

# Thermochemical properties of copper forms of zeolite ZSM5 containing dimethylethylenediamine

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## Abstract

Synthetic zeolite ZSM5 and its copper forms containing *N,N*-dimethylethylenediamine (dmen) have been investigated by CHN, energy dispersive spectroscopy (EDS) analysis, X-ray powder diffractometry, X-ray photoelectron spectroscopy and continuous waves hydrogen nuclear magnetic resonance (CW <sup>1</sup>H NMR) spectroscopy. Thermal properties have been studied by methods of thermal analysis—TG, DTA and DTG in the temperature range 20–1000 °C in air atmosphere. Mass spectroscopy method was used for the study of the released gas products of thermal decomposition.

The results of thermal analyses of two zeolitic samples Cu-ZSM5 and Cu(dmen)<sub>x</sub>ZSM5 (*x* depends on the mode of preparation) demonstrated their different thermal properties. The main part of the decomposition process of the samples Cu(dmen)<sub>x</sub>ZSM5 occurs at considerably higher temperatures than the boiling point of dimethylethylenediamine, proving strong bond and irreversibility of dmen–zeolite interaction. According to the results of mass spectroscopy the decomposition process in inert atmosphere is characterized by the development of a large spectrum of products with atomic mass from 18 to 447 atomic mass units as a consequence of the catalytic effect of the silicate surface.

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## 1. Introduction

The present study of the preparation and characterization of copper forms of the synthetic zeolite ZSM5 with *N,N*-dimethylethylenediamine (dmen) content is a continuation of our previous study of the organomodified copper forms of ZSM5, particularly with a content of organic diamines [1–3].

The 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

and Rh) in many kinds of matrices (ZSM5, ZSM11, mordenit, USY and ferrierit) play an active role at the decomposition of N<sub>2</sub>O and other oxides of nitrogen [4–7]. The mentioned oxides belong among atmospheric pollutants, they are often a product of combustion processes and chemical production too. The organomodified copper forms are interesting for their catalytic properties too.

In our previous studies [1,2] of copper forms of synthetic zeolite ZSM5 containing ethylenediamine (en) the methods of thermal analysis—TG, DTA, DTG, X-ray photoelectron spectroscopy and NMR spectroscopy significantly contributed to the characterization of the zeolitic materials. Ethylenediamine in copper forms of synthetic zeolite ZSM5 was connected to Cu(II) ions by coordinative bonds. The main part of the decomposition

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process of the products  $\text{Cu}(\text{en})_x\text{ZSM5}$  was at the temperatures remarkably higher than the boiling point of ethylenediamine. The presence of ethylenediamine changed the original properties of Cu-ZSM5 which changes were influenced by the ethylenediamine content and also by the mode of preparation. The main reaction of copper form of the synthetic zeolite ZSM5 and ethylenediamine [1,2] gives rise to a complex cation  $[\text{Cu}(\text{en})_x]^{2+}$ , which is a process similar to the processes in some other synthetic zeolites and clay minerals [8,9].

Our previous knowledge about how the mode of preparation influences the chemical composition and thermal properties of the coordination complexes with organic ligands (mainly ethylenediamine) [10–12] was also used at the synthesis of our recent zeolitic products with dimethylethylenediamine.

The methods of thermal analysis significantly contributed to the characterization of zeolitic [2,13–17] and other aluminosilicate materials [18,19].

The aim of our present study was the preparation of copper form of synthetic zeolite ZSM5 with *N,N*-dimethylethylenediamine and its characterization by the CHN, EDX analyses, X-ray photoelectron spectroscopy, CW  $^1\text{H}$ NMR spectroscopy and X-ray powder diffractometry. The thermochemical properties were studied by using the thermal analysis—TG, DTA, DTG and the released gas products of thermal decomposition by the mass spectroscopy.

## 2. Experimental

### 2.1. Chemicals and materials

In our study we have used a synthetic zeolite ZSM5 (Slovaft a.s. Bratislava) with the chemical composition (without water):  $x\text{Na}_2\text{O}\cdot x\text{Al}_2\text{O}_3\cdot y\text{SiO}_2$  ( $x = 0.8 \pm 0.15$ ,  $y = 20\text{--}45$ ). ZSM5 was thermally activated for 3–4 h by heating at continuously increasing temperature in the range from 150 to 400 °C (1 h at 400 °C).

