

A Study of the Silver Form of a Natural Zeolitic Material of the Clinoptilolite Type

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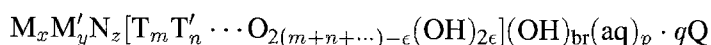
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Abstract. The silver forms of a natural zeolitic material (from the East Slovakian deposit) of the clinoptilolite type has been prepared. The silver forms of the natural zeolitic material were investigated by X-ray powder diffractometry, IR spectroscopy, ESCA measurements, scanning electron microscopy and conductivity measurements. Depending on the preparation conditions, the content of silver ions in the zeolitic products was found to be in the range from 16 to 24%. In the sample with a silver loading of 18.6%, the silver uptake is due to an ion exchange process, mostly involving Na(I), Ca(II) and Mg(II) ions.

Key words: Natural zeolite, clinoptilolite, silver, silver ions.

1. Introduction

Zeolitic materials have the property of absorbing molecules and ions with differentiated functions in the zeolitic structure. Molecules may substitute the sorbate Q, ions can exchange with other ions in the cationic part of the host [1], and sometimes they may be sorbed in an intrazeolitic manner [2]. Halogenides, such as AgI [3], may also be included by substituting the sorbate. Meier's general formula [4] for zeolites:



is very open to these substitutions. In general, all these substitutions allow the properties of the zeolitic material to be changed.

The aim of our present study was the preparation and characterization of silver forms of a natural zeolitic material of the clinoptilolite type.

2. Experimental

2.1. CHEMICALS AND MATERIALS

For our study we used a natural zeolitic material of the clinoptilolite (CT) type from the East Slovakian deposit in Nižný Hrabovec. This natural material contains on average 57.2% [5] of the CT zeolitic mineral. Silver nitrate and other chemicals were of p.a. purity (Lachema Brno).

2.2. PREPARATION

Silver forms of natural clinoptilolite can be obtained by treating the solid with a silver nitrate solution at room temperature. By changing the contact time between the solid and the AgNO_3 solution (from 2 h to 10 days) and the concentration (0.1 or 1 M) and the volume of the solution, silver zeolitic products were obtained with silver contents ranging from 16 to 24%.

In particular, the material containing 18.6% of silver was prepared by the following method: the natural zeolite (5 g), after drying at 100–110 °C for 1 h, was mixed with 20 mL of a 1 M solution of AgNO_3 . The heterogeneous mixture was left to stand for 10 days (with occasional mixing) and then decanted 3× with distilled water and centrifuged (after this treatment the absence of Ag(I) in the washing water was tested by adding a solution of 0.05 M NH_4SCN). The zeolitic product was dried at 60 °C for about 30 min. This product is denoted as CTA_g.

2.3. INSTRUMENTATION

The amounts of silver and other elements in the zeolitic material were determined by Electron Microsonda measurements (JXA-5A, JEOL) applying KeveX. Parameters used: accelerating voltage 25 kV, sample current 1.5×10^{-7} A; analysing crystal LiF-PED. CHN analysis was performed with a Perkin Elmer 2400 Elemental Analyser.

IR spectra of the zeolitic products were obtained with the KBr disc technique using a Specord M 80 IR spectrometer (Carl Zeiss, Jena). X-ray powder diffraction patterns were taken with a Dron-2.0 Diffractometer by using FeK_α radiation. A Jeol scanning microscope, Model JSM 840A, was used to study the morphology.

ESCA spectra were obtained in Catania with a LHX1 Leibold Spectrometer by using an unmonochromated $\text{AlK}_{\alpha,1,2}$ (1486.6 eV) photon source operating at 14 KV and 20 mA. The binding energies (BE) are corrected by referring to the Si_{2p} peak at 103 eV; under this condition the BE of the graphitic C_{1s} peak is 284.6 eV. Sensitivity factors used in this work were obtained from Ref. [6] since the dependence of the spectrometer transmission from KE is compatible with that of the spectrometer used by those authors. The samples, as powders, were mounted on the probe tip of the spectrometer by means of double-sided adhesive tape.

Alternating current (ac) conductivity measurements were performed in Perugia. Pellets, 10 mm in diameter and 1.3–1.5 mm thick, were prepared by pressing ~200 mg of material at 50 kN/cm². The two opposite surfaces of the pellet were coated with pressed Pt-black or graphite powder mixed with the material in 3 : 1 ratio. Conductivity measurements were done using a sealed-off stainless steel cell connected to a Hewlett Packard 4192 A Impedance Analyzer in the frequency range 10 Hz–10 MHz at a signal voltage lower than 1 V. Before measurements the pellets were equilibrated at room temperature for 1 or 2 days at a relative humidity of 53% (obtained by using a saturated salt solution of Mg(NO₃)₂·6H₂O). All measurements were taken in the temperature range from 20 to –25 °C.

