

Natural Zeolitic Material of the Clinoptilolite Type Doped with Iodine and Its Ions

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Abstract. The aim of this study was the preparation of natural zeolitic materials doped with iodine and its ions. Natural zeolite from an East Slovakian deposit was used. The content of iodine in the zeolitic products depended on the experimental conditions used for the preparation. The products and their intermediates obtained at 100, 200, 400 and 900°C were identified.

Key words. Natural zeolite, clinoptilolite, iodine, iodide, host-guest complexes, electrical conductivity.

1. Introduction

The synthetic and natural zeolites have been the object of research in different branches of chemistry for a long time. The natural zeolites, being non-toxic materials, are widely used in practice. In both types of zeolites the guest component is water [1, 2]. It is known that zeolites may have the original guest component substituted by different organic or inorganic compounds, forming a sorbate [3, 4]. The presence of guests confers some characteristic properties on the complexes, which are associated with different uses.

The preparation of our zeolitic products containing iodine and its ions arises from the study of other inclusion compounds doped with iodine, which have electrical properties [6]. Information about the possibility of using some cationic form of clinoptilolite for the extraction of radioactive iodine and other ions from wastes has been published [4]. Inclusion compounds containing polyiodide ions [7, 8] and polymeric adducts containing iodine and its ions [9] (exhibiting different electrical properties depending on the conditions of their preparation) have been reported.

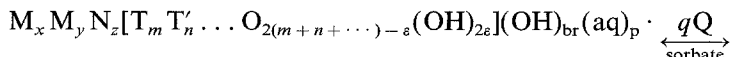
The aim of the present study was to change the properties of the natural zeolitic materials by doping it with iodine and to examine the different methods for such preparations.

2. Experimental

2.1. PREPARATION AND METHODS

Natural zeolitic materials of the clinoptilolite (CT) type from the East Slovakian deposit in Nižný Hrabovec was used. It contains on average 57.2% [11] of the

zeolitic mineral clinoptilolite (CT). The composition of the natural zeolitic material can be expressed by Meier's [10] formula as:



It enables one to see the large substitution of atoms in the cationic and anionic part of the host and the changes and differentiations in the water molecules. The chemical composition of the original zeolitic material used in our preparation [11] has a Si/Al proportion: 5,19, suitable for the sorption of organic compounds.

Different methods and different iodine-containing reactants were used for the preparation of the new zeolitic products. The zeolitic material was used after partial thermal activation or in its natural form.

- I. The zeolite was dried at 100–110°C for one hour for the more effective sorption of new guests. The partially activated zeolite was used in the following way:
 - (a) 5 g of this zeolitic sample was added to different (5–20 mL) quantities of iodine (solution 1 or 2) or potassium iodide (1 M or 0.1 M) solutions. After two hours of intensive mixing the heterogeneous mixture was decanted three times with distilled water and centrifuged. The zeolitic product (product A) was then dried in a desiccator (over silicagel) or in a drying oven at 60°C.
 - (b) After adding the iodine or the potassium iodide solution (5–20 mL) to the zeolitic sample (5 g) it was left to stand for ten days (with occasional mixing). The zeolitic product was decanted and then treated as above.
- II. The zeolitic products were prepared without the partial thermal activation of the zeolite.
The modes II(a) and II(b) are analogous to modes I(a) and I(b).
- III. The zeolitic products were prepared as in I and II, but the decantation was done only after three months standing.

Iodine was used as solution (in KI) with different concentrations of iodine and potassium iodide. The most frequently used solutions had the composition: 1.5 g I₂, 5 g KI in 30 mL H₂O (solution 1); 1 g I₂, 5 g KI in 24 mL H₂O (solution 2).

The zeolitic product was also prepared with pure potassium iodide solution 1 mol · dm⁻³ or 0.1 mol · dm⁻³.

The iodine and potassium iodide were of p.a. purity (Lachema, Brno).

When the preparation of the physical mixture of the natural zeolite with solid iodine was attempted only by cogrinding, the product gained was brown coloured. A part of the iodine was liberated in the gaseous form from the mixture. The IR spectra measured immediately after the mixing were similar to those of the original zeolite.

2.2. INSTRUMENTATION

The iodine content and other elements were determined by Electron Microsonda measurements (JXA-5A, JEOL) applying Kevec. Parameters used: accelerating voltage 25 kV, sample current 1.5 × 10⁻⁷ A; analysing crystal LiF-PED.