Copper sulphate, dimethylethylenediamine and other chemicals were of p.a. purity (MERCK).

#### 2.1.1. Material preparation

**2.1.1.1. Cu-ZSM5.** The copper form of the synthetic zeolite ZSM5 (denoted as Cu-ZSM5) was prepared by ion exchange starting from a thermally activated Na-ZSM5 (10 g) with a copper sulphate solution (30 mL) with different concentrations (mainly 0.1 M solution of  $\text{CuSO}_4$ ) at room temperature. After 2 h of intensive mixing the heterogeneous mixture was decanted with distilled water and centrifuged (the presence of  $\text{SO}_4^{2-}$  ions in water after the decanting was checked by a solution of  $\text{BaCl}_2$ ). The zeolitic product was dried at 60–80 °C [1].

**2.1.1.2. Cu-dmen-ZSM5.** Cu-ZSM5 (3 g) was mixed with 5 mL *N,N*-dimethylethylenediamine. The heterogeneous mixture was left to stand for 1 h with occasional mixing (at room temperature) and then was decanted with distilled water and centrifuged. The zeolitic product was dried at 60–80 °C.

### 2.2. Methods

The CHN elemental analyses were performed on a Perkin-Elmer 2400 Elemental Analyser.

The copper and other elements were determined by the energy dispersive spectroscopy (EDS) analysis using a TESLA BS 340 scanning electron microscope (TESLA ELMI a.s. with a LINK ISIS 300 microanalyser).

The X-ray powder diffraction patterns were recorded with a Philips PW 1710 Diffractometer using  $\text{Cu K}\alpha$  radiation.

The X-ray photoelectron spectroscopy was carried out in two laboratories: in Catania and in Prague.

In Catania the X-ray photoelectron spectra (XPS) were recorded with a VG MT 500 Instruments electron spectrometer equipped with CLAM II analyser and a twin anode Mg/Al, using a Mg  $\text{K}\alpha$  X-ray source (1253.6 eV). The base pressure of the instrument was  $7 \times 10^{-8}$  Pa and the operating pressure was typically  $3 \times 10^{-6}$  Pa. The X-ray source in the standard conditions was working at 100 W, 10 kV and 10 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 45° with respect to the surface of the sample. The data analysis was accomplished using VGX900x (version 6) software. Binding energies were referenced to the C 1s level at 285.0 eV.

In Prague the X-ray photoelectron spectra were obtained with high resolution electron spectrometer ESCA 310 (Gamma-data Scienta, Sweden) equipped with rotating anode of special UHV design. Photoelectrons were excited using monochromatized Al  $\text{K}\alpha$  X-rays ( $h\nu = 1486.6$  eV), eliminating thus the bremsstrahlung radiation which might cause reduction of  $\text{Cu}^{2+}$  species. 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 Cu 2p, Si 2p, O 1s, C 1s and N 1s spectral regions. The instrument was calibrated so that the difference between the Au 4f<sub>7/2</sub> 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  $\sim 10^{-7}$  Pa. The Si 2p binding energy (103.4 eV) was used as 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 [20] background. Quantification of the element surface concentration ratios was accomplished by correcting the integral intensities of the photoemission peaks for their cross-sections [21] and accounting for the dependence of the analyser transmission [22] and electron mean free paths on kinetic energy of electrons [23]. Core level binding energies were determined with an accuracy of  $\pm 0.2$  eV. The results obtained did not depend on the angle of electron detection, indicating thus the absence of measurable surface concentration gradients.

The thermal analyses TG, DTA and DTG were carried out at temperature up to 1000 °C in air on a Derivatograph Q-1500D ASI Budapest under the conditions—sample weight 100 mg, sensitivities: 50 mg, heating rate 10 °C/min, reference

material  $\text{Al}_2\text{O}_3$ . Before the thermal analyses the samples were equilibrated at room temperature for 2 or 3 days at relative humidity (RH) 53% obtained by using a saturated salt solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . For a more detailed results about the mass loss of the samples the TG was recorded also on a thermogravimetric analyzer TGA 7 in air atmosphere from 50 to 800 °C, the sample weight 5 mg, heating rate was 10 °C/min.

The released gas products during the thermal decomposition were investigated by the mass spectroscopy methods. The mass detector for the measurements was a VG Instrument, typ Trio 1000 linked to Perkin-Elmer automated thermal desorption system. The conditions of measurements: mass of sample, 10 mg; heating rate, 20 °C/min; carrier gas, helium; temperature of MS detector, 220 °C.

