

IR Studies of the Activation of C=C Bond in Alkenes by Cu⁺ Ions in Zeolites

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IR studies show that Cu⁺ ions in zeolites CuX, CuY, and CuZSM-5 are able to activate C=C bond in alkenes (ethene, propene, but-1-ene, and *cis*-but-2-ene). The stretching frequency of the C=C— band decreased by 78–115 cm^{−1}, indicating a significant weakening of the double bond. In ethene, the IR inactive C=C stretching became IR active when interacting with Cu⁺ as the result of the loss of symmetry. The band of C=C interacting with alkenes was split into two submaxima suggesting that Cu⁺ ions activate alkenes to a different extent. The IR bands corresponding to C–H stretching, deformation, and bending of the =CH₂ and =C–H groups near the double bond also shifted to lower frequencies. At high loadings, some of the Cu⁺ ions were able to bond two alkene molecules. The interaction of alkenes with Cu⁺ was so strong that alkenes replaced CO and NO in relatively stable Cu⁺CO and Cu⁺(NO)₂. Very strong interaction of alkenes with Cu⁺ was also evidenced by a large shift of IR band of oxygen ring which was deformed by the interaction with Cu⁺ and relaxed when Cu⁺ was withdrawn from the ring by alkene. Most probably the mechanism of the activation of alkenes by Cu⁺ is similar to the mechanism of activation of NO, that is, involves the π -back-donation of *d* electrons of Cu⁺ to π^* antibonding orbitals of the alkenes.

Introduction

Since the early reports by Iwamoto et al.^{1–4} on the activity of CuZSM-5 in the decomposition of nitrogen oxides, copper-containing zeolites attracted a great deal of attention. DFT calculations showed^{5–8} that the high activity of Cu⁺ in CuZSM-5 could be related to the high energy of the HOMO orbital of Cu⁺ in MFI and to the π -back-donation of electrons from the *d* orbitals of Cu to π^* antibonding orbitals of NO, resulting in a distinct weakening and dissociation of the N=O bond. The role of zeolite was the partial neutralization of the electrical charge of Cu⁺: the charge decreased from +1 to +0.3 when Cu⁺ was placed in a cluster simulating a fragment of the MFI structure and therefore an increase of the HOMO energy. According to Goursot et al.,⁹ zeolitic framework acts as a reservoir of electrons; the negative charge transferred to NO comes mostly from the framework with only a small variation in the charge on the Cu⁺ ion.

Apart from the activity in the “denox” reaction, Cu-containing zeolites were also active catalysts in some reactions of organic molecules.^{10–26} It was recently reported^{11,12} that CuMCM-41 was active in *n*-butene isomerization to isobutene known as acid-catalyzed reaction. CuMCM-41 was more active in butene isomerization than HMCM-41, despite the fact that it showed lower Brønsted acidity, indicating the important role of Cu⁺ ions as active sites in this reaction. The activity of Cu-containing faujasites in Diels–Alder cyclodimerization of 1,3 butadiene to vinylcyclohexene was reported by Piffer et al.²³ Cu-zeolites are also active in some reactions of alkene oxidation.^{13–16,18–22}

Since most of the aforementioned reactions concern alkenes, we undertook IR studies of the activation of the alkene double bond by Cu⁺. The studies of interaction of ethane with Cu⁺ in CuY were already done by Hübner et al.^{27,28} We performed IR studies on the adsorption of but-1-ene, *cis*-but-2-ene, *trans*-but-

2-ene, propene, and ethene on Cu⁺ sites in zeolites CuX, CuY, and CuZSM-5. In most cases, the alkene adsorption was followed at room temperature, but in CuZSM-5, which besides Cu⁺ sites contains strongly acidic protonic sites which may catalyze but-1-ene isomerization and oligomerization, butenes were adsorbed at low temperature (170 K) to slow the undesired reactions.

Experimental Methods

Zeolites CuX, CuY, and CuZSM-5 were prepared from a parent zeolite NaX (Si/Al = 1.31) synthesized at Department of Chemical Technology UJ, and zeolites NaY and NaZSM-5 (Si/Al = 2.56 and 35, respectively) were synthesized in Institute of Industrial Chemistry (Warsaw) by treatment with Cu(CH₃COO)₂ at 350 K. Following the ion exchange, the samples 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. We also used silicalite synthesized at the Department of Chemical Technology Jagiellonian University.

But-1-ene, *cis*-but-2-ene, *trans*-but-2-ene, and propene (Fluka – 99.9% pure), as well as ethene (UCAR, 99.5% pure), were used as received.

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

Results and Discussion

Interaction of But-1-ene with Cu⁺ in CuX, CuY, and CuZSM-5. The spectra of but-1-ene sorbed in CuX, CuY, and CuZSM-5 as well as physisorbed in silicalite are shown in Figure 1. But-1-ene was adsorbed at room temperature in CuX and CuY, and at 170 K in CuZSM-5 and silicalite. A comparison of the spectra of physisorbed but-1-ene and that of but-1-ene

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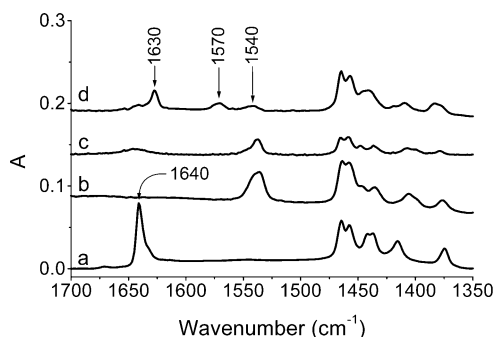


Figure 1. IR spectra of but-1-ene physisorbed in silicalite (a) and sorbed in CuX (b), CuY (c), and CuZSM-5 (d).

