Preparation and Characterization of a Composite of Silver Iodide and Synthetic Mordenite

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Abstract. A composite material made up of AgI and the potassium form of mordenite has been prepared by treating the silver form of synthetic mordenite with potassium iodide. The composite as well as the silver and potassium forms of mordenite have been characterised by X-ray powder diffractometry, X-ray photoelectron spectroscopy, EDS analyses and ac conductivity measurements. It has been inferred that, in the composite material, AgI grows at the entrance of the zeolite channels without forming a continuous conducting phase. The silver form of mordenite has been proved to be a silver ion conductor by dc conductivity measurements.

Key words: synthetic mordenite, silver, silver iodide, ac conductivity measurements

1. Introduction

Zeolites are well known microporous alumino-silicates where the negative charge of a rigid framework of silicon, aluminum and oxygen atoms is compensated by mobile cations situated in cavities and channels of the framework. These features make zeolites both ion-exchangers and suitable host materials for inclusion of molecular species [1, 2].

It was reported that synthetic sodium mordenite is able to include AgI when heated at a temperature close to the AgI melting point [3, 4]. In our recent papers, AgI inclusion in synthetic ZSM5 [5] and in natural clinoptilolite [6] was attempted by reacting the zeolite silver forms with solutions of potassium iodide. While clinoptilolite was claimed to be able to include AgI, the reaction of ZSM5 and

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KI gives a composite where AgI forms a thin conductive shell on the surface of potassium exchanged ZSM5 particles.

The present study deals with the preparation by ion-exchange of the silver and potassium forms of mordenite (hereafter Ag-MD and K-MD, respectively) starting from synthetic sodium mordenite. Taking into account the results reported in Refs. 5 and 6, it was thought of interest to investigate the reaction of Ag-MD with aqueous KI and to compare the structural features and the electrical properties of the composite obtained with those of Ag-MD and K-MD.

2. Experimental

2.1. CHEMICALS AND MATERIALS

Synthetic mordenite MORSIT SM 315/500 (Slovnaft a.s., Bratislava) [7] was used as a starting material for the preparation of Ag-MD and K-MD. It was thermally activated by increasing the temperature from 150 to 400 $^\circ$C in 6 steps ($\sim$20 minutes per step) and maintaining constant temperature at 400 $^\circ$C for 1 hour). The chemical composition of MORSIT SM 315/500 is: Na_2O 5.26%, CaO 0.89%, Al_2O_3 10.99%, Fe_2O_3 0.024%, SiO_2 82.87%.

Silver nitrate, potassium iodide and other chemicals were of p.a. purity (Lachema Brno). Silver iodide used for the preparation of physical mixtures of K-MD and AgI was Carlo Erba RPE.

2.2. MATERIALS PREPARATION

Ag-MD. Synthetic mordenite (3g) was mixed with a solution of 1M $AgNO_3$ (20 mL). After two hours of intensive mixing, the heterogeneous mixture was decanted and centrifuged several times with distilled water until the water was free of silver ions (checked by adding a solution of 0.05 M NH_4SCN). The solid was then dried at 6O $^\circ$C.

K-MD. Synthetic mordenite (3.5g) was equilibrated with 1M potassium iodide (20 mL) under the same conditions as reported for Ag-MD (the absence of iodide ions was checked by adding a solution of 0.1M $AgNO_3$). The final product was dried at 60–70 $^\circ$C.

Reaction of Ag-MD with KI. Ag-MD (3g) was mixed with 1M potassium iodide (20 mL) and kept under stirring for one hour at room temperature and for the last ten minutes at 60–80 $^\circ$C. The heterogeneous mixture was left to stand for 7days (with occasional mixing) and then decanted and centrifuged several times with distilled water until the water was free of iodide ions (checked by adding a solution of 0.1 M $AgNO_3$). The final product was dried at 60 $^\circ$C.

2.3. METHODS

The content of silver and other elements in the zeolitic materials was determined by Electron Microsonda measurements (JXA-5A, JEOL) applying Kevex and by EDS analyses using a scanning electron microscope TESLA BS 340 (TESLA ELMI a.s. with a LINK ISIS 300 microanalyser).

X-ray powder diffraction patterns were recorded with a Siemens D5000 diffractometer using $CuK_{\alpha 1}$ radiation.

The X-ray photoelectron spectra (XPS) were collected with a VG ESCA 3 MkII spectrometer using AlK_α achromatic radiation ($h\nu = 1486.6$ eV). The instrument was calibrated so that the difference between the Au $4f_{7/2}$ photoelectron peak and the Fermi level of Pd was 84.0 eV. The spectrometer was operated in the fixed analyser transmission mode. The background pressure of the residual gases during the spectrum accumulation was typically of the order of 10^{-6} Pa. The C 1s binding energy (284.8 eV) of adventitious carbon was used in calibration to compensate for charging effects. The XPS measurements were carried out on the samples in the as received state at liquid nitrogen temperature. 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 accuracy of ± 0.2 eV.

