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Preparation and Characterization of a Composite of Silver Iodide and Synthetic Zeolite ZSM5

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Abstract. A composite material made up of AgI and the potassium form of the synthetic zeolite ZSM5 has been prepared by treating the silver form of ZSM5 with potassium iodide. The composite has been characterised by X-ray powder diffractometry, IR and X-ray photoelectron spectroscopy, electron microsonde analyses and ac conductivity measurements. The AgI content in the composite material is 11.5%. On the basis of the conductivity data obtained for the composite material as well as for K-ZSM5, Ag-ZSM5, microcrystalline AgI and a physical mixture of AgI and K-ZSM5, it has been inferred that, in the composite material, AgI forms a thin conductive shell on the surface of the K-ZSM5 particles.

Key words: Synthetic zeolite ZSM5, silver, silver iodide, ac conductivity measurements.

1. Introduction

Inclusion compounds can be synthesized using zeolites as host materials, where various inorganic salts and inorganic or organic molecules are included in the zeolite channels [1–3].

The synthetic zeolite sodium mordenite can include AgI [4, 5] and the photosensitive properties of AgI change due to its inclusion in the zeolite.

It has been known for many years [6] that AgI undergoes a phase transition at 146 °C and that the high-temperature form, α-AgI, has an exceptionally high conductivity, ~ 1 S cm^{-1}, which is about four orders of magnitude higher than the room temperature value.

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This paper describes the preparation of a composite material, made up of AgI and the potassium form of the zeolite ZSM5, by treatment of the silver form of synthetic ZSM5 with potassium iodide. The composite has been characterised by X-ray powder diffractometry, IR and X-ray photoelectron spectroscopy, electron microsonde analyses and ac conductivity measurements.

2. Experimental

2.1. CHEMICALS AND MATERIALS

For our study we used synthetic zeolite ZSM5 (Slovnaft a.s., Bratislava) [7]. Its chemical composition (without water) is $x\mathrm{Na_2O}\cdot x\mathrm{Al_2O_3}\cdot y\mathrm{SiO_2}$ ($x = 0.8 \pm 0.15$, y = 20–45). ZSM5 was thermally activated for 3–4 h by heating at continuosly increasing temperature in the range from 150 to 400 °C (1 h at 400 °C).

Silver nitrate, potassium iodide and other chemicals were of p.a. purity (Lachema, Brno).

2.2. MATERIAL PREPARATION

1. Thermally activated ZSM5 (5 g) was mixed with 20 mL of 1 M silver nitrate solution. After two hours of intensive mixing the heterogeneous mixture was decanted with distilled water and centrifuged (the presence of silver ions in water after decanting was checked by adding a solution of 0.05 M NH_4SCN). The zeolitic product was dried at 60–80 °C. This product is denoted as Ag-ZSM5.

2. Ag-ZSM5 (5 g) was mixed with 20 mL of 1 M potassium iodide solution. The heterogeneous mixture was intensively mixed for two hours and then was left to stand for 7 days (with occasional mixing). After 7 days the heterogeneous mixture was decanted three times with distilled water and centrifuged. The final zeolitic product was dried at 60 °C. This product is denoted as K-ZSM5/AgI.

3. The potassium form of ZSM5, silver iodide as well as physical mixtures of AgI and synthetic zeolite in the potassium form were prepared for comparison with the structure and properties of K-ZSM5/AgI.

(*a*) ZSM5 in the sodium form (3.5 g) was mixed with 1 M potassium iodide solution (20 mL). The heterogeneous mixture was intensively mixed for 2 h and then decanted with distilled water and centrifuged. (The presence of iodide ions in water after the decanting was checked by adding a solution of 0.1 M $AgNO_3$.) This zeolitic product is denoted as K-ZSM5.

(*b*) Silver iodide was 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 60–80 °C. (The solid was characterised by X-ray diffraction measurements, IR and thermal analysis).