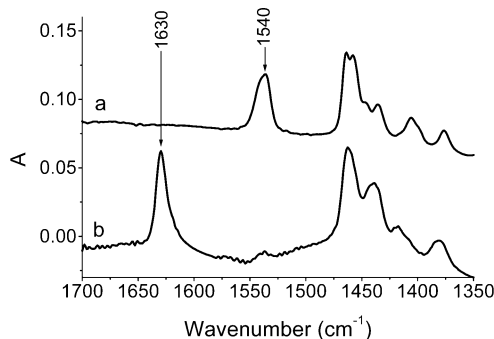


Figure 2. IR spectra of but-1-ene sorbed in CuX pretreated at 630 K in a vacuum (a) and in dry air (b).

sorbed in Cu-zeolites shows that the interaction with Cu sites resulted in an important weakening of the C=C bond: the IR band shifted from 1641 cm^{-1} (position typical of physisorbed molecules) to about 1540 cm^{-1} ($\Delta\nu \approx 100 \text{ cm}^{-1}$). In CuZSM-5, a second maximum at ca. 1570 cm^{-1} is also present. The nature of the species responsible for the band at 1570 cm^{-1} will be discussed later.

Cu-containing zeolites pretreated at vacuum above 570 K contain mostly Cu^+ but a small amount of Cu^{2+} is also present.²⁹ It was therefore important to know if Cu^+ or Cu^{2+} is responsible for weakening the C=C bond in but-1-ene. To answer this question, but-1-ene was sorbed in CuX which had been oxidized (at 720 K) in dry air, followed by evacuation at 670 K. Our earlier study²⁹ demonstrated that most of the Cu^+ was oxidized to Cu^{2+} by this treatment. The spectrum of but-1-ene sorbed in oxidized CuX zeolite (Figure 2) showed only a very small band at 1540 cm^{-1} and a distinct band (at 1630 cm^{-1}) of but-1-ene hydrogen bonded to OH groups. The distinct weakening of C=C in but-1-ene is therefore due to interaction with Cu^+ cations. It is very possible that this is the effect of π -back-donation of d electrons of Cu^+ ions to π^* antibonding orbitals of alkenes. Such an interpretation was proposed by Hübner et al.^{28,30} for ethane and ethyne adsorbed. As mentioned in the Introduction, quantum-chemical DFT calculations show that the location of Cu^+ in cationic positions of ZSM-5 results in a partial neutralization of its electrical charge and in a distinct increase of HOMO energy and therefore in an increase of electrodonor properties of Cu^+ .^{7,8}

The C=C and C-H Bonds in Alkenes Interacting with Cu^+ in Cu-Zeolites. The spectra of but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene, propene, and ethene interacting with Cu^+ in CuX are shown in Figures 3 and 4. In all the alkenes (except *trans*-but-2-ene), the interaction with Cu^+ resulted in a red shift of the C=C band by 78 cm^{-1} (for ethene) to 115 cm^{-1} (for *cis*-but-2-ene). The vibration of the C=C bond in ethene, which

is IR inactive in free molecule, became active upon the adsorption on Cu^+ . (Figure 4). Physisorbed ethene showed a very weak band at 1616 cm^{-1} , but upon adsorption on CuX a distinct band at 1538 cm^{-1} ($\Delta\nu = 78 \text{ cm}^{-1}$) is visible. This result indicated that ethene molecule lost its symmetry when interacting with Cu^+ . Such a loss of symmetry was, however, not observed in *trans*-but-2-ene; no C=C band was seen when *trans*-but-2-ene was sorbed on CuX (Figure 3).

Analysis of the spectra in Figures 3 and 4 showed that not only was the C=C bond affected by the interaction with Cu^+ , but also the =CH₂ and =C-H bonds were perturbed. The IR bands of =CH₂ and =C-H stretching (3000–3100 cm^{-1}) were red shifted by 12 cm^{-1} (but-1-ene) to 30 cm^{-1} (*cis*-but-2-ene). The bands of =CH₂ scissoring (1400–1450 cm^{-1}) were red shifted by 10–12 cm^{-1} (for but-1-ene, propene, and ethene), and the band of =C-H bending (1400 cm^{-1}) in *cis*-but-2-ene by 20 cm^{-1} . The bands corresponding to vibrations of CH₃ and CH₂ groups more distant from the double bond were less perturbed. Similar results of distinct weakening of C=C bonds and some perturbation of =CH₂ and =C-H bonds were also observed if alkenes were sorbed in CuY and CuZSM-5 (spectra not shown). In ethene sorbed in CuY (Figure 4), the band of C=C vibration is split into two maxima at 1535 and 1546 cm^{-1} ($\Delta\nu = 81$ and 70 cm^{-1}). Similar results were obtained by Hübner et al.^{27,28} who reported distinct red shifts and splitting of both C=C stretching and =CH₂ scissoring bands in ethene interacting with Cu^+ in CuY. The values of $\Delta\nu_{\text{C}=\text{C}} = 78$ and 88 cm^{-1} , reported by Hübner et al.,^{27,28} are very close to those obtained in our study (70 and 81 cm^{-1}). The analysis of the spectra presented in Figures 3, 4, and 6A suggests that the C=C band is also split if other alkenes (propene and but-1-ene) interact with Cu^+ in CuX and CuY. This splitting is not always as visible as in the ethene in CuY, but two overlapping submaxima can be observed. It seems that the most probable reason of such a splitting may be the presence of Cu^+ ions in various cationic positions in CuY. According to Hübner et al.,^{28,30} Cu^+ sites in CuY bond ethene and ethyne with different C=C stretching frequencies. Moreover, several authors^{31–35} reported various frequencies of CO bonded to various Cu^+ sites in CuY.