The continuous waves hydrogen nuclear magnetic resonance (CW  $^1\text{H}$  NMR) spectra were recorded at room temperature by the CW  $^1\text{H}$  NMR spectrometer designed at the Department of Physics, Technical University in Košice, with frequency 10.545 MHz. The derivative recordings were averaged out of 16 accumulated repetitions [24].

### 3. Results and discussion

The copper form of synthetic zeolite ZSM5 was prepared by an ion exchange starting from Na-ZSM5 with a copper sulphate solution. The reaction of Cu-ZSM5 with *N,N*-dimethylethylenediamine gave a blue-violet zeolitic product denoted as Cu-(dmen)<sub>x</sub>-ZSM5. By different preparation techniques different modified zeolitic compounds were obtained [1,2,25]. The content of copper and dmen as well as the thermal and other properties of the obtained zeolitic products were considerably influenced by the conditions of their synthesis. Our attention was focussed to the copper form of ZSM5 which was prepared as described in Section 2.1.1. with 0.1 M  $\text{CuSO}_4$  solution.

The copper form of the synthetic zeolite ZSM5 with dimethylethylenediamine as well as the starting sample Cu-ZSM5 were analyzed by the CHN, EDS, X-ray powder diffractometry, X-ray photoelectron spectroscopy, CW  $^1\text{H}$  NMR and thermal analyses—TG, DTG and DTA. The released gas products of the thermal decomposition were investigated by the mass spectroscopy.

It is known from the literature [26], that zeolites with large open frameworks are also able to reversibly intercalate salts as neutral ion pairs into the intracrystalline cavities. During the preparation of Cu-ZSM5 it is necessary to wash out the  $\text{CuSO}_4$  from the zeolitic channel thoroughly. In cases, where a part of the  $\text{CuSO}_4$  was not thoroughly washed out from the channels, the XPS analysis confirmed the presence of sulphur. But after adding dimethylethylenediamine, the  $\text{CuSO}_4$  was washed out from the channels very easily in the form of a dark-blue solution of the coordinate salt (copper cations form coordination complexes with dmen).

The presence of copper in both products Cu-ZSM5 and Cu-dmen-ZSM5 was confirmed by the EDS and XPS analyses. The results of the CHN analyses as well as of XPS and thermal analyses checked the presence of dimethylethylenediamine in

Table 1

Chemical analysis of the product Cu-dmen-ZSM5 according to the results of EDS (for copper content), CHN (for dmen and  $\text{H}_2\text{O}$  content) and TG (for dmen and  $\text{H}_2\text{O}$  content)

Sample	Colour	Cu (wt.%)	dmen (wt.%)	$\text{H}_2\text{O}$ (wt.%)
Cu-dmen-ZSM5	Blue-violet	3.8	6.45	3.5–4

Table 2

Surface atomic concentrations of elements calculated from XPS data (relative to Si) of the product Cu-dmen-ZSM5

Sample	Colour	Element			
		Cu	O	N	C
Cu-dmen-ZSM5	Blue-violet	0.02	1.89	0.06	0.17

the product Cu-dmen-ZSM5. The molar ratio of Cu:dmen for Cu-dmen-ZSM5 was 1:1.22. According to the CHN analyses the content of dmen in Cu-dmen-ZSM5 was 6.45 wt.% (Table 1). The results of the CHN analyses were in a good agreement with the results of the TG.

The surface atomic concentration of copper and other elements of Cu-dmen-ZSM5 calculated from the XPS data (relative to Si = 1) is listed in Table 2. The measured core level binding energies for this product are summarized in Table 3. The binding energy of Cu  $2p_{3/2}$  electrons obtained for samples Cu-ZSM5, 934.5 eV is characteristic for divalent, paramagnetic  $\text{Cu}^{2+}$  ions. The intense satellite structure in the spectra of Cu 2p electrons (Fig. 1) is consistent with this conclusion. For the sample Cu-dmen-ZSM5 two components in the spectrum of Cu  $2p_{3/2}$  electrons were observed with binding energies equal to 934.7 and 933.4 eV. The component with higher binding energy corresponds to Cu(II) and the second one which is shifted by 1.3 eV towards lower binding energy corresponds to Cu(I). In our previous study [1] of copper forms of ZSM5 with a higher content of ethylenediamine we found that with the increasing content

