THERMAL ANALYSIS OF THE SYNTHETIC ZEOLITE ZSM5 AND ITS SILVER IODIDE FORM

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Abstract

TG, DTG and DTA measurements were used to study the thermal properties of the synthetic zeolite ZSM5, its silver form (Ag-ZSM5) and a zeolitic product containing silver iodide (K-ZSM5/AgI). Thermoanalytical measurements were supplemented by morphology studies.

Keywords: silver iodide, synthetic zeolite, ZSM5

Introduction

Natural and synthetic zeolites as host materials can sorb different inorganic or ogranic molecules. Zeolites with large open frameworks are also capable of reversibly intercalating salts (e.g. alkali halides) as neutral ion pairs into the intracrystalline cavities [1].

The presence of AgI in the zeolitic material can change the original properties. Sodium mordenite, one of the synthetic zeolites, can include AgI. Photosensitive properties were observed in a hydrated mordenite–AgI inclusion compound. In the hydrated mordenite–AgI compounds, silver and iodide ions become diffusible from the mordenite channels to the surface due to hydration [2].

In our previous work [3] a composite material made up of AgI and the potassium form of the synthetic zeolite ZSM5 has been studied. In this zeolitic material AgI forms a thin conductive shell on the surface of the K-ZSM5 particles.

The present investigations of the thermal behaviour of the synthetic zeolite ZSM5 containing AgI were carried out as a continuation of our study of the preparation, characterization and determination of the electrical properties of natural and synthetic zeolite containing iodine, iodide ions, silver ions and also AgI [3–5].

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Experimental

Materials and methods of preparation

For our study we used synthetic zeolite ZSM5 (Slovnaft a.s., Bratislava). Its chemical composition (without water) is $xNa_2O{\cdot}xAl_2O_3{\cdot}ySiO_2$ (x=0.8±0.15, y=20–45).

The silver form of the synthetic zeolite ZSM5 was prepared by treatment of thermally activated zeolite ZSM5 (at 400°C) with silver nitrate solution. By reaction of the silver form of ZSM5 with potassium iodide solution the zeolitic product containing silver iodide was obtained [3]. The silver form is denoted as Ag-ZSM5 and the zeolitic product containing AgI as K-ZSM5/AgI.

For comparison, the thermal properties of the potassium form of ZSM5, of silver iodide and of a physical mixture of K-ZSM5 (88%) and AgI (12%) were also studied [3]. The potassium form is denoted as K-ZSM5 and the physical mixture as K-ZSM5+AgI.

Silver nitrate, potassium iodide and other chemicals were of analytical grade (Lachema, Brno).

Instrumentation

The contents of silver, iodine and other elements in the solid zeolitic materials were determined by Electron Microprobe measurements (JXA-5A, Jeol) applying Kevex [3]. For studying the morphology, a scanning electron microscope (TESLA BS 300) with an EDAX 9100/60 microanalyser (TESLA ELMI a.s., Brno) was used.

Thermal analyses were carried out up to a temperature of 1050°C in air with MOM derivatograph type 102 (Paulik-Paulik-Erdey, Budapest). The conditions used were: sample mass: 150 mg, heating rate 10°C min^{-1} reference material Al_2O_3 (in the case of silver iodide the mass and the composition of the analysed sample was: 18 mg AgI+132 mg Al_2O_3, and in the case of the physical mixture: 18 mg AgI+132 mg K-ZSM5).

Results and discussion

By treating the synthetic zeolite ZSM5 with silver nitrate solution, the silver form of zeolite ZSM5 (Ag-ZSM5) was obtained. The zolitic product containing silver iodide (K-ZSM5/AgI) was prepared by reaction of Ag-ZSM5 with potassium iodide solution [3]. In our previous paper [3] the synthetic zeolite ZSM5 in the potassium form (K-ZSM5), silver form and the zeolitic product containing AgI have been investigated by X-ray powder diffractometry, X-ray photoelectron spectroscopy (XPS), Electron microprobe measurements, IR and ac conductivity measurements.

The results of XPS measurements and electron microprobe measurements confirmed the presence of silver in Ag-ZSM5 (7.9 wt%) and silver, potassium and iodine in the zeolitic product K-ZSM5/AgI (11.5 wt% of AgI).

According to the results of X-ray measurements, Ag-ZSM5 treated with KI solution becomes K-ZSM5 by ion exchange and silver iodide is formed as a separate phase. Ac conductivity measurements also confirmed the presence of AgI [3]. The zeolitic material K-ZSM5/AgI is made up of K-ZSM5 particles surrounded by a thin conductive shell of silver iodide [3].

The thermal decomposition of the zeolitic product K-ZSM5/AgI was not completed up to 900°C, therefore, the thermal analysis of this zeolitic product as well as of the starting zeolite Na-ZSM5, the potassium form K-ZSM5, and the physical mixture K-ZSM5+AgI and AgI was conducted up to 1050°C.