IR spectra were obtained with the KBr disc technique using a Specord M80 IR spectrometer (Carl Zeiss, Jena).

Thermal analyses were carried out at temperatures up to 600 and 1100 °C in air on 100 mg samples by using a Derivatograph MOM OD 102 (Paulik-Paulik-Erdey) operated at the following sensitivities: TG 100 mg, DTA 1/3, DTG 1/3; reference material was Al_2O_3. All samples were equilibrated at room temperature for at least two days at 53 and 75% relative humidity (obtained by using saturated salt solutions of $Mg(NO_3)_2 \cdot 6H_2O$ and NaCl, respectively).

Ac conductivity measurements were carried out on pressed powders by using the impedance technique. Pellets, 10 mm in diameter and 1.3–1.5 mm thick, were prepared by pressing about 200 mg of material at 40 kN/cm². The two opposite surfaces of the pellet were coated, under pressure, with a mixture of the material and platinum powder in the weight ratio 3:1. Impedance measurements in the range 20–25 °C were carried out in a sealed-off stainless steel cell connected to a Hewlett Packard 4192 A Impedance Analyzer in the frequency range 10 Hz to 10 MHz at a signal voltage lower than 1 V. The pellets were previously equilibrated at room temperature for at least 2 days at 75% relative humidity. Ac measurements were also performed in the range 200 to 100 °C by using a cell purged with a flow of dry nitrogen. Before starting measurements, the pellets were held overnight in the measuring cell at 200 °C. Dc conductivity measurements were performed at 20 °C and 53% relative humidity by applying a 0.2 V dc load with composite electrodes consisting of a mixture of the material with graphite or silver powder in the weight ratio 1 : 3.
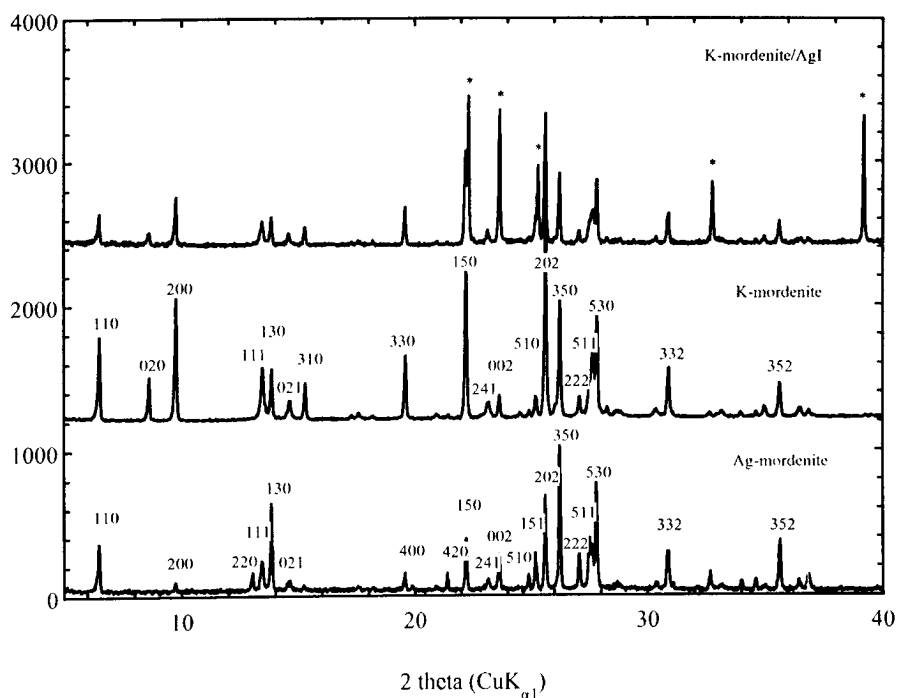
Figure 1. X-ray powder diffraction patterns of Ag-mordenite, K-mordenite and K-mordenite/AgI. * Indicate presence of β-AgI. For two of the patterns Miller indices have been indicated for the strongest peaks.

Nitrogen adsorption measurements were made automatically by a SORPTOMATIC 1800 (Carlo Erba Strumentazione). Before nitrogen absorption, the samples were out-gassed at 100 °C.

