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The activation of acetylene by Cu^+ ions in zeolites studied by IR spectroscopy

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Abstract

The interaction of acetylene with Cu^+ ions in zeolites CuX, CuY, CuZSM-5 and CuMCM-41 was studied by IR spectroscopy. The C≡C bond was strongly activated, what resulted in a distinct weakening of the triple bond and of ≡C–H bond ($\Delta\nu_{C\equiv C}$ = 156–168 cm^{-1}, $\Delta\nu_{\equiv C-H}$ = 93–122 cm^{-1}). The ability of Cu^+ ions to activate acetylene molecule increases in the order: CuMCM-41 < CuZSM-5 < CuY < CuX. It may be related to increasing amount of AlO_4^- tetrahedra, and to increasing negative charge of zeolite framework. IR experiments evidenced, that Cu^+ in various cationic sites activate acetylene molecule in a different extend. It has been shown, that Cu^+ ions are also able to bond two acetylene molecules. The molecules of pyridine when bonded to Cu^+ ions increase the electron donor properties of Cu^+ ions and their ability to activate acetylene molecule. This effect is however very small. The adsorption of acetylene removes pre-adsorbed CO.

Keywords: IR spectroscopy; Acetylene; Zeolites; Cu^+ cations

1. Introduction

Transition metal cations in zeolites attract a great deal of attention because of their interesting physicochemical properties and of their catalytic activity in "redox" reactions. A specially important point is the modification of cation properties by the zeolite framework. Cu^+ containing zeolites were the subject of special interest because of their activity in the decomposition and reduction of NO_x (e.g. review papers [1–5]). Most probably, monovalent Cu^+ ions were formed by the reduction of Cu^{2+} by intrazeolitic water [6]. Quantum-chemical calculations evidenced [7–11] that the "denox" activity of zeolitic Cu^+ could be related to partial neutralization of positive charge of Cu^+ cations by framework oxygen atoms, what increased their HOMO energy. Consequently, π back donation of electrons from Cu^+ to π^* antibonding orbitals of NO resulted in a distinct weakening of N–O bond and molecule dissociation.

Besides of "denox" activity Cu^+ ions in zeolites were also active in several reactions of organic molecules. As alkenes and alkynes are reactants in many of these reactions, the problem of activation of double C=C or triple C≡C bond by Cu^+ ions in zeolites seems to be interesting. IR studies of interaction of alkenes with Cu^+ in zeolites [12–16] evidenced a significant weakening of double C=C bond and therefore a distinct red shift of IR band of C=C stretching ($\Delta\nu$ = 78–115 cm^{-1}), as well as some perturbation of =C–H vibrations neighbouring the double bond. Moreover, in the case of ethene interacting with Cu^+ IR inactive C=C stretching became IR active. Quantum-chemical calculations evidenced a bond order decrease, and bond lengthening; the calculated $\Delta\nu$ values were very close to experimental ones. The calculations showed also a change of the geometry of ethene molecule. DFT calculations [13,16] evidenced also a net charge transfer from Cu^+ ions in zeolites acting as electron donors to alkenes. The π back donation to π^* antibonding orbitals of alkenes resulted in a distinct double bond weakening.

Our recent IR study [17] of acetone sorption in Cu-zeolites showed also a C=O bond weakening due to π back donation, but in that case the C=O frequency shift $\Delta\nu$ (39–51 cm^{-1}) was lower than for alkenes. Quantum-chemical DFT calculations [16,17] evidenced the net charge transfer from acetone to Cu^+ ions in zeolites. Both in the case of alkenes and acetone, the zeolite framework, which

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neutralized partially positive charge of Cu^+ acted also as reservoir of electrons. Only a part of negative charge transmitted to alkene came from Cu^+, and the rest was came from the framework (via Cu^+). In the case of acetone, all the charge from acetone was transmitted to the framework via Cu^+ cations, the charge on Cu^+ ions did not change.

