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THERMOCHEMICAL PROPERTIES OF COMPOSITES OF SYNTHETIC ZEOLITE ZSM5 AND SILVER IODIDE

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Thermochemical properties of two kinds of composite material of synthetic zeolite ZSM5 in potassium form (K-ZSM5) with AgI have been studied. The composites have been prepared by treating the silver form of synthetic zeolite ZSM5 (Ag-ZSM5) with potassium iodide solution under different experimental conditions. One of the composites was additionally sintered at temperature 500°C for 20 h. Both composites have been characterized by TG, DTG, DTA, EDS analysis, X-ray powder diffractometry and X-ray photoelectron spectroscopy. The methods of thermal analysis as well as X-ray powder diffractometry and XPS confirmed the differences between the two composites caused by sintering during the synthesis. The content of AgI in the surface layer was different. No changes of the zeolitic mineral dimensions are observed.

Keywords: *silver iodide, synthetic zeolite, thermal analysis, XPS, X-ray, ZSM5*

Introduction

The inclusion compounds on the basis of zeolites or some composite materials containing silver iodide are interesting with regard to their optical and electrical properties [1–4]. The present study of the preparation and characterization of composite material of synthetic zeolite ZSM5 and AgI is a continuation of our previous study of the composite materials of synthetic zeolite with AgI prepared by different ways of synthesis [3, 5].

It is known from literature that sodium mordenite (NaMD), one of the synthetic zeolites, can include AgI and the photosensitive properties of AgI change due to its inclusion in the zeolite [1, 2]. The NaMD–AgI inclusion compound was obtained by sintering a mixture of NaMD and AgI (in air at 500°C for about 50 h). According to the X-ray powder diffraction results the AgI peaks, which appeared in the diffraction patterns of the physical mixture, were not observed in the sintered sample. All peaks for the sintered sample were attributed to the NaMD lattice. The results of differential thermal analysis for NaMD, AgI and the sintered sample NaMD–AgI also showed that the peak observed for AgI at 146°C, which corresponds to the transition from α to β phase, was not observed in the sintered sample [2].

Photochromic properties of the hydrated mordenite–AgI inclusion compounds are based on the reversible movements of Ag^+ and I^- ions from inside to outside the lattice and vice versa through the mordenite channels [2].

In our previous papers the composite materials of the potassium form of the synthetic zeolite ZSM5 and AgI (K-ZSM5/AgI) [3] and the potassium form of synthetic mordenite and AgI (K-MD/AgI) [5] were studied and compared. The composites were prepared by a reaction of the silver forms of synthetic zeolites (Ag-ZSM5 and Ag-mordenite) with a solution of potassium iodide. It was the composite on the basis of synthetic zeolite ZSM5 prepared by the above mentioned reaction that appeared to be interesting from the point of its electrical properties. On the basis of ac conductivity data obtained for the composite material K-ZSM5/AgI it was concluded that AgI forms a thin conductive shell on the surface of the K-ZSM5 particles. However, as for the composite K-MD/AgI, the ac conductivity measurements confirmed the absence of continuous pathways of silver iodide around the K-MD particles.

By alternating the way of preparation we have obtained composites with different properties. When we prepared the composite of K/ZSM5 and AgI by sintering K-ZSM5 with AgI at the temperature 500°C for 20 h, the obtained composite was not interesting from the point of its electrical properties.

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The methods of thermal analysis significantly contribute to the characterization of zeolitic [6–14] and other aluminosilicate materials [15–20].

In this stage of our research the attention has been focussed to the study of the thermochemical properties of two kinds of composite material of ZSM5 in potassium form (K-ZSM5) with AgI. The first composite was prepared according to our previous paper [3], i.e. by the reaction of ZSM5 in silver form (Ag-ZSM5) with solution of KI. The second kind of composite was prepared by the same way as the first one but, in addition, it was also sintered at 500°C for 20 h. The composites before and after the sintering were characterized by methods of thermal analysis – DTA, DTG, TG, as well as EDS, X-ray powder diffractometry and X-ray photoelectron spectroscopy and compared.