Direct current (dc) measurements were performed with composite graphite electrodes and a dc load of 0.5 V. During these experiments the ac conductivity was measured at regular time intervals without the dc load. The dc to ac conductivity ratio reached a constant value after about 1 day.

3. Results and Discussion

3.1. MATERIAL CHARACTERIZATION

As already mentioned in the Experimental Section, zeolitic products with different silver contents were obtained by putting the natural zeolitic material in contact with a silver nitrate solution, under different experimental conditions; the silver content ranged from 16–24%.

The presence of silver in the zeolitic products was also observed by the colour, as in the case of other zeolitic products which contain iodine and its ions [7] or Cu(II) ions [8]. The colour of the silver forms was grey.

In this paper our attention is focused on a zeolitic product containing 18.6% of silver (CTAg). The composition of the natural zeolitic material of the clinoptilolite type (CT) and its silver form, CTAg, was obtained by Electron Microsonda measurements. From the data of Table I it can be calculated that the silver uptake (0.78 equivalents per Al mole) is equal, within experimental error, to the total loss of sodium, calcium and magnesium (0.75 equivalents per Al mole). In addition, CTAg contains 1.03 equivalents of Ag(I) + Ca(II) + Mg(II) per Al mole, as expected for any zeolitic material where the excess of negative charge associated with one aluminum mole must be compensated by one cation equivalent. According to these data, the silver uptake from natural clinoptilolite can be interpreted as an ion exchange process occurring in the zeolitic material.

The results of CHN analysis (hydrogen: 0.95–0.91%) confirmed the presence of water in the exchanged material (8.19–8.55%) but at a lower percentage in comparison with the starting CT zeolitic material (water content 10.5%). One part of the water content was substituted by intrazeolitic silver ions, probably as a consequence of the exchange of two Ag(I) ions for one divalent cation. The presence of water in the starting CT zeolitic material and its silver form was confirmed by two absorption bands. The first one corresponds to the stretching vibrations of

TABLE I. Analysis of natural zeolitic material of the clinoptilolite type (CT) and its silver form (CTAg).

Sample	Weight [%]								Total
	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	CaO	FeO + Fe ₂ O ₃	MgO	Ag ⁺	
CT	73.94	12.31	3.78	0.5	5.24	3.48	0.75	–	100
CTAg	62.20	11.24	4.66	–	1.09	1.87	0.29	18.65	100

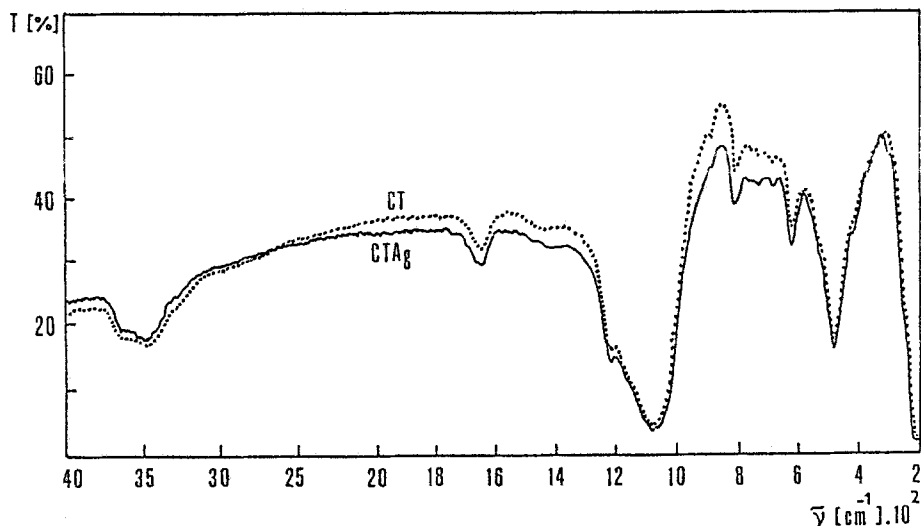


Fig. 1. IR spectra of the natural clinoptilolite CT (.....) and of the silver zeolitic product CTAg (_____).

water (3350–3650 cm^{-1}) and the second one corresponds to the bending vibration of water at 1620 cm^{-1} (Figure 1).