Various Loadings of Alkenes in Cu-Zeolites. The spectra shown in Figure 5 were recorded upon the adsorption of increasing amounts of but-1-ene at room temperature on CuX. At lower coverages, only the bands of but-1-ene interacting with Cu^+ were present (the most characteristic band at 1540 cm^{-1}), and they increased with the amount of butene adsorbed. At higher coverages, the 1540 cm^{-1} band increases no more and the band of but-1-ene bonded with OH groups (1630 cm^{-1}) appears. This result indicates that but-1-ene molecules reacted in the first order with Cu^+ cations, and, after their saturation, formed hydrogen bonding with OH groups. The bonding of but-1-ene with Cu^+ was therefore stronger than the hydrogen bonding with OH. At higher loadings, a new band at 1570 cm^{-1} appeared (Figure 5), similar as in the but-1-ene sorbed at 170 K in CuZSM-5 (Figure 1). Similar results were also obtained with all other alkenes and all the Cu-zeolites. In all these cases, the bands of alkene interacting with Cu^+ appeared before the band of hydrogen-bonded alkenes. At higher loadings, the band at ca. 1570 cm^{-1} appeared. As mentioned above, the band about 1570 cm^{-1} was also present if but-1-ene was sorbed at 170 K in CuZSM-5 zeolite.

To obtain more information on the nature of species represented by the 1570 cm^{-1} band, the spectra were recorded upon the sorption of various amounts of alkenes: but-1-ene,

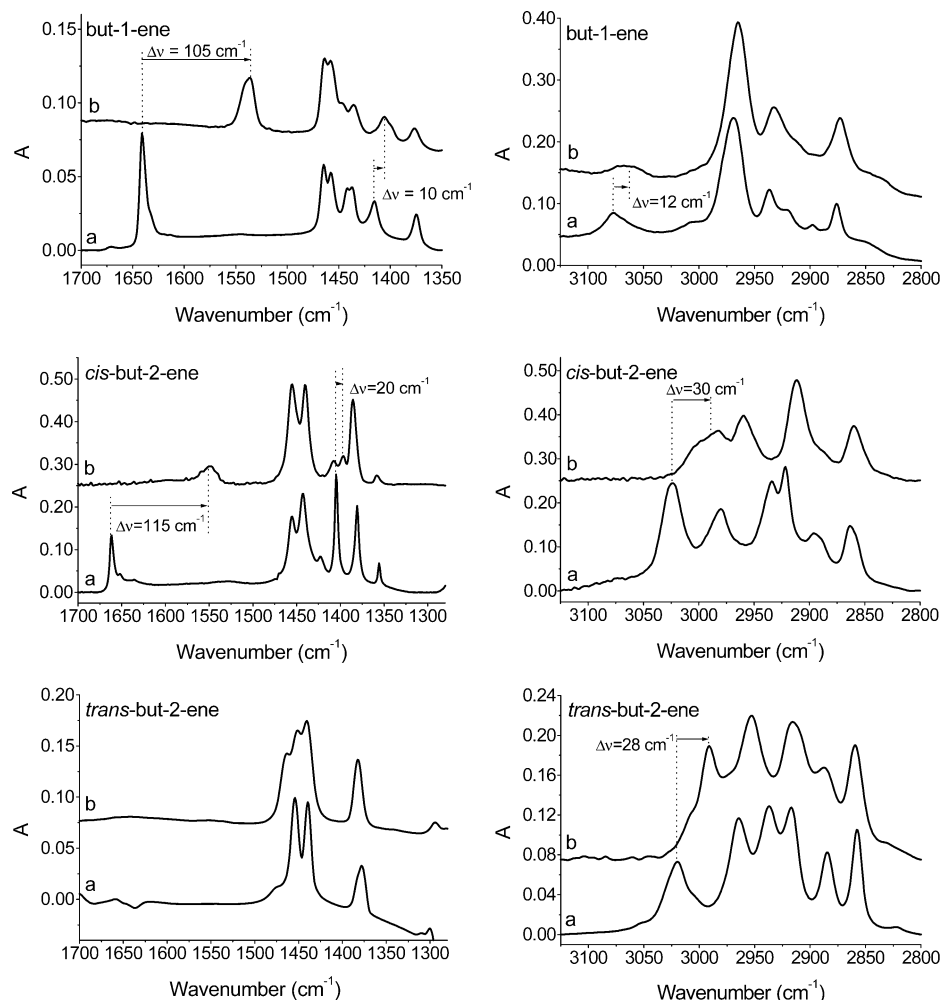


Figure 3. IR spectra of but-1-ene, *cis*-but-2-ene, and *trans*-but-2-ene physisorbed in silicalite (a) and sorbed in CuX (b).