Experimental

Chemicals and materials

In our study we used the synthetic zeolite ZSM5 (Slovnaft a.s., Bratislava) with chemical composition (without water): $x\mathrm{Na_2O}\cdot x\mathrm{Al_2O_3}\cdot y\mathrm{SiO_2}$ (x=0.8±0.15, y=20–45). The ZSM5 was thermally activated for 3 h by heating at continuously increasing temperature in the range from 150 to 400°C (1 h at 400°C).

Potassium iodide, silver nitrate and other chemicals were of p.a. purity (Merck and Fluka).

Silver form of synthetic zeolite ZSM5

Thermally activated ZSM5 (5 g) was mixed with 20 mL of silver nitrate solution with the concentration 1 mol dm^{-3}. 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 $\mathrm{NH_4SCN}$ with concentration 0.05 mol dm^{-3}). The obtained zeolitic product was dried at 60–80°C. This product is denoted as Ag-ZSM5.

Composite of K-ZSM5 and AgI

Ag-ZSM5 (3 g) was mixed with 20 mL of potassium iodide solution with the concentration 1 mol dm^{-3}. The heterogeneous mixture was intensively mixed for 2 h and then was left to stand for seven days (with occasional mixing). Then the heterogeneous mixture was decanted and centrifuged with distilled water (the presence of iodide ions in water after decanting was checked by adding a solution of $\mathrm{AgNO_3}$ with the concentration 0.1 mol dm^{-3}). The final zeolitic product was dried at 60–80°C. This product is denoted as K-ZSM5/AgI before heating (or simply K-ZSM5/AgI B.H.).

Composite of K-ZSM5 and AgI after sintering

The zeolitic product K-ZSM5/AgI was sintered four times for 5 h during four days at temperature 500°C, overall 20 h. This product is denoted as K-ZSM5/AgI after heating (or simply K-ZSM5/AgI A.H.).

Methods

The silver, iodine and other elements were determined by EDS analysis using a Jeol JSM-35CF scanning electron microscope with a LINK AN 10 000 microanalyser.

The thermal analyses – TG, DTG and DTA were carried out at temperatures up to 1000°C in air on a thermoanalyser SDT 2960 (TA Instruments, USA) under the conditions: sample mass 17–23 mg, heating rate 10°C min^{-1}, reference material $\mathrm{Al_2O_3}$, Pt crucible. The thermal analysis of AgI was carried out only up to temperature 550°C, close to its melting point. Before the thermal analyses the samples were equilibrated at room temperature for two or three days at relative humidity 53% obtained by using a saturated salt solution of $\mathrm{Mg(NO_3)_2\cdot 6H_2O}$.

X-ray powder diffraction patterns were recorded with a Philips PW 1710 Diffractometer using $\mathrm{CuK_{\alpha}}$ radiation in Bratislava.

The X-ray photoelectron spectroscopic measurements were carried out in two laboratories: in Catania and Prague.

In Catania the X-ray photoelectron spectra (XPS) were recorded with a VG Instruments electron spectrometer, using a $\mathrm{MgK_{\alpha,1,2}}$ X-ray source (1253.6 eV). The base pressure of the instrument was $5\cdot 10^{-10}$ torr and the operating pressure was typically $2\cdot 10^{-8}$ torr. The X-ray source in the standard conditions was working at 300 W, 15 kV and 20 mA. A pass energy of 100 and 50 eV was used for wide scans and narrow scans, respectively. The take-off angle of electron was 80° with respect to the macroscopic surface of the sample. The data analysis was accomplished using VGX900× (version 6) software. Binding energies were referenced to the C–H level at 285.0 eV.

In Prague the X-ray photoelectron spectra (XPS) were obtained with electron spectrometer ESCA 310 (Gammadata Scienta, Sweden) equipped with rotating anode of special UHV design. The photoelectrons were excited using monochromatized $\mathrm{AlK_{\alpha}}$ X-rays ($h\nu$=1486.6 eV). The samples were spread on gold plates which were mounted on a sample probe by means of tantalum clips. Detailed spectral scans were taken over the Ag 3d, Ag MNN, K 2p, Si 2p, Al 2p, O 1s and I 3d spectral regions. The instrument was calibrated so that the difference between the Au $4f_{7/2}$ photoelectron peak and the Fermi level was 84.0 eV.