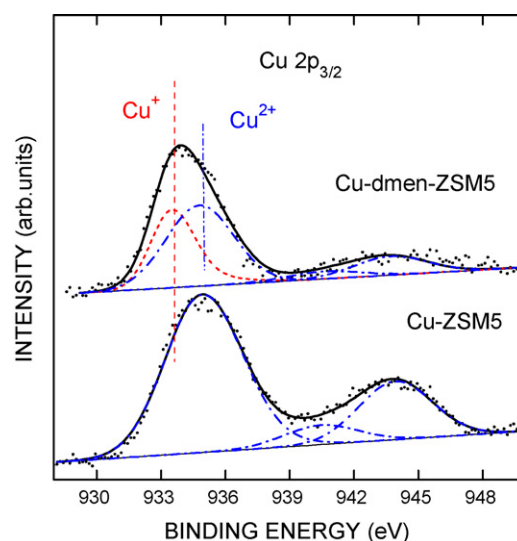


Fig. 1. Photoelectron spectra of Cu  $2p_{3/2}$  electrons of the sample Cu-ZSM5 and Cu-dmen-ZSM5.

Table 3  
Binding energies of core level electrons, widths of the measured lines at half-height (in parentheses)

Sample	Line					
	Si (2p)	Cu (2p)		O (1s)	N (1s)	C (1s)
		Cu (2p <sub>3/2</sub> )	Sat			
Cu-ZSM5	103.4 (2.5)	934.5 (4.0)	943.5 (4.0)	532.7 (2.5)	–	284.9 (2.8), 288.5 (2.8)
Cu-dmen-ZSM5	103.4 (2.4)	Cu(II) 934.7 (3.7), Cu(I) 933.4 (2.3) Cu(II) 943.6 (4.0)		532.9 (2.5)	400.4 (2.7), 402.4 (2.7)	285.1 (2.7), 286.5 (2.7)

All values are in eV.

of ethylenediamine in the samples prepared by various preparation modes the binding energy of Cu 2p<sub>3/2</sub> electrons was shifted downwards by 1.1 eV in comparison with the Cu-ZSM5. The intensity of the “shake-up” satellites was significantly lower compared to the samples Cu-en-ZSM5 with a low content of en and to the sample Cu-ZSM5, showing thus the lower spin density on Cu atoms.

The sample Cu-dmen-ZSM5 was analyzed by XPS method also after the thermal analysis up to 950 °C. The binding energy of Cu 2p<sub>3/2</sub> electrons measured for the ash of the sample Cu-dmen-ZSM5 is 933.5 eV (full width at half-maximum, FWHM = 2.4 eV) which is consistent with presence of Cu(I).

The X-ray powder diffraction patterns of Cu-dmen-ZSM5 and Cu-ZSM5 are similar except for some minor amplitude variations (Fig. 2). The zeolitic structure is dominant. In Fig. 2 we can see some differences of the intensity of peaks in the range

