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Thermochemical study of sorption of pyridine derivates by copper forms of synthetic and natural zeolites

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Abstract Sorption of hazardous pyridine derivates by copper forms of synthetic zeolite ZSM5 and natural zeolite of the clinoptilolite type (CT) has been investigated. Sorption of 2-chloropyridine (clpy) and 2-ethylpyridine (ethylpy) from liquid and gas phase by copper forms of zeolites (Cu-ZSM5 and Cu-CT) has been studied by CHN analysis, thermal (TG, DTG and DTA) analysis, FTIR spectroscopy, X-ray powder diffractometry and determination of the surface areas and the pore volumes by low-temperature adsorption of nitrogen. The results of thermal analyses of Cu-ZSM5, Cu-(clpy)$_x$-ZSM5, Cu-(ethylpy)$_x$-ZSM5, Cu-CT, Cu-(clpy)$_x$-CT and Cu-(ethylpy)$_x$-CT zeolitic products with different composition (x depends on the experimental conditions of sorption of pyridine derivates) clearly confirmed their different thermal properties and the sorption of pyridine derivates. The main part of the decomposition process of zeolitic samples containing pyridine derivates occurs at considerably higher temperatures than the boiling point of pyridine derivates proving strong bond and irreversibility of clpy- and/or ethylpy–zeolite interaction. FTIR spectra showed well-resolved bands for pyridine derivates in the Cu-(clpy)$_x$-zeolite and Cu-(ethylpy)$_x$-zeolite. Surface area and pore volumes of the samples Cu-clpy-ZSM5, Cu-ethylpy-ZSM5, Cu-clpy-CT and Cu-ethylpy-CT in comparison with Cu-ZSM5 and Cu-CT decreased due to the adsorption of pyridine derivates.

Keywords Clinoptilolite · Copper · Zeolite · ZSM5 · 2-Chloropyridine · 2-Ethylpyridine

Introduction

The study of the sorption of pyridine derivates by copper forms of synthetic zeolite ZSM5 and natural zeolite of the clinoptilolite type (CT) is a continuation of our previous study of copper forms of zeosorbents for removing pyridine from the liquid and gas phase, as well as other organic compounds [1–3].

Pyridine and its derivates constitute an important class of compounds with applications in pharmaceuticals, cosmetics and pesticides [4–6]. Alkylpyridines are toxic environmental pollutants commonly found in many surface waters and groundwaters near industries for the production

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of synthetic liquid fuel. Pyridine derivates are harmful and present high carcinogenic and mutagenic activity. The destruction of pyridine and its derivates has always been of interest in practice and in scientific research and methods such as biodegradation [7–11], adsorption [12, 13], combustion and photocatalysis [4–6, 14, 15] have been proposed for their removal. Biodegradation of pyridine is possible by various types of microorganisms [7–11], but chloropyridines, in particular, are known to be hardly biodegradable and highly toxic to fresh water and marine bacteria [15].

Amongst various treatment methods adsorption on zeolites looks like the most attractive one when effective, low-cost adsorbents and ion exchangers are used. Zeolite‘s use as adsorbents for environmental protection and other applications are stimulated by the good results obtained, the nontoxic nature of these materials, their availability in many parts of the world and low cost [16–23].

The methods of thermal analysis significantly contribute to the characterization of zeolitic [1–3, 24–28] and other silicate materials [29].

The aim of our present study was the sorption of pyridine derivates: 2-chloropyridine (from the liquid and gas phase) and 2-ethylpyridine (from the gas phase) by copper forms of the synthetic zeolite ZSM5 (Cu-ZSM5) and natural zeolite of CT (Cu-CT). The zeolitic products containing pyridine derivates as well as starting zeolitic adsorbents Cu-ZSM5 and Cu-CT were characterized by CHN, FTIR spectroscopy, X-ray powder diffractometry, analysis of the surface areas and the pore volumes by low-temperature adsorption of nitrogen. The thermochemical properties were studied using thermal (TG, DTG and DTA) analyses and intermediate products of thermal decomposition were analysed by FTIR 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): $Na_2O = 2.683\%$, $CaO = 0.528\%$, $Al_2O_3 = 3.717\%$, $SiO_2 = 93.072\%$ (ratio $SiO_2/Al_2O_3 = 42.94$) and natural zeolite of the CT from East Slovakian deposit in Nižný Hrabovec with content of clinoptilolite 84% and the chemical composition (without water): 65.0–71.3% SiO_2, 11.5–13.1% Al_2O_3, 2.7–5.2% CaO, 2.2–3.4% K_2O, 0.7–1.9% Fe_2O_3, 0.6–1.2% MgO, 0.2–1.3% Na_2O, 0.1–0.3% TiO_2 (ratio $SiO_2/Al_2O_3 = 4.8–5.4$) [23].