The spectrometer was operated in the fixed analyser transmission mode. The background pressure of the residual gases during spectral accumulation was typically of the order of ~10^{-7} Pa. The Si 2p binding energy (103.4 eV) was used as an internal standard in calibration to compensate for static surface charging of the sample. The XPS measurements were carried out on the samples in the as-received state. The peak positions and areas were determined by fitting the unsmoothed experimental data after subtraction of the Shirley [21] background. Quantification of the element surface concentration ratios was accomplished by correcting the integral intensities of the photoemission peaks for their cross-sections [22] and accounting for the dependence of the analyser transmission [23] and electron mean free paths on kinetic energy of electrons [24]. Core level binding energies were determined with an accuracy of ±0.2 eV.

Results and discussion

Two kinds of composite zeolitic materials containing K-ZSM5 and AgI (K-ZSM5/AgI) were prepared. The first one was obtained by the reaction of silver form of synthetic zeolite ZSM5 (Ag-ZSM5) with a solution of potassium iodide. In our previous study [3] the composite as well as the starting silver form of synthetic zeolite ZSM5 (Ag-ZSM5) were characterized by X-ray diffractometry, X-ray photoelectron spectroscopy, electron microprobe analyses and ac conductivity measurements. According to the results of X-ray powder diffractometry, the Ag-ZSM5 treated with solution of potassium iodide becomes K-ZSM5 by ion exchange and silver iodide is formed as a separate phase. On the basis of the conductivity data of the composite material K-ZSM5/AgI 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.

The second composite was prepared by the same way of preparation as the first one but, in addition, it was also sintered at 500°C for 20 h. Both composites were characterized by EDS, thermal analyses – DTA, DTG, TG, X-ray photoelectron spectroscopy and X-ray powder diffractometry. The composites were compared to obtain information whether the sintering causes some changes of their properties.

The results of EDS and XPS checked the presence of silver and iodine (Table 1) as well as potassium, silicon and aluminum in the composites. The molar ratio of silver and iodine in pure silver iodide is 1:1.176. The molar ratio of silver and iodine in the composite K-ZSM5/AgI before heating is similar within the experimental error. According to the results of EDS and XPS the content of silver is higher in the composite K-ZSM5/AgI after heating. The molar ratio of silver and iodine was changed and is 1:0.897. During the sintering a part of iodine was released from the composite. The results of EDS and XPS are in good agreement with the results of thermal analyses.

Table 1 Surface atomic concentrations of silver, iodine and potassium calculated from XPS data (relative to Si) of the product K-ZSM5/AgI before heating

		Element			
Sample	Colour	Si	Ag	I	K
KZSM5/AgI	yellow	1	0.027	0.030	0.070

The results of thermal analyses of the composites confirmed the presence of water in both composites (Figs 1 and 2), but with a lower amount in comparison with the starting zeolites Ag-ZSM5. The content of water in both composites was similar. The composite before heating contained 6.87% and after heating 6.18%. The results of DTA confirmed the presence of

