Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **23:** 157–163, 1995.

Natural Zeolitic Material of the Clinoptilolite Type and Its AgI Form

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(Received: 4 May 1995; in final form: 25 September 1995)

Abstract. The aim of this study was the preparation of the natural zeolitic material of the clinoptilolite type doped with silver iodide. Natural zeolite from the East Slovakian deposit was used. This natural zeolitic material doped with AgI (content of AgI: 28.5%) has been investigated by X-ray powder diffractometry, EDS analysis, scanning electron microscopy, IR spectroscopy and thermal analysis.

Key words: Natural zeolite, clinoptilolite, silver iodide.

1. Introduction

Natural materials are nowadays used for many interesting purposes and are comparable with the synthetic ones. The smectites, mainly the montmorillonites (first used in 1887 by Le Châtelier) are continually being studied for the sorption of different cations and also organic molecules. Their dehydration, dehydroxylation, amorphisation and rehydration has been studied during heating [1–3].

The second important type of natural clays are the zeolites, particularly clinoptilolite and mordenite. The clinoptilolitic (CT) natural zeolites may be used in practice for the sorption of fertilizers [4], agrochemicals such as insecticides [5, 6] or growth stimulators, perfumes [5], toxic elements [7], cyclodextrins, and pharmaceuticals [8,9]. The natural CT zeolite from Slovakia [5–9] was used in this paper.

Clinoptilolitic zeolitic material coming from different deposits in the world is used for technical purposes. The destruction of the zeolitic host structure starts only at about 750°C and a new hydrated amorphous phase of clinoptilolite is obtained [5, 10].

Recently, its thermostability, in combination with reversible desorption and absorption of water, was also found to be an advantage in technological processes and it has therefore often been studied [11].

The doping of natural zeolites by iodine has benefits in veterinary pharmacy [9]. In the case of the synthetic and natural zeolites as well as other compounds the presence of iodine and iodide ions contributes to an alteration of the electrical properties (an increase of electrical conductivity) [12, 13].

The mordenite–AgI inclusion compound and its properties are known from the literature [14].

The aim of our present study was the preparation and characterisation of natural clinoptilolite–AgI inclusion compound.

2. Experimental

2.1. CHEMICAL AND MATERIALS

For our study we used natural zeolite of the clinoptilolite (CT) type from the East Slovakian deposit in Nižný Hrabovec. This natural zeolitic material contains on average 57.2% of the CT zeolite.

Potassium iodide and other chemicals were p.a. purity (Lachema Brno).

2.2. MATERIAL PREPARATION

1. The silver form [15] of the natural zeolitic material of CT type (3 g) was mixed with 1M potassium iodide solution (20 mL). The heterogeneous mixture was intensively mixed for one hour (the final ten minutes at a temperature of 60–80 °C). It was then left to stand for seven days (with occasional mixing) and then decanted with distilled water and centrifuged (the content of silver and iodide ions in water after the decanting was checked by the analytical method). The zeolitic product was dried at 60 °C ($\frac{1}{2}$ h). This product will be indicated as CTAgI.

2. The physical mixture of CT and AgI was prepared by the cogrinding of CT (71.5%) and AgI (28.5%).

3. For the comparison of the structure of the natural zeolitic product CTAgI, AgI was also prepared by reaction of a 1 M solution of potassium iodide and a 1 M solution of silver nitrate (in stoichiometric ratio). The precipitate of AgI was decanted with distilled water, centrifuged and dried at 60 °C. (The purity was checked by X-ray diffractographic measurements, IR and analytical methods.)

2.3. INSTRUMENTATION

The amounts of silver, iodine and other elements were determined by EDS analyses using a scanning electron microscope (TESLA BS 300) with an EDAX 9100/60 microanalyser. The morphology of the products was studied by a scanning electron microscope TESLA BS 340 (TESLA ELMI a.s. Brno). CHN analyses were performed by a Perkin Elmer 2400 Elemental Analyser.

X-ray powder diffraction patterns were obtained with the Dron-2 diffractometer using a GUR-5 goniometer with Mn-filtered FeK_α radiation (λ = 1.9373 Å).

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

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, sensitivies: TG 50 mg, DTA 1/3, DTG 1/3, heating rate 9 °C min, reference material Al_2O_3).