The 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). Natural zeolite of the CT was thermally activated for 2 h by heating at 110 °C. Based on our long-term experimental experience, the thermal activation of natural zeolite was realized at lower temperature and shorter time than the thermal activation of synthetic ZSM5 [1, 28, 30]. The temperature and time of the thermal activation proved to be sufficient in such case if, after the thermal activation, the modification is realized using aqueous solution.

Copper sulphate (Merck), 2-chloropyridine (ACROS), 2-ethylpyridine (Aldrich) and other chemicals were of p.a. purity.

Material preparation

The copper forms of synthetic zeolite ZSM5 and natural clinoptilolite were prepared by reaction of thermally activated Na-ZSM5 and natural clinoptilolite by a reaction with $CuSO_4$ solution of two concentrations 0.1 and 1.0 mol dm^{-3}. The heterogeneous mixtures were after 2 h of stirring decanted several times and centrifuged to get rid of sulphate ions and then dried for 2 h at 90–100 °C. The copper forms were denoted as Cu-ZSM5 and Cu-CT, marked by (0.1 M) or (1 M) denotation according to the solution concentration used.

The prepared copper forms of ZSM5 and clinoptilolite were used for sorption of 2-chloropyridine from the liquid and gas phase, 2-ethylpyridine only from the gas phase.

The products obtained by sorption of 2-chloropyridine from the liquid phase were prepared from the copper forms of zeolites (6 g) by adding 2-chloropyridine in liquid phase (for Cu-ZSM5 12 mL, for Cu-CT 8 mL). The heterogeneous mixtures were left to stand (in fume hood) for 1 h with occasional mixing, decanted several times and centrifuged. The final products were dried at room temperature in a dark desiccator over silica gel. The products were denoted as Cu-clpy-ZSM5 (L) and Cu-clpy-CT (L).

The products obtained by sorption from the gas phase of pyridine derivates: 2-chloropyridine and/or 2-ethylpyridine were prepared by exposing a layer of copper forms Cu-ZSM5 and Cu-CT (5 g) to vapours of pyridine derivate for 10 days at room temperature in dark desiccators (desiccators were placed in fume hood). Then the samples were left in the desiccators without vapours of pyridine derivate for the next 3 days. The products were denoted as Cu-clpy-ZSM5 (G), Cu-clpy-CT (G), Cu-ethylpy-ZSM5 (G) and Cu-ethylpy-CT (G).

Measurements

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

Thermal analyses TG, DTA and DTG were carried out at temperature up to 800 °C in air on a NETZSCH STA

409 PC/PG under the conditions: sample weight 25 mg, heating rate 10 °C min^{-1}, and Al_2O_3 crucible.

Infrared spectra were obtained using the KBr disc technique in the range 400–4000 cm^{-1} using an AVATAR 330 FTIR Thermo Nicolet IR spectrometer.

X-ray powder diffraction patterns were recorded on a Bragg-Brentano diffractometer Philips PW 1730/1050, using β-filtered Co K_α radiation, 40 kV/35 mA in the range of 2θ 3°–71°, step 0.02°.

The analysis of surface areas and the pore volumes of the zeolitic samples were performed on a GEMINI 2360 (Micrometrics USA). The specific surface area was determined by low-temperature adsorption of nitrogen. The samples were heated for 2 h at 105 °C before measurements.

Results and discussion

The zeoadsorbents on the basis of copper forms of synthetic zeolite ZSM5 and natural zeolite of the CT from the East Slovakian deposit in Nižný Hrabovec were used for removal of toxic 2-chloropyridine from the liquid and gas phase and 2-ethylpyridine from the gas phase. The removal of pyridine derivates was based on ion-exchange and sorption properties of zeolites. Both copper forms of synthetic ZSM5 and natural clinoptilolite (Cu-ZSM5, Cu-CT) were obtained in consequence of an ionic-exchange mechanism, starting from Na-ZSM5 and natural zeolite of the CT with copper sulphate solution with two different concentrations 0.1 and 1.0 mol dm^{-3}. It was found [26] that extra framework cations in zeolites have influence on the adsorption of organic compounds, affecting both the initial adsorption in the micropores as well as ordering of the adsorbed molecules.

