energy (BE) of adventitious carbon was 285.1 eV. Sensitivity factors used in this work were taken from [10] since the spectrometer transmission function was compatible with that of the spectrometer used [11].

In Prague the XPS measurements were carried out with a VG ESCA 3 MkII spectrometer using the same radiation as above. The instrument was calibrated so that the difference between the Au 4f7/2 photoelectron peak and the Fermi level of Pd was 84.0 eV. The spectrometer was operated in fixed analyzer transmission mode. The background pressure of residual gases during the spectra accumulation was typically of the order of 10^{-6} Pa. The C binding energy (284.8 eV) of adventitious carbon was used in calibration to compensate for charging effects. To avoid the sublimation of iodine the XPS measurements were carried out on the samples in the as received state at liquid nitrogen temperature. The measured lines included Si 2p, Al 2p, K 2p, Ca 2p, I 3d, C 1s, O 1s and Al KLL Auger transition. The XPS peak positions and areas were determined by fitting the unsmoothed experimental data after subtraction of the linear background. Core level binding energies were determined with an accurancy of ±0.2 eV. The sample CT2KI was analysed by XPS after heating to 200°C and after thermal analysis which was carried out at temperatures up to 900°C.

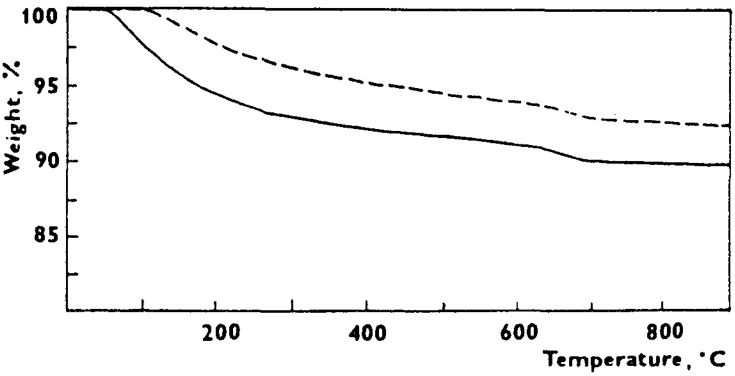

Fig. 1 TG curves of the iodine-doped zeolitic product CT2KI (—) and the natural zeolitic material CT after thermal activation at 100–110°C (- - -)