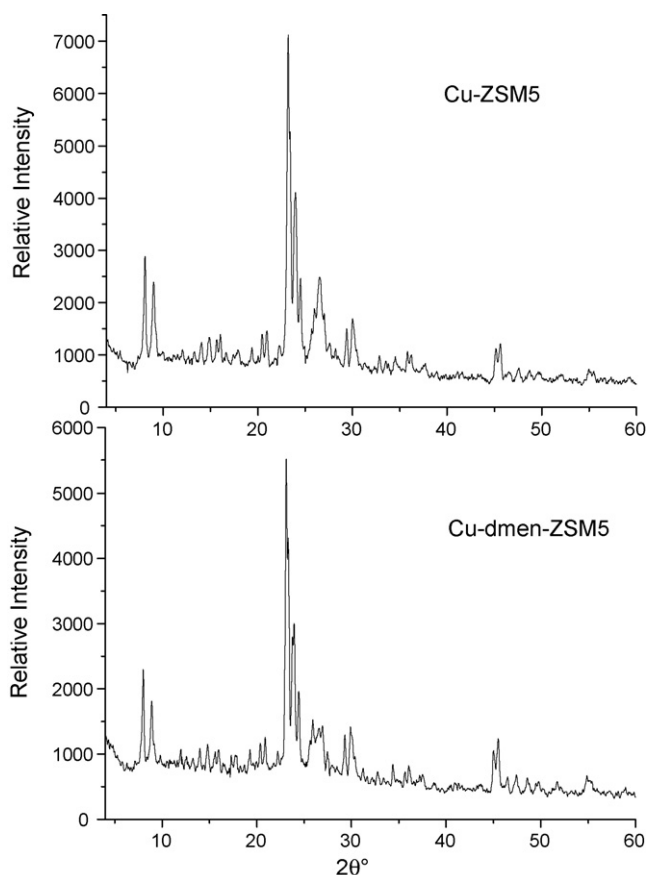


Fig. 2. X-ray powder diffraction patterns of the sample Cu-ZSM5 and Cu-dmen-ZSM5.

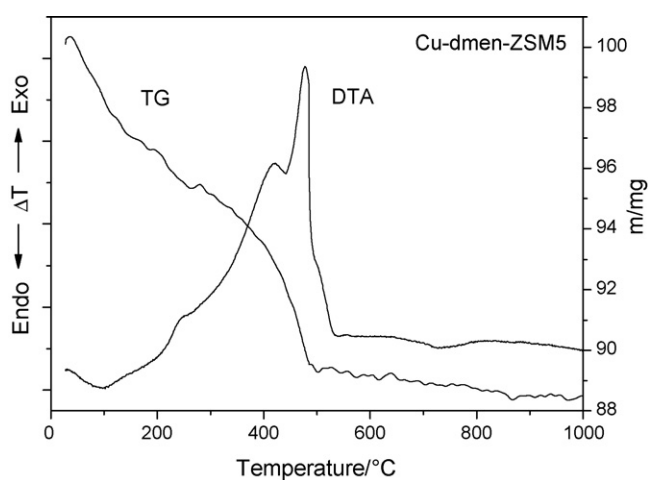


Fig. 3. DTA and TG curves of Cu-dmen-ZSM5 (before thermal analysis the sample was equilibrated at room temperature for 2 or 3 days at RH 53%).

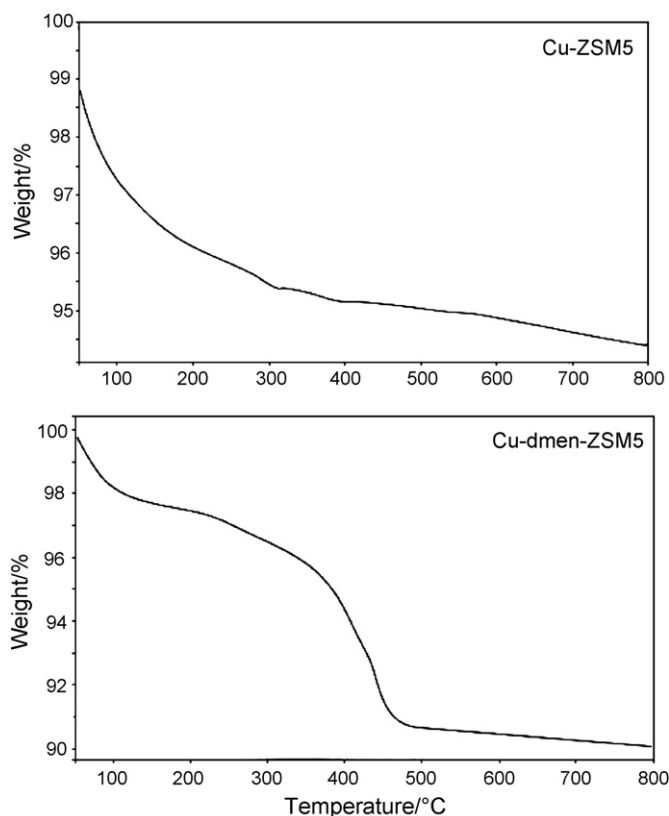


Fig. 4. TG curves of the sample Cu-ZSM5 and Cu-dmen-ZSM5.

from  $5^\circ$  to  $10^\circ$   $2\theta$  and also from  $20^\circ$  to  $28^\circ$   $2\theta$ . The broad peak, medium strong at  $2\theta = 26.5^\circ$ , corresponding to  $d = 3.35\text{--}3.36$  Å, may be due to the strongest of few characteristic  $\text{SiO}_2$  signals. Dimethylethylenediamine itself does not give any diffraction characteristics and is thus distributed in the zeolitic channels. The results of X-ray powder diffraction patterns of Cu-dmen-ZSM5 are similar to the results of X-ray powder diffraction patterns of copper form of ZSM5 containing ethylenediamine (Cu-en-ZSM5) [1].