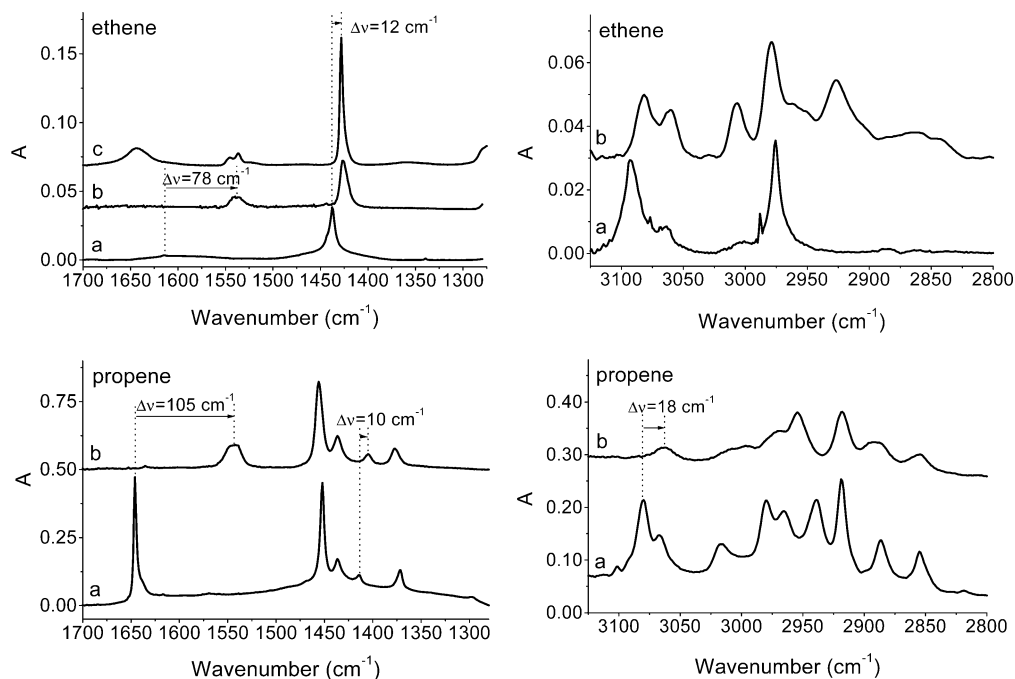


Figure 4. IR spectra of propene and ethene physisorbed in silicalite (a) as well as sorbed in CuX (b) and CuY (c).

cis-but-2-ene, and propene in CuX and CuY. The spectra recorded upon the sorption of amounts of alkenes comparable to the amount of Cu^+ , the excess of alkenes (1–3 mbar in gas

phase), as well as difference spectra are presented in Figure 6 A. In most cases, alkenes were sorbed at room temperature; only but-1-ene was sorbed in CuY at 260 K to avoid isomer-

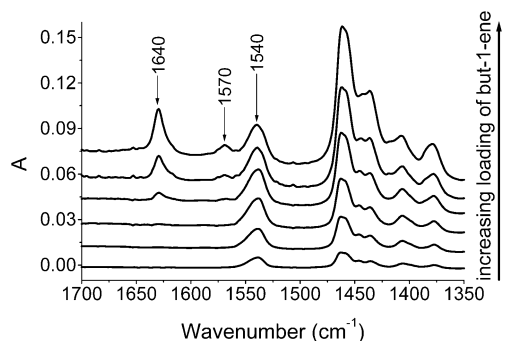


Figure 5. IR spectra recorded upon the sorption of increasing amounts of but-1-ene in CuX.

ization. For propene sorbed in CuY, the spectrum recorded upon the evacuation which followed the sorption of an excess of propene is also given.

In all these cases, the sorption of excess alkenes resulted in an increase of 1570 cm^{-1} band and in a decrease of the 1540 cm^{-1} one. These effects (seen well in the different spectra) are more pronounced in CuY than in CuX. An opposite effect of a decrease of 1570 cm^{-1} band accompanied by an increase of 1540 cm^{-1} band can be observed upon the evacuation of CuY in which an excess of propene has been sorbed.

All these results suggest that the band 1570 cm^{-1} may correspond to the situation in which two alkene molecules are bonded to one Cu^+ ion. The ability of Cu^+ ions to bond two NO molecules or two to three CO molecules has been already reported.^{36–40} It is not excluded that they may also bond two alkene molecules.

As mentioned in the previous section, in the spectra shown in Figure 6A (recorded at lower alkenes loadings), two submaxima are seen at the 1540 cm^{-1} C=C band. Comparing these spectra with difference spectra shows that the low-frequency

submaximum (at higher $\Delta\nu$) was eroded first when a large amount of alkenes is sorbed. This suggests that the Cu^+ ions which bonded alkenes with higher $\Delta\nu$ were more prone to bond a second alkene molecule.