By different experimental conditions of sorption of pyridine derivates from liquid and gas phase zeolitic products with different content of 2-chloropyridine and/or 2-ethylpyridine were obtained. The reaction of Cu-ZSM5 and Cu-CT with pyridine derivates gave a zeolitic product denoted as Cu-$(\text{clpy})_x$-ZSM5, Cu-$(\text{clpy})_x$-CT, Cu-$(\text{ethylpy})_x$-ZSM5 and Cu-$(\text{ethylpy})_x$-CT (x depends on the experimental conditions of sorption of 2-chloropyridine and 2-ethylpyridine).

The copper forms of both zeolites containing pyridine derivates as well as the starting sample Cu-ZSM5 and Cu-CT were analysed by the CHN, thermal (TG, DTG and DTA) analyses, FTIR spectroscopy, XRD and determination of the surface areas and the pore volumes by low-temperature adsorption of nitrogen. The content of copper in the starting copper zeolitic forms was determined by X-ray photoelectron spectroscopy [1, 2]. According to the results of XPS, the sample Cu-ZSM5 (0.1 M) prepared with lower concentration (0.1 mol dm^{-3}) of the $CuSO_4$ solution contains also a very small amount of sodium ions and the sample Cu-CT (0.1 M) contains a very small amount of calcium and potassium ions. The contents of these ions in the samples were not determined. The content of copper ions in the samples Cu-ZSM5 (1 M) and Cu-CT (1 M) was a little higher in comparison with the samples Cu-ZSM5 (0.1 M) and Cu-CT (0.1 M).

The results of CHN analyses and thermal analyses checked the presence of pyridine derivates after sorption by copper forms of synthetic ZSM5 and natural clinoptilolite. The results of the CHN analyses were in a good agreement with the results of thermal analyses. The comparison of the sorption ability of the copper forms of synthetic zeolite ZSM5 and natural zeolite CT showed that the synthetic zeolite sorbed more pyridine derivates than natural CT. The copper forms prepared with the higher concentration of the starting solution (1 mol dm^{-3}) sorbed a little more pyridine derivates in comparison with the copper forms prepared with the lower concentration of the starting solution (0.1 mol dm^{-3}). The average content of pyridine derivates in the zeolitic products after the sorption was as follows: Cu-clpy-ZSM5 8.8%, Cu-clpy-CT 4.8%, Cu-ethylpy-ZSM5 7.5% and Cu-ethylpy-CT 5%.

The odour of derivates of pyridine is very offensive. However, during the decanting of the products Cu-Clpy-CT, we noticed that their odour was different from the odour of the original 2-chloropyridine. After the sorption of 2-chloropyridine by the copper form of natural zeolite of CT (Cu-CT) the unpleasant smell has changed and the smell of the products Cu-clpy-CT resembled odour of certain natural plant materials. The new odour was difficult to characterize (it slightly resembled mint or peppermint). However, we did not observe this change of the odour after the sorption of 2-chloropyridine by Cu-ZSM5. In our present study the change of odour was not studied but it can be the object of further study.

The sorption of 2-ethylpyridine by zeoadsorbents has only been studied from a gas phase, because of the intensive and rapidly spreading toxic odour of 2-ethylpyridine the decantation and centrifugation would be very complicated.

Thermal analysis

The results of thermal analyses clearly show different properties of the starting zeosorbents Cu-ZSM5, Cu-CT and zeosorbents containing pyridine derivates Cu-clpy-ZSM5, Cu-clpy-CT, Cu-ethylpy-ZSM5 and Cu-ethylpy-CT (Figs. 1, 2, 3 and 4). The products containing pyridine derivates have different TG, DTG and DTA curves in comparison with starting copper forms Cu-ZSM5 and Cu-CT. The results of thermal analysis obtained for Cu-ZSM5 sample were reported in our previous article [2] and for Cu-CT in [1].

