Journal of Inclusion Phenomena and Macrocyclic Chemistry **39:** 181–186, 2001.

Study of Copper Forms of the Synthetic Zeolite ZSM5 Containing Ethylenediamine

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(Received: 11 February 2000; in final form: 3 June 2000)

Key words: synthetic zeolite, ZSM5, ethylenediamine, copper, complex, NMR, XPS, DTA

Abstract

Synthetic zeolite ZSM5 and its copper forms containing ethylenediamine (en) have been investigated by X-ray powder diffractometry, NMR and X-ray photoelectron spectroscopies, CHN, EDS and thermal analyses. Copper cations exchanged into the channels of synthetic zeolite ZSM5 formed coordination complexes with ethylenediamene. By different modes of preparation we obtained three Cu-en-ZSM5 zeolitic products with different composition, colour and other properties. The content of the ethylenediamine in the zeolitic products was 1.5–6 wt.% (dependent of the mode of preparation).

Introduction

Many new inclusion compounds can be prepared by using natural and synthetic zeolites as host materials, where various inorganic or organic molecules are included in the zeolitic channels [1, 2].

The natural zeolite of the clinoptilolite type may be used in practice for the sorption of fertilizers, agrochemicals such as insecticides or growth stimulators, disinfectants, perfumes, toxic elements, cyclodextrins and pharmaceuticals [3–8]. In previous papers the electrical properties of natural and synthetic zeolitic products containing iodine, iodide and silver ions have been studied [8–12]. The presence of iodine and iodide ions in the zeolitic products contributed to their higher electrical conductivity [7, 8]. The composite material of K-ZSM5 and AgI is also interesting. In this composite material the silver iodide forms a thin conductive shell on the surface of the K-ZSM5 particles [9].

The exchange of $[\mathrm{Cu(en)}_x]^{2+}$ on A type, X, Y zeolites and montmorillonite is known from the literature [13]. Adsorption of ethylenediamine (in the gas phase) on a dehydrated CuA zeolite gives only $[\mathrm{Cu(en)}]^{2+}$. In the presence of water $[\mathrm{Cu(en)}_2]^{2+}$ and $[\mathrm{Cu(en)}_3]^{2+}$ were synthesised on the surface [14]. The effect of ethylenediamine on Co^{2+} ion exchange in zeolite ZSM5 was also studied. According to the results of the spectroscopic and magnetic studies the compound formed with cobalt is the adduct $([\mathrm{Co(en)}_3]^{2+})\mathrm{O}^{\cdot-}$, in which the cationic complex is the high spin octahedral cobalt species (the first coordination sphere) and the superoxide ($\mathrm{O}_2^{\cdot-}$) is the low-spin one (the second coordination sphere). The structure of the zeolite ZSM5 promotes the migration of the adduct to the surface. The stability of the adduct on the surface can be explained by its negative charge density [14].

The present study was aimed at the preparation and characterization of copper forms of synthetic zeolite ZSM5 containing ethylenediamine by different methods and to the investigation of the influence of the different modes of preparation on the properties of the obtained products. Several techniques have been applied in order to understand the measurements: XRD, XPS, TA, NMR, EDS, morphology, colour and washing. The first four techniques give information on both surface and bulk properties whereas the remaining four are surface connected.

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Experimental

Chemicals and materials

In our study we have used a synthetic zeolite ZSM5 (Slovnaft a.s.Bratislava) with the chemical composition (without water): $x\mathrm{Na_2O}\cdot x\mathrm{Al_2O_3}\cdot y\mathrm{SiO_2}$ ($x = 0.8 \pm 0.15$, $y = 20$–45). ZSM5 was thermally activated for 3–4 hours by heating at continuously increasing temperature in the range from 150 to 400 °C (1 hour at 400°C). Copper sulphate, ethylenediamine and other chemicals were of p.a. purity (Lachema Brno).

Material preparation

Cu-ZSM5

Thermally activated ZSM5 was mixed with $CuSO_4$ solution [15]. After two hours of intensive mixing the heterogeneous mixture was decanted with distilled water and centrifuged (the presence of SO_4^{2-} ions in water after the decanting was checked by a solution of $BaCl_2$). The zeolitic product was dried at 60-80 °C.

Cu-en-ZSM5 I (mode I)

Cu-ZSM5 (3 g) was mixed with 5 mL ethylenediamine. The heterogeneous mixture was left to stand for 1 hour with occasional mixing (at room temperature) and then was decanted with distilled water and centrifuged. The zeolitic product was dried at 70–75 °C.