3. Results and Discussion

3.1. MATERIAL CHARACTERISATION

The silver and potassium forms of synthetic mordenite were prepared according to the procedure described in Section 2.2. EDS analyses of the exchanged compounds show the presence of silver and potassium and the absence of sodium and calcium. Within the error limits, the Al/Si molar ratio in both compounds is the same as that in the starting material (0.16) and equal to the Ag/Si molar ratio in Ag-MD (0.18) and K/Si in K-MD (0.16). These data show that Ag^+ and K^+ are fully exchanged for Na^+ and Ca^{2+}. The X-ray powder patterns of Ag-MD and K-MD (Figure 1) were indexed as orthorhombic; cell parameters are listed in Table I.

The water content of Ag-MD and K-MD, previously equilibrated at 53% relative humidity, was 10.5% and 11.5%, corresponding to H_2O/Si molar ratios of 0.57 and

Table I. The unit cell dimensions of Na-mordenite, K-mordenite, Ag-mordenite and K-mordenite/AgI.

	a(Å)	b(Å)	c(Å)	V(Å^3)
Na-mordenite	18.078 (3)	20.440 (3)	7.509 (1)	2774.2
K-mordenite	18.112 (2)	20.504 (3)	7.515 (1)	2790.8
Ag-mordenite	18.124 (2)	20.473 (2)	7.517 (1)	2789.0
K-mordenite/AgI	18.118 (2)	20.504 (3)	7.516 (1)	2792.1

0.55, respectively. At 75% relative humidity the water contents increased to 11.8% for Ag-MD and 12.5% for K-MD.

The zeolitic water is characterised by two absorption bands in the IR spectra at 3350–3650 cm^{-1} (stretching vibration) and at 1620 cm^{-1} (bending vibration).

Figure 1 shows the X-ray powder pattern of the composite obtained by reacting Ag-MD with aqueous KI. The pattern can be indexed as orthorhombic. Taking into account the standard deviation, the cell parameters of the composite (Table I) are the same as those of K-MD. Reflections which cannot be indexed belong to AgI in the form of iodargyrit (hexagonal β-AgI form). Since the integrated intensity ratios of K-MD diffraction lines in the composite are the same as in the pure compound, K-MD and silver iodide are present as separate phases. The analysis of the composite by EDS gives, within the error limits, equal K/Si and Al/Si ratios (0.16 and 0.17, respectively) thus confirming that K$^+$ is exchanged for Ag$^+$, according to the reaction:

$$(AgAlO_2)_{0.16}(SiO_2) + 0.16K^+ + 0.16\,I^- \rightarrow (KAlO_2)_{0.16}(SiO_2) + 0.16AgI$$
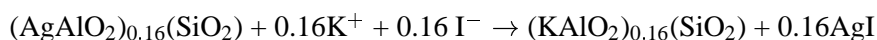
The composite will be hereafter denoted as K-MD/AgI. The presence of silver iodide in K-MD/AgI is also confirmed by thermal analysis up to 1100 °C. The DTA curve shows two peaks of weak intensity: the first one corresponds to the phase transition from β-AgI (hexagonal) to α-AgI (cubic) at 146 °C and the second one to the melting of α-AgI at 558 °C (Figure 2). The water content of K-MD/AgI, calculated from the weight loss up to 500 °C assuming a AgI/Si molar ratio of 0.16, is 0.58 H$_2$O molecules per silicon atom, close to the corresponding ratio found for K-MD.