3. Results and Discussion

The natural zeolitic material of the clinoptilolite type doped with silver iodide CTAgI was obtained by reaction of the silver form of the natural zeolitic material [15] with potassium iodide solution. According to EDS analysis the product CTAgI contains on average 28.5% of AgI (13.1% Ag, 15.4% I).

The results of X-ray measurements confirmed the presence of AgI which can be indexed as iodargyrite. Figure 1 shows X-ray powder diffraction patterns of the natural zeolite of the clinoptilolite type CT (Figure 1a), natural zeolitic products CTAgI (Figure 1b) and AgI (Figure 1c). In accordance with Figure 1b the characteristic diffraction signals for AgI are detected with the reflecting technique.

From the SEM picture we assume a mean particle dimension of 1 μm.

If it is dispersed to preferred places in the bulk or on the surface corresponding to channels, AgI will not give rise to characteristic XRD patterns. But if the silver iodide is evenly coated over the surface of each particle and distributed to all tunnel positions, a typical XRD pattern will occur using this diffraction method.

The integrated intensity ratio of the selected diffraction lines corresponding to the clinoptilolite was different in the X-ray diffraction pattern of natural clinoptilolite CT and in the X-ray diffraction pattern of its product CTAgI. Similarly the integral intensity ratio of selected diffraction lines corresponding to AgI was different in the X-ray diffraction pattern of AgI and the X-ray diffraction patterns of CTAgI. The differences of the integral intensity ratio of the selected diffraction lines of CT and AgI indicates the formation of the inclusion compounds.

The electron micrographs of the natural zeolite CT, its zeolitic product CTAgI and pure AgI are shown in Figure 2. According to the electron micrographs, the starting CT material, (Figure 2a) has a relatively undeformed surface. But in the product CTAgI (Figure 2b), in contrast to the original CT material we can see some 'pits', showing that the AgI was sorbed into the zeolitic material CT and therefore it is, in some way, 'impregnated' by silver iodide. We found similar 'pits' in all our zeolitic products [5]. We can also find them in the paper by Galaway [10], but the author describes them as some sort of foaming structure.