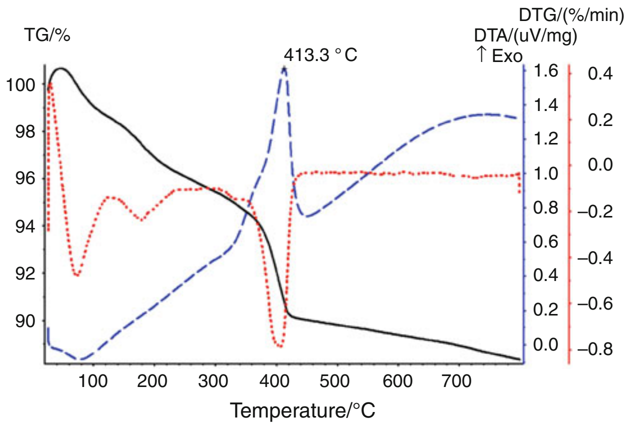

Fig. 1 TG (*solid line*), DTG (*dotted line*) and DTA (*dashed line*) curves of the sample Cu-clpy-ZSM5 (G) 1 M

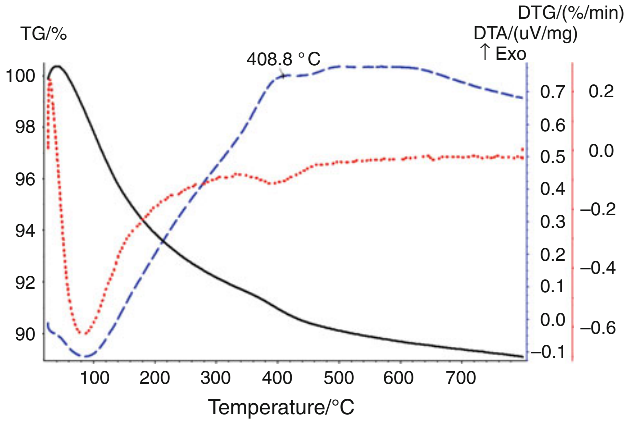

Fig. 2 TG (*solid line*), DTG (*dotted line*) and DTA (*dashed line*) curves of the sample Cu-clpy-CT (G) 1 M

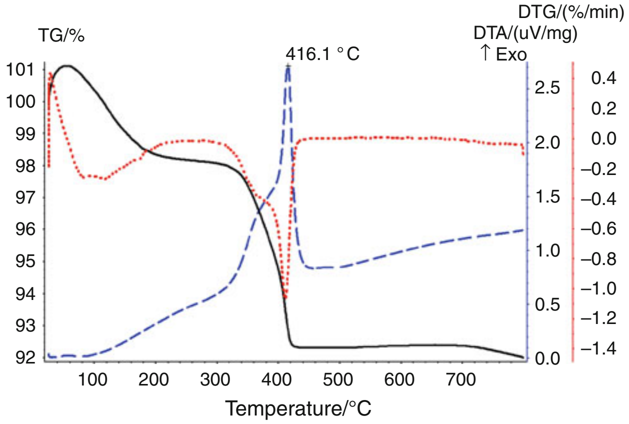

Fig. 3 TG (*solid line*), DTG (*dotted line*) and DTA (*dashed line*) curves of the sample Cu-ethylpy-ZSM5 (G) 1 M

It is known from literature [31, 32] that during thermal analysis pyridine is released in several steps from Brönsted and Lewis sites. Pyridine derivates are released from the zeolitic structure in several steps too.

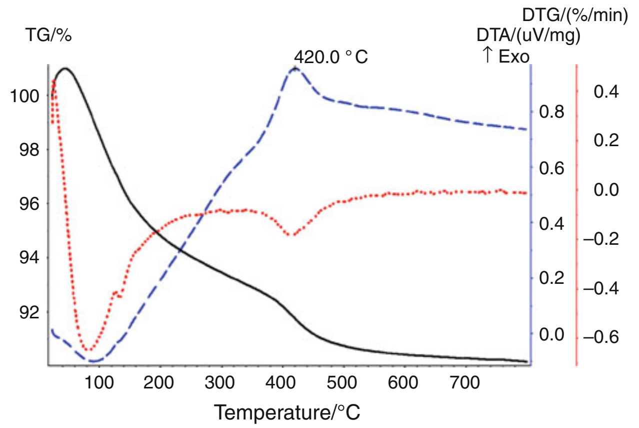

Fig. 4 TG (*solid line*), DTG (*dotted line*) and DTA (*dashed line*) curves of the sample Cu-ethylpy-CT (G) 1 M

During thermal analysis of the samples Cu-clpy-ZSM5 obtained by the sorption of 2-chloropyridine from the liquid and gas phase (Fig. 1) 2-chloropyridine was released at 130–450 °C in three steps: the first step at 130–240 °C, the second at 300–350 °C, the third step up to 450 °C with a maximum of the strong exothermic peak on the DTA curve at 413 °C and with a clear weight loss on the TG curve. It can be assumed that the releasing of 2-chloropyridine in the third step refers to 2-chloropyridine coordinated to copper ions. In the endothermic process up to the temperature 130 °C water is released. A small amount of 2-chloropyridine of the sample Cu-clpy-ZSM5 (G) obtained by the sorption of 2-chloropyridine from the gas phase can be released together with water in the endothermic process up to 130 °C.