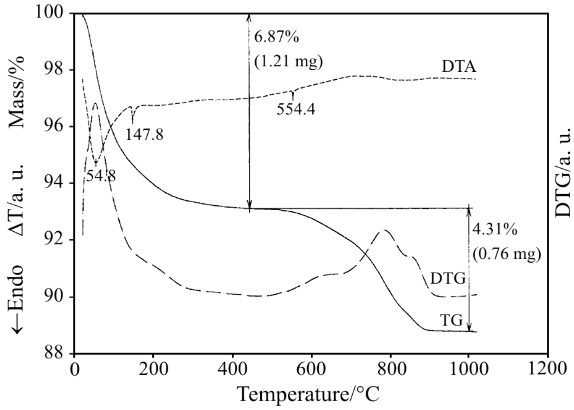

Fig. 1 TG, DTA and DTG curves of the sample K-ZSM5/AgI before heating

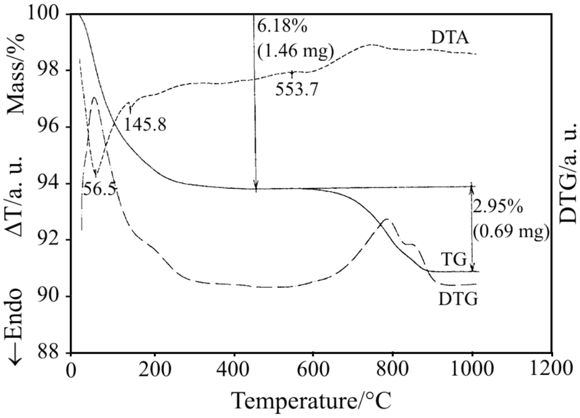

Fig. 2 TG, DTA and DTG curves of the sample K-ZSM5/AgI after heating

Table 2 Core level binding energies, kinetic energies of Ag Auger electrons, Auger parameter (AP) and full widths at half maxima of the spectral lines (in parentheses) of the Ag-ZSM5, K-ZSM5/AgI before heating and K-ZSM5/AgI after heating

Line sample	Si (2p)	Al (2p)	O (1s)	K ($2p_{3/2}$)	Ag ($3d_{5/2}$)	Ag (M4N45N45)	AP	I ($3d_{5/2}$)
Ag-ZSM5	103.4 (2.3)	74.4 (2.8)	532.8 (2.4)	–	369.0 (2.4)	355.8 (3.7)	724.8	–
K-ZSM5/AgI before heating	103.4 (2.1)	74.6 (2.7)	532.8 (2.1)	294.3 (2.4)	369.3 (1.5)	355.1 (3.2)	724.4	620.4 (2.0)
K-ZSM5/AgI after heating	103.4 (2.1)	74.6 (2.7)	532.8 (1.9)	294.2 (2.4)	369.1 (1.7)	355.4 (3.6)	724.5	620.2 (1.9)

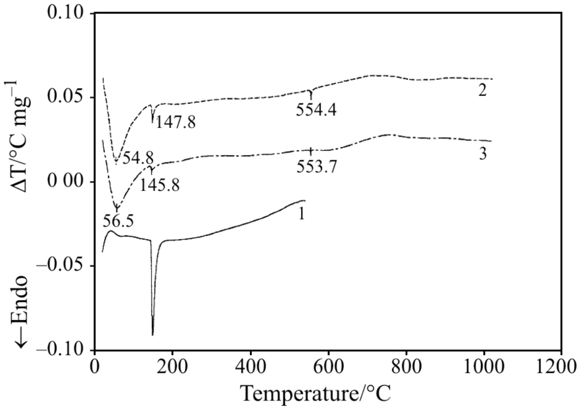

Fig. 3 DTA curves of three samples: 1 – AgI, 2 – K-ZSM5/AgI before heating and 3 – K-ZSM5/AgI after heating

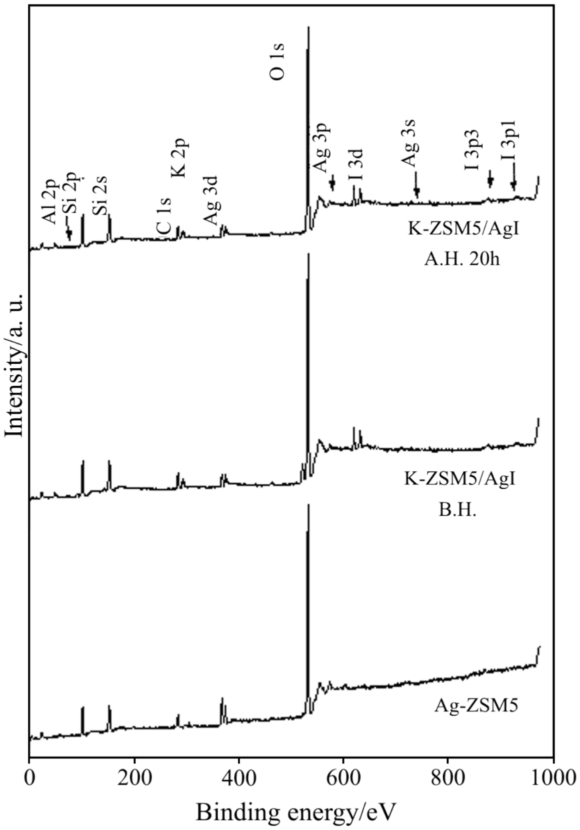

Fig. 4 XPS spectrum of Ag-ZSM5, K-ZSM5/AgI before heating and K-ZSM5/AgI after heating