The results of thermal analysis of the zeolitic products confirmed the presence of water but at a lower percentage in comparison with the starting zeolite Na-ZSM5. The presence of water was checked by means of IR spectra [3]. The starting zeolite Na-ZSM5 contained 12% of water (Fig. 1), the silver form Ag-ZSM5 10% and the zeolitic product K-ZSM5/AgI 7.5% of water (at 75% RH). In the Ag-ZSM5 a part of the water content was substituted by intrazeolitic silver ions [6] which was checked by morphology studies (Fig. 2).

The TG, DTA and DTG curves of the zeolitic material K-ZSM5/AgI are shown in Fig. 1 in comparison with the curves obtained for K-ZSM5. In the DTA

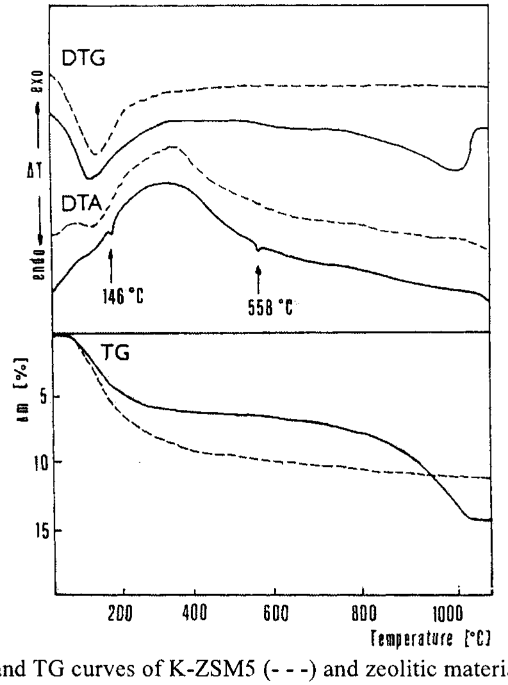

Fig. 1 DTA, DTG and TG curves of K-ZSM5 (- - -) and zeolitic material K-ZSM5/AgI (—)

a

b

c

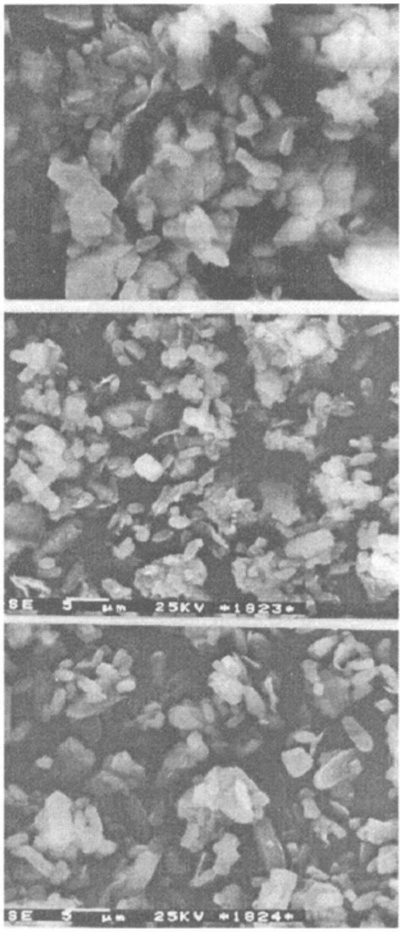

Fig. 2 Scanning electron micrograph of: a) the starting synthetic zeolite Na-ZSM5 (1 cm=3 μm); b) its silver form Ag-ZSM5 and c) zeolitic material K-ZSM5/AgI

curve of K-ZSM5/AgI, two small endothermic peaks at 146 and 558°C confirmed the presence of AgI. In the DTA curve of AgI we find two endothermic peaks at the same temperatures. The first one at 146°C corresponds to the phase transition [7, 8], the second one at 558°C corresponds to the start of decomposition of AgI. The TG curve of K-ZSM5/AgI up to 558°C showed the liberation of water. The decomposition of silver iodide started at 558°C. The loss of iodine from the sample K-ZSM5/AgI in the temperature range from 558 to 1020°C was 6.5% which is in a good agreement with the results of electron microprobe analysis.

The thermal decomposition of Ag-ZSM5 is similar to that of K-ZSM5. The difference is in the loss of water because the water content is lower in Ag-ZSM5.

Comparison of the results of our morphological study of the starting zeolite Na-ZSM5 (Fig. 2a), its silver form Ag-ZSM5 (Fig. 2b) and the new zeolitic product with silver iodide (Fig. 2c) revealed some differences. According to previous studies [3] the volume fraction of silver iodide in K-ZSM5/AgI turns out to be 0.041. Silver iodide coating in a thin layer the particles of K-ZSM5 changed the originally smooth plates to partially pitted ones (similarly as in [5, 9]).

Conclusions

Thermal analysis of the zeolitic products Ag-ZSM5 and K-ZSM5/AgI revealed the presence of water molecules but in a reduced amount in comparison with the original zeolite Na-ZSM5. The presence of silver iodide was checked in the composite material K-ZSM5/AgI.

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