Thermal analysis of the samples Cu-clpy-CT confirmed the release of 2-chloropyridine too (Fig. 2), but in lower amount. 2-chloropyridine was released in temperature range from 130 to 470 °C. On the DTA curve we can see endothermic process up to 150 °C. In this process water is released. Small amount of 2-chloropyridine from the samples Cu-clpy-CT (G) can release together with water at lower temperature. 2-chloropyridine coordinated to copper ions is released at 320–470 °C in the exothermic process with a maximum on DTA curve at 408 °C.

The desorption of 2-ethylpyridine from the samples Cu-ethylpy-ZSM5 (G) is similar to the desorption of 2-chloropyridine from Cu-clpy-ZSM5. A part of 2-ethylpyridine from the samples Cu-ethylpy-ZSM5 is released at 100–200 °C. The main part of 2-ethylpyridine is released at 300–450 °C in exothermic process with a strong maximum on the DTA curve at 416 °C (Fig. 3).

During thermal analysis 2-ethylpyridine from the samples Cu-ethylpy-CT (G) is released in several steps. The desorption of a part of 2-ethylpyridine from the samples Cu-ethylpy-CT (G) starts at lower temperatures during endothermic process together with water (Fig. 4). A very small peak on DTG curve is observed at 125 °C and the next, strong peak, is observed at 350–470 °C corresponding to a clear weight loss on the TG curve. In this exothermic process with maximum on DTA curve at 420 °C the part of 2-ethylpyridine coordinated to copper ions is released.

The main part of the pyridine derivates release from the products Cu-clpy-zeolite and Cu-ethylpy-zeolite occurs at remarkably higher temperatures than the boiling point of 2-chloropyridine (168 °C) and 2-ethylpyridine (149 °C). It provides evidence in favour of strong bond and irreversibility of the clpy– and ethylpy–zeolite interaction.

The IR measurements of the intermediate products of thermal decomposition of the sample Cu-clpy-ZSM5 (G) and Cu-ethylpy-ZSM5 (G) were performed to better understanding of the 2-chloropyridine and 2-ethylpyridine elimination. The results of the characterization of the intermediate products by FTIR spectroscopy are in the part FTIR spectroscopy (Figs. 7, 8).

The main part of pyridine derivates is chemisorbed on Brönsted and Lewis acid sites. Only in the case of the samples Cu-clpy-ZSM5 (G), Cu-ethylpy-ZSM5 (G), Cu-clpy-CT (G) and Cu-ethylpy-CT (G), which were obtained by the sorption of pyridine derivates from the gas phase a small amount of physisorbed pyridine derivates is released from the samples, together with water at lower temperature during endothermic process.

To obtain more information about the thermal decomposition of the samples Cu-clpy-ZSM5, Cu-ethylpy-ZSM5, Cu-clpy-CT and Cu-ethylpy-CT, mainly those concerning the decomposition products of thermal analysis, it will be necessary to analyse the decomposition products by mass spectroscopy too. The previous studies of the thermal decomposition of the copper forms of synthetic zeolite ZSM5 containing organic diamines (ethylenediamine and dimethylethylenediamine) confirmed that as a consequence of the catalytic effect of the silicate surface condensation and polymerisation reactions of the primarily releasing products occur [3, 27]. In the case of the study of copper forms of synthetic zeolite ZSM5 and natural clinoptilolite with pyridine derivates content there occurs oxidation (in air atmosphere) of the released pyridine derivates during exothermic process of thermal analysis [33] as well as there may occur other reactions of the released products as a result of the catalytic effect of the silicate surface.