AgI in both composites (Fig. 3). Two endothermic peaks on the DTA curve of AgI (Fig. 3) correspond to phase transition at 146 and 555°C. There are also observed two endothermic peaks on the DTA curves of composites before and after heating, but the intensities of the peaks are significantly lower. When we compare the endothermic peaks corresponding to the phase transition of the composites before and after heating, the peaks of the composite after heating are smaller. The temperatures of the endothermic peaks are slightly shifted, too. The decomposition of AgI in the sample of the composite before heating occurs in the temperature range from 550 to 900°C and in the sample of the composite after heating from 600 to 900°C. According to the DTG curves the decomposition in this temperature region occurs in two steps. The mass loss of the composite sample before heating in this temperature range is 4.31%, but in the sample after heating it is lower 2.95%. The results of thermal analysis checked changes caused by sintering.

The results of XPS measurements confirmed the presence of silver in Ag-ZSM5 and silver, potassium and iodine in the both composites K-ZSM5/AgI before and after heating (Figs 4 and 5). The values of the Ag ($3d_{5/2}$) core level binding energies and widths of photoemission lines, displayed in Table 2, are within the experimental error the same for Ag-ZSM5 and both composites 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) listed also in Table 2 and calculated as a sum of the Ag ($3d_{5/2}$) core level binding energy and Ag (M4N45N45) kinetic energy differ by 0.4 eV between Ag-ZSM5 and K-ZSM5/AgI before heating and by 0.3 eV between Ag-ZSM5 and K-ZSM5/AgI after heating. The AP values obtained for the composites K-ZSM5/AgI before and after heating agree within experimental error with values reported in [25, 26] 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 ob-

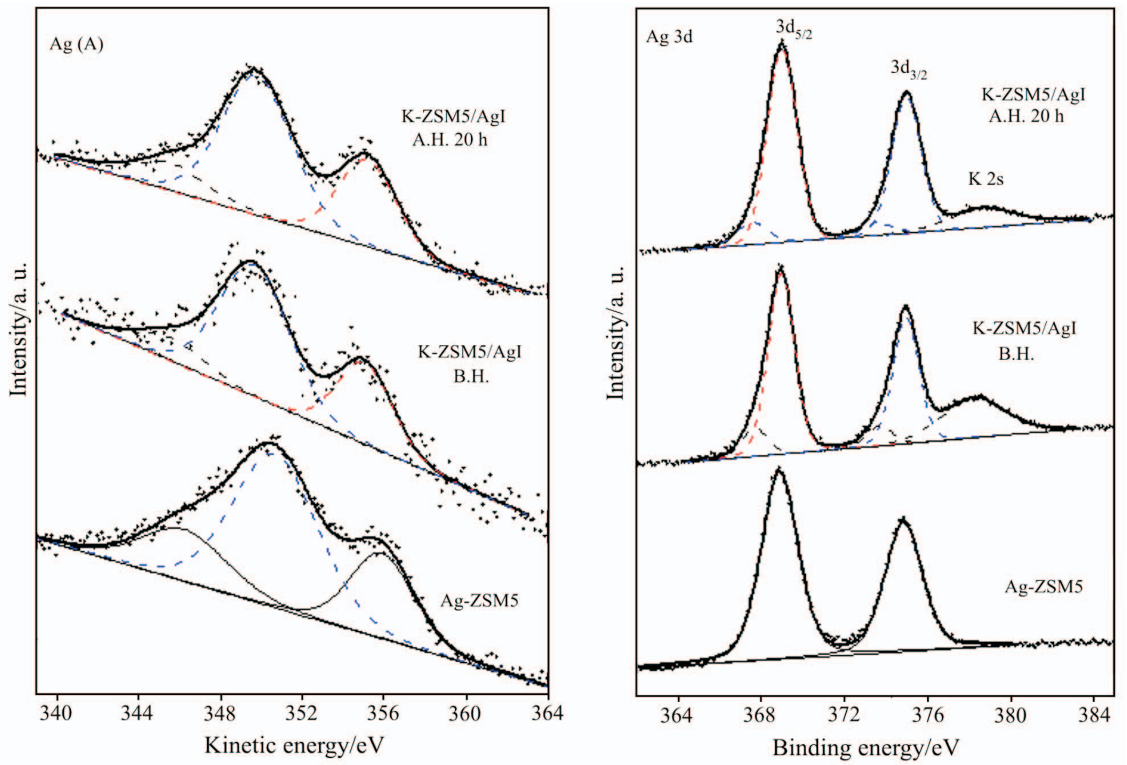

Fig. 5 Photoelectron spectra of Ag $3d_{5/2}$ electrons of the sample Ag-ZSM5, K-ZSM5/AgI before heating and K-ZSM5/AgI after heating