The present study concerns the activation of the triple $C{\equiv}C$ bond in acetylene by Cu^+ cations in zeolites. This problem was already studied by Hűbner et al. [18] by IR spectroscopy and by quantum-chemical calculations. Both experiment and calculations showed a distinct $C{\equiv}C$ bond weakening and a net electron transfer from Cu^+ to acetylene. In the case of CuY two kinds of acetylene-Cu^+ complexes of various $C{\equiv}C$ stretching frequencies due to the presence of Cu^+ in various cationic sites S_{II} and S_{III} were found. Sites S_{II} are located inside supercages above 6-ring of hexagonal prism. Sites S_{III} are situated between two 4-rings on the wall of 12-ring window.

We undertook further IR studies of acetylene activation by Cu^+ ions in various zeolites. As Hűbner et al. [18] studied the effect of position of Cu^+ ions in zeolite CuY on the properties of adsorbed acetylene, we followed the effect of zeolite composition, by using zeolites CuX, CuY and CuZSM-5, of various content of negatively charged $[AlO_4]^-$ tetrahedra, i.e. of various negative charge of the whole framework on the extend of acetylene activation. We also compared highly crystalline CuZSM-5 and amorphous CuMCM-41. Another interesting problem was the status of acetylene adsorbed in Cu-zeolites at high loadings. Our previous IR studies evidenced, that at high alkenes (butenes, propene) loadings one Cu^+ cation bonded two alkene molecules. In this study we investigated the problem of binding two acetylene molecules by one Cu^+.

In this study, we also investigated the coadsorption of acetylene and CO (which is often used as a probe molecule for Cu^+ in zeolites), as well as pyridine on one Cu^+ ion. Pyridine is bonded to cation by one lone electron pair of nitrogen and acts as electron donor, it was therefore interesting to know, how the increase of electron density of Cu^+ affects the activation of acetylene.

As mentioned, we studied zeolites: CuX, CuY, CuZSM-5 and CuMCM-41. In most cases, acetylene was adsorbed at room temperature, but in the case of CuZSM-5, which contains besides of Cu^+ ions also strongly acidic Si–OH–Al groups, acetylene was sorbed at lower temperature (250 K) to slow down the undesired reactions of acetylene oligomerisation (reported already by Bordiga et al. [19]).

2. Experimental

2.1. Samples preparation

CuX, CuY and CuZSM-5 zeolites were obtained from a parent NaX (Si/Al = 1.31) synthesized at Department of Chemical Technology UJ, NaY and NaZSM-5 (Si/Al = 2.56 and 35, respectively) synthesized in the Institute of Industrial Chemistry (Warsaw) by treatment with $Cu(CH_3COO)_2$ solution at 80 °C. Upon the ionic exchange, the zeolites were washed with distilled water and dried in air at 370 K. The exchange degrees (Cu/Al) were 0.43, 0.31 and 0.45 for CuX, CuY, and CuZSM-5 respectively. CuMCM-41 (of Cu content 2.3%) was the same as used in a previous study [20].

Acetylene (Messer, 99.6%) was used. As acetylene contained traces of acetone, we purified it by the bulb-to-bulb distillation until no carbonyl band (ca. 1720 cm^{-1}) was seen in the IR spectra.

2.2. IR

For IR studies, all the materials studied were pressed into thin wafers and activated in situ in IR cell at 730 K at vacuum for 1 h. IR spectra were recorded by BRUKER IFS 48 spectrometer equipped with an MCT detector. The spectral resolution was 2 cm^{-1}.