CHN analysis was performed by a Perkin Elmer 2400 Elemental Analyser.

All TG, DTG and DTA analyses were measured up to 900°C in air on a Derivatograph MOM OD 102 (Paulik-Paulik-Erdey, Budapest) under the same conditions (weight of sample 100 mg, sensitivities: TG 100 mg, DTA 1/5, DTG 1/5; heating rate 9° min⁻¹; reference material Al₂O₃).

IR spectra of the zeolitic products were obtained with the KBr disc technique using a Specord M 80 IR spectrometer (Carl Zeiss, Jena).

A Jeol scanning microscope Model JSM 840A and for some samples also a Jeol scanning microscope Model JSM 35 CF were used to study the morphology.

3. Results and Discussion

3.1. PREPARATION

The chemical composition [11] of the starting zeolitic CT material agreed with our results obtained by the Electron Microsonda measurements and CHN analysis. The results of CHN analysis (hydrogen: 1.15%) confirmed that the content of water in the original zeolite amounted to 10.9% water (the literature [11–13] value is 9.97–10.9%). The water was still present in the zeolitic materials doped with the iodine, but at a lower percentage.

By putting the zeolite into contact with iodine (I₂/KI) or pure potassium iodide solution under different experimental conditions products were obtained which differed from each other in iodine content and in other properties. The iodine content was in a wide range from 0.24% up to 43.26%, according to the synthesis conditions. However, for the products with higher iodine content it was observed that iodine was slowly lost from the zeolitic products, even at laboratory temperature.

The presence of the iodine in the zeolitic products was also observed by the colour. In the case of very low contents (<1%) it was not distinctly visible, but with increasing content of iodine the colour was deeper yellow and also yellowish brown.

The products prepared without using decantation (III) always had a higher iodine content. After three months standing these products were decanted additionally for the elution of the absorbed iodine. After decantation the content of iodine was only slightly decreased. The products prepared by methods Ia and IIa had a lower iodine content.

Potassium iodide solution alone was effective in the doping of the zeolites, the product changing color to yellow. For example contact of the KI solution with zeolite (5 mL of 1 M KI solution, mode III(b)) yielded a product containing 13.45% iodine (compare also in Figure 1 TG curve 6 of the product against curve 2 of the thermally activated zeolite). But when a lower concentration of KI solution (0.1 M) was used, the product contained only 4.43% of iodine (compare TG curve 4 against the thermally treated CT zeolite). The products prepared using methods I(a) and II(a) had only a low iodine content.

3.2. THERMAL ANALYSIS

The thermal degradation of the products were studied in comparison with the original zeolitic materials. The TG curves of all zeolitic products prepared by the