Cu-en-ZSM5 II (mode II)

Cu-ZSM5 (3 g) was mixed with 7 mL of solution of $[Cu(en)_2]SO_4$ (preparation: 100 mL of 1M $CuSO_4$ + 1.5 mL of en). The heterogeneous mixture was left to stand for 1 hour with occasional mixing (at room temperature) and then decanted with distilled water and centrifuged. The zeolitic product was dried at 70-75 °C.

Cu-en-ZSM5 III (mode III)

ZSM5 (3g) was mixed with 6 mL of solution of $[Cu(en)_2]SO_4$(preparation: 100 mL of 1M $CuSO_4$ + 1.5 mL of en).The heterogeneous mixture was left to stand for 1 hour with occasional mixing (at room temperature) and then was decanted with distilled water and centrifuged. The zeolitic product was dried at 70-75 °C.

Instrumental methods

The content of copper and other elements in the solid zeolitic materials was determined by electron microprobe measurements (JXA-5A, JEOL) applying Kevex and by EDS analyses using a TESLA BS 34O scanning electron microscope (TESLA ELMI a.s. with a LINK ISIS 300 microanalyser).

CHN analyses were performed on a Perkin Elmer 2400 Elemental Analyser. X-ray powder diffraction patterns were recorded with a Philips PW 1710 Diffractometer using CuK_α radiation.

X-ray photoelectron spectra (XPS) and X-ray excited Auger spectra were obtained with a VG ESCA 3 MkII spectrometer using AlK_α achromatic radiation ($h\nu = 1486.6$ 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 Cu 2p, Si 2p, O 1s, C 1s, N 1s, S 2p and Cu $L_3M_{45}M_{45}$ regions. 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 spectral accumulation 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. The peak positions and areas were determined by fitting the unsmoothed experimental data after subtraction of the Shirley [16] background. Quantification of the element surface concentration ratios was accomplished by correcting the integral intensities of the photoemission peaks for their cross-sections [17] and accounting for the dependence of the analyser transmission [18] and electron mean free paths on kinetic energy [19]. Core level binding energies were determined with an accuracy of ±0.2 eV. The results obtained did not depend on the angle of electron detection, showing thus the absence of measurable surface concentration gradients.

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 (also 200 mg), sensitivities: 50 mg (also 20 and 100 mg), DTA 1/3, DTG 1/3, heating rate 9 °C min^{-1}).

All NMR spectra were taken at room temperature by using a CW-NMR spectrometer constructed at the Department of Physics, Technical University in Košice [20], working at a frequency of 10.545 MHz. The derivative recordings were averaged out of 14 accumulated repetitions. Two series of measurements were carried out. The first series on the samples prepared as mentioned above, and the second one on the same samples that had been heated up to 100 °C and left for 10 minutes at this temperature to remove at least a part of the adsorbed water molecules in the ZSM5 channels.

Results and discussion

The copper form of the synthetic zeolite ZSM5 (Cu-ZSM5) was prepared by ion exchange starting from Na-ZSM5 with a copper sulfate solution. The reaction of Cu-ZSM5 with ethylenediamine (in the liquid phase) gave a light-violet zeolitic product containing Cu(II) ions and ethylenediamine (Cu-en-ZSM5 I, mode I). Using the next two modes (II and III) of preparation starting from Cu-ZSM5 and from Na-ZSM5, two products were obtained which were different in colour and other properties. The product Cu-en-ZSM5 II (mode II) was light-blue and Cu-en-ZSM5 III (mode III) was light-violet.

It is known from the literature [1], 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 $CuSO_4$ from the zeolitic channels thoroughly. In cases,

Table 1. Chemical analyses of the products Cu-en-ZSM5 I, II and III according to the results of electron microprobe measurements and EDS (for copper content), CHN (for en and H_2O content) and TG (for H_2O content).

Sample	Colour	Cu (wt, %)	en (wt, %)	H_2O (wt, %)
Cu-en-ZSM5 I	Light-violet	5.36	6.0	3.0
Cu-en-ZSM5 II	Light-blue	9.15	1.5	6.5
Cu-en-ZSM5 III	Light-violet	4.94	3.0	5.0

Table 2. Surface concentrations of elements calculated from XPS data (relative to Si = 1).