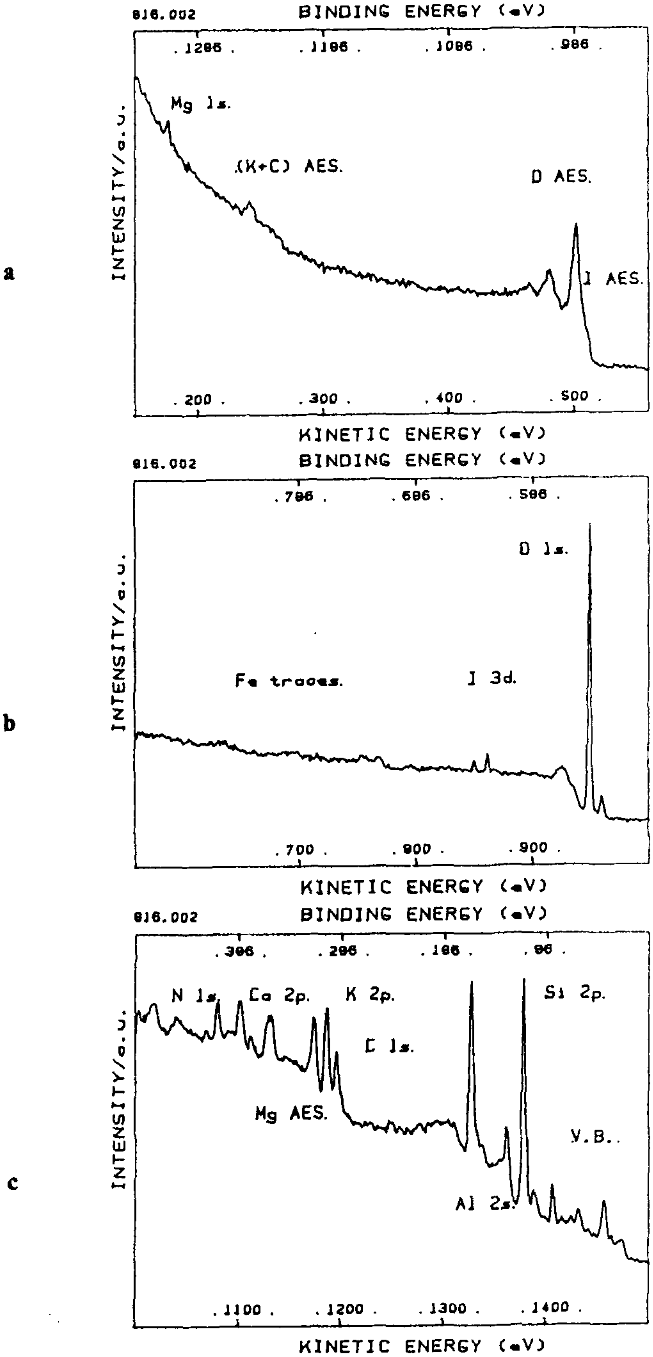

Fig. 2a, b, c Three different regions of wide spectra of the zeolitic sample CT2KI showing all the elements detected

Results and discussion

By treating the natural zeolitic material with potassium iodide solution under different experimental conditions, products were obtained which differed in iodine content and in their properties [8, 9]. In our previous papers [8, 9] the natural zeolite of clinoptilolite type and its iodine products have been investigated by means of IR spectroscopy, X-ray powder diffractometry, thermal analysis, scanning electron microscopy and ac-dc conductivity as well as by electromotive force measurements. The iodine content and the content of other elements were determined by Electron Microprobe measurements and EDS analysis.

The IR spectra and X-ray powder analysis revealed no significant differences between the original zeolite and its iodine-doped forms. It may be supposed that iodine enters the channels of the zeolite as a monodispersed phase [10] similarly as in other products [1]. The results of thermal analysis obtained for an East Slovakian natural zeolitic material have been described in [9, 12, 13]. Pechar and Rykl [13] described the gradual loss of water molecules. The total water content was in their case 10.9 wt%. The partial loss of water up to 220°C was 7.2 wt%. After heating to 900°C, 9.4 wt% of water was released, the zeolitic material retained 1.5 wt% of its total water content.

We obtained similar results with our zeolitic products doped with iodine (content of iodine: 2.48 wt%) and degraded by heating to 900°C (content of iodine: 0.19 wt%) [9]. The decomposed sample still exhibited the presence of a small amount of iodine.

The TG curve of the CT2KI product is shown in Fig. 1 in comparison with the curve obtained with the natural zeolitic material thermally activated at 100–110°C for 1 h. The product doped with iodine showed a gradual loss of water and iodine during thermal decomposition. The iodine replaced part of the water in the original zeolite (the sample CT2KI, according CHN analysis, contained [8] 5.4 wt% of water and, according to the results of electron microprobe analysis, 6.5 wt% of iodine). The TG curve of the sample CT1KI is very similar to the curve of the sample CT2KI (the sample CT1KI, according CHN analysis, contained 8.1 wt% of water and, according to the results of electron microprobe analysis, 4.2 wt% of iodine).

The results of XPS measurements obtained in both ESCA laboratories indicate presence of both elementary iodine and iodides in the product CT2KI. Under the low-pressure conditions of measurements a non-significant proportion of iodine may escaped – mainly from the surface of the sample. Figures 2a, b, c depict three different portions of wide spectra showing all the elements detected (sampling depth is about 3–5 monolayers). Detailed scans of the regions of interest were analyzed to obtain BE values and widths of lines (FWHM). In some cases detailed scans were analyzed by proper analysis software [14] to discriminate component peaks and to subtract overlapped features. From peak areas elemental concentration ratios were calculated. Two peaks arising from surface Al atoms have been measured, namely the Al 2p photoemission peak and Al KLL Auger peak. The sum of the Al 2p binding energy and the kinetic energy of the Auger KLL electrons yields the modified Auger parameter α'. The value of this parameter may be related to the polarizability of the near neighbour oxygen atoms [15] and to the coordination state of Al. For the CT2KI sample we obtained α'=1460.9 eV. This value is close to that reported for pyrophyllite [16] in which Al is six-fold coordinated. This indicates that the surface of the studied CT sample contains Al species which are probably octahedrally coordinated.