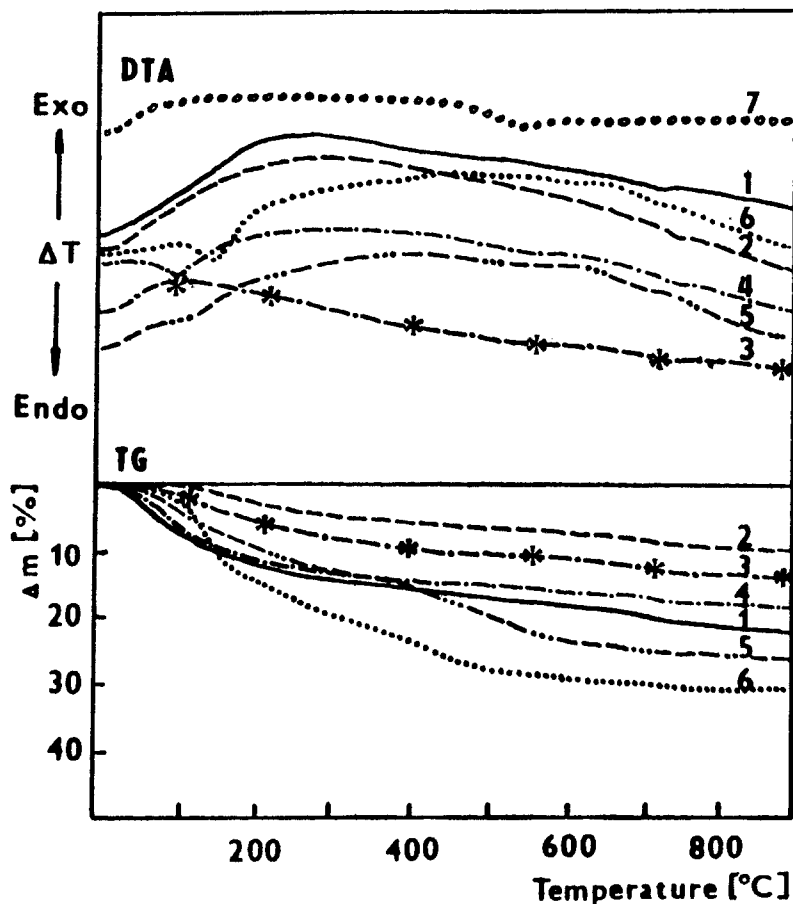


Fig. 1. TG and DTA curves of the original natural zeolitic material (curve 1), of the zeolitic material after partial thermal activation at 110°C (curve 2) and the zeolitic products prepared: (curve 3) with iodine solution (product A); (curve 4) with 0.1 M KI solution (preparation I(a)); (curve 5) with iodine solution (II(b) preparation); (curve 6) with 1 M KI solution (III(b) preparation); (curve 7) original zeolitic material (heating rate 3°/min). The curves 1–6 measured with 9°/min heating rate.

use of iodine or KI solution showed a higher weight loss in comparison with the original zeolite or the thermally activated sample.

In Figure 1 the original and the activated (by heating to 100–110°C) zeolites are compared with the zeolitic products containing different amounts of iodine (cf. curves 5 and 6 with curve 1 and curves 3 and 4 with curve 2).

Product A, containing 2.48% of iodine (Figure 1, TG curve 3), was prepared by method I(a) with iodine solution (20 mL, solution 2). The heating of this product was interrupted at temperatures of 200, 400 and 900°C and the intermediates analysed. The iodine content in the individual intermediates is given in Table I.

As shown in Table I the iodine is partially lost during the thermal decomposition. But the product obtained at 900°C still contains a small amount of iodine: 0.19% (which represents 7.66% of the total content). This is confirmation that the iodine

Table I. Iodine content in the zeolitic product (A) at 25°C and after the heating to 200, 400 and 900°C. The zeolitic product (A) was prepared with iodine solution (I(a))

Zeolitic product (A)	25°C	After heating to		
		200°C	400°C	900°C
Iodine content (%)	2.48	1.19	0.59	0.19

enclosed in the zeolite substituted for the original water. The zeolite alone contained 1.5% of its original water content after heating to 900°C [13]. The partial loss of water from the natural zeolite up to 220°C was 7.2%. The next weight loss was only 2% up to 335°C. During the heating to 900°C 9.4% of the total water was released. The original water content was 10.9%.