3. Results and discussion

3.1. Activation of acetylene by Cu^+ in zeolites

Due to high symmetry, the IR spectrum of acetylene shows only two bands: asymmetric $\equiv$C–H stretching, and bending, on the other hand, the band of $C{\equiv}C$ stretching is IR inactive. The spectrum of acetylene interacting with Cu^+ in CuX is presented in Fig. 1A and B. Two bands of $C{\equiv}C$ stretching are seen at 1806 and 1822 cm^{-1} ($\Delta\nu = 168$ and 152 cm^{-1}). The spectrum of adsorbed acetylene shows also two bands of $\equiv$C–H stretching at 2160 and 2193 cm^{-1} ($\Delta\nu = 122$ and 89 cm^{-1}). The observed bands are similar to those reported for CuY by Hűbner et al. [18] who assigned these bands to acetylene bonded to Cu^+ in sites S_{III} and S_{II}. Low frequency maxima (of higher $\Delta\nu$) were assigned to sites more electron donor S_{III}, and low frequency ones (of lower $\Delta\nu$) to less electron donor sites S_{II}. As far as we know, the positions of Cu^+ cations in zeolites CuX are not reported, but it may be supposed, that observed in our study low frequency $C{\equiv}C$ and $\equiv$C–H maxima corresponds to acetylene bonded to more electron donor Cu^+ sites, and high frequency ones to acetylene bonded to less electron donor Cu^+. The observed distinct red shifts of both $C{\equiv}C$ and $\equiv$C–H bands (if comparing with free molecule) indicate, that the interaction of acetylene with Cu^+ sites in zeolites results not only in an important weakening of $C{\equiv}C$, but also of weakening of $\equiv$C–H bond neighbouring to the triple bond. It should be noted that similar effects were also observed in the case of alkenes, the interaction with Cu^+ resulted [12,13,15,16] in a distinct weakening of the double bond ($\Delta\nu = 78$–115 cm^{-1}) and in some weakening of =C–H bond ($\Delta\nu = 10$–30 cm^{-1}). The perturbation of $\equiv$C–H bond in acetylene is, however, more distinct than of =C–H bond in alkenes. May be it is due