Element Sample	Cu	O	N	C	S
Cu-en-ZSM5 I	0.02	2.0	0.077	0.33	0
Cu-en-ZSM5 II	0.12	2.2	0.019	0.29	0.030
Cu-en-ZSM5 III	0.01	2.0	0.020	0.28	0

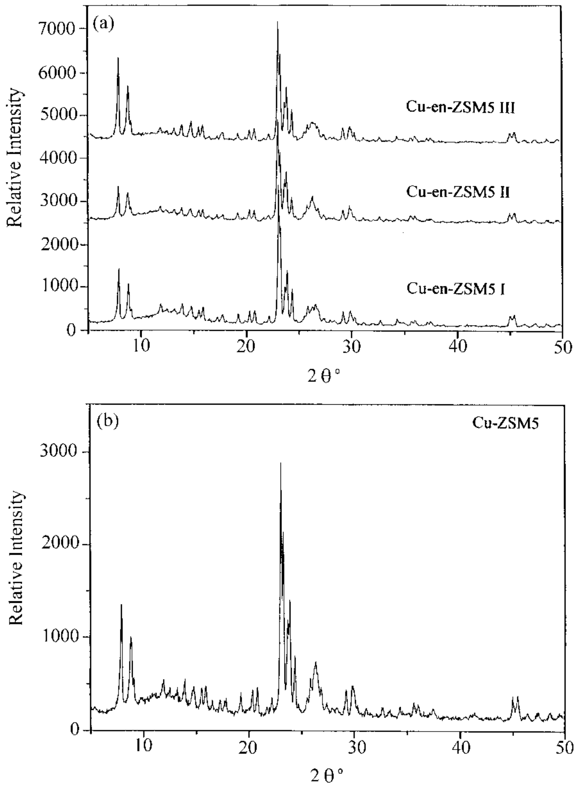

Figure 1. X-ray powder diffraction patterns of Cu-en-ZSM5 I, II, III (a) and Cu-ZSM5 (b).

where a part of the $CuSO_4$ was not thoroughly washed out from the channels, XPS analysis confirmed the presence of sulphur. But after adding ethylenediamine, the $CuSO_4$ is washed out from the channels very easily in the form of dark-blue solutions of coordinate salt (containing the $[Cu(en)_2]^{2+}$ cationic complex).

Electron microprobe, EDS analyses and XPS (Tables 1 and 2) confirmed the presence of copper in Cu-ZSM5 and in all products Cu-en-ZSM5 I, II, III. Within the error limits the molar ratio Si/Al = 20.4 in the product Cu-ZSM5 was the same as that in the starting material Na-ZSM5 (Si/Al = 20.1). According to EDS analyses the content of sodium in Cu-en-ZSM5 I (0.186 wt, %), Cu-en-ZSM5 II (0.181 wt, %) and Cu-en-ZSM5 III (0.170 wt, %) was also analysed. The 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. CHN analyses confirmed the presence of ethylenediamine in all three products prepared by modes I–III (Table I). The results of CHN analyses were in good agreement with the results of TG. The highest content of en was found in Cu-en-ZSM5 I and the lowest content in Cu-en-ZSM5 II. The product Cu-en ZSM5 I was prepared by mode I, where en solution was used, unlike the modes II and III where a solution containing complex cation Cu(II)-en was used. The zeolitic products Cu-en-ZSM5 I and III are similar not only by colour but also by other properties.

The surface atomic composition (relative to Si = 1) of the samples obtained by XPS analysis is listed in Table 2. It follows from these data that the concentration of Cu is an order of magnitude lower for samples Cu-en-ZSM5 I and III (within the experimental error) than for the sample Cu-en-ZSM5 II. The sample Cu-en-ZSM5 II contains also sulphur, so that $CuSO_4$ or $[Cu(en)_x]SO_4$ included in the channels can be assumed.

In Table 3 the measured core level binding energies and values of the modified Auger parameters (calculated as a sum of the binding energy of Cu $2p_{3/2}$ electrons and the kinetic energy of Cu $L_3M_{45}M_{45}$ Auger electrons) are summarized. The binding energy of Cu $2p_{3/2}$ electrons obtained for samples Cu-ZSM5 and Cu-en-ZSM5 II, 935 ± 0.1 eV, is characteristic for divalent, paramagnetic Cu^{2+} ions. The intense satellite structure in the spectra of Cu 2p electrons (see Figure 4) as well as the calculated values of the modified Auger parameter, α, are consistent with this conclusion. For the samples Cu-en-ZSM5 I and III the binding energy of Cu $2p_{3/2}$ electrons is shifted by 1.1 eV towards lower binding energy. The intensity of the “shake-up” satellites is significantly lower compared to samples Cu-en-ZSM5 II and Cu-ZSM5, thus showing the lower spin density on Cu atoms [21].