The results of the thermal analyses (Figs. 3 and 4) and XPS clearly show different properties of the two solids Cu-ZSM5 and Cu-dmen-ZSM5. The products containing dimethylethylenediamine have different DTA curve in comparison with Cu-ZSM5 (which was already presented in refs. [1,2]). On the DTA curve of the product Cu-dmen-ZSM5 (Fig. 3) we can see a strong double exothermic peak (unlike the DTA curve of Cu-ZSM5 which is without it [1,2]) with the maximum at  $500^\circ\text{C}$  and with a clear loss of mass on the TG curve. Fig. 4 presents a more detailed comparison of the mass loss of Cu-ZSM5 and Cu-dmen-ZSM5. Both the products contain water, the water content depends on the relative humidity of the surrounding. The mass loss on the TG curve of Cu-ZSM5 corresponds to about 6–10 wt.% of water. At the RH 53% the water content was 10% (Fig. 3). In the sample Cu-dmen-ZSM5 the water content is

lower (3–4%). The main part of the decomposition process of the product Cu-dmen-ZSM5 is at remarkably higher temperatures than the boiling point of dimethylethylenediamine ( $116^\circ\text{C}$ ). It provides evidence in favour of “strong” bond and irreversibility of the dmen–zeolite interaction.

To obtain more information about the thermal decomposition of the “dmen–zeolite complex” the pyrolysis gas products of the sample Cu-dmen-ZSM5 were studied by the mass spectroscopy in inert atmosphere (in helium). The study of the decomposition gas products in the inert atmosphere corresponds with the DTA and TG results in air. The decomposition process can be documented by the curve of the total ion current on the mass detector versus sample temperature (Fig. 5) and by the total mass spectrum of the substances released during the whole decomposition process (Fig. 6). In Fig. 5 there are two curves of two products Cu-dmen-ZSM5 prepared with different mode of preparation. The first product is prepared with 0.1 M  $\text{CuSO}_4$  solution (Fig. 5a) and the second one (Fig. 5b) with 1 M  $\text{CuSO}_4$  solution. In the temperature range from 25 up to  $200^\circ\text{C}$  (Fig. 6a) the results of the mass spectroscopy confirmed released water, but also a beginning of the decomposition of the organic ligand. The spectrum of the released products (Fig. 6a and b) is large and includes substances developed by the decomposition of the dimethylethylenediamine as well as by their following conden-

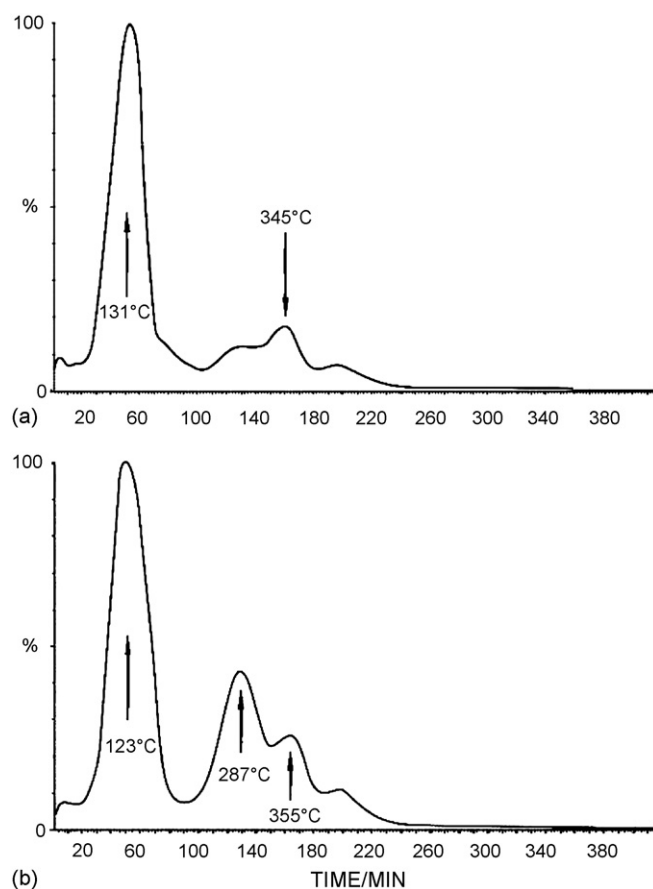


Fig. 5. Total ion current during dynamic heating of the sample Cu-dmen-ZSM5 prepared with 0.1 M solution of  $\text{CuSO}_4$  (a) and with 1 M solution of  $\text{CuSO}_4$  (b) carried out by combination of thermal analysis and mass spectroscopy in inert atmosphere in temperature range from 25 to  $600^\circ\text{C}$ .