In CuZSM-5 zeolite, in which but-1-ene was sorbed at low temperature (170 K), both 1540 and 1470 cm^{-1} bands appeared together even at relatively low loadings. It may be explained by the condensation of but-1-ene at the entrance to pores and in a high concentration of but-1-ene which favored the bonding of two molecules by one Cu^+ .

It is not excluded that the higher C=C stretching frequency of 1570 cm^{-1} band (lower $\Delta\nu$) may be because the electrical charge transferred by Cu^+ to alkenes is shared between two molecules. This problem will be the subject of our future quantum-chemical calculations.

The ability of Cu^+ ions in CuX, CuY, and CuZSM-5 zeolites to bond two alkene molecules was compared in experiments in which the excess of but-1-ene was sorbed at 170 K (Figure 6B). The ratio of intensities of the 1570 to 1540 cm^{-1} bands increases in the order $\text{CuX} < \text{CuZSM-5} < \text{CuY}$, indicating that the ability of Cu^+ to bond two alkene molecules increases in the same order.

Interesting results were obtained in experiments in which but-1-ene was sorbed at 170 K in CuZSM-5 with preadsorbed pyridine (Figure 6C). The sorption of pyridine (spectrum a) resulted in the appearance of bands of pyridinium ions (1490 , 1545 , 1635 cm^{-1}) and of pyridine bonded to Cu^+ ions (1450 and 1612 cm^{-1}). The sorption of but-1-ene (spectrum b) resulted in a small red shift of 1490 and 1612 cm^{-1} bands of adsorbed pyridine and in the appearance of 1540 cm^{-1} band of but-1-ene bonded to Cu^+ . This band is the only band of C=C interacting with Cu^+ . The band at 1570 cm^{-1} was absent even though it was present if but-1-ene was sorbed at the same experimental conditions in zeolite without pyridine (spectrum

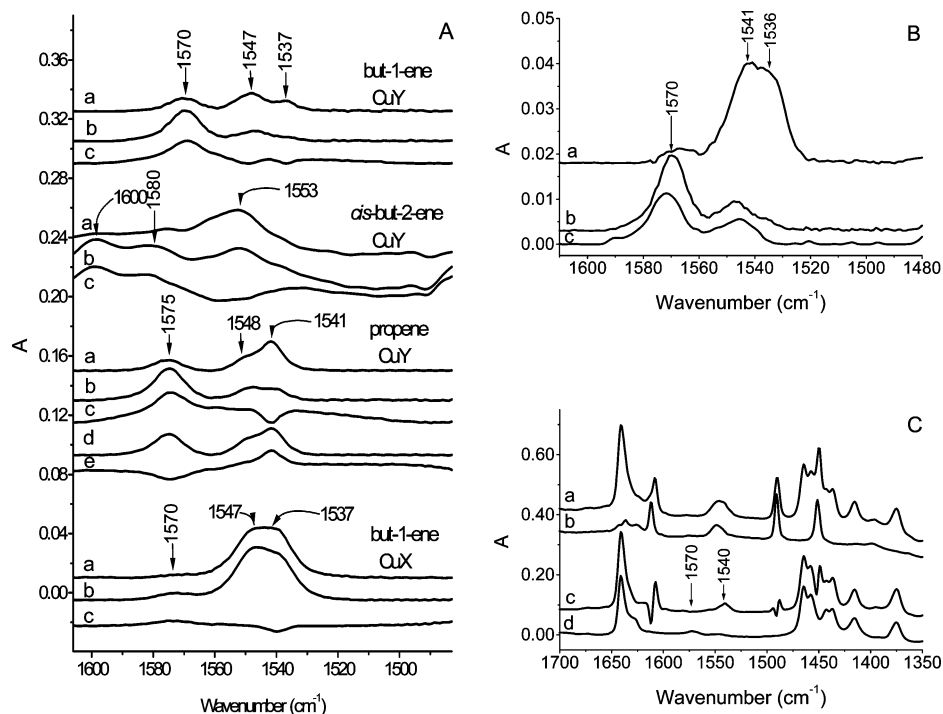


Figure 6. The spectra of but-1-ene, *cis*-but-2-ene, and propene sorbed in CuY and CuX. (A) But-1-ene, *cis*-but-2-ene, and propene sorbed in CuY (at 260 K) and CuX (room temperature): a, alkenes sorbed in amount comparable to the amount of Cu^+ ; b, alkenes sorbed in excess ($1\text{--}3\text{ mbar}$ in gas phase); c, difference spectra ($c = b - a$); d, evacuation of CuY zeolite with excess of propene sorbed; e, difference spectrum ($e = d - b$). (B) The spectra of excess but-1-ene sorbed at 170 K in CuX (a), CuY (b), and CuZSM-5 (c). (C) The spectra of but-1-ene sorbed at 170 K in CuZSM-5 with preadsorbed pyridine: a, spectrum of zeolite with sorbed pyridine (sorption of pyridine at 450 K followed by desorption at 590 K); b, but-1-ene sorbed in zeolite with pyridine; c, difference spectrum ($c = b - a$); d, but-1-ene sorbed in zeolite without pyridine.