The X-ray powder diffraction patterns revealed by the transmission and reflecting techniques are very similar, except for some minor amplitude variations (Figure 1a,b). The zeolitic structure is dominant. No extra signals are observed although about 10% by weight of additives have been introduced. In Figure 1a we can see some differences of the intensity of peaks in the range from 5° to 10° 2θ and also from 20° to 28° 2θ. The broad, medium strong peak at 2θ = 26.5°, corresponding to d = 3.35–3.36 Å, may be due to the strongest of a few characteristic SiO_2 signals. Ethylenediamine itself does not give any diffraction characteristics and is thus distributed in the zeolitic channels.

The results of thermal analyses (Figure 2a–d), EDS and XPS clearly shows the different properties of the four solids. The products containing ethylenediamine (Figure 2a–c) have different DTA curves in comparison with Cu-ZSM5 (Figure 2d). According to the thermal analysis Cu-ZSM5

Table 3. Binding energies of core level electrons, widths of the measured lines at half-height (in parentheses) and modified Auger parameters, α. All values are in eV.

Line Sample	Si 2p	Cu $2p_{3/2}$	O 1s	N 1s	C 1s	S 2p	α
Cu-en-ZSM5 I	102.7 (2.5)	933.9 (3.8)	532.0 (2.6)	399.7 (2.9)	284.8 (3.1) 288.6 (3.1)	–	1848.3
Cu-en-ZSM5 II	103.0 (2.5)	935.1 (3.8)	532.3 (2.8)	401.1 (3.3)	284.8 (2.9) 288.7 (2.9)	168.3 (2.8)	1850.6
Cu-en-ZSM5 III	103.0 (2.6)	933.9 (3.7)	532.3 (2.7)	400.5 (3.5)	284.8 (2.8) 288.4 (2.8)	–	1846.9

contains 7.5% of water. In Figure 2a–c we can see that the different modes of preparation correspond to different thermal properties. All three products with en contain water. A part of the water was replaced by ethylenediamine. The Cu-en-ZSM5 I has the highest content of en but the lowest content of water (Table 1). In the sample Cu-en-ZSM5 II it is the opposite. On the DTA curve of the product Cu-en-ZSM5 I (Figure 2a) we can see first an exothermic peak with a maximum at 200 °C and in the next exothermic process a strong double exothermic peak with a maximum at 400 °C (in the temperature range from 290 °C to 480 °C). During thermal decomposition of the product Cu-en ZSM III the exothermic process occurs in the similar temperature range with the maximum of the exothermic peak on the DTA curve at 400 °C. On the DTA curve of Cu-en-ZSM5 II only one double exothermic peak with maximum at 300 °C is observed. The identification of released gas products from the samples Cu-ZSM5 and Cu-en-ZSM5 I, II, III by the combination of thermal analysis and mass spectrometry is the subject of our next paper [22]. The first results of the combination of thermal analyses and mass spectrometry measurements in an inert atmosphere confirmed a release of water from the products Cu-en-ZSM5 I, II, III. The main part of the decomposition process of all three products is remarkably higher than the boiling point of ethylenediamine. It provides evidence in favour of a “strong” bond and irreversible interaction of en-zeolite. These studies proved a similarity of the products Cu-en-ZSM5 I and III and a difference of the product Cu-en-ZSM5 II, and also a release of SO_2 in Cu-en-ZSM5 II, in accordance with the EDS and XPS results.