No significant changes were observed on examining the IR spectra of the original CT zeolitic material and its silver forms (Figure 1). A small change appeared in the band at 1200–900 cm^{-1} , corresponding to the asymmetric stretching vibration of the (Al,Si)O group (this band changes from a sharp to a broader one). Similar but stronger changes of this band were also found in other zeolitic products [1, 8] prepared in Kosice as a consequence of the sorption of different organic or inorganic compounds into the microcrystalline zeolitic material.

As already observed for copper and calcium forms of natural clinoptilolite [8], the silver uptake from natural clinoptilolite does not change significantly the X-ray pattern of the starting material (Figure 2), apart from the intensity of some reflections, e.g., 6° , and the appearance of a few new reflections in the θ range from 20 to 25° .

The ESCA spectrum of the silver zeolitic form shows a large peak (FWHM = 1.9 eV) for $\text{Ag}_{3d5/2}$ at BE = 368.3 eV. This value is close to that reported in

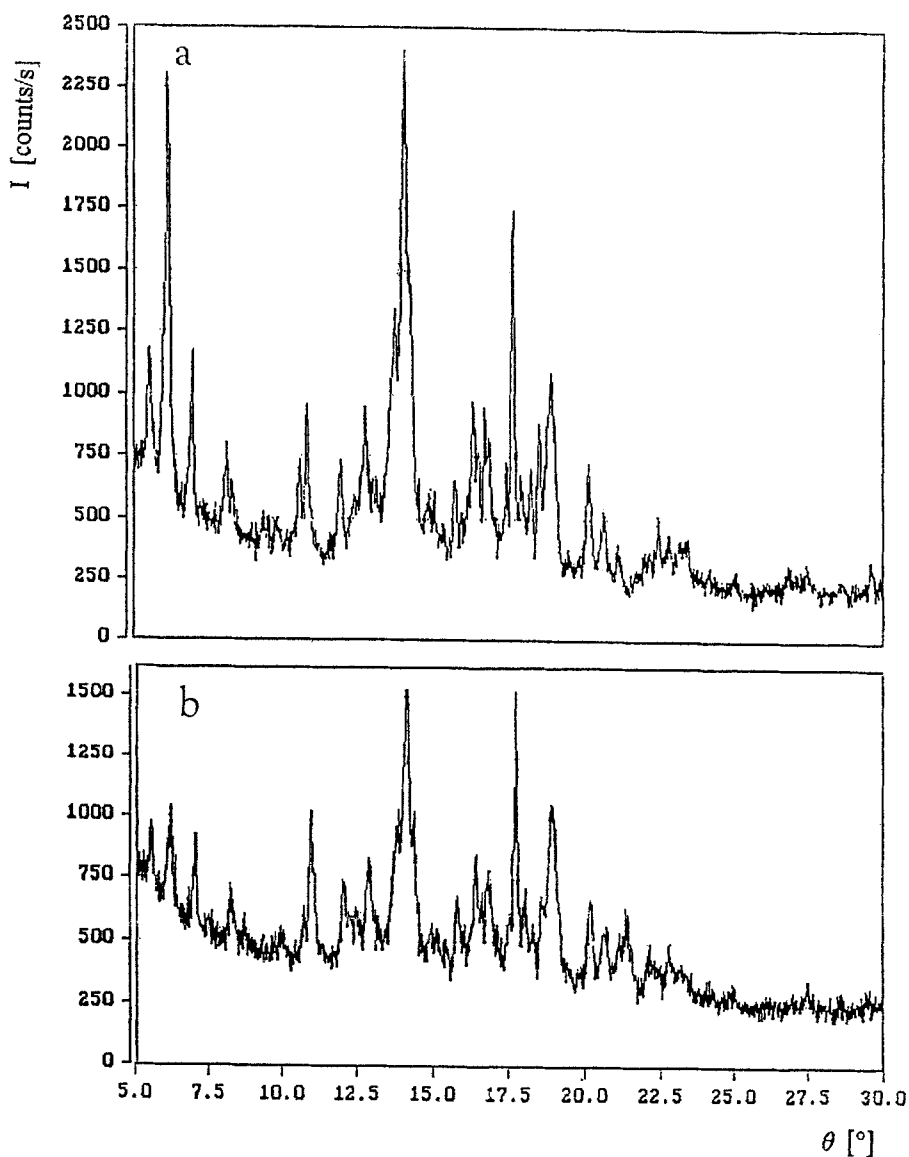


Fig. 2. X-ray powder diffraction patterns of the natural zeolite CT (a) and of the silver zeolitic product CTAg (b).

the literature for metallic Ag (BE = 368.2 eV, FWHM = 1.15 eV) [9]; however, the high value of the FWHM found for our samples seems to indicate that this peak can be better interpreted as indicative of silver (I) bonded to the negatively charged zeolitic oxygen. Auger electron spectroscopy is superior to ESCA in differentiating metallic Ag from Ag(I), but the technique was not available to us.