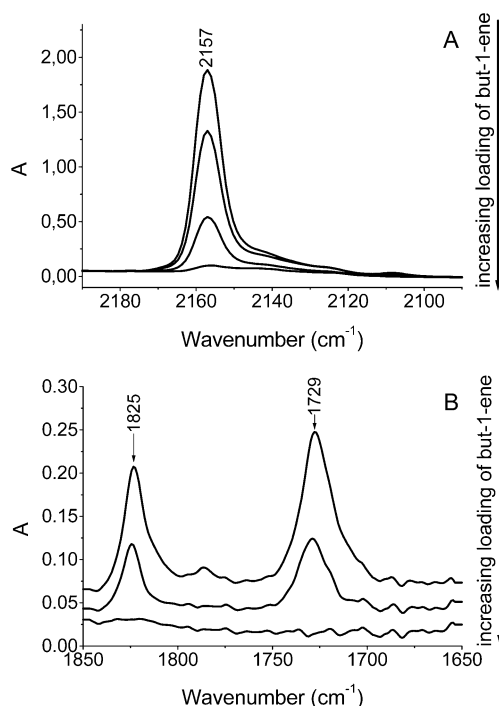


Figure 7. IR spectra of Cu^+CO and $\text{Cu}^+(\text{NO})_2$ complexes upon the sorption of increasing amounts of but-1-ene.

d). This result supports the hypothesis that the 1570 cm^{-1} band corresponds to two alkene molecules bonded to one Cu^+ ion. If Cu^+ bonded a pyridine molecule, there was no space to bond two alkene molecules. The intensity of the 1540 cm^{-1} band was higher than without pyridine. It seems that with pyridine most of Cu^+ was able to bond one alkene molecule, whereas without pyridine only some Cu^+ form 1:1 complexes with alkenes, whereas most of them bonded two alkene molecules.

Sorption of Alkenes in Cu-Zeolites with Preadsorbed CO and NO. Important information on the strength of alkenes to Cu^+ bonding was obtained in the experiments in which alkenes were sorbed in zeolites with preadsorbed CO and NO.

Figure 7A presents the results of experiments obtained with but-1-ene sorption in CuZSM-5 with preadsorbed CO. The excess of CO sufficient to cover all the Cu^+ ions was sorbed in CuZSM-5 at room temperature. It resulted in the formation of Cu^+CO monocarbonyls (IR band at 2157 cm^{-1}) and in a certain amount of $\text{Cu}^+(\text{CO})_2$ dicarbonyls (IR bands at 2150 and 2180 cm^{-1}). Evacuation at room temperature resulted in the decomposition of dicarbonyls and all the Cu^+ ions were in the form of Cu^+CO monocarbonyls. The sorption of but-1-ene at 170 K in such a zeolite resulted in a decrease of 2157 cm^{-1} bands of monocarbonyls and in an appearance and increase of the bands of but-1-ene interacting with Cu^+ (the most characteristic was 1540 cm^{-1}). Similar results were also obtained with other alkenes (propene and ethene) sorbed in all the Cu-zeolites (CuX, CuY, and CuZSM-5). In all the cases, alkenes replaced CO in Cu^+CO forms.

The results obtained with preadsorbed NO are shown in Figure 7B. NO was sorbed at a low temperature (170 K) to avoid the oxidation of Cu^+ to Cu^{2+} . NO sorbed at low temperature formed dinitrosyls $\text{Cu}^+(\text{NO})_2$ for which two bands, at 1825 and 1729 cm^{-1} , were characteristic. The sorption of but-1-ene at 170 K resulted (similarly to the preadsorbed CO) in a disappearance of the bands of $\text{Cu}^+(\text{NO})_2$ and in an appearance of the bands of but-1-ene interacting with Cu^+ .

All the results obtained in the experiments with CO and NO preadsorbed demonstrated that alkenes were so strongly bonded

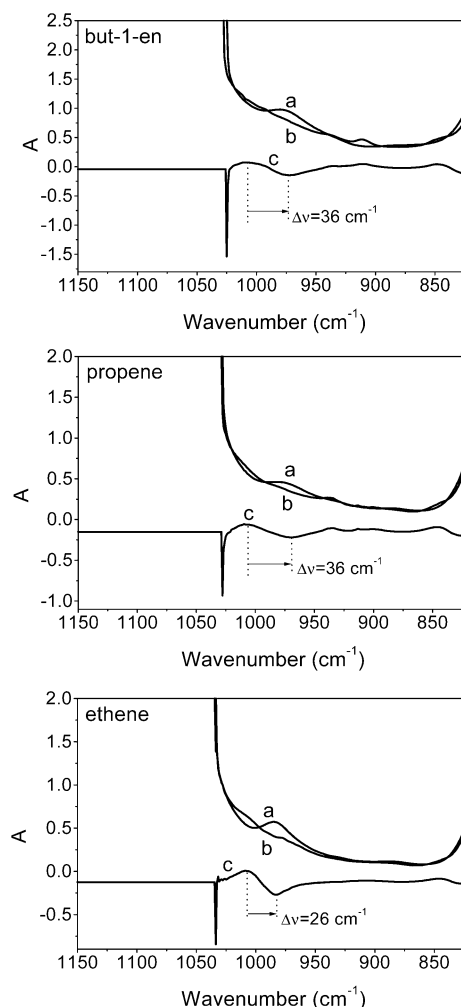


Figure 8. IR spectra of framework oxygen rings in CuZSM-5 (recorded at 170 K) before (a) and after the sorption of but-1-ene, propene, and ethene (b), as well as difference spectra $c = b - a$.