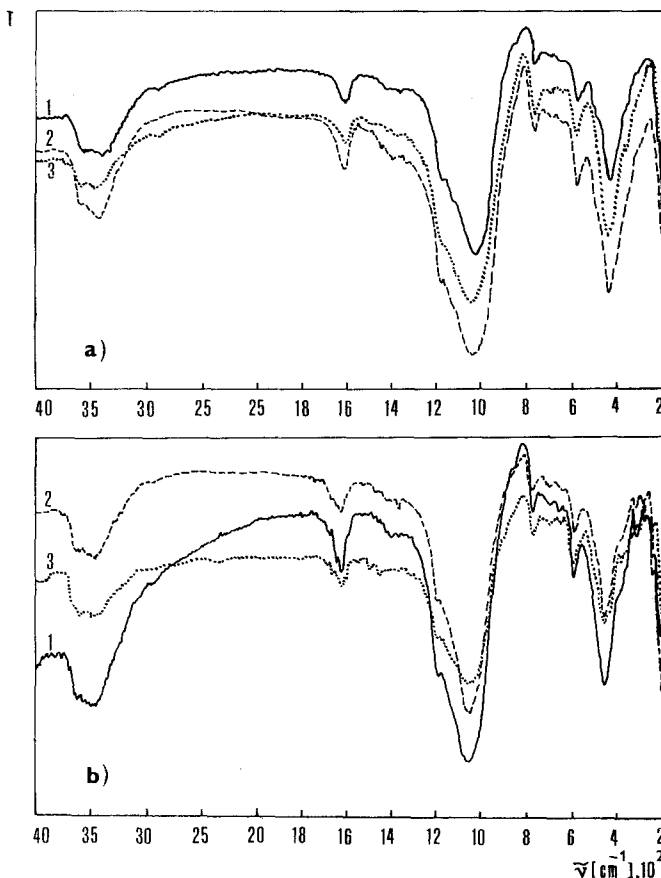


Fig. 2. (a) IR spectra of: the original natural zeolites CT (1); the zeolitic product A containing 2.48% of iodine (2) and the zeolitic product A after heating to 900°C (3). (b) IR spectra of the product A heated to 100 (1), 200 (2) and 400°C (3).

The DTA curves of the original zeolitic material (curve 1) and of the thermally activated material (curve 2) are mostly analogous and in the natural zeolites they show [14] a very weakly differentiated course of the changes, concurrent with the gradual loss of the appropriate amounts of H_2O or OH . We compared them with the DTA curve measured using a slower ($3^\circ\text{C}/\text{min}$) heating rate.

Only in products prepared with KI solutions (1 M or 0.1 M) do their DTA curves (6 or 4) show, in addition to less distinct maxima, a strong endothermic process with maxima at about 100 and 145°C , respectively. The products show (on curves 6 and 4) further weak maxima existing at about 650 and 700°C .

3.3. IR SPECTRA

Only some less significant changes were observed by examining the IR spectra of the original zeolites and their products containing iodine (Figure 2). An important change appeared in the bands in the $1200\text{--}800\text{ cm}^{-1}$ region which correspond to the asymmetric stretching vibration of the $(\text{Al}, \text{Si})\text{O}$ group. This is further proof that iodine and its ions penetrated into the cavities.

After heating to 900°C the zeolite alone is always in the amorphous form [13, 14] which is manifested by a broader band from this vibration. The IR spectrum of product A (curve 2 in Figure 2a) prepared and measured without heating shows the characteristics of the amorphous form. A similar broader band is observed after

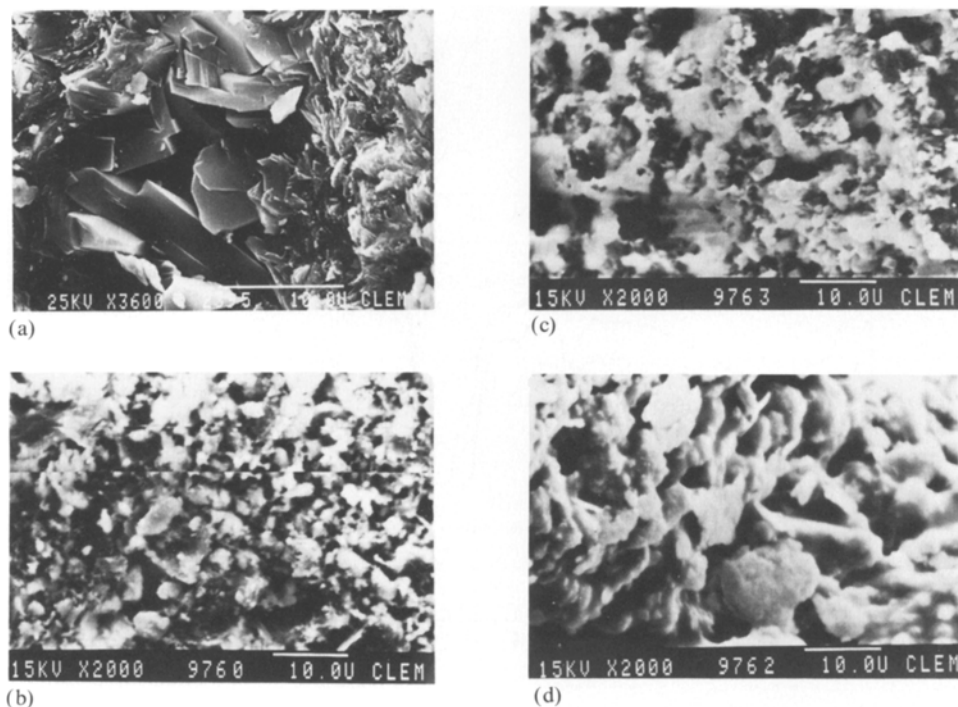


Fig. 3. Scanning electron micrograph of: the original natural [11] zeolite (a); the zeolitic product prepared with iodine solution (b) and the zeolitic product prepared with KI solution (c), (d).

heating product A to 900°C (curve 3). The original crystalline zeolite (curve 1) shows the sharp band.