The XPS spectrum of Ag-mordenite and K-mordenite/AgI is shown in Figure 3. The values of the Ag (3d5/2) core level binding energies and widths of photoemission lines are displayed in Table II. Furthermore, the X-ray excited spectra of Ag (M45N45N45) Auger electrons were measured and the sum of the kinetic energy of Ag (M5NN) Auger electrons and binding energy of Ag (3d5/2) electrons calculated. This sum is defined as the Auger parameter, A.P. The advantage of A.P. is that its value does not depend on static sample charging and is therefore obtained with higher accuracy than the energy of electrons alone. In addition, the value of the Auger parameter is frequently more sensitive to changes in chemical
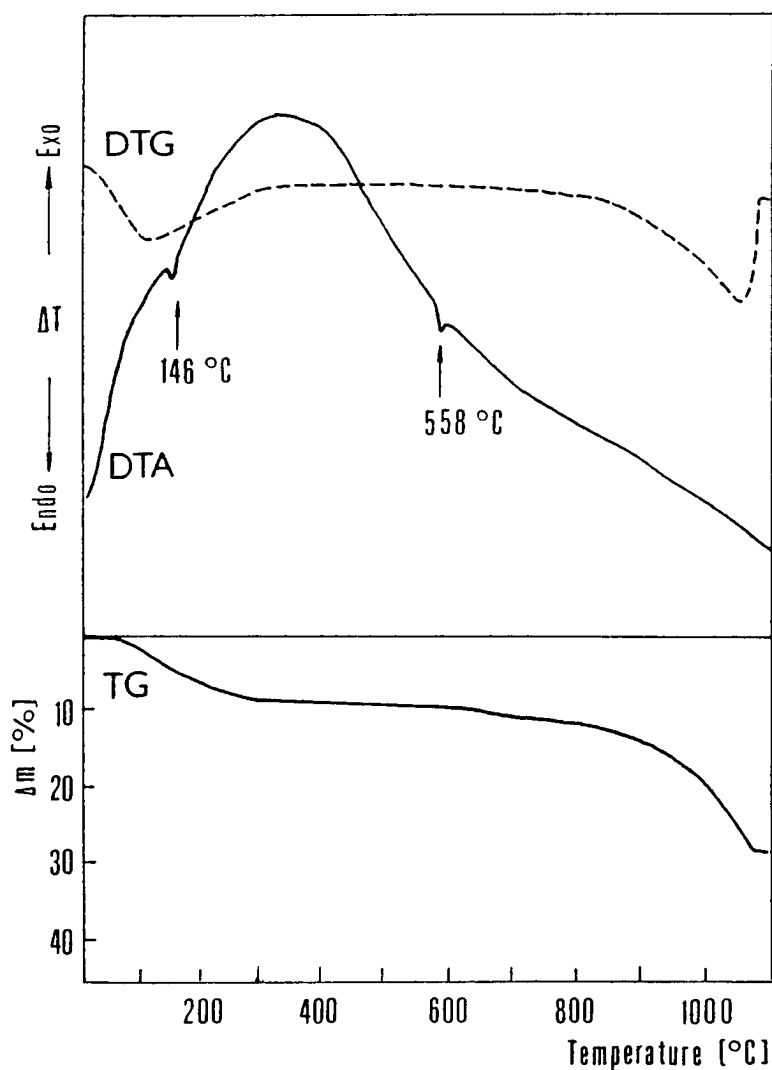
Figure 2. TG, DTG and DTA curves of K-mordenite/AgI.

environment than that of the core level binding energy. In Table III the A.P. value for Ag-mordenite and K-mordenite/AgI are displayed together with the published values for relevant standards [8]. The A.P. value for the K-mordenite/AgI sample agrees within the experimental error (±0.2 eV) with that for AgI. As already reported for AgZSM5 [5], the rather low A.P. value obtained for Ag-MD is most likely a consequence of the interaction of Ag with the zeolite matrix. Namely, it can be ascribed to the effects of decreasaed extraatomic relaxation due to the higher ionicity of Ag bonding to zeolitic oxygens compared to bonding in Ag oxides.
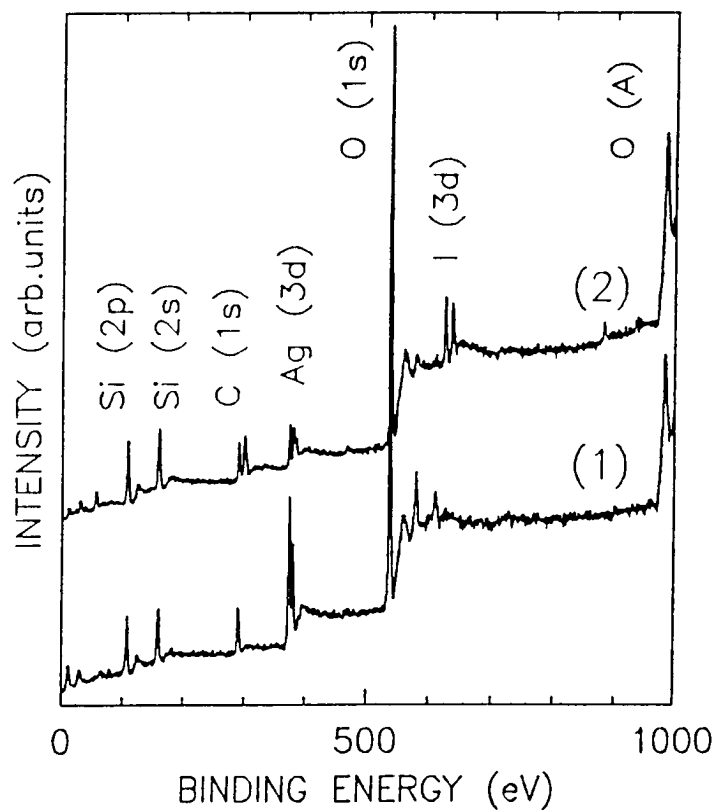
Figure 3. XPS spectrum of Ag-mordenite (1) and K-mordenite/AgI (2).