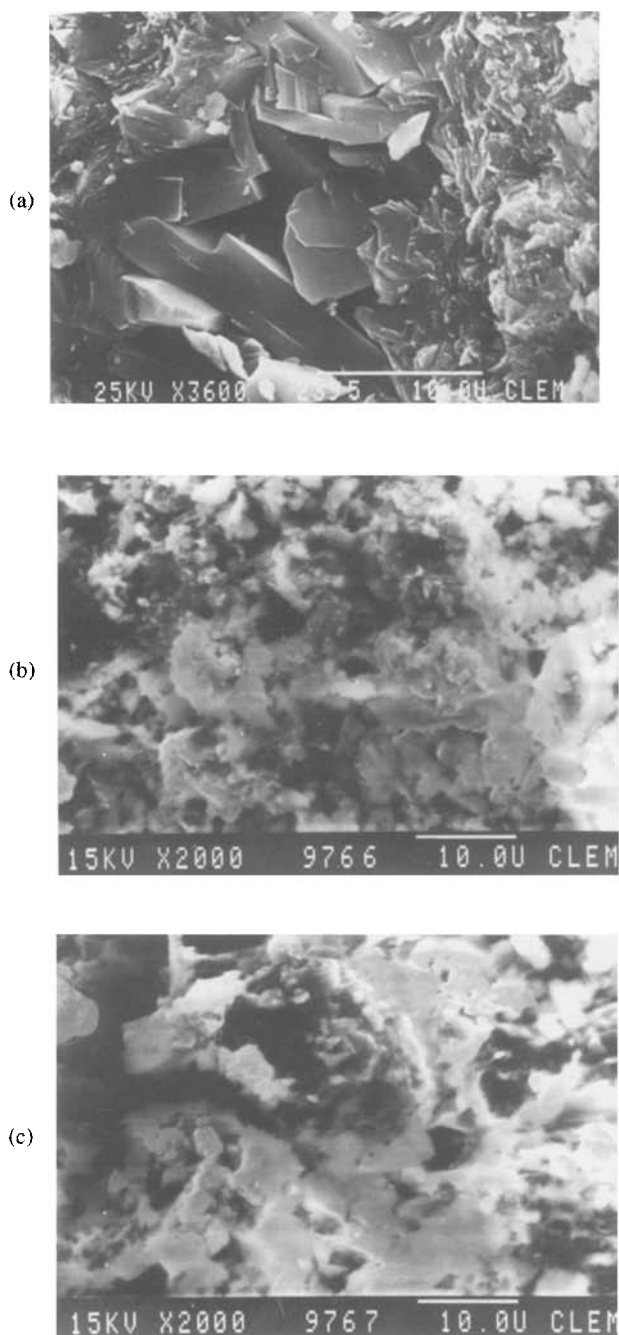


Fig. 3. Scanning electron micrograph of the original natural [5] zeolite (a) and the silver zeolitic products (3b-content of silver: 16.4%; 3c-content of silver: 18.6%).