The IR spectra of the intermediates gained from product A (iodine content 2.48%) at 100, 200 and 400°C are shown in Figure 2b. The absorption band at 1200–800 cm^{-1} shows only minor changes, but the broader bands showing the amorphous characteristics against the original zeolitic material (Figure 2a) are evident.

3.4. MORPHOLOGICAL STUDY

The morphological study of the zeolitic products containing iodine indicate, together with the $\nu_{\text{as}}(\text{Al, Si-O})$ band, some mode of their ‘impregnation’ or ‘preparation’ similar to that described in other products gained by the interaction of the zeolitic material with different [14] inorganic (potassium chloride, N-P, N-P-K fertilisers) or organic (perfumes, insecticides and other) compounds. This corresponds to the change of the originally crystalline form to the amorphous form which was observed in the IR spectra of all our products.

The very smooth surface of the original zeolite (Figure 3a) disappeared in all the products with iodine (Figures 3b and 3c). Some kind of little ‘pits’ are to be seen, differing from the original CT sample. These little cavities in Figure 4 become more evident during the heating of product A.

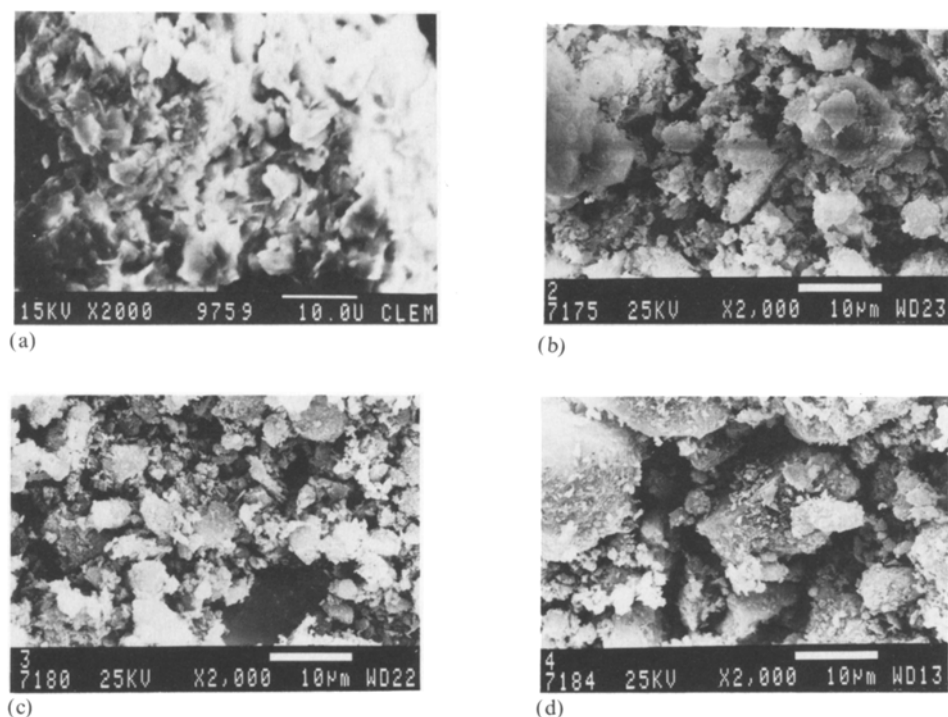


Fig. 4. Scanning electron micrograph of: the zeolitic product A at 25°C, containing 2.48% of iodine (a) and after heating to 100°C (b), 200°C (c) and 400°C (d).

4. Conclusion

The action of the iodine solution (in KI) and of pure potassium iodide solution on the natural zeolitic material of the clinoptilolite type yielded products with different amounts of sorbed iodine. The iodine content (0.24–43.26%) depends on the mode of the preparation. The presence of the iodine may contribute to the specific properties of the host–guest complexes gained from the natural zeolites. Preliminary measurements of the products give values of the electrical conductivity equal to 10^{-5} S cm⁻¹. Further studies using these host–guest complexes should clarify the mode of enclosure of the iodine.

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