Table I. The unit cell dimensions of the products K-ZSM5, Ag-ZSM5 and K-ZSM5/AgI

Sample	a (Å)	b (Å)	c (Å)	V (Å^3)
K-ZSM5	20.151 (2)	19.941 (2)	13.432 (1)	5397.3
Ag-ZSM5	20.141 (3)	19.928 (2)	13.426 (2)	5388.6
K-ZSM5/AgI	20.154 (3)	19.940 (3)	13.428 (2)	5396.2

(*c*) The physical mixture of K-ZSM5 and AgI was prepared by cogrinding K-ZSM5 (88%) and AgI (12%). This mixture is denoted as K-ZSM5+AgI.

2.3. METHODS

The concentrations of silver, iodine and other elements in the solid zeolitic materials were determined by electron microsonde measurements (JXA-5A, JEOL) applying Kevex; parameters used: accelerating voltage 25 kV, sample current 1.5×10^{-7} A; analysing crystal LiF-PEP.

X-ray powder diffraction patterns were recorded with a Philips PW 1710 Diffractometer and with a Siemens D5000 diffractometer by using CuK_α radiation. The Siemens patterns were indexed; the unit cells are given in Table I.

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 accumulation of the spectra 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).

All thermal analyses were carried out at temperatures up to 900 °C in air on a Derivatograph MOM OD 102 (Paulik-Paulik-Erdey) under the same conditions (sample weight: 100 mg, sensitivities: TG 50 mg, DTA 1/3, DTG 1/3, heating rate 9 °C min^{-1}, reference material Al_2O_3). For the determination of water the zeolitic samples were also heated (in an oven) to 450 °C for 1 h. Before heating, the zeolitic samples were equilibrated at room temperature for one or two days at 53 and 75% relative humidity (obtained by using saturated salt solution of $Mg(NO_3)_2{\cdot}6H_2O$ and NaCl).

Ac conductivity measurements were carried out at the University of Perugia. Pellets, 10 mm in diameter and 1.3–1.5 mm thick, were prepared by pressing ≈200 mg of material at 50 kN/cm^2. The two opposite surfaces of the pellet were coated with pressed Pt-black or graphite powder mixed with the material in the ratio 3 : 1. Impedance measurements in the range 20 to −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. Before measurements the pellets were equilibrated at room temperature for 1 or 2 days at 75% relative humidity. Some measurements were taken in air in the temperature range from 200 to 100 °C, after heating the pellets overnight at 200 °C. In all cases the impedance plot (reactance versus resistance) consisted of a single depressed semicircle (pellet impedance) ending in a low frequency tail (electrode-pellet interface). The ac conductivity was calculated by arc extrapolation to the resistance axis on the low frequency side taking into account the pellet geometrical size.

3. Results and Discussion

3.1. MATERIAL CHARACTERIZATION

The silver form of the synthetic ZSM5 (Ag-ZSM5) was obtained by mixing Na-ZSM5 with a silver nitrate solution. The X-ray powder pattern of Ag-ZSM5 (Figure 1) was indexed as orthorhombic; cell parameters are listed in Table I. The reaction of Ag-ZSM5 with a potassium iodide solution gave a zeolitic product (here after K-ZSM5/AgI) containing silver iodide. This is clearly seen from the X-ray powder pattern of K-ZSM5/AgI (Figure 1), where the silver iodide phase is indexed as iodargyrite syn (JCPDS 9-374). The remaining lines can be indexed on the basis of an orthorhombic cell (Table I) which is slightly larger than that of Ag-ZSM5. The presence of AgI as a separate phase suggests that the zeolitic phase is converted by treatment with potassium iodide into the potassium form K-ZSM5. In agreement with this hypothesis, K-ZSM5, prepared by ion exchange starting from Na-ZSM5, has the same unit cell as K-ZSM5/AgI.