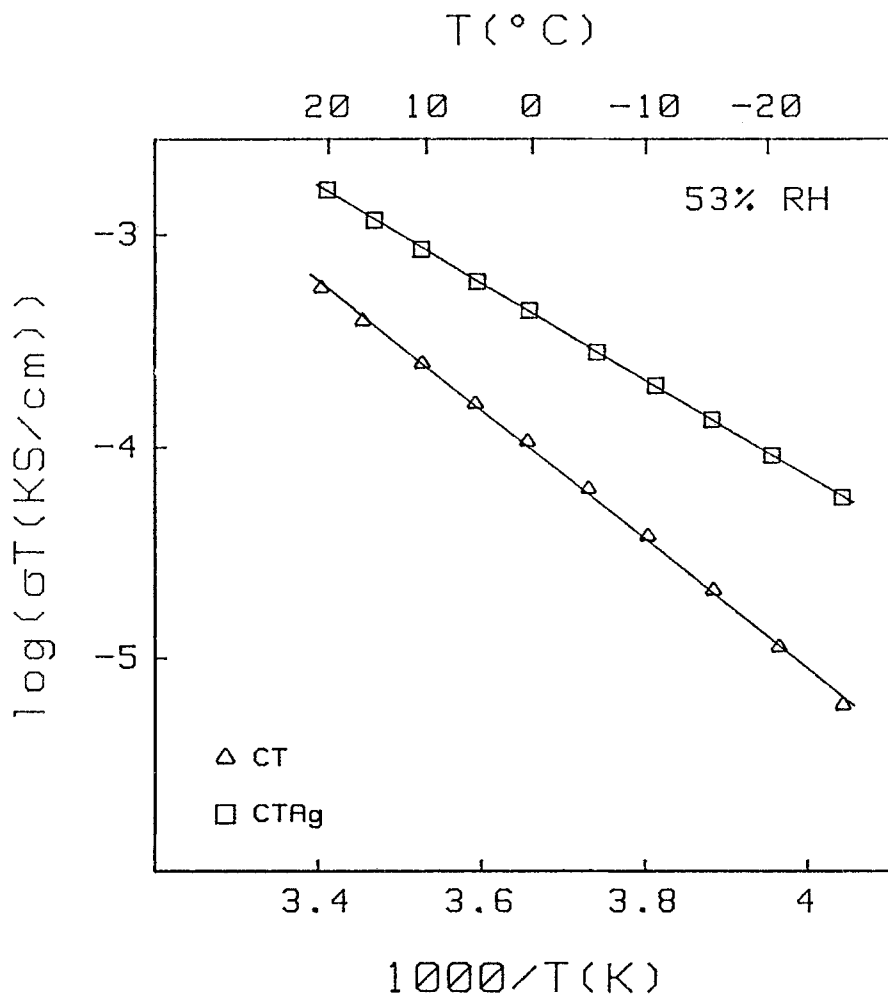


Fig. 4. Arrhenius plot of a pellet of the silver zeolitic product CTAg compared to that of the natural zeolitic material of clinoptilolite type (CT): measurements were carried out on pellets previously equilibrated at 53% relative humidity.

ESCA measurements gave an Ag/Al ratio of 0.8, which agrees well with the results of Electron Microsonda determinations.

3.2. MORPHOLOGICAL STUDY

The morphological study of the silver products indicate some type of 'impregnation' similar to what is observed in all products obtained from zeolites with different organic or inorganic compounds. The quite smooth surface of the original zeolite (Figure 3a) disappears in the silver products (Figures 3b,c).

3.3. CONDUCTIVITY MEASUREMENTS

Combined ac/dc measurements were carried out on CTA_g pellets using ionic blocking graphite electrodes (see Experimental Section) to evaluate the relative extent of ionic and electronic conductivity. At the steady state, the ac conductivity (measured by the impedance technique) gives the overall (ionic + electronic) conductivity, while the dc conductivity is due only to the electronic component [10]. This kind of measurement was performed at 20 °C and 53% RH; the ac conductivity turned out to be three orders of magnitude higher than the dc conductivity, thus indicating that the conduction process is dominated by the ionic component.

Further ac conductivity measurements were carried out as a function of temperature in the range 20 to –25 °C, on pellets previously equilibrated at 53% RH. In all cases the impedance plots consisted of a single, semicircular arc going through the origin of the complex plane; the pellet conductivity was calculated by arc extrapolation to the real axis on the low frequency side. Figure 4 shows the Arrhenius plot of a pellet of CTA_g previously equilibrated at room temperature and at 53% RH, together with that of the natural CT material. Compared with natural clinoptilolite (the conductivity of which was reported in a previous paper [7]), CTA_g shows a slightly higher conductivity ($\sigma = 5 \times 10^{-6} \text{ S cm}^{-1}$ against $1.9 \times 10^{-6} \text{ S cm}^{-1}$) with a lower activation energy (10.3 kcal/mol versus 14 kcal/mol).

3.4. CONCLUSION

The natural zeolitic material of the clinoptilolite type is able to sorb silver ions in different amounts (16–24%) according to the preparation conditions. In the case of the material containing 18.6% of silver, it has been shown that Ag(I) was exchanged for Na(I), Ca(II) and Mg(II) ions. The original water content of the zeolite was lowered after the exchange of Ag(I), but water is still present according to the CHN analysis and IR spectroscopy. The presence of residual water molecules should allow this silver form to be used for sorbing iodine or other compounds.

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