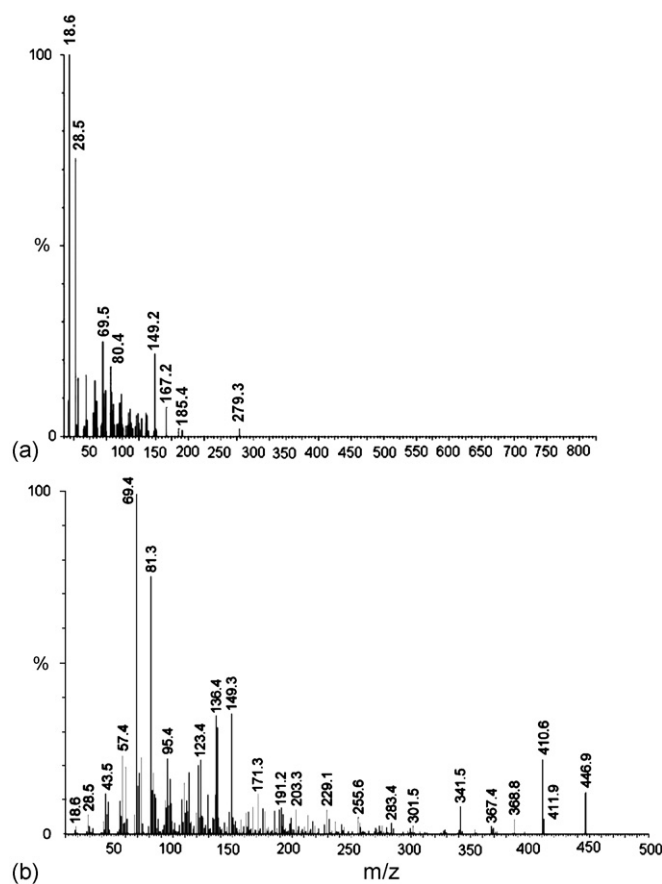


Fig. 6. The mass spectrum of ions releasing during dynamic heating of the sample Cu-dmen-ZSM5 (prepared with 0.1 M solution of  $\text{CuSO}_4$ ) in inert atmosphere in temperature range from 25 to  $200^\circ\text{C}$  (a) and from  $200^\circ\text{C}$  (b).

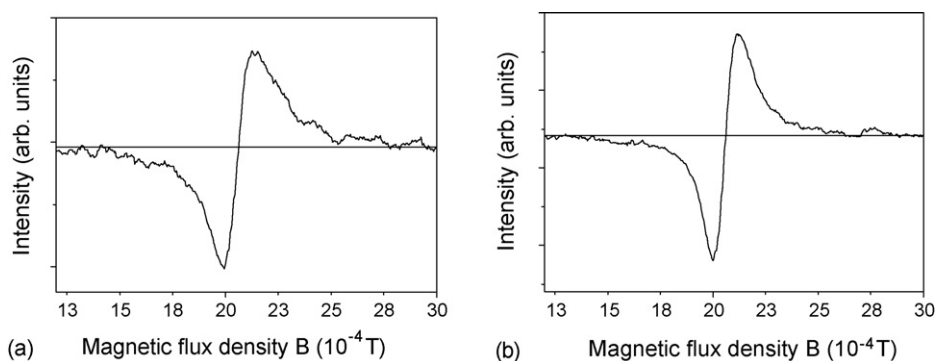


Fig. 7. The derivative CW  $^1\text{H}$  NMR spectra of the products Cu-ZSM5 (a) and Cu-dmen-ZSM5 (b), both measured at room temperature.

sation and polymerization. The releasing of the components with the molar masses higher than the mass of the primarily present components (molar mass of  $\text{H}_2\text{O}$  is 18.015 g/mol and of dimethylethylenediamine is 88.15) documents a complex mechanism of the decomposition process, which process involves the condensation and polymerization of the primarily releasing products. It is assumed to be a consequence of the catalytic effect of the silicate surface.

