THERMOCHEMICAL PROPERTIES OF COPPER FORMS OF ZEOLITE ZSM5 CONTAINING ETHYLENEDIAMINE

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Abstract

Copper forms of synthetic zeolite ZSM5 containing ethylenediamine (*en*) were characterised by methods of thermal analyses – TG, DTA and DTG in the temperature range 20–1000°C, in air and in argon atmosphere. Mass spectroscopy was used for the study of the released gas products of thermal decomposition. The results of thermal analyses of three $Cu(en)_x ZSM5$ zeolitic products with different composition (*x* depends on the mode of preparation) checked their different thermal properties. The main part of the decomposition process occurs at considerably higher temperatures than the boiling point of ethylenediamine of all three products, it proves strong bond and irreversibility of en-zeolite interaction. According to the results of the mass spectroscopy method the decomposition process in inert atmosphere is characterised by the development of a large spectrum of products with atomic mass from 28 to 178 atomic mass units, and there is a correlation between the mode of sample preparation and the spectrum of the released products.

Keywords: copper, ethylenediamine, mass spectroscopy, thermal analysis, zeolite, ZSM5

Introduction

The organomodified copper forms of synthetic zeolites are interesting for their catalytic properties. It is known from literature that the zeolites with exchangeable cations of transition metals (Fe, Co, Cu, Rh) in many kinds of matrices (ZSM5, ZSM11, mordenit, USY, ferrierit) play an active role at the decomposition of N_2O and other oxides of nitrogen [1]. The mentioned oxides belong among atmospheric pollutants; they are often a product of combustion processes and chemical production too.

The main reaction of the copper form of the synthetic zeolite ZSM5 and ethylenediamine is the rise of a complex cation $[Cu(en)_x]^{2+}$ [2], which is a process similar to the processes of some other synthetic zeolites and clay minerals. The ex-

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change of $[Cu(en)_x]^{2+}$ on A type, X,Y zeolites and montmorillonite is known from [3]. The adsorption of ethylenediamine (in the gas phase) on a dehydrated CuA zeolite gives only $[Cu(en)]^{2+}$. In the presence of water $[Cu(en)_2]^{2+}$ and $[Cu(en)_3]^{2+}$ were also synthetised on the surface. The effect of ethylenediamine on Co^{2+} ion exchange in zeolite ZSM5 was also studied [4].

The reaction of copper forms of ZSM5 and ethylenediamine can give rise to a series of products with properties significantly influenced by the experimental conditions during their preparation [2, 5]. Our previous knowledge about how the mode of preparation influences the chemical composition and thermal properties of the coordination complexes with ethylenediamine ligands was also used at the synthesis of the zeolitic products [6–10].

In our previous studies [2] the copper forms of the synthetic zeolite ZSM5 containing ethylenediamine were characterised by CHN analysis, electron micro-probe measurements, EDS, X-ray powder diffractometry, XPS, IR and NMR spectroscopy. The mentioned methods can explain several links between the methods of the preparation and properties, but they cannot give information that are important for the application.

The methods of thermal analysis significantly contribute to the characterisation of zeolitic [11–16] and other aluminosilicate [17–20] materials aimed for application, as well as to the study of zeolitic materials prepared by the interaction of zeolites with organic compounds within the framework of basic research.

The aim of our present investigation is the study of thermal properties of copper forms of synthetic zeolite ZSM5 containing ethylenediamine by using methods of thermal analysis and characterisation of the gas products of thermal decomposition by mass spectroscopy.

Experimental

Chemicals and materials

In our study we have used a synthetic zeolite ZSM5 (Slovnaft a.s.Bratislava) with the chemical composition (without water): xNa$_2$O xAl$_2$O$_3$ ySiO$_2$ (x=0.8 0.15, y=20–45).

Copper sulphate, ethylenediamine and other chemicals were of p.a. purity (Lachema Brno and Merck).

Material preparation

Cu-ZSM5 as well as Na-ZSM5 have been used for the preparation of the zeolitic products. The copper form of the synthetic zeolite ZSM5 (denoted as Cu-ZSM5) has been prepared by ion exchange starting from a thermaly activated Na-ZSM5 with a copper sulphate solution [2].