Table II. Core level binding energies and widths (in parentheses) of photoemission lines of Ag-mordenite and K-mordenite/AgI (in eV).

Sample	Line					
	Si (2p)	Al (2p)	O (1s)	Ag (3d5/2)	I (3d5/2)	K (2p3/2)
Ag-MD	102.4 (2.1)	73.9 (1.7)	531.6 (2.2)	368.7 (1.7)	–	–
K-MD/AgI	102.5 (2.0)	73.9 (1.9)	531.8 (2.3)	368.6 (1.4)	619.9 (1.7)	293.8 (1.9)

In order to obtain further insight into the composite nature, nitrogen adsorption determinations were carried both for K-MD and the composite. As a consequence

Table III. Auger parameters (A.P.) of Ag for Ag-MD and K-MD/AgI, displayed together with the published values for relevant bulk standards [8].

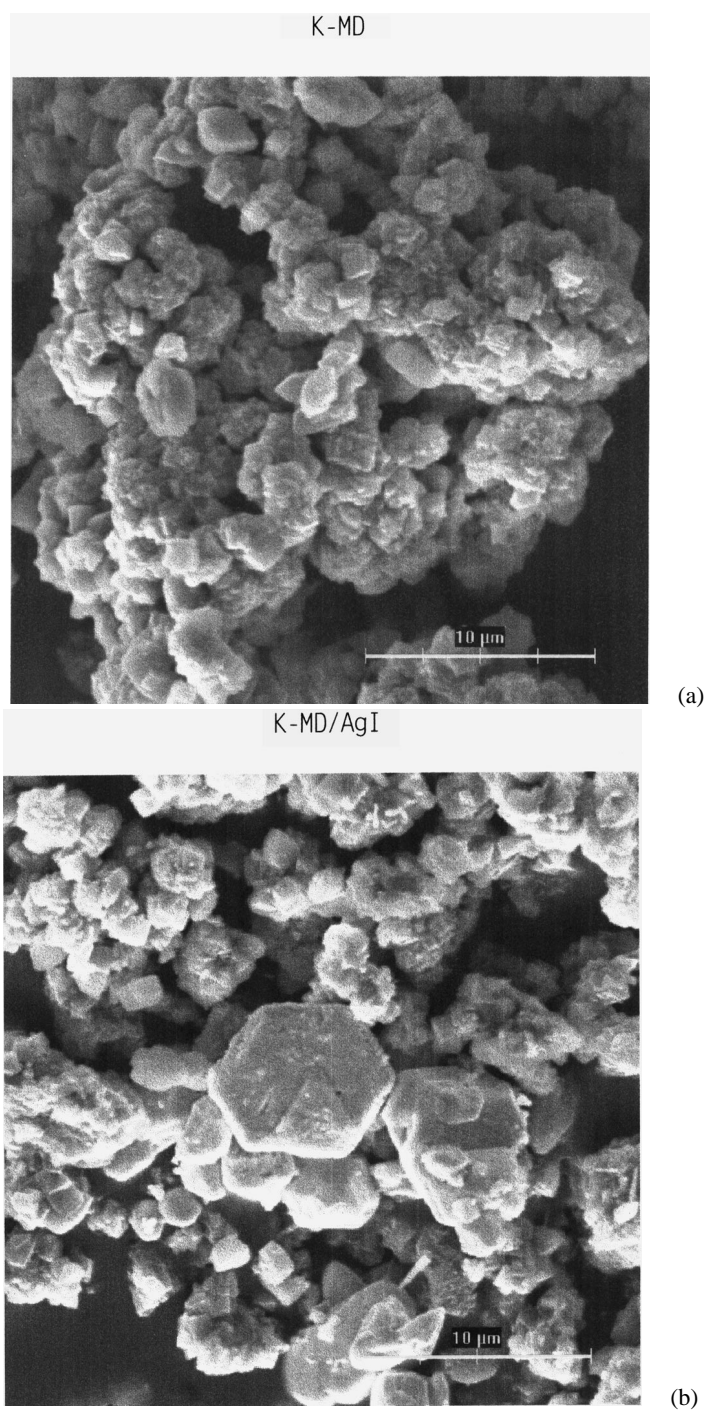|	Ag-MD	Ag-MD/AgI	Ag bulk	AgI	AgO	Ag_2O
A.P. (eV)	722.5	723.8	726.1	724.1	724.0	724.5

(a)

(b)