The results of XPS measurements (Figures 2, 3) confirmed the presence of silver in Ag-ZSM5 and silver, potassium and iodine in K-ZSM5/AgI. The values of the Ag (3*d*5) core level binding energies and widths of photoemission lines, displayed in Table II are within the experimental error the same for both zeolitic products Ag-ZSM5 and K-ZSM5/AgI and consequently they do not allow us to discern likely different chemical states of Ag. On the other hand, the values of the modified Auger parameter (AP), also listed in Table II and calculated as a sum of the Ag (3*d*5) core level binding energy and Ag (M4N45N45) kinetic energy, differ by 0.7 eV. The AP value obtained for the K-ZSM5/AgI sample agrees within experimental error with values reported in the literature [8, 9] for AgI. The AP value measured for Ag-ZSM5 is rather close to the values published for AgO but this assignment is not consistent with the obtained Ag (3*d*5) core level binding

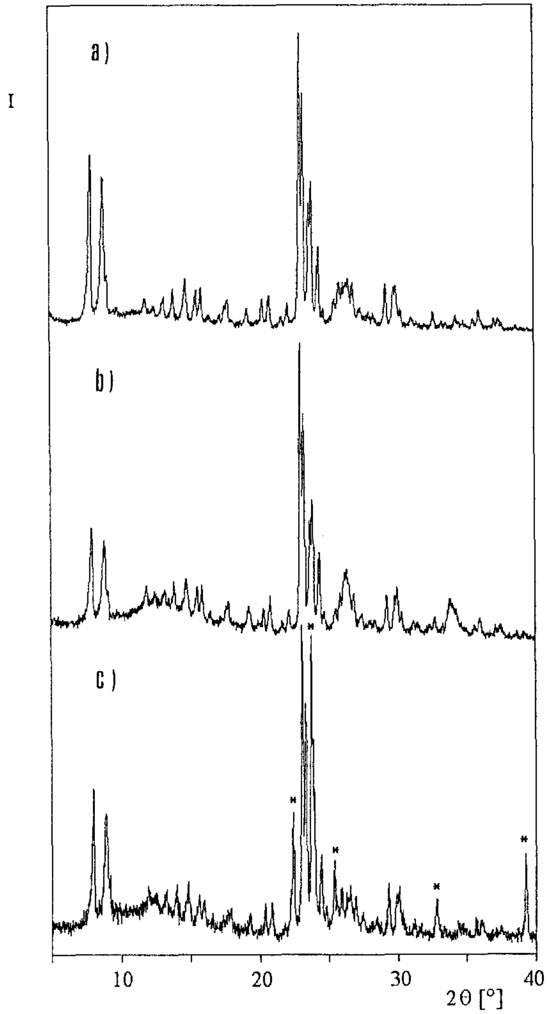

Figure 1. X-ray powder diffraction patterns of K-ZSM5 (a) Ag-ZSM5; (b) and K-ZSM5/AgI; (c, * – characteristic of AgI).

energy which is 1.4 eV higher than reported for Ag oxide [8, 9]. However, it cannot be ruled out that this shift can be attributed to the effects of bonding to zeolitic oxygen ions. It is worth mentioning that both values, the AP and Ag (3*d*5) binding energies, agree well with those obtained for highly dispersed Ag on Al_2O_3 and SiO_2 [10, 11]. Also the large width of the Ag (3*d*5) photoemission line (1.9 eV) compared to that of metallic Ag (1.15 eV) is characteristic of supported dispersed Ag [11]. Anyway, bulk silver has to be present as Ag^+, otherwise it would be impossible to use Ag-ZSM5 as a starting material for the preparation of K-ZSM5 by ion exchange.

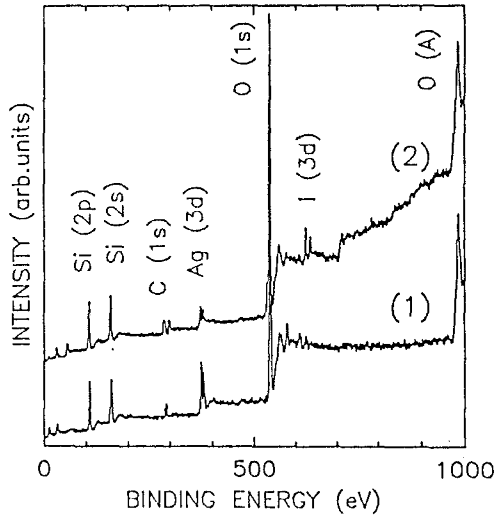

Figure 2. XPS spectrum of Ag-ZSM5 (1) and K-ZSM5/Ag (2).