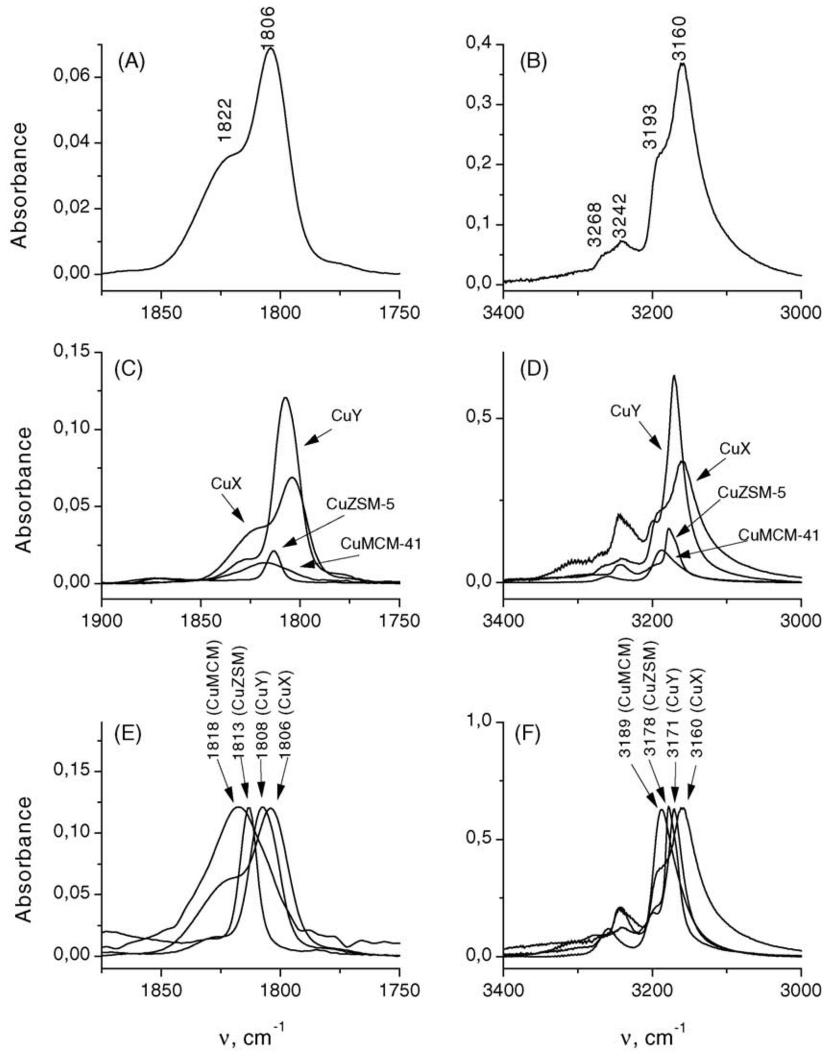

Fig. 1. (A, B) IR spectra of acetylene sorbed in zeolite CuX. (C–F) The spectra of acetylene sorbed in CuX, CuY, CuZSM-5, CuMCM-41 normalized to the same sample mass (C, D) and to the same intensitiy of C≡C and ≡C–H bands (E, F).

to higher polarization of C–H bond in acetylene and its more acidic character.

According to the data presented in Fig. 1, the C≡C and symmetric ≡C–H stretching, which is IR inactive in free molecule, became active if acetylene interacted with Cu^+. Similar situation was observed in ethene [12–15], and in acetylene [18]. Quantum-chemical calculations evidenced, that both ethene and acetylene was deformed (ethene became no more flat and acetylene no more linear) when interacting with Cu^+.

The spectra of acetylene interacting with Cu^+ in CuX, CuY, CuZSM-5 and CuMCM-41 are presented in Fig. 1C–F. Acetylene was sorbed in CuX, CuY and CuMCM-41 at room temperature, but in CuZSM-5 (which contains strongly acidic Si–OH–Al groups which may catalyse acetylene oligomerisation) at 250 K. The spectra presented in Fig. 1C and D are normalized to the same mass of zeolite, and those in Fig. 1E and F to the same intensity of main C≡C or ≡C–H bands. Various intensities of C≡C bands in the spectra normalized to the same mass (Fig. 1C and D) can be, due to various contents of Cu^+ accessible to acetylene and/or to various extinction coefficients. The spectrum of acetylene sorbed in CuY is practically the same as that reported by Hűbner et al. [18]. Two maxima, a stronger one at 1808 cm^{-1} and a weaker one at 1830 cm^{-1} of acetylene interacting with Cu^+ in sites S_{III} and S_{II}, respectively. The spectra of acetylene interacting with Cu^+ in CuZSM-5 and CuMCM-41 show only one C≡C band.

According to the data presented in Fig. 1, the position of the main C≡C and ≡C–H maxima is different in various zeolites. The frequency of C≡C band increases in the order CuX < CuY < CuZSM-5 < CuMCM-41, indicating that the activation of the triple bond is the strongest in CuX and the weakest in CuMCM-41. It may be related to different electron donor properties of Cu^+ cation in various zeolites, and to the effect of zeolite framework to the electrical charge of cation.

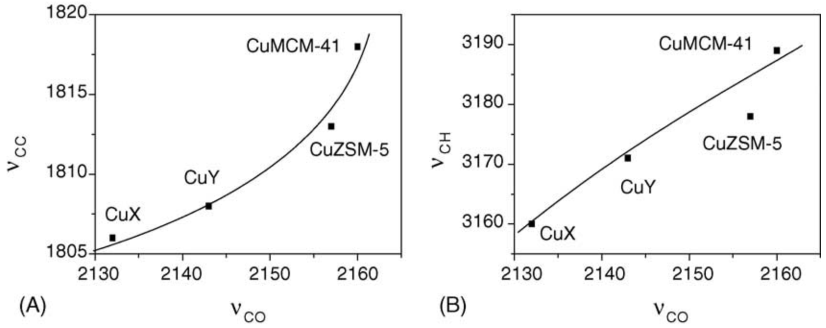

Fig. 2. The correlations between the frequencies of C≡C and ≡C–H bands of acetylene sorbed in various Cu-zeolites and the frequency of CO sorbed.