The  $^1\text{H}$  NMR spectra of the products Cu-ZSM5 and Cu-dmen-ZSM5 prepared by using 0.1 M solution of  $\text{CuSO}_4$  are in Fig. 7. In Cu-ZSM5 the NMR signal arises from the resonating protons of the water molecules that occupy various sites in the ZSM5 channels while in the sample Cu-dmen-ZSM5 it arises from resonating protons of both the water molecules and the dmen molecules. Their separation is not possible within the CW  $^1\text{H}$  NMR experiment. However, by using the method of second moment some conclusions about the state of the dmen molecules can be made. The parameter second moment  $M_2$  can be calculated from an experimentally obtained  $^1\text{H}$  NMR line by using a formula [27]. The calculation gives the values  $M_2 = 4.60 \text{ G}^2$  for Cu-ZSM5 and  $M_2 = 3.54 \text{ G}^2$  for Cu-dmen-ZSM5. The second moment represents the contribution of the nearest magnetic moments in the matter to the local magnetic field in the place of the resonating nuclei and is generally composed of a diamagnetic and a paramagnetic part:

$$M_2 = M_{2d} + M_{2p},$$

because the elementary magnetic dipoles in the matter are either induced by the applied magnetic field or they are permanently present there. The induced dipoles orient antiparallely to the field, while the permanent dipoles show tendency to turn parallelly to the field which means that the diamagnetic part may partly compensate the paramagnetic part.

When the matter contains both diamagnetic and paramagnetic atoms or molecules and when the diamagnetic molecules are coordinated in close vicinity of the paramagnetic ones, their diamagnetic effect partly reduces the local magnetic field in the place of the resonating nuclei in the measured sample. So that the lower value of the second moment in the Cu-dmen-ZSM5 compared with the Cu-ZSM5 may be explained by the presence of diamagnetic component in the former in the following way: if a part of the formerly paramagnetic Cu(II) present in the product Cu-ZSM5 changed in the process of preparation of the product

Cu-dmen-ZSM5 to the univalent state Cu(I) that is not paramagnetic, then the second moment decreases. The similar effect on the decrease of the second moment may have also the diamagnetic dmen molecules in the sample Cu-dmen-ZSM5. This can explain why the value of  $M_2$  of the sample Cu-dmen-ZSM5 with more resonating hydrogen nuclei is smaller than that of Cu-ZSM5.

As far as the NMR linewidths are concerned, their values determined as the distance between the peaks of the derivative recordings of the experimentally observed  $^1\text{H}$  NMR lines are:  $\Delta H = 1.70 \text{ G}$  for Cu-ZSM5 and  $\Delta H = 1.39 \text{ G}$  for Cu-dmen-ZSM5. It follows from the NMR theory that the linewidths of the NMR resonance lines are in inverse proportion to the hydrogen nuclei mobility which fact in our case indicates an intensification of the hydrogen nuclei motion in the sample Cu-dmen-ZSM5 compared to the sample Cu-ZSM5. The intensification can be caused by the rotation of  $\text{CH}_2$  and  $\text{CH}_3$  groups that are present in the dmen contained in the Cu-dmen-ZSM5 zeolite.

The results of the NMR measurements confirmed the different properties of two studied products Cu-ZSM5 and Cu-dmen-ZSM5.

Further study is now in progress to find out if there is some possibility of redox reaction between copper and dmen and if there occur some changes of the organic ligands.

#### 4. Conclusion

The thermal analyses and XPS significantly contributed to the characterization of the organomodified copper form of the synthetic zeolite ZSM5 containing dimethylethylenediamine. The methods of thermal analysis as well as the study of the released gas products by the mass spectroscopy contributed also to the explanation of the interaction of dimethylethylenediamine and copper forms of synthetic zeolite ZSM5.

The main part of the decomposition process of the product Cu-dmen-ZSM5 occurs at the remarkably higher temperatures than the boiling point of dimethylethylenediamine. It provides evidence in favour of “strong” bond and irreversible interaction of dmen–zeolite. The decomposition process of the zeolitic products with dimethylethylenediamine is characterized by the development of a wide spectrum of substances with atomic mass from 18 to higher atomic mass units.

Further study would be required for more detailed characterization of the organic ligand as well as about the released gas products.

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