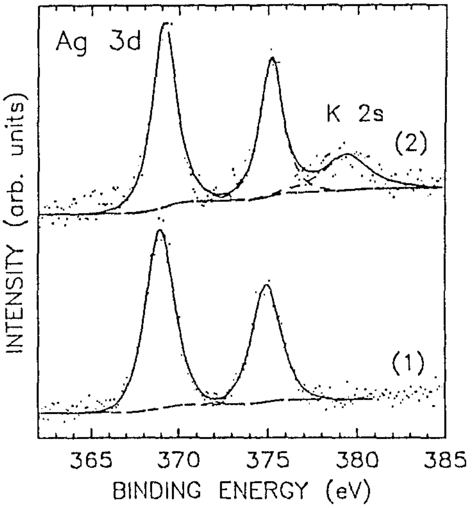

Figure 3. Ag 3d core level spectra of Ag-ZSM5 (1) and K-ZSM5/AgI (2).

According to the results of electron microsonde measurements the content of silver in the Ag-ZSM5 sample is 7.9%, while the K-ZSM5/AgI sample contains on average 11.5% of silver iodide.

The results of IR measurements and thermal analysis confirmed the presence of water in the zeolitic products. At 75% RH, the starting Na-ZSM5 contained 12% of water, the product Ag-ZSM5 10% and K-ZSM5/AgI 7.5%. At 53% RH, the water content of Ag-ZSM5 was 6.9% and K-ZSM5/AgI 5.5%. The presence of

Table II. Core level binding energies, kinetic energies of Ag Auger electrons, Auger parameters (AP) and full widths at half maxima of the spectral lines (in parentheses) of the Ag-ZSM5 and K-ZSM5/AgI samples (in eV).

Line/sample	Si(2*p*)	Al(2*p*)	O(1*s*)	K(2*p*3)
Ag-ZSM5	103.4 (2.1)	74.4 (2.2)	532.6 (2.1)	–
K-ZSM5/AgI	103.6 (2.1)	74.4 (2.3)	532.8 (2.0)	294.3 (2.4)
Line/sample	Ag(3*d*5)	Ag(M4N45N45)	AP	I(3*d*5)
Ag-ZSM5	369.0 (1.9)	354.7 (3.9)	723.7	–
K-ZSM5/AgI	369.1 (1.6)	355.3 (4.0)	724.4	620.4(1.8)

water in Na-ZSM5 as well as in Ag-ZSM5 and K-ZSM5/AgI was confirmed by two absorption bands in the IR spectra at 3350–3650 cm^{-1} (the stretching vibration) and at 1620 cm^{-1} (the bending vibration).

The results of thermal analysis confirmed the presence of AgI also in the K-ZSM5/AgI sample. On the DTA curve of AgI an endothermic peak at 146 °C corresponds to the phase transition. The second endothermic peak at 558 °C corresponds to the start of decomposition of AgI. These peaks, but with small intensity, are also present on the DTA curve of the K-ZSM5/AgI sample. According to a thermal analysis carried out up to 1050 °C silver iodide was decomposed in the temperature range from 558 to 1020 °C [12]. (The loss of iodine from K-ZSM5/AgI is 6.5%.)

3.2. CONDUCTIVITY MEASUREMENTS

The presence of AgI as a separate phase in K-ZSM5/AgI is also clearly seen from the Arrhenius plot of Figure 4 which shows the ac conductivity of K-ZSM5 and K-ZSM5/AgI in the range 100–200 °C. The sharp conductivity change occurring between 142 and 147 °C is due to AgI undergoing the well known phase transition from hexagonal to cubic symmetry at 146 °C [6]. Above the transition temperature, due to the high conductivity of AgI, K-ZSM5/AgI is two orders of magnitude more conductive than K-ZSM5.