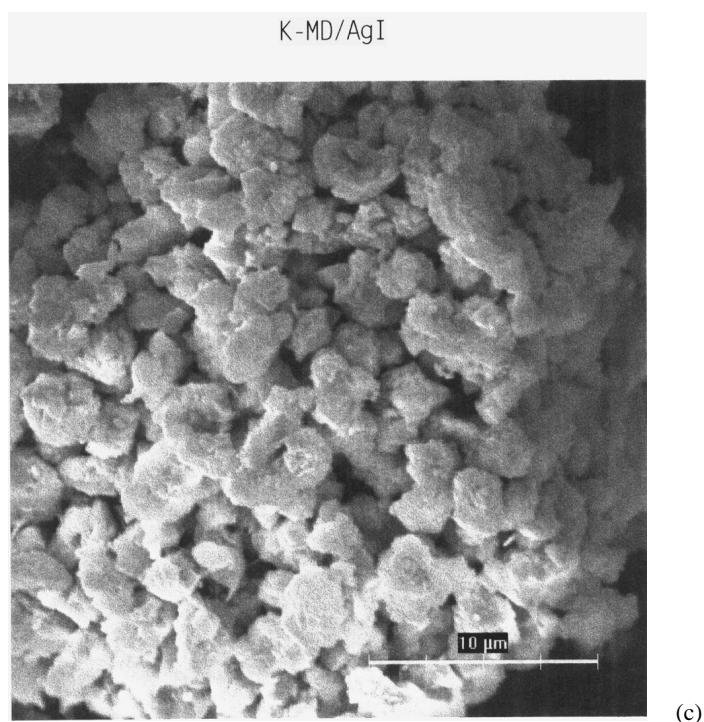*Figure 4*. Scanning electron micrograph of K-mordenite (a) and K-mordenite/AgI (b,c).

Figure 4.

of the composite formation, the nitrogen uptake (in terms of surface of a nitrogen monolayer) was reduced from 230 to 30 m^2/g. It can therefore be inferred that some silver iodide is formed at the entrance of the zeolite channels thus hindering nitrogen diffusion into the zeolite.

Scanning electron micrographs of K-MD and K-MD/AgI are shown in Figure 4. In Figure 4b can be seen a hexagonal crystal of AgI.

3.2. CONDUCTIVITY MEASUREMENTS

Ag-MD, K-MD and K-MD/AgI were also characterised by impedance measurements carried out between 20 and $-20\,^{\circ}$C on pellets previously equilibrated at 75% relative humidity. In all cases the impedance plot (reactance versus resistance) consists of an arc (pellet impedance) ending with a low frequency tail (impedance of electrode–pellet interface); the ac conductivity of the pellet is obtained by arc extrapolation to the resistance axis on the low frequency side. The ac conductivity at 20 $^{\circ}$C and the activation energy of conduction for pellets previously equilibrated at 75% relative humidity are listed in Table IV; the dependence of conductivity on temperature is shown in Figure 5.

Table IV. Conductivities (σ) and activation energies (E) for Ag-MD, K-MD, K-MD/AgI and AgI.

	σ (20 °C, 75% (S cm^{-1})	E($-20/+20$ °C, 75% RH) (kJ mol^{-1})
Ag-MD	8.1×10^{-6}	44.8
K-MD	1.4×10^{-5}	42.3
K-MD/AgI	9.5×10^{-6}	41.0
AgI	$4.4 \times 10^{-4*}$	

* From Ref. 5.

Dc conductivity measurements were also carried out on Ag-MD to see whether its conductivity arises from Ag$^+$ diffusion. A dc load of 0.2 V was applied by using reversible silver composite electrodes and the dc conductivity measured as a function of time over two days. After a sharp decrease during the first hour, the dc conductivity remained nearly constant for all the remaining time, being about 70% of the ac conductivity. A similar experiment was carried out by using Ag$^+$ blocking graphite electrodes to estimate electronic conductivity. In this case the dc conductivity decreased by three orders of magnitude during two days while the ac conductivity remained constant. These findings show that Ag-MD is a silver ion conductor with negligible electronic conductivity and that the difference between ac and dc conductivity is due to the resistance of the electrode/electrolyte interface.

From Table IV and Figure 5 it can be seen that the ac conductivity of K-MD is slightly higher than the conductivity of K-MD/AgI. On the other hand, in a previous paper [5] it was found that the ac conductivity of the composite of AgI and K-ZSM5 [5] is significantly higher than the ac conductivity of K-ZSM5, both in hydrated and anhydrous form. This is due to the fact that the zeolite particles are coated by a thin shell of silver iodide, which is more conductive than K-ZSM5. From Table IV it can be seen that the conductivity of AgI is also higher than that of K-MD. Therefore, since K-MD/AgI is slightly less conductive than K-MD, it can be suggested that silver iodide in the mordenite composite does not form a conductive shell around the zeolite particles.