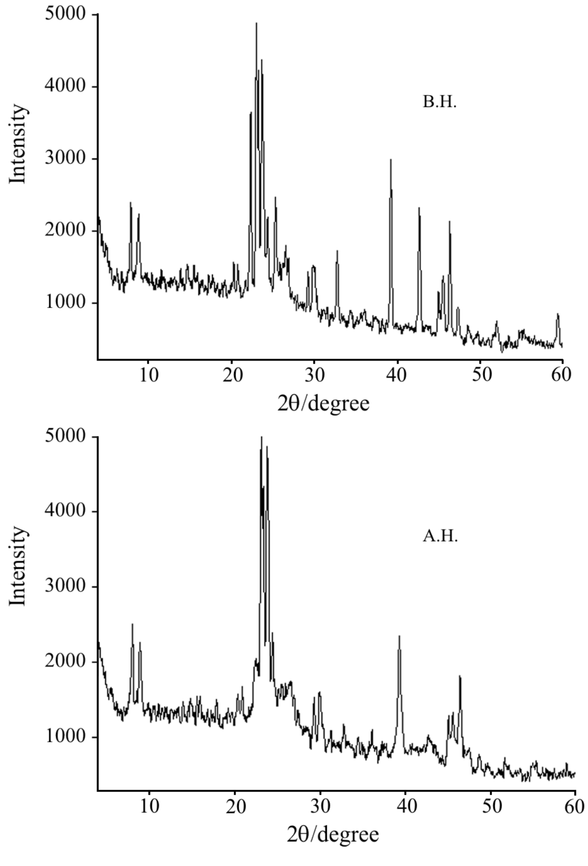

Fig. 6 X-ray powder diffraction patterns of the samples K-ZSM5/AgI before heating and K-ZSM5/AgI after heating

tained Ag ($3d_{5/2}$) core level binding energy which is by 1.4 eV higher than reported for Ag oxide [25, 26]. However, it cannot be excluded 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 ($3d_{5/2}$) binding energies agree well with those obtained for highly dispersed Ag on Al_2O_3 and SiO_2 [27, 28]. Also the large width of the Ag ($3d_{5/2}$) photoemission line (1.9 eV) compared to that of metallic Ag (1.15 eV) is characteristic of supported dispersed Ag [28]. It can not be excluded that during XP spectra acquisition reduction of Ag^+ to metallic Ag takes place. 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.

The X-ray measurements of the composite after heating also confirmed the changes caused by sintering. Both composites, before and after heating, were analysed by reflecting technique which mainly gives data from surface (Fig. 6). According to the results of the composite after heating at temperature 500°C (20 h heating) there are not observed any changes of the mineral dimensions indicating true host-guest reaction. 25–30% of the initial amount of AgI remains after the heat treatment.

To obtain more information about the changes caused by sintering there is necessary next study including conductivity measurements.

Conclusions

The methods of thermal analysis as well as X-ray photoelectron spectroscopy and X-ray powder diffractometry significantly contributed to the characterization of the composite zeolitic materials containing K-ZSM5 and AgI, prepared by different ways. The used methods demonstrated the presence of AgI in both composites and the changes of the composite caused by sintering. Two endothermic peaks on the DTA curves corresponding to the phase transitions of AgI at 146 and 555°C are less intensive in the composite prepared by sintering. The results of thermal analysis are in good agreement with the results of X-ray diffractometry measurements. No changes of the zeolitic mineral dimensions indicating true host-guest reaction are observed. The measured changes in the intensity of the X-ray reflection peaks of AgI indicate different content of AgI in the surface layer. Further information is however necessary to know in which form silver and iodide ions are built in the host channels after sintering.

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