Measurements were also carried out in the temperature range −20 to +20 °C on pellets previously conditioned at 75% relative humidity. From Figure 5 and Table III it is seen that K-ZSM5/AgI is more conductive than K-ZSM5 and Ag-ZSM5 and that the activation energy of K-ZSM5 (37.7 kJ mol^{-1}) is significantly higher than that of K-ZSM5/AgI (30.1 kJ mol^{-1}). To see whether the different conductivities of K-ZSM5 and K-ZSM5/AgI arose from different hydration of the zeolitic phases, the water content of K-ZSM5 was determined at 75% relative humidity. It turned out to be 9.5%. If it is assumed that the hydration of the composite is mainly due to the zeolitic phase, the water content of K-ZSM5 in the composite can be estimated to be 8.5%, being therefore close to that of the pure phase. From these data it can

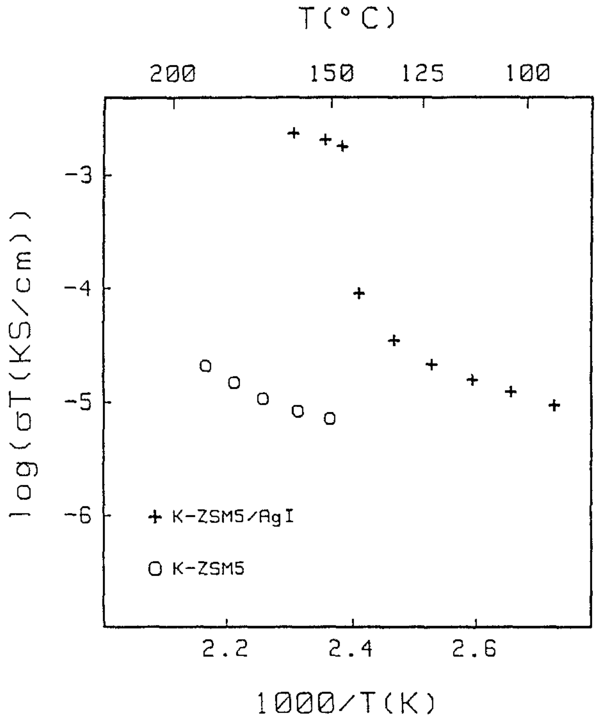

Figure 4. Arrhenius plot for the conductivity of the indicated materials (measurements taken in air).

Table III. Conductivities (σ) and activation energies (E) for K-ZSM5, Ag-ZSM5, K-ZSM/AgI and for the physical mixture K-ZSM5+AgI.

	σ(150 °C, air) S cm^{-1}	σ(20 °C, 75% RH) S cm^{-1}	E(−20/+20 °C, 75% RH) kJ mol^{-1}
K-ZSM5	1.7×10^{-8}	2.5×10^{-5}	37.7
Ag-ZSM5		5.2×10^{-6}	34.3
K-ZSM5/AgI	4.7×10^{-6}	5.3×10^{-5}	30.1
K-ZSM5 + AgI		2.6×10^{-5}	38.5
AgI		4.4×10^{-4}	24.3

be concluded that the higher conductivity of the composite compared to that of K-ZSM5 is not due to a different water content of the zeolitic phases.

To gain some insight into the conduction properties of K-ZSM5/AgI, measurements were also carried out on microcrystalline AgI and on a physical mixture of AgI and K-ZSM5 having the same composition as K-ZSM5/AgI. The results (Figures 4, 5 and Table III) show that the conductivity of AgI is on average an order of magnitude higher than that of K-ZSM5/AgI, while within the errors, the physical mixture has the same conductivity as K-ZSM5.