To check this hypothesis, ac conductivity measurements were carried out in anhydrous conditions at temperatures below and above the temperature (146 °C) at which AgI changes from the hexagonal phase to the superconducting cubic phase. Under these conditions the conductivity of K-ZSM5/AgI [5] was found to increase by more than one order of magnitude since AgI forms continuous conduction pathways around the ZSM5 particles. The impedance plots of K-MD/AgI are shown in Figure 6. While the impedance plots of K-MD have the usual semicircular shape (Figure 6), those of the composite are rather flat in the low frequency region so that the pellet resistance cannot be calculated accurately by extrapolating the high frequency arc. Nevertheless, comparison of the impedance plots obtained at different temperatures does not reveal any discontinuity in the correspondence of
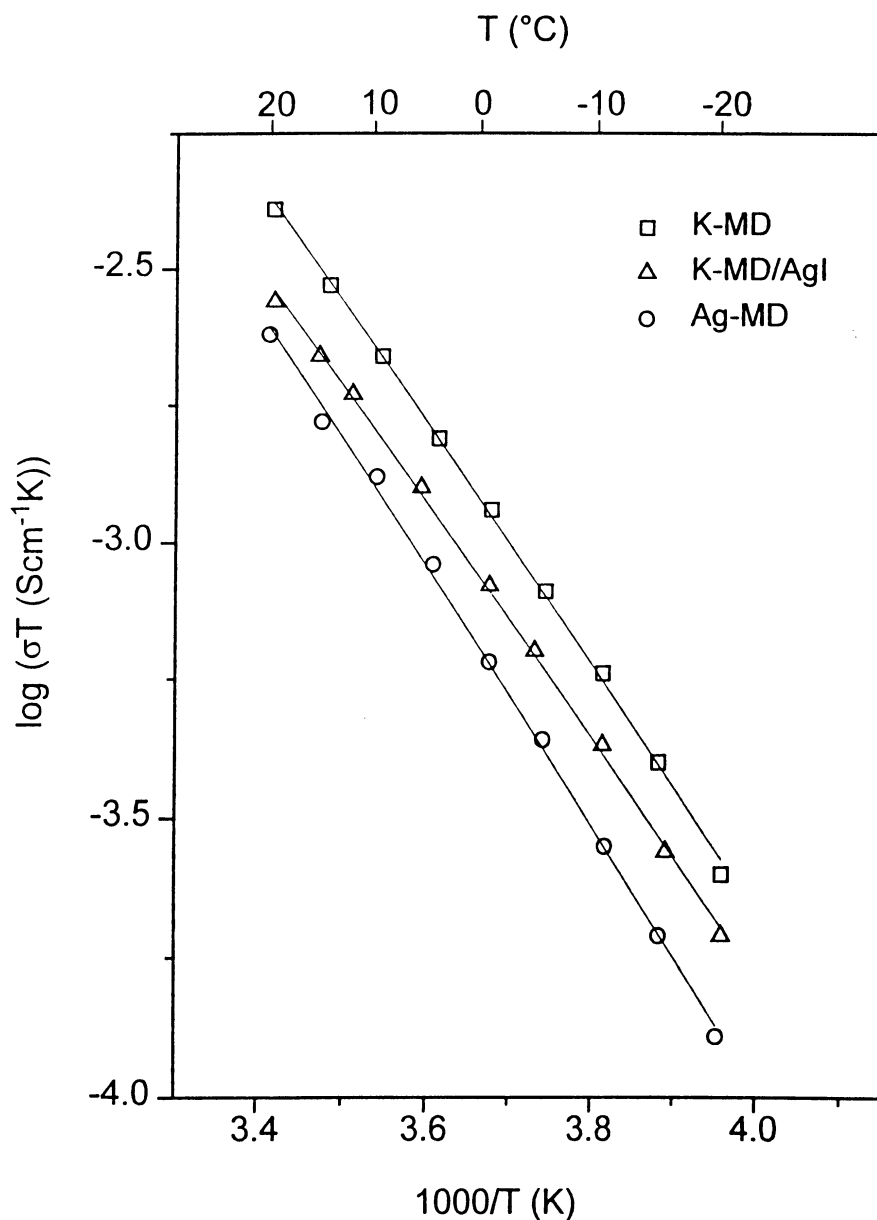
Figure 5. Arrhenius plots for Ag-MD, K-MD and K-MD/AgI pellets previously equilibrated at 75% relative humidity.