to Cu^+ in zeolites that they replaced CO and NO from relatively stable Cu^+CO and $\text{Cu}^+(\text{NO})_2$ complexes. However, the results obtained with but-1-ene sorbed in zeolite with preadsorbed pyridine (Figure 6C) proved that but-1-ene could not replace pyridine bonded to Cu^+ .

The Effect of Alkene Sorption on the Framework Vibrations of CuZSM-5 Zeolites. The introduction of cations into cation positions of MFI zeolites, as well as of other zeolites (for example, ferrierites), resulted in some deformation of the oxygen ring and therefore in a shift of IR band of ring vibration from about 1020 cm^{-1} (position of unperturbed rings) to lower frequencies. A weak maximum or a shoulder between 930 and 980 cm^{-1} (in the so-called “transmission window”) appeared, the position of which depended on the extent of deformation of the ring by cation and their intensity on the cation amount. The interaction of cations with adsorbed molecules such as CO, NO, NO_2 , NH_3 , and H_2O resulted in some cation withdrawal from the oxygen ring and in the ring relaxation. The IR band of ring vibration shifted to a higher frequency toward the position of unperturbed ring. Therefore, the observation of the band of oxygen ring vibration (about 930 – 980 cm^{-1}) may be helpful in studies of the properties of cations in zeolites and their interaction with adsorbed molecules. This is especially useful in the highly siliceous zeolites in which the properties of cations cannot be studied by XRD. The method based on observation of the IR band in the “transmission window” was

first proposed by Sarkany^{41–45} and then developed by other authors.^{46–49}

The spectra of CuZSM-5 in the “transmission window” are shown in Figure 8. The spectra recorded at 170 K before and after alkene sorption as well as difference spectrum are given.

A weak band at 960 cm^{−1} seen in the spectrum of activated CuZSM-5 can be interpreted as the vibration of oxygen rings deformed by Cu⁺. The effect of alkene adsorption can be best seen in different spectra. The band shift was 26–36 cm^{−1} for ethene, propene, and but-1-ene adsorbed. These $\Delta\nu$ values were distinctly higher than for CO adsorbed ($\Delta\nu = 7$ cm^{−1} ref 45), proving that relaxation of the oxygen ring by withdrawing Cu⁺ by alkenes was more pronounced than by CO. These results indicate again that the interaction of Cu⁺ with alkenes was very strong, much stronger than with CO.

Conclusions

The interaction of the alkenes ethene, propene, but-1-ene, and *cis*-but-2-ene with Cu⁺ cations in zeolites resulted in a strong activation of the C=C bond. The double-bond stretching band shifted to lower frequencies by 78–115 cm^{−1}, indicating a distinct C=C bond weakening. The interaction of the C=C group with Cu⁺ cation also resulted in a shift of IR bands with stretching, deformation, and bending of C–H bonds in =CH₂ and =C–H groups in the vicinity of the double bond.

In ethene, the stretching of the C=C bond which was IR inactive in free molecules became IR active when interacting with Cu⁺, indicating the loss of symmetry. By contrast, the C=C stretching in *trans*-but-2-ene was still IR inactive when *trans*-but-2-ene interacted with Cu⁺.

In most cases, the band of C=C interacting with Cu⁺ was split into two submaxima suggesting the presence of Cu⁺ sites activating alkenes to a different extent.

At high loadings, some Cu⁺ ions were able to bond two alkene molecules. The Cu⁺ ions which bond alkenes with the highest $\Delta\nu$ are the most prone to bond two alkenes. The ability to bond two alkene molecules increased in the order CuX < CuZSM-5 < CuY.

The interaction of alkenes with Cu⁺ was so strong that they replaced both CO and NO from relatively stable Cu⁺CO and Cu⁺(NO)₂ complexes. Further evidence of the strong interaction of alkenes with Cu⁺ was a large shift in the IR band of framework oxygen rings perturbed by Cu⁺ upon alkene sorption, indicating a distinct relaxation of the rings because of withdrawing cation by alkenes.

It is concluded that the mechanism of alkene activation by Cu⁺ in zeolites is similar as in NO activation, that is, the π -back-donation of d electrons of Cu⁺ to antibonding π^* orbitals of alkenes. Our earlier quantum-chemical DFT calculations showed that the location of Cu⁺ in cationic positions distinctly lowered their electrical charge and increased the HOMO energy, enhancing the electrodonor properties of cations.