FTIR spectroscopy

The presence of 2-chloropyridine and 2-ethylpyridine in the samples Cu-clpy-ZSM5, Cu-clpy-CT, Cu-ethylpy-ZSM5 and Cu-ethylpy-CT was confirmed by the IR spectra. The vibrations of the frameworks of zeolites give rise to typical bands at 1052–1059 cm^{-1} (stretching vibrations of Si–O groups), 547 cm^{-1} (deformation vibrations of Al–O–Si groups) and 444–454 cm^{-1} (deformation vibrations of Si–O–Si groups). In the O–H stretching region there is a peak observed at 3609 cm^{-1} assigned to O–H groups attached to extra framework alumina species [34–37]. Deformation vibration of water is at 1635 cm^{-1}. The pyridine ring vibration region of 1400–1650 cm^{-1} is commonly used to characterize the concentrations of Brönsted and Lewis acid sites [31, 36, 37]. Pyridine adsorbed on the Brönsted acid sites gives rise to the band at 1545 cm^{-1} and on the Lewis acid sites to the band at 1450 cm^{-1}, whilst the band at 1490 cm^{-1} is attributed to the adsorbed pyridine species on both Brönsted and Lewis acid sites.

The IR spectra of the adsorbed 2-chloropyridine in the ring vibration region are shown in Fig. 5. There are bands at 1592, 1570, 1539, 1465 and 1425 cm^{-1} in the 2-chloropyridine ring vibration region. The bands at 1592 and 1570 cm^{-1} are assigned to the ring stretching vibrations of the 2-chloropyridinium ion and ligated 2-chloropyridine. The 1539 and 1465 cm^{-1} bands are attributed to the ring stretching vibration of 2-chloropyridinium ion. The evidence for the coordination of 2-chloropyridine at Lewis acid sites is also provided by the strongest band at 1425 cm^{-1}. This is attributed to the ring stretching vibration of 2-chloropyridine coordinated to the copper ions.

The IR spectra of the adsorbed 2-ethylpyridine are shown in Fig. 6. The bands at 1540 and 1560 cm^{-1} may be assigned to 2-ethylpyridine adsorbed on Brönsted acid sites (2-ethylpyridinium ion). The Lewis acid sites can correspond to the 1475 cm^{-1} band which may be attributed to 2-ethylpyridine coordinatively bound to copper ions.

The IR measurements of the intermediate products of the thermal decomposition of the sample Cu-clpy-ZSM5 (G) at temperatures 150, 350, 400 and 480 °C (Fig. 7) and Cu-ethylpy-ZSM5 (G) at temperatures 200, 350, 400 and