the AgI phase transition. It is interesting to observe that the impedance plots of K-MD/AgI have the same shape as those of a pellet made of a physical mixture of AgI and K-MD with a Ag/Si molar ratio of 0.16. The flat shape of the impedance plots has therefore to be ascribed to a non-negligible impedance of the anhydrous
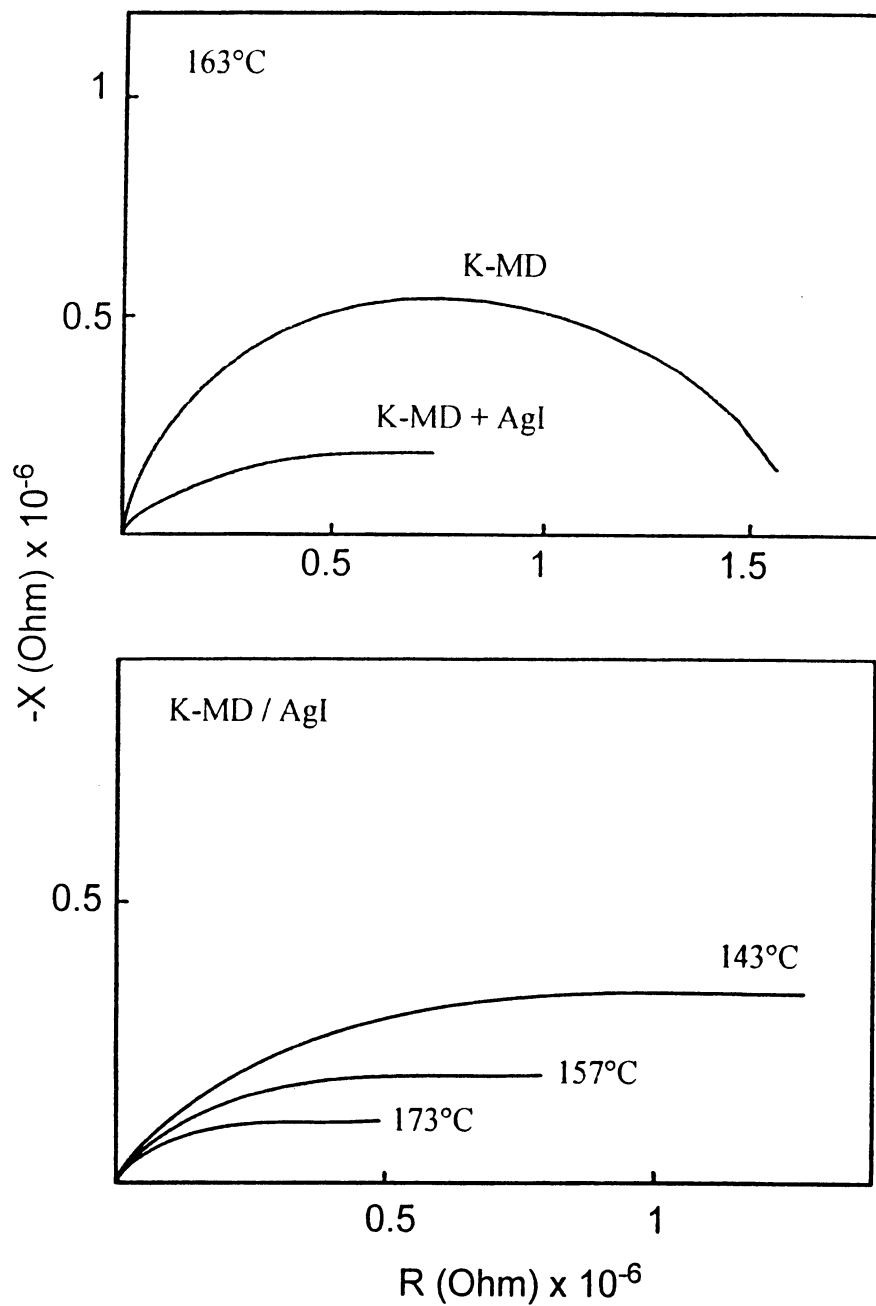
Figure 6. Impedance plots for K-MD, K-MD/AgI and the physical mixture K-MD+AgI in a flow of dry nitrogen, at the indicated temperatures.

interface between AgI and K-MD particles. These findings confirm the absence of continuous conduction pathways of silver iodide around the K-MD particles.

4. Conclusion

The reaction of the silver form of synthetic mordenite with potassium iodide leads to the formation of a composite material made of AgI, in the beta phase, and the potassium form of mordenite. From nitrogen adsorption determinations it is inferred that silver iodide is formed at the entrance of K-MD channels. In contrast to K-ZSM5/AgI [5] silver iodide in K-MD/AgI does not form continuous conducting pathways around the K-MD particles and the frequency response of K-MD/AgI is similar to that of a physical mixture of AgI and K-MD.

Materials with different AgI contents and properties are expected to be obtained by changing the conditions used in the ion exchange reaction between Ag-MD and KI as well as by suitable thermal treatments of the composite.

Acknowledgement

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