The information on the electrical charge of Cu^+ in zeolites can be obtained by IR studies of CO sorption. CO molecule bonds with Cu^+ site by σ-donation (the donation of electrons from σ orbital of CO to electroacceptor site) and by π back donation (donation of d electrons of Cu^+ to π^* antibonding orbitals of CO). The more electron donor is Cu^+ site, weaker is σ-donation and stronger is π back donation, the C≡O stretching frequency decreases. The correlation between stretching frequencies of adsorbed acetylene (both C≡C and ≡C–H) and C≡O is presented in Fig. 2. The CO frequency decreases in the order: CuMCM-41 > CuZSM-5 > CuY > CuX, indicating, that the electron donor properties of Cu^+ increase in the same order. It may be the result of the increase in amount of AlO_4^- in the framework and the neutralization of Cu^+ charge by more and more negative framework. The less positive the Cu^+ cation is, the stronger its electron donor properties, and stronger is the π back donation effect and lower C≡C stretching frequency. According to the data presented in Fig. 2B, the asymmetric stretching frequency of ≡C–H does also decrease in the same order (CuMCM-41 > CuZSM-5 > CuY > CuX), i.e. with the increase of π back donation.

The bands of C≡C and ≡C–H in acetylene sorbed in CuMCM-41 are distinctly larger than in CuZSM-5, suggesting that in amorphous CuMCM-41 structure there are Cu^+ ions in various environments of various electron donor properties and of various ability of activation of acetylene molecules.

3.2. Increasing loading of acetylene

The spectra recorded upon the sorption of increasing amounts of acetylene at room temperature in CuX are presented in Fig. 3. Two bands of C≡C, 1806–1812 cm^{-1} and 1822 cm^{-1} as well as two bands of ≡C–H, 3163 and 3190 cm^{-1} are present. Low frequency bands (of higher $\Delta\nu$) correspond to acetylene bonded to more electron donor Cu^+, whereas high frequency ones (of lower $\Delta\nu$) to acetylene bonded to less electron donor Cu^+. The proportions between high frequency and low frequency bands increase with acetylene loading, suggesting that at lower loadings acetylene reacts preferentially with more electron donor Cu^+. The desorption at increasing temperature (from room temperature to 470 K) resulted in decrease of the bands of acetylene desorbing from less electron donor Cu^+ in first order (at lower temperatures), whereas acetylene was bonded to more electron donor Cu^+ more strongly. According to the data presented in Fig. 3A, the band of acetylene bonded to more electron donor Cu^+ shifts to lower frequency (from 1812 to 1806 cm^{-1}) with the increase of acetylene loading. It suggests that even more electron donor

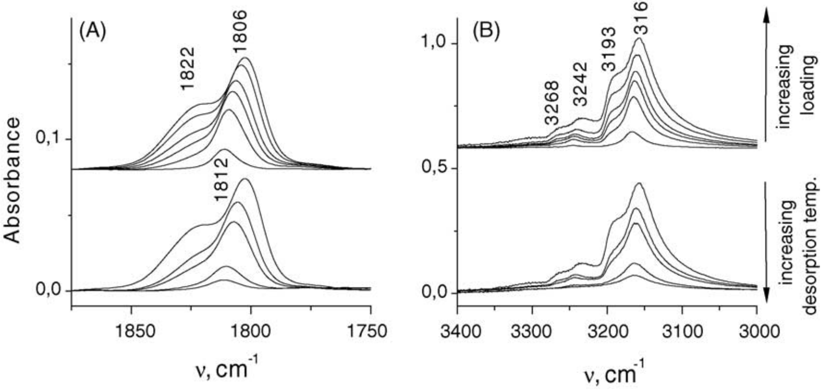

Fig. 3. The spectra of acetylene adsorbed at room temperature at increasing loadings in zeolite CuX, and at the desorption at increasing temperatures from CuX (from room temperature to 470 K).

Cu^+ sites show somewhat different properties and different ability to activate acetylene molecules.

The results obtained in our previous study of alkenes sorption in Cu-zeolites showed that at high loading one Cu^+ cation was able to bond two alkene molecules. It was interesting to know, if one Cu^+ can also bond two acetylene molecules.