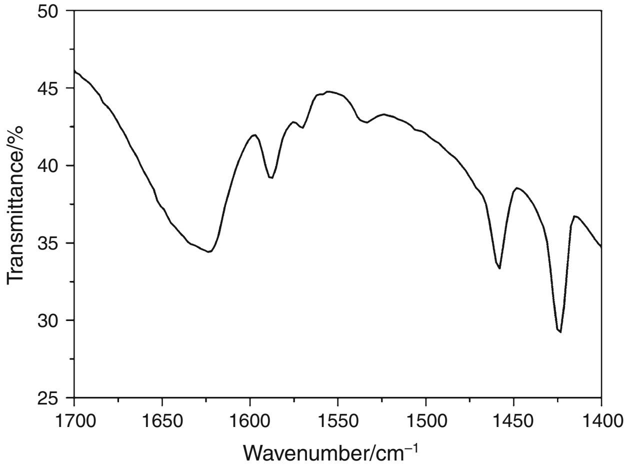

Fig. 5 IR spectrum of Cu-clpy-ZSM5 (G) in the range from 1700 to 1400 cm^{-1}

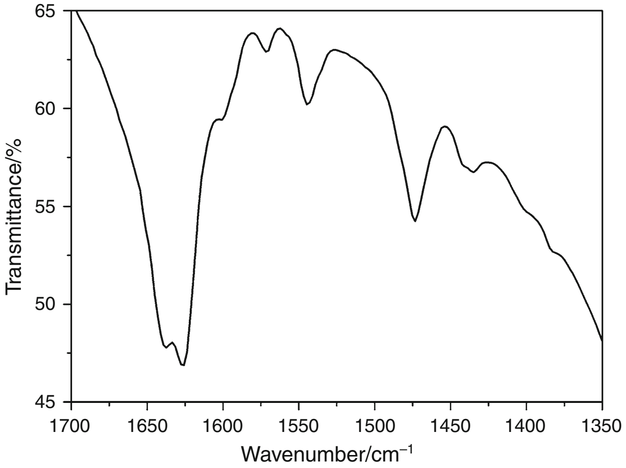

Fig. 6 IR spectrum of Cu-ethylpy-ZSM5 (G) in the range from 1700 to 1350 cm^{-1}

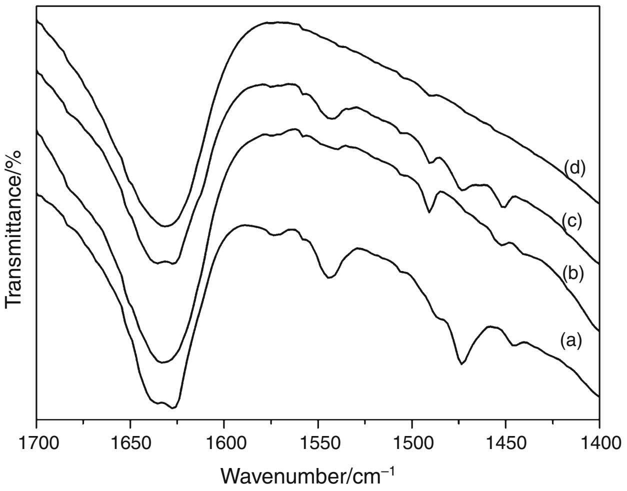

Fig. 8 IR spectrum of Cu-ethylpy-ZSM5 (G) after heating at: (*a*) 200 °C, (*b*) 350 °C, (*c*) 400 °C and (*d*) 450 °C

450 °C (Fig. 8) were performed. In the IR spectra of the intermediate products obtained after the heating up 400 °C the vibrations of pyridine derivates were already missing. These results are in good agreement with the results of thermal analyses.

X-ray diffraction analysis

There are X-ray diffraction patterns of the samples Cu-ZSM5, Cu-clpy-ZSM5 and Cu-ethylpy-ZSM5 and selected regions of peaks at $2\theta = 25°–30°$, which correspond to the specific peaks of ZSM5 zeolite [38, 39] in Fig. 9. The selected regions show that the characteristic peaks for Cu-exchanged zeolites are similar to those of pure ZSM5. No significant diffraction lines assigned to any new phase, as are extra-framework 2-chloro and 2-ethylpyridine complexes of Cu, are observed. Moreover, there is a shift of 2θ peak position at about 27° which indicates changes due to the presence of pyridine derivates bonded to Brönsted, Lewis acid sites and copper ions in intra-framework spaces of synthetic zeolite ZSM5. Also the integral intensity ratio of the selected diffraction lines of Cu-ZSM5, Cu-clpy-ZSM5 and Cu-ethylpy-ZSM5 in the range of $2\theta = 9.5–11°$ and 26–29° is a little different.

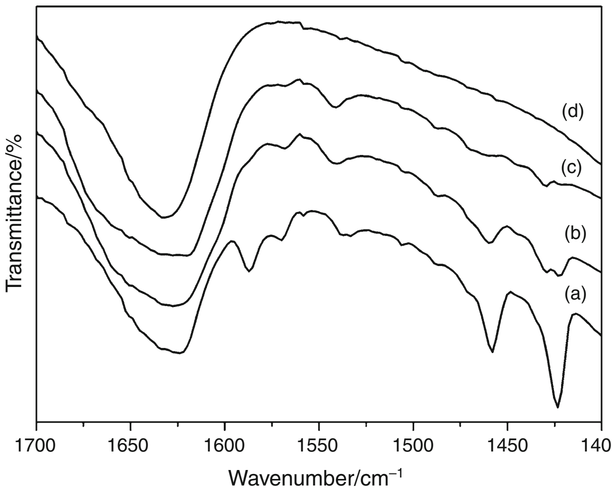

Fig. 7 IR spectrum of Cu-clpy-ZSM5 (G) after heating at: (*a*) 150 °C, (*b*) 350 °C, (*c*) 400 °C and (*d*) 480 °C