By using three different modes of preparation we have obtained three different copper forms of ZSM5 containing Cu(II) ions and ethylenediamine [2]:

- the reaction of Cu-ZSM5 with ethylenediamine has given rise to a light-violet zeolitic product, which was denoted as Cu-en-ZSM5 I
- starting from Cu-ZSM5 with the solution of $[Cu(en)_2]SO_4$ we have obtained a light-blue product, which was denoted as Cu-en-ZSM5 II
- the reaction of Na-ZSM5 with the solution of $[Cu(en)_2]SO_4$ has given rise to a light-violet zeolitic product, which was denoted as Cu-en-ZSM5 III.

Methods

The thermal analyses TG, DTG and DTA were carried out at temperatures up to 900°C in air on a Derivatograph-OD 102 (Paulik–Paulik–Erdey) under the conditions: sample mass 100 mg, sensitivities: 50 mg (also 20 and 100 mg), DTA 1/3, DTG 1/3, heating rate 9°C min^{-1}, reference material Al_2O_3. The DTA was carried out also in argon atmosphere at temperatures up to 1000°C on a Netzsch DTA 404 (sample mass: 70 mg, heating rate 10°C min^{-1}, sensitivities 0.1 mV, thermocouple: platinum–platinum/rhodium).

The gas products released during thermal decomposition were investigated by the mass spectroscopy method, as follows: the thermal decomposition of the sample was performed in a small oven with a linear increase of temperature in helium atmosphere. The samples were placed in a silica tube and the decomposition products were passed through a restrictor to the mass detector (type: Voyager GC/MS, firm: Thermoquest, USA). The details about this apparatus were published in [5, 21]. The spectra were analyzed by the commercial software and database 'NIST 98' for identification of the samples analyzed by the gas chromatography. The conditions of measurements: mass of sample: 10 mg, heating rate: 14°C min^{-1}, carrier gas: helium (purity: 99.99%), restrictor: fussed silica (1 m×0.1 mm), temperature of MS detector: 250°C, frequency of recording spectra in SCAN mode: 0.2 Hz, region of m/z: 10–350 amu.

Results and discussion

The copper forms of synthetic zeolite ZSM5 containing ethylenediamine were prepared by three different modes and three different zeolitic products (denoted as Cu-en-ZSM5 I, Cu-en-ZSM5 II and Cu-en-ZSM5 III) were obtained. They have different composition, colour and properties and their composition can be expressed simply as $Cu(en)_x$-ZSM5 (x depends on the preparation mode). The final products of the interaction of the ethylenediamine and Cu-ZSM5 or Na-ZSM5 are considerably influenced by the conditions of their synthesis.

The copper forms of synthetic zeolite ZSM5 with ethylenediamine were analysed by CHN, EDS, electron microprobe measurements, X-ray powder diffractometry, NMR and X-ray photoelectron spectroscopies [2].

The results of EDS, electron microprobe analyses and XPS confirmed the presence of copper in Cu-ZSM5 and in all three zeolitic products [2]. The results of CHN analyses confirmed the presence of ethylenediamine in the products Cu-en-ZSM5 I (6%), II (1.5%) and III (3%). The highest content of en was found in Cu-en-ZSM5 I and the

lowest content in Cu-en-ZSM5 II. Molar ratio of Cu: ethylenediamine for Cu-en-ZSM5 I was 1:1.185; for Cu-en-ZSM5 II 1:0.174 and for Cu-en-ZSM5 III 1:0.643. The presence of water in Cu-ZSM5 (7.5%) and in all three products with en (Cu-en-ZSM5 I 3%; Cu-en-ZSM5 II 6.5%; Cu-en-ZSM5 III 5.0%) was checked too. A part of water in the synthetic zeolite was replaced by ethylenediamine. The Cu-en-ZSM5 I with the highest content of en contains the lowest amount of water, in the sample Cu-en-ZSM5 II it is opposite. The results of CHN analyses were in a good agreement with the results of TG (e.g. in Cu-en-ZSM5 I the content of ethylenediamine was in average 5.96 and 6.0% by CHN and TG analyses, respectively).

The product Cu-en ZSM5 I was prepared by the reaction of Cu-ZSM5 with ethylenediamine (in liquid phase) unlike the preparation of the products II and III where a solution containing complex cation $[Cu(en)_2]^{2+}$ was used. The zeolitic products Cu-en-ZSM5 I and III are of similar colour and their other properties are similar to each other too; their colour is light-violet, the colour of Cu-en-ZSM5 II is light-blue.