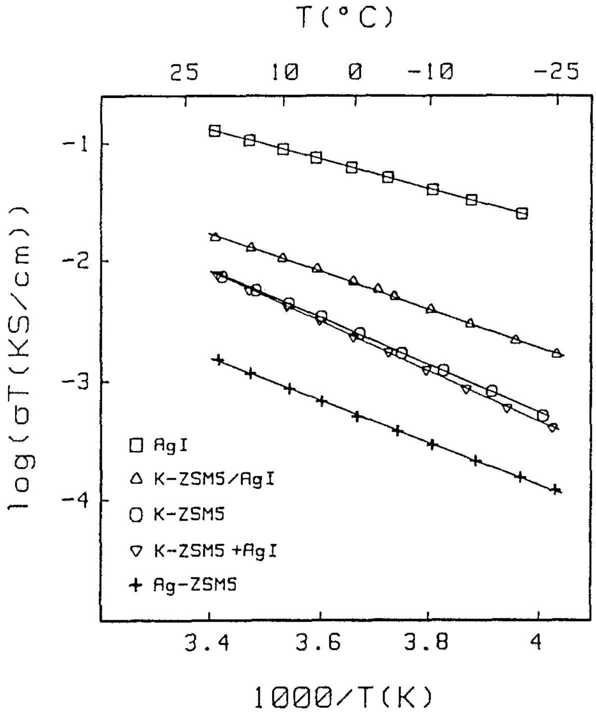

Figure 5. Arrhenius plot for the conductivity of the indicated materials; pellets were previously stored at 75% relative humidity.

Let us discuss these findings on the basis of different distributions of the two phases in K-ZSM5/AgI. The density of hexagonal AgI is 5.68 g/mL [13]; the density of K-ZSM5 can be estimated around 1.78 g/mL taking into account the unit cell parameters and assuming eight water molecules per unit-formula and four unit-formulae per unit cell. From density and weight % data, the volume fraction of silver iodide in K-ZSM5/AgI turns out to be 0.041. Two limit situations can be considered: (i) AgI particles are dispersed uniformly in K-ZSM5 so that each AgI particle is fully surrounded by K-ZSM5 particles; (ii) each K-ZSM5 particle is coated by a thin layer of AgI. In the first case, due to the small volume fraction of AgI, the conductivity is dominated by K-ZSM5, as proved by the conductivity of the physical mixture K-ZSM5 + AgI. In the second case, the conductivity of K-ZSM5 is enhanced by the more conductive AgI shell forming continuous conduction pathways on the surface of K-ZSM5 particles. This latter model accounts qualitatively for the influence of the small AgI percentage on the conductivity of K-ZSM5/AgI and is consistent with the fact that, as a consequence of the Ag^+/K^+ exchange, AgI is formed at the solution-zeolite interface.

It can be pointed out that the conductivity upper-limit (σ_1) of a two-component system is achieved when they are connected in parallel. In the case of K-ZSM5/AgI, σ_1 is given by

$$\sigma_1 = \sigma_{\text{AgI}} f_{\text{AgI}} + \sigma_{\text{K-ZSM5}} f_{\text{K-ZSM5}}$$

where f_{AgI} and $f_{\text{K-ZSM5}}$ are the volume fractions of AgI and K-ZSM5. By using the conductivities σ_1 listed in Table III and assuming $f_{\text{AgI}} = 0.041$, σ_1 turns out to be 4.2×10^{-5} S cm^{-1} at 20 °C, 75% RH. Since σ_1 is lower than the conductivity of K-ZSM5/AgI, it has to be concluded that one component, or both, are more conductive in K-ZSM5/AgI than in the separate phases. This can be due to a number of factors, such as different degree of crystallinity, particle size and associated interparticle resistances.

4. Conclusion

Reaction of the silver form of synthetic ZSM5 with potassium iodide leads to the formation of a composite material, made up of AgI and the ZSM5 potassium form. Comparison of the composite conductivity with the conductivity of K-ZSM5, of polycrystalline AgI as well as of the physical mixture K-ZSM5 + AgI suggests that the composite is made up of K-ZSM5 particles surrounded by a thin shell of silver iodide.

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