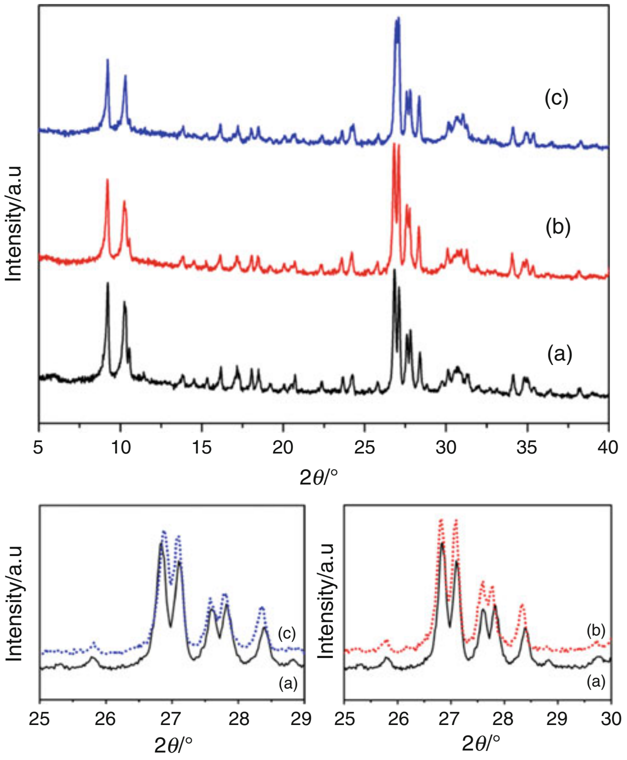

Fig. 9 The X-ray diffraction patterns of: (*a*) Cu-ZSM5, (*b*) Cu-ethylpy-ZSM5 and (*c*) Cu-clpy-ZSM5

Table 1 The surface areas (S_{BET}) and pore volumes of the studied zeolitic samples

Samples	S_{BET}/m^2/g	Pore volume/cm^3/g
Cu-ZSM5 1 M	133.6106	0.0876
Cu-clpy-ZSM5 (L) 1 M	12.9088	0.0184
Cu-clpy-ZSM5 (G) 1 M	12.8137	0.0186
Cu-ethylpy-ZSM5 (G) 1 M	12.3623	0.0190
Cu-CT 1 M	23.9645	0.0384
Cu-clpy-CT (L) 1 M	20.7414	0.0360
Cu-clpy-CT (G) 1 M	20.8723	0.0364
Cu-ethylpy-CT (G) 1 M	20.9187	0.0377

Analysis of the surface areas and the pore volumes

The surface areas of the starting zeoadsorbents and zeoadsorbents after sorption of pyridine derivates were measured only for comparison of the changes. The results of the study of the surface areas changes of the zeolitic samples before and after sorption of 2-chloropyridine and 2-ethylpyridine are in a good agreement with the results of the pore volumes (Table 1). After the comparison of the results of the starting copper zeolitic samples and the samples after the sorption of the pyridine derivates it was found that the surface area and pore volumes decreased due to the adsorption of 2-chloropyridine and 2-ethylpyridine.

The surface areas and pore volumes of the starting samples are relatively low because before the measurements all samples were heated only at temperature 105 °C for 2 h. The samples could not be heated to a higher temperature before the measurements to remove water from the zeolitic channels, since at the higher temperatures the desorption of pyridine derivates could already occur.

The copper forms Cu-ZSM5 1 M and Cu-CT 1 M prepared by using higher concentration of the starting solution (1 mol dm^{-3}) sorbed a little more pyridine derivates in comparison with the samples Cu-ZSM5 0.1 M and Cu-CT 0.1 M prepared by using lower concentration of the starting solution (0.1 mol dm^{-3}). For example, the surface areas (S_{BET}) of the sample Cu-ethylpy-ZSM5 1 M was 12.3623 m^2 g^{-1} (Table 1). The surface areas (S_{BET}) and pore volumes of the sample Cu-ethylpy-ZSM5 0.1 M are higher: 22.1559 m^2 g^{-1} and 0.036 cm^3 g^{-1}, respectively, which indicates that this sample sorbed a lower amount of 2-ethylpyridine.

Conclusions

Copper forms of synthetic zeolite ZSM5 (Cu-ZSM5) and natural zeolite of the CT (Cu-CT) from East Slovakian deposit in Nižný Hrabovec were used for sorption of harmful pyridine derivates: 2-chloropyridine (from the liquid and gas phase) and 2-ethylpyridine (from the gas phase). The content of the sorbed 2-chloropyridine and 2-ethylpyridine in the zeosorbents depended on the experimental conditions during the preparation of the modified copper forms of synthetic and natural zeosorbents, as well as on experimental conditions during the sorption process. The methods of thermal analysis, FTIR and analysis of the surface areas and the pore volumes clearly confirmed the sorption of pyridine derivates. Thermal analysis and FTIR spectroscopy contributed to the characterization of the sorption processes and the interaction of the pyridine derivates with the zeolitic structure.

The copper forms of the zeosorbents were studied for their environmental application in removing harmful 2-chloropyridine and 2-ethylpyridine.

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