The methods of thermal analyses are often used for the study of inclusion compounds. However, there is a general problem how to identify the processes related with the decomposition of various organic compounds, which problem of the identification often arises from the low content of the organic components in the samples.

The first results of thermal analyses – TG, DTG and DTA (in air) clearly showed the different thermal properties of the three zeolitic products with different content of *en* [2]. To obtain more detailed information about the thermal decomposition of 'en-zeolite' complexes as well as about the pyrolysis gas products, the samples Cu-en-ZSM5 I, II and III were studied by thermal analyses in two kinds of atmosphere – in air and in inert atmosphere argon – and the gas products released during the thermal decomposition in inert atmosphere were investigated by mass spectroscopy.

The DTA curves of the Cu-en-ZSM5 I, II and III, in air (Fig. 1) show exothermic peaks that confirm the presence of ethylenediamine (unlike the DTA curve of the Cu-ZSM5 which is without them [2]). There are two exothermic peaks on the DTA curve of the Cu-en-ZSM5 I , the maximum of the first, weaker peak is at 200°C, and the maximum of the second, strong double peak is at 400°C. The second exothermic peak corresponds with the clear loss of mass on the TG curve (Fig. 1). The DTA curve of the Cu-en-ZSM5 III shows that the exothermic process occurs in the similar temperature range as at the product Cu-en-ZSM5 I, from 290 to 480°C, with the maximum of the strong exothermic peak at 400°C. It corresponds with a slight mass loss on the TG curve, which mass loss is smaller at Cu-en-ZSM5 III than at Cu-en-ZSM5 I (Fig. 1). On the DTA curve of Cu-en-ZSM5 II there is observed one double exothermic peak with the maximum at 300°C, but the corresponding mass loss on the TG curve is hardly visible (Fig. 1).

The thermal analysis performed in argon atmosphere also confirmed the similarity of the thermal properties of the products Cu-en-ZSM5 I and III and their difference from the Cu-en-ZSM5 II (Fig. 2). There are two exothermic peaks with maximum at 280 and 530°C on the DTA curve of the Cu-en-ZSM5 I. Similarly, there are observed two exothermic processes on the DTA curve of the Cu-en-ZSM5 III; the second exothermic peak has maximum at 620°C (Fig. 2).
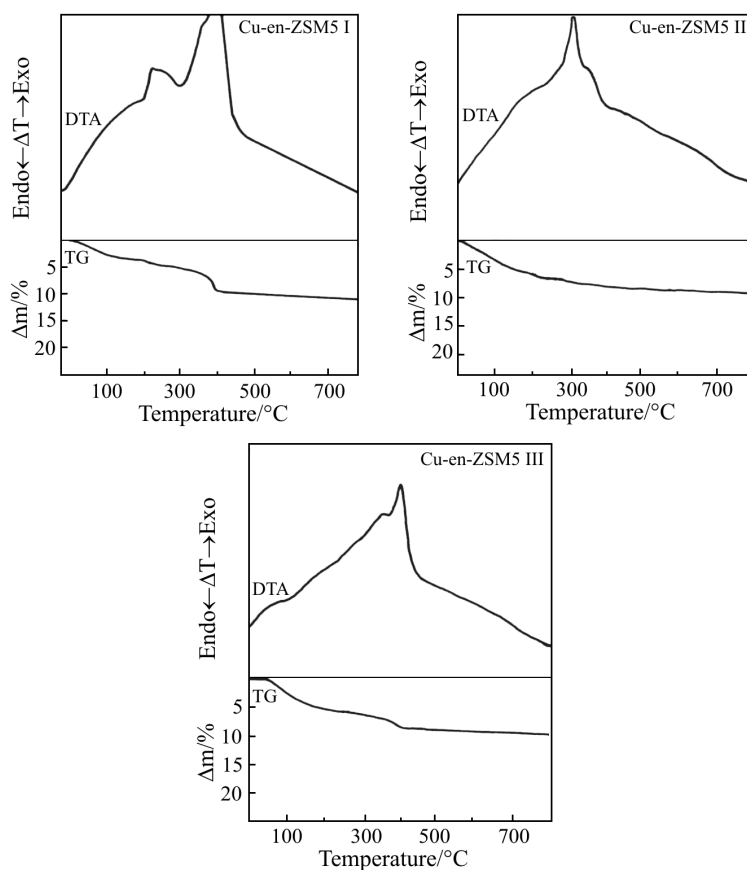
Fig. 1 DTA and TG curves of Cu-en-ZSM5 I, II and III (in air)