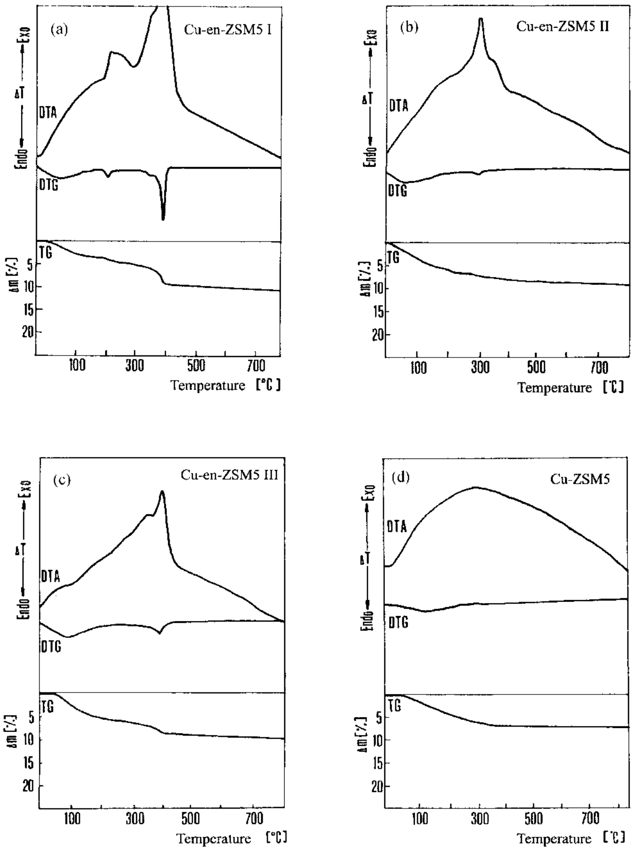

Figure 2. DTG, DTA and TG curves of Cu-en-ZSM5 I (a), Cu-en-ZSM5 II (b), Cu-en-ZSM5 III (c) and Cu-ZSM5 (d).

The ^{1}H NMR spectra are given in Figure 3. The lines consist of at least two components that are well observed in sample Cu-ZSM5 and Cu-en-ZSM5 II. The Cu-ZSM5 does not contain en, and the Cu-en-ZSM5 II has the lowest content of en. The lineshape of the next two samples Cu-en-ZSM5 I and III is apparently different from the lineshape of the previous ones, which in fact is likely caused by their higher en content. The NMR signal stems both from the protons of the resonating water molecules and the protons in the en molecules, and separating these two signals is not possible. Despite this some conclusions about the en content can be made.

In the following text the spectra of thermally treated samples Cu-ZSM5 and Cu-en-ZSM5 I, II, III are compared. In Cu-ZSM5 the NMR signal arises from the resonating protons of water molecules that occupy various sites in the ZSM5 channels. The NMR lineshape of the Cu-en-ZSM5 II (the lowest en content) has a similar form to that of Cu-ZSM5. The main difference observed is in the intensity of the narrow line and in its linewidth. The intensity increases and the linewidth is smaller than that in Cu-ZSM5. Its value is 2.20 G in Cu-ZSM5 and 1.38 G in Cu-en-ZSM5 II. The narrowing of the linewidth indicates either the intensification of the molecular motion, or more distant resonating nuclei. The lineshapes of Cu-en-ZSM5 I and III apparently differ from those of Cu-ZSM5 and Cu-en-ZSM5 II. It can be seen in Figure 3, that the first two samples, i.e., Cu-en-ZSM5 I and III have remarkably narrower lines when

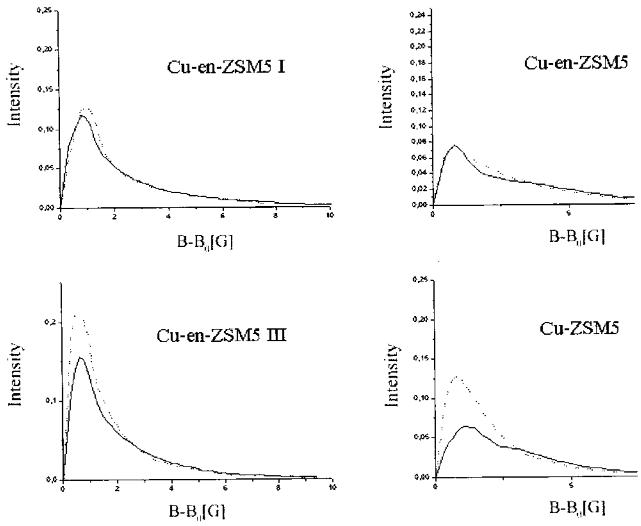

Figure 3. Normalized ^{1}H NMR spectra of Cu-en-ZSM5 I, II, III and Cu-ZSM5 before (– – –) and after (——) thermal treatment. The spectra were taken at a resonance frequency 10.545 MHz.