In the present study, this problem was investigated by the adsorption of consecutive doses of acetylene at 250 K in zeolite CuX, CuY and CuZSM-5 in which the amounts of acetylene sufficient to form 1:1 complexes (one acetylene per one Cu^+) had been pre-adsorbed at room temperature. The spectra are presented in Fig. 4. In the case of zeolite CuX (Fig. 4A), the spectrum of 1:1 complex (spectrum a) shows two maxima, 1806 and 1822 $\mathrm{cm^{-1}}$ related to more and less electron donor Cu^+. The sorption of increasing amounts of acetylene at 250 K results in the decrease of 1806 $\mathrm{cm^{-1}}$ maximum and in the appearance of a weak and broad maximum at ca. 1850 $\mathrm{cm^{-1}}$ ($\Delta\nu \approx 120\ \mathrm{cm^{-1}}$). These effect are best seen in a difference spectrum (spectrum e). It may be supposed that the 1850 $\mathrm{cm^{-1}}$ band may correspond to the situation in which one Cu^+ binds two acetylene molecules (2:1 complexes). A short evacuation at 250 K (spectrum f) resulted in disappearance of 1850 $\mathrm{cm^{-1}}$ band and in restoring the 1806 $\mathrm{cm^{-1}}$ one of 1:1 complex. A low intensity of 1850 $\mathrm{cm^{-1}}$ band may suggest that the deformation of acetylene molecule which was responsible for the loss of symmetry and appearance of IR inactive $C\equiv C$ band is less pronounced in the case of 2:1 complexes than in 1:1 ones. Also the activation of acetylene molecule in 2:1 complexes (expressed by red shift of $C\equiv C$ band) is smaller than in 1:1 ones ($\Delta\nu = 120$ and 168 $\mathrm{cm^{-1}}$, respectively). Similar effects were observed in the case of alkenes interacting with Cu^+ sites in zeolites [15]. According to the data presented in Fig. 4A, only more electron donor Cu^+ sites (acetylene band at 1806 $\mathrm{cm^{-1}}$) are able to bind two acetylene molecules, the band at 1822 $\mathrm{cm^{-1}}$ of acetylene bonded to less electron donor Cu^+ sites does not change at high loading of acetylene. Similar situation was also observed in the case of alkenes [15]. The band of 1:1 complexes of alkenes composed of two submaxima (not as well seen as for acetylene) and mostly Cu^+ ions for which low frequency submaximum was responsible for forming 2:1 complexes.

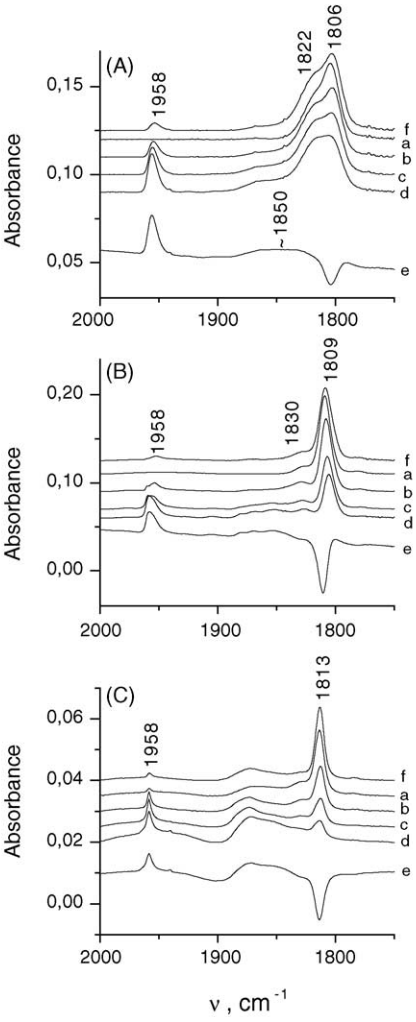

Fig. 4. The spectra of acetylene sorbed at 250 K in zeolites CuX (A), CuY (B), CuZSM-5 (C). (a) Covering of all Cu^+ by one acetylene molecule at room temperature (CuX and CuY) or at 250 K (CuZSM-5); (b, c) sorption of increasing amounts of acetylene at 250 K on zeolite with acetylene pre-adsorbed at room temperature (represented by spectrum a); (d) sorption of large amount of acetylene at 250 K (ca. 1 Torr of acetylene in gas phase); (e) difference spectrum (spectrum d minus spectrum a); (f) evacuation at 250 K.