The study of the decomposition gas products in an inert atmosphere by using mass spectroscopy also corresponds with the DTA results in argon. The decomposition process can be documented by the curve of the total ion current on the mass detector *vs.* sample temperature (Fig. 3) and by the total mass spectrum of the substances released during the whole decomposition process (Fig. 4). In Fig. 3 we can see that the decomposition of the samples Cu-en-ZSM5 I and Cu-en-ZSM5 III (Figs 3a and c) begins at the temperature about 220°C. The main part of the decomposition of the products Cu-en-ZSM5 I and Cu-en-ZSM5 III is divided into two stages. The decomposition curve of the products Cu-en-ZSM5 I and Cu-en-ZSM5 III is similar to each other but it is different from the decomposition curve of Cu-en-ZSM5 II. The first stage of the decomposition of the Cu-en-ZSM5 I shows maximum at 450°C and the first stage of the decomposition of the product Cu-en-ZSM5 III is localized in the temperature range 350–450°C. The second stage of the decomposition of the Cu-en-ZSM5 I and Cu-en-ZSM5 III shows maximum at 700°C. The main part of the decomposition of the
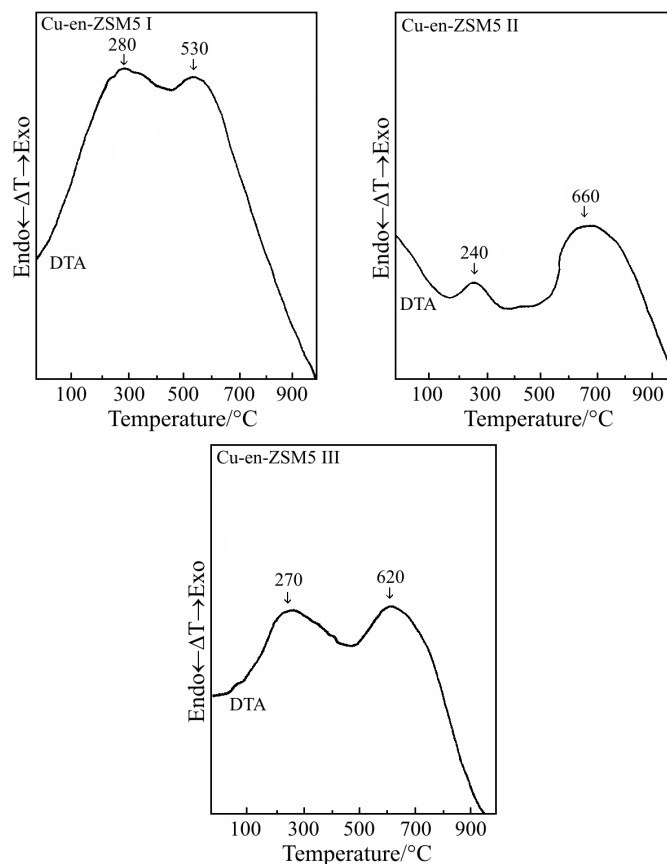
Fig. 2 DTA curves of Cu-en-ZSM5 I, II and III (in argon)

product Cu-en-ZSM5 II is in a relatively narrow temperature range 340–430°C (Fig. 3b) with maximum at 350°C. In that case there was identified a smaller amount of the gas products, including SO_2. The results are in a good agreement with the results of XPS, where the presence of sulphur was proved [2]. So we can deduce that in the channel system there was also a small amount of $CuSO_4$ or $Cu(en)_xSO_4$.

Since the main part of the decomposition process of all three products occurs at temperatures considerably higher than the boiling point of ethylenediamine (116°C), it proves 'strong' bond and irreversibility of the en-zeolite interaction.