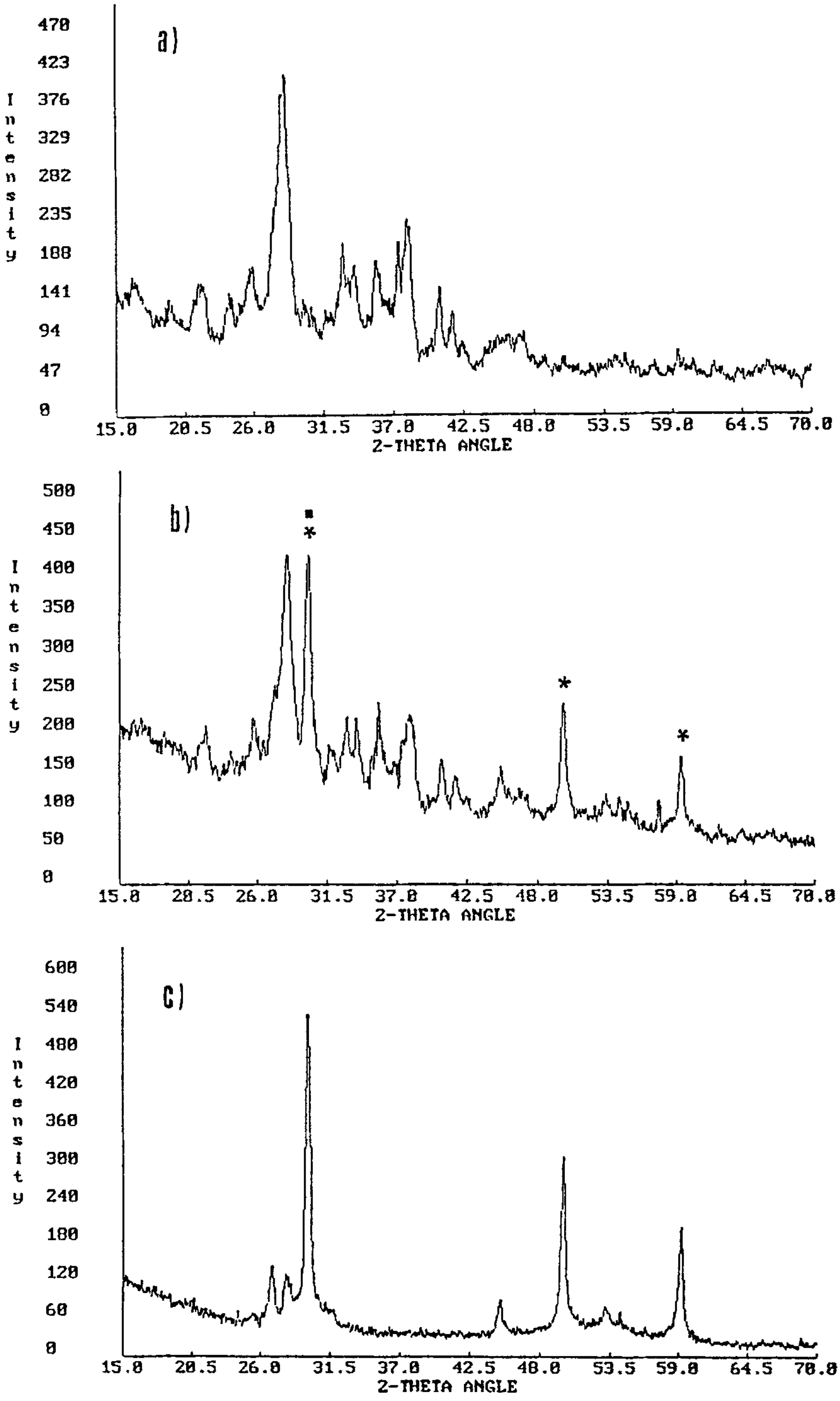
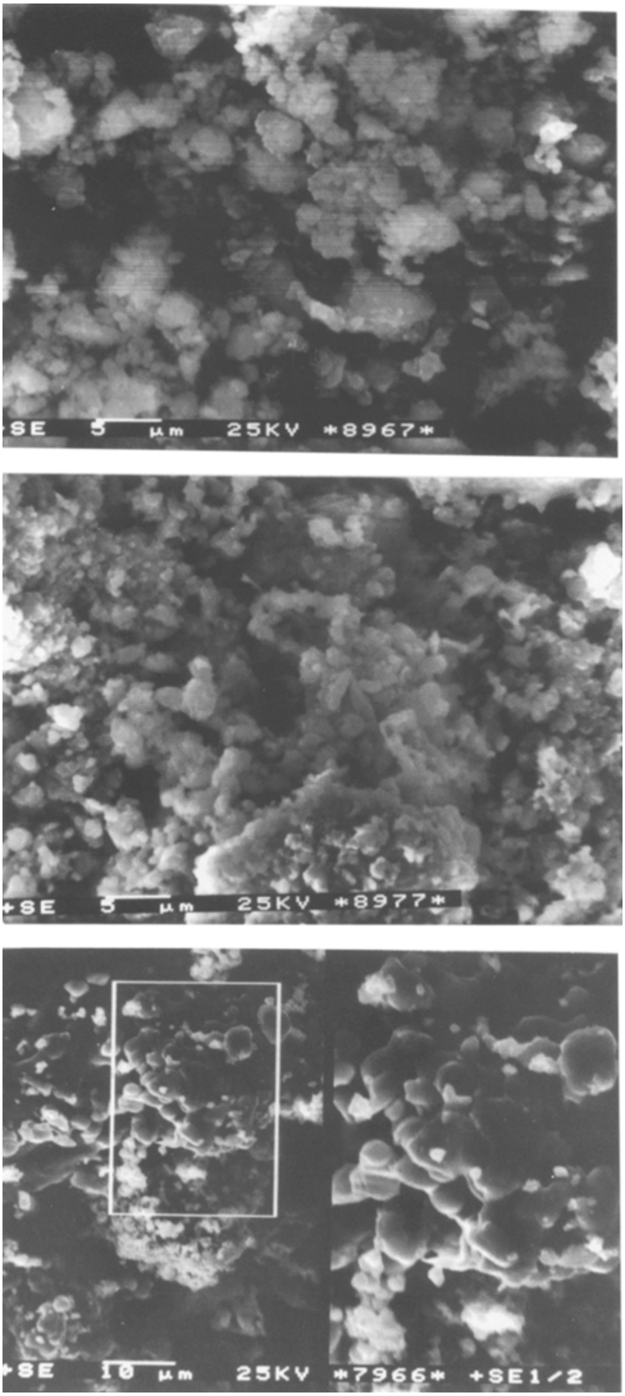