Similar results were obtained with zeolite CuY (Fig. 4B). The band of acetylene interacting with Cu^+ in sites S_{III} (1809 $\mathrm{cm^{-1}}$) does also decrease at high loadings of acetylene adsorbed at 250 K, and new weak bands of 2:1 complex around 1860–1885 $\mathrm{cm^{-1}}$ appear. As in the case of zeolite CuX, short evacuation removed 1860–1885 $\mathrm{cm^{-1}}$ bands and restored the 1809 $\mathrm{cm^{-1}}$ band of 1:1 complex.

The spectra of acetylene sorbed at high loadings in CuZSM-5 (Fig. 4C) show a decrease of $C\equiv C$ band at 1813 $\mathrm{cm^{-1}}$, but the appearance of new band of 2:1 complexes is less clear: a band around 1850 $\mathrm{cm^{-1}}$ appears, but the fact that the spectral background in the region 1800–1900 $\mathrm{cm^{-1}}$ changes makes the interpretation not certain.

Further arguments on the formation of 2:1 complexes were obtained in experiments, in which acetylene was sorbed in CuZSM-5 with pre-adsorbed pyridine. Pyridine, if bonded to Cu^+ ions blocks the possibility of bonding the second acetylene molecule, and the decrease of 1813 $\mathrm{cm^{-1}}$ at high loading (replacing of 1:1 complexes by 2:1 ones) should not occur. The spectra presented in Fig. 5 shows that it is really the case. Spectrum a was recorded upon the sorption of pyridine at 420 K: the bands of pyridinium ions 1490 and 1545 $\mathrm{cm^{-1}}$ (Bronsted sites were formed by hydrolysis) as well as pyridine bonded to Cu^+ (1450 and 1609 $\mathrm{cm^{-1}}$) are present. The sorption of acetylene at room temperature (spectra b, c) results in small red shift of 1450 and 1609 $\mathrm{cm^{-1}}$ and in appearing of 1811 $\mathrm{cm^{-1}}$ $C\equiv C$ band. Contrary to zeolite without pyridine (spectrum e), if pyridine

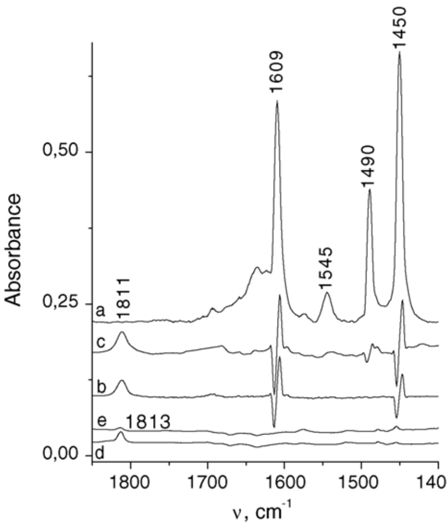

Fig. 5. IR spectra of acetylene sorbed at 250 K in CuZSM-5 with pre-adsorbed pyridine (b, c), and without pyridine (d, e). (a) Sorption of excess of pyridine in CuZSM-5 at 420 K and removal of physisorbed, pyridine by evacuation at 570 K; (b, d) sorption of acetylene (amount of acetylene comparable to the amount of Cu^+) in zeolite with pyridine (b) and without pyridine (d); (c, e) sorption of large amount of acetylene at 250 K (ca. 1 Torr of acetylene in gas, phase) in zeolite with pyridine (c) and without pyridine (e).

is present (spectrum c) the 1811 cm^{-1} band does not decrease at high acetylene loading. It supports hypothesis, that the decrease of 1813 cm^{-1} band is really due to replacing of 1:1 complexes by 2:1 ones.