The spectrum of the released products (Fig. 4) is large and includes substances developed by the decomposition of the ethylenediamine as well as by their following condensation. The decomposition process in the inert atmosphere is characterised by a development of a wide spectrum of components with their mass from 28 to 178 atomic mass units, and there exists a correlation between the mode of preparation and the spectrum of the releasing components. The releasing of components with molar masses higher than the mass of
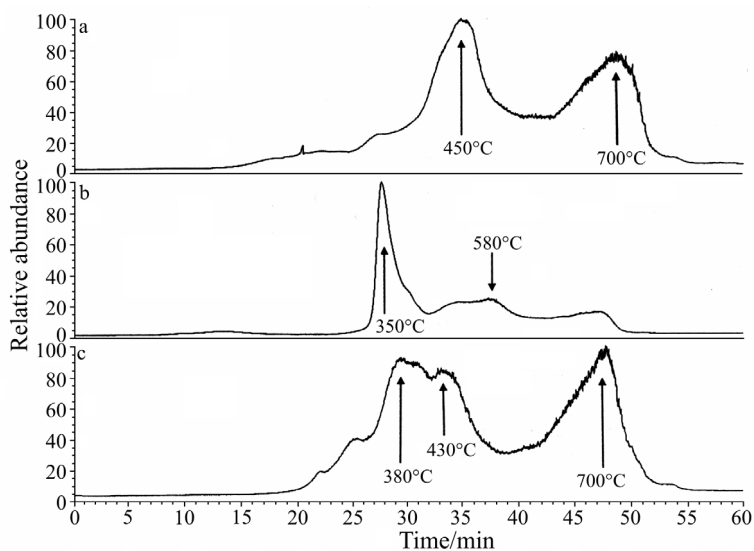
Fig. 3 Total ion current during dynamic heating of zeolitic complexes a – Cu-en-ZSM5 I,
b – Cu-en-ZSM5 II and c – Cu-en-ZSM5 III in inert atmosphere (carried out by
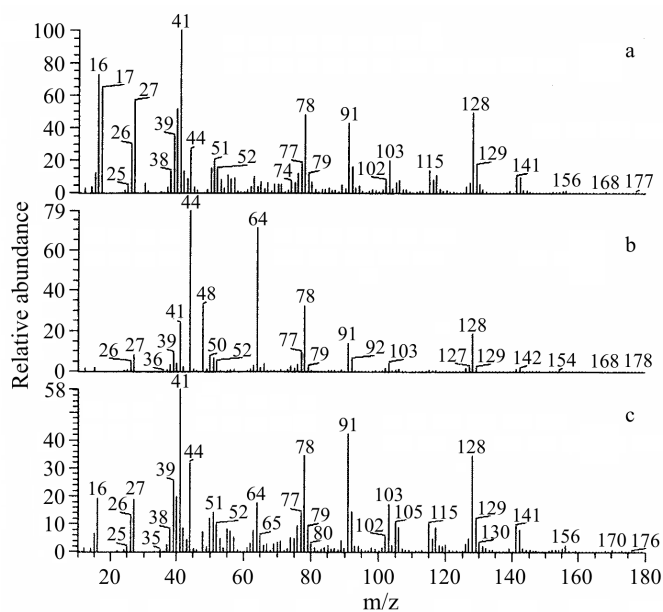combination of thermal analysis and mass spectroscopy)

Fig. 4 The mass spectrum of ions releasing during dynamic heating in inert atmosphere
in temperature range from 20 to 800°C: a – Cu-en-ZSM5 I, b – Cu-en-ZSM5 II
and c – Cu-en-ZSM5 III

the primarily present component (molar mass of H_2O is 18.015 g mol^{-1} and of ethylenediamine is 60.10 g mol^{-1}) documents a complex mechanism of the decomposition process, which process involves the condensation of the primarily releasing products as a consequence of the catalytic effect of the silicate surface.

Conclusions

The thermal analysis significantly contributed to the characterisation of the organo-modified copper forms of the synthetic zeolite ZSM5 containing ethylenediamine. The methods of thermal analyses as well as the study of released gas products by mass spectroscopy contributed also to the explanation of the interaction of ethylenediamine and copper forms of synthetic zeolite ZSM5.

The thermochemical properties of the products Cu-en-ZSM5 I and Cu-en-ZSM5 III (light-violet colour) are similar but they differ from the product Cu-en-ZSM5 II (light-blue, with the lowest content of ethylenediamine).

The main part of the decomposition process of all three products Cu-en-ZSM5 I, II and III is at temperatures remarkably higher than the boiling point of ethylenediamine. It provides evidence in favour of 'strong' bond and irreversible interaction of en-zeolite. As a consequence of the catalytic effect of silicate surface the decomposition process of the zeolitic products with ethylenediamine is characterised by the developing of a wide spectrum of substances with higher molecular mass. Further study would be required for more detailed characterisation of this process.

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