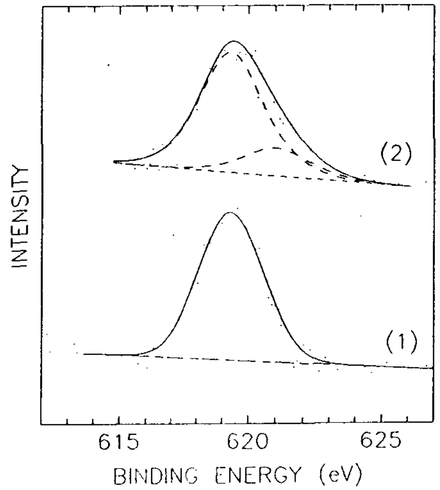

Fig. 3 I 3d5/2 spectra of samples CT1KI (1) and CT2KI (2)

Table 1 Binding energies and widths (in parentheses) of photoelectron lines in eV

Line	Sample			
	CT1KI	CT2KI	CT2KI after heating at	
			200°C	900°C
K 2p3/2	294.1(2.5)	293.3(2.2)	294.2(2.0)	294.0(2.3)
I 3d5/2	619.3(2.9)	619.3(2.8)	619.2(2.5)	619.3(2.6)
	–	621.1(2.8)	–	–
Si 2p	103.0(2.5)	103.0(2.6)	102.9(2.1)	103.0(2.4)

The I 3d5/2 photoemission line can be fitted by two components (Fig. 3), corresponding to iodide ions and iodine.

Table 2 Surface atomic concentration of K and I in the studied zeolitic samples CT1KI and CT2KI (relative to Si concentration)

Element	Sample		
	CT1KI	CT2KI	CT2KI after heating at 200°C
Si	1.00	1.00	1.00
K	0.13	0.089	1.0
I	0.005	0.011	0.004

The XPS study showed presence of only iodide ions in the sample CT1KI (as in KI [16]). The core level binding energies of the measured peaks are displayed in Table 1. In Table 2 the results of determination of the surface concentration of potassium and iodine in both zeolite samples are summarized. Because of the different preparation procedures [8], the sample CT2KI contains more iodine than the sample CT1KI (some sorbed I_2 is lost from the sample CT1KI during the drying process at 60°C during the preparation) and the sample CT1KI contains more potassium than the sample CT2KI. The results from XPS measurements (Table 2) agree with those from electron microprobe analysis, giving K content of 5.85 wt% for CT1KI and 5.1 wt% for CT2KI [8]).

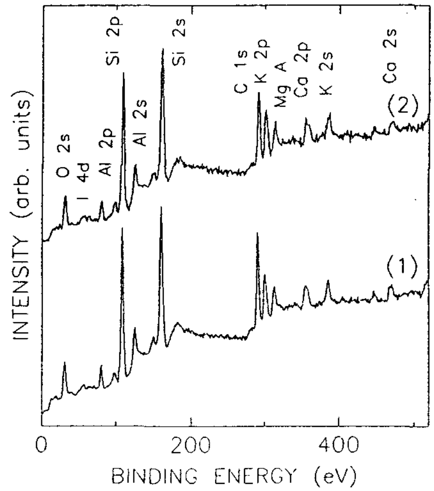

Fig. 4 XPS spectrum of the iodine-doped zeolitic product CT2KI after heating up to 200°C (1) and of the CT2KI product after heating up to 900°C (2)

In these studies only iodides were identified in the CT2KI sample heated to 200°C (Tables 1, 2, Fig. 4, curve 1). Heating up to 900°C yielded a product which contained only a small amount of iodide ions (Table 1, Fig. 4, curve 2). Their presence influences the thermal and electrical properties as discussed in our previous paper [8, 9].

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Zusammenfassung — Ein jodhaltiges natürliches Zeolith-Material vom Typ Klinoptilolit wurde nach Aufheizen auf verschiedene Temperaturen mittels Röntgen-Photoelektronenspektroskopie und thermoanalytischen Methoden untersucht. Bei Raumtemperatur ist Jod – in Abhängigkeit von der Herstellungsmethode – in Form von Jodid oder in Form von Jodid und elementarem Jod zugegen. Nach Erhitzen auf 200°C wurde nur noch Jodid beobachtet, was nach dem Erhitzen auf 900°C auch im Produkt in geringen Mengen weiter vorhanden bleibt.