3.3. Coadsorption of acetylene, pyridine and CO

According to the results of Hűbner et al. concerning both ethene [13] and acetylene [18], the position of the band of C=C and C≡C depends on the position of Cu^+ in zeolite. It may be due to the influence of the environment of Cu^+ ions on its ability to activate adsorbed molecule. It was interesting to know if another factor such as the presence of electron donor pyridine molecule bonded to the same Cu^+ cation affects the interaction of Cu^+ with acetylene. In order to answer this question, acetylene was sorbed at 250 K in zeolite CuZSM-5 in which pyridine was pre-adsorbed. According to the results presented in Fig. 5, the frequency of C≡C band was 1811 cm^{-1}, i.e. of 2 cm^{-1} lower than without pyridine (1813 cm^{-1}). This result indicates that pyridine which bonds to Cu^+ with lone electron pair acts as electron donor, enhances the electron donor properties of Cu^+, and the affectivity of π back donation, but this effect is very small. The effect of pyridine is distinctly smaller than the effect of various localization of Cu^+ in zeolites in various oxygen environments (Cu^+ in sites S_{II} and S_{III} [18]).

We studied also the coadsorption of acetylene and CO. CO was first sorbed in CuZSM-5 until all the Cu^+ ions were formed Cu^+CO monocarbonyls (IR band 2157 cm^{-1}). The sorption of acetylene (Fig. 6) in zeolite with pre-adsorbed CO resulted in the decrease of the band of CO bonded to Cu^+ (2157 cm^{-1}) and in appearance of the band around 2140 cm^{-1}, the position of which is practically the same as in free CO. This band may be due to physisorbed or very weakly bonded CO. It disappears upon short evacuation at room temperature (spectrum not shown). At higher acetylene loading the 2157 cm^{-1} band of Cu^+CO disappears. Such result indicates, that acetylene is so strongly bonded to Cu^+ that it replaces CO from relatively stable Cu^+CO monocarbonyls.

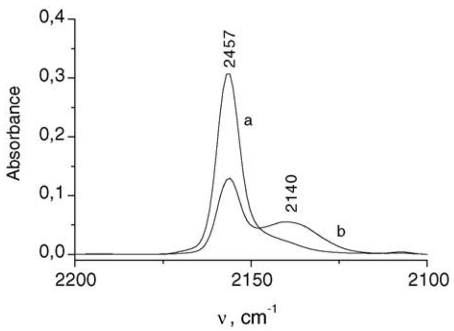

Fig. 6. IR spectra of CO in zeolite CuZSM-5 before (a) and upon the sorption of acetylene (b).

4. Conclusions

Cu^+ ions in zeolites strongly activate acetylene by π back donation. It results in a distinct weakening of C≡C ($\Delta\nu = 152–168\ cm^{-1}$) and ≡C–H ($\Delta\nu = 89–156\ cm^{-1}$) bonds.

In zeolites CuX and CuY there are two distinct bands of C≡C and ≡C–H stretching of acetylene bonded to different Cu^+ sites. According to the interpretation of Hűbner et al. [18], the S_{II} and S_{III} sites in CuY have different ability of activation of acetylene molecules.

The frequencies of both C≡C and ≡C–H bands decreases in the order: CuMCM-41 > CuZSM-5 > CuY > CuX, indicating that the ability of activation of acetylene molecule by π back donation increases from CuMCM-41 to CuX. It may be related with an increase of the amount of $[AlO_4]^-$ increase of the negative charge of zeolitic framework and increase of electron donor properties of Cu^+.

At high loadings one Cu^+ cation can bond two acetylene molecules. In zeolite CuX only more electron donor Cu^+ sites are able to bond two acetylene molecules.

The experiments of pyridine and acetylene coadsorption evidenced that electron donor pyridine molecule bonded to Cu^+ ion increases its ability of activation of acetylene by π back donation. This effect is, however, very small if comparing with the effect of location of Cu^+ in various sites (S_{II} and S_{III}) in CuY.

The bonding of acetylene with Cu^+ ions is so strong that it replaces CO from Cu^+CO monocarbonyls.

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