Fig. 1. X-ray powder diffraction patterns of the natural clinoptilolite CT (a), zeolitic product CTAgI (b), and AgI (c). (* characteristic peaks for AgI, ■* overlaping of the peaks of CT and AgI).



(a) CT

(b) CTAgI

(c) AgI

Fig. 2. Scanning electron micrograph of: natural zeolite CT (a), zeolitic product CTAgI (b) and AgI (c).

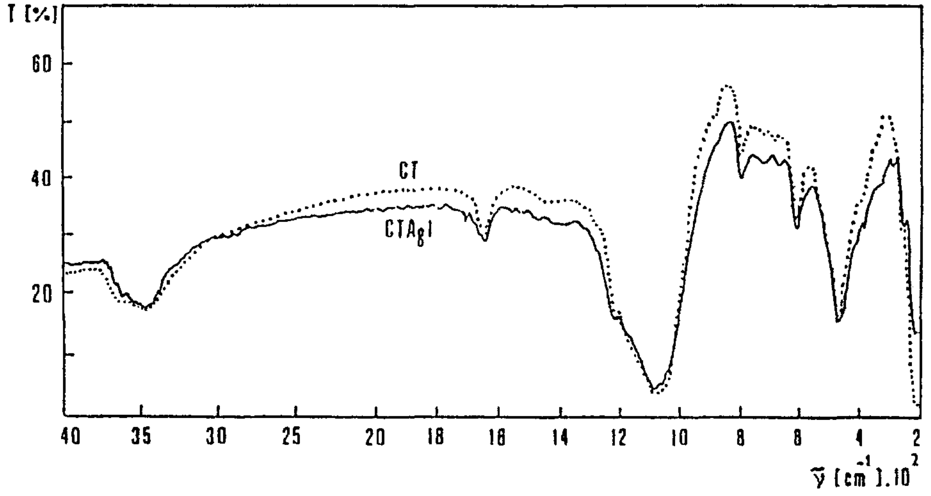


Fig. 3. IR spectra of natural zeolite CT and its product CTAgI.

The results of IR spectra and thermal analysis confirmed the presence of water in the product CTAgI but a lower percentage (5.5%) in comparison with the starting natural zeolite CT (10.9%) [12,15]. The presence of water in the starting zeolite and its CTAgI product was observed by two absorption bands in the IR spectra (Figure 3). The first one corresponds to the stretching vibration (3350–3650 cm^{-1}) and the second to the bending vibration of water at 1630 cm^{-1}. A change appeared in the bands in the 1200–900 cm^{-1} region which correspond to the asymmetric vibration of the (Al, Si)O group. Similar changes of this band (the band changes from a sharp to a broader and less intense one) were also found in other zeolitic products [5,8] as a consequence of the sorption of different organic or inorganic compounds into the microcrystalline zeolitic material.

The results of thermal analysis also confirmed the presence of AgI in the product CTAgI. On the DTA curve of pure AgI we find an endothermic peak at 146 °C which corresponds to the phase transition. The second endothermic peak is at 558 °C. These peaks are also present on the DTA curve of the product CTAgI, but with very small intensity. According to the results of the thermal analysis carried out to 900 °C, the thermal decomposition of the product CTAgI is not complete at 900 °C, but the decomposition of AgI can be seen in the temperature range from 560 to 900 °C.

Conductivity measurements of the product CTAgI will be reported in a subsequent paper.

4. Conclusion

Our measurements (XRD, SEM, thermal analysis and IR) indicate that a new inclusion compound (natural clinoptilolite–AgI) has been prepared. The XRD study shows that the AgI can both enter into the tunnels and be deposited on the surface of the CT particles. The coating of the zeolitic particles by the silver iodide is also revealed in the morphological study.

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