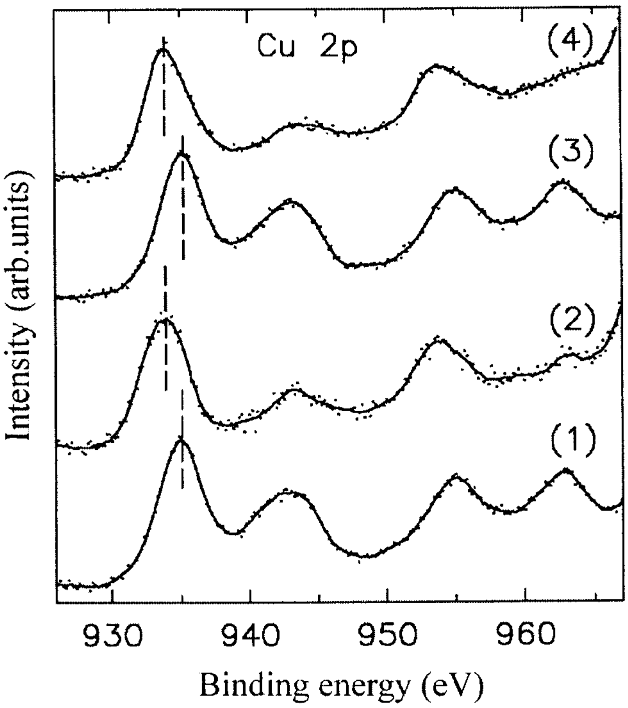

Figure 4. Photoelectron spectra of Cu 2p electrons for samples Cu-ZSM5, Cu-en-ZSM5, I, II and III, spectra (1), (2), (3) and (4), respectively. The spectra are normalized to the same height.

compared to the other two samples, i.e., Cu-en-ZSM5 II and Cu-ZSM5. As for their linewidths, there is only a slight tendency of narrowing when these two groups are compared. The linewidths, evaluated as the distance between two peaks, are 1.53 G for Cu-en-ZSM5 I and 1.25 G for Cu-en-ZSM5 III. Another remarkable NMR parameter is the second moment M_2, that can provide information about the surrounding of the resonating atoms [23]. However, there is also thermal motion that influences the second moment. M_2 is composed of a diamagnetic and a paramagnetic part:

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

Here M_{2d} is the contribution of the nearest protons and M_{2p} is the contribution of the spins of the paramagnetic species in the sample.The calculation of M_2 gives the values 5.91 G^2, 6.89 G^2, 5.18 G^2, 7.39 G^2 for the series of the thermally treated samples Cu-en-ZSM5 I, II, III and Cu-ZSM5, respectively. The changes of M_2 can originate from more factors, as mentioned above. Generally, more homogeneous distribution of the resonating nuclei results in a higher second moment value. When the second moment M_2 values of the four samples are compared, then we can say, that the samples Cu-ZSM5 and Cu-en-ZSM5 II with low en content have a more homogeneous distribution of resonating nuclei than the samples with higher en content, i.e., Cu-en-ZSM5 I and III. The difference is remarkable, and it can be suggested that the NMR resonance lines depend on the en content. Because the Cu atom is paramagnetic and en is diamagnetic, the en coordinated to Cu(II) supresses the influence of Cu ions on the NMR resonance line. The higher the concentration of en, the more the lineshape resembles its original form. Similar effects were reported in the literature (see e.g., reference [23], p. 328). There, in a commercial zeolite with iron impurity, a small amount of diamagnetic platinum had been introduced. Making definite conclusions from the NMR experiments is not possible at the moment. The main problem is that the NMR signal of ethylenediamine is partially obscured by the undesirable NMR signal of water protons that are present in the measured samples.

According to our first measurements of ac conductivity the presence of ethylenediamine in the zeolitic products Cu-en-ZSM5 I, II, III contribute to the higher values of electrical conductivity in comparison with Cu-ZSM5. In our previous paper about inclusion compounds of tetracyanonickelates containing etylenediamine ligands, the presence of ethylenediamine contributed in all the studied samples to higher values of the electrical conductivity [24, 25].

Conclusion

By different preparation techniques three different zeolitic inclusion compounds were obtained which contain ethylenediamine (1.5–6%) in the zeolitic channels. By using preparation modes I and III copper (II) ethylenediamine zeolite complexes with similar properties including colour were obtained, unlike the product prepared by using the preparation mode II. It is different from the mentioned products and it has the lowest ethylenediamine content.

Ethylenediamine is connected to Cu(II) ions by coordinative bonds. The presence of ethylenediamine changed the original properties of Cu-ZSM5. The changes are influenced by the ethylenediamine content and also by the mode of preparation.

Acknowledgement

The authors wish to thank Dr. Loredana Massinelli and Dr. Sonia Murchia Mascaros from Department of Chemistry, University of Perugia in Italy for the X-ray powder diffractometry measurements.

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