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References and Notes

- (1) Iwamoto, M.; Furokawa, H.; Mine, Y.; Uemura, F.; Mikuriya, S.; Kagawa, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1272.
- (2) Iwamoto, M.; Yakoo, S.; Sakai, K.; Kagawa, S. *J. Chem. Soc., Faraday Trans.* **1981**, 77, 1629.
- (3) Iwamoto, M.; Yachiro, H.; Mine, Y.; Kagawa, S. *Chem. Lett.* **1989**, 213.
- (4) Iwamoto, M.; Yachiro, H.; Kutsuno, T.; Bunyu, S.; Kagawa, S. *Bull. Chem. Soc. Jpn.* **1989**, 62, 583.
- (5) Broclawik, E.; Datka, J.; Gil, B.; Piskorz, W.; Kozyra, P. *Top. Catal.* **2000**, 11/12, 335.
- (6) Broclawik, E.; Datka, J.; Gil, B.; Kozyra, P. Zeolites and mesoporous materials at the dawn of the 21st century. In *Studies in surface science and catalysis*, electronic ed.; Galarneau, A., Di Renzo, F., Fajula, F., Vedrine, J., Eds.; Elsevier: 2001; 135, 15P13.
- (7) Broclawik, E.; Datka, J.; Gil, B.; Kozyra, P. Impact of zeolites and other porous materials on the new technologies at the beginning of the new millennium. In *Studies in surface science and catalysis*; Aiello, R., Giordano, G., Testa, F., Eds.; Elsevier: 2002; 142, 1971.
- (8) Datka, J.; Kukulska-Zajac, E.; Kozyra, P. *Catal. Today* **2004**, 90, 109.
- (9) Goursot, A.; Coq, B.; Fajula, F. *J. Catal.* **2003**, 216, 324–332.
- (10) Velu, S.; Wang, L.; Okazaki, M.; Tomura, S. *Microporous Mesoporous Mater.* **2002**, 54, 113.
- (11) Kumar, N.; Nieminen, V.; Lindfors, L. E.; Salmi, T.; Murzin, D. Y.; Laine, E.; Heikkilä, T. *Catal. Lett.* **2002**, 78, 105.
- (12) Nieminen, V.; Kumar, N.; Päiväranta, J.; Datka, J.; Hotokka, M.; Laine, E.; Salmi, T.; Murzin, D. Y. *Microporous Mesoporous Mater.* **2003**, 60, 159.
- (13) Zulfugarova, S. Zeolites and mesoporous materials at the dawn of the 21st century. In *Studies in surface science and catalysis*, electronic ed.; Galarneau, A., Di Renzo, F., Fajula, F., Vedrine, J., Eds.; Elsevier 2001; 135, 27P13.
- (14) Arnold, U.; da Cruz, R. S.; Mandelli, D.; Schuchardt, U. Zeolites and mesoporous materials at the dawn of the 21st century. In *Studies in surface science and catalysis*, electronic ed.; Galarneau, A., Di Renzo, F., Fajula, F., Vedrine, J., Eds.; Elsevier: 2001; 135, 27P06.
- (15) Batista, M. S.; Urquieta-Gonzales, E. A. Zeolites and mesoporous materials at the dawn of the 21st century. In *Studies in surface science and catalysis*, electronic ed.; Galarneau, A., Di Renzo, F., Fajula, F., Vedrine, J., Eds.; Elsevier 2001; 135, 27P12.
- (16) Antunes, A. P.; Silva, J. M.; Ribeiro, M. F.; Ribeiro, F. R.; Magnoux, P.; Guisnet, M. Zeolites and mesoporous materials at the dawn of the 21st century. In *Studies in surface science and catalysis*, electronic ed.; Galarneau, A., Di Renzo, F., Fajula, F., Vedrine, J., Eds.; Elsevier: 2001; 135, 30P23.
- (17) Łaniecki, M. Zeolites and mesoporous materials at the dawn of the 21st century. In *Studies in surface science and catalysis*, electronic ed.; Galarneau, A., Di Renzo, F., Fajula, F., Vedrine, J., Eds.; Elsevier: 2001; 135, 24P23.
- (18) Kubota, T.; Kumada, F.; Tominaga, H. *Int. Chem. Eng.* **1973**, 13, 539.
- (19) Arai, H.; Yamashiro, T.; Kubo, T.; Tominaga, H. *Bull. Jpn. Pet. Inst.* **1976**, 18, 39.
- (20) Espeel, P. H.; de Peuter, G.; Tielen, M. C.; Jacobs, P. A. *J. Phys. Chem.* **1994**, 98, 11588.
- (21) Minachev, Kh.; Kharlamov, V. V. *Acta Phys. Chem.* **1985**, 31, 497.
- (22) Mochida, I.; Hayata, S.; Kato, A.; Seiyama, T. *J. Catal.* **1970**, 19, 405.
- (23) Piffer, R.; Förster, H.; Niemann, W. *Catal. Today* **1991**, 9, 491.
- (24) Langham, C.; Piaggio, P.; Bethell, D.; Lee, D. F.; McMorn, P.; Bulman Page, P. C.; Willock, D. J.; Sly, C.; Hancock, F. E.; King, F.; Hutchins, *Chem. Commun.* **1998**, 15, 1601.
- (25) Traa, Y.; Murphy, D. M.; Farley, R. D.; Hutchings, *Phys. Chem. Chem. Phys.* **2001**, 3, 1073.
- (26) Armengold, E.; Corma, A.; Garcia, H.; Primo, J. *Eur. J. Org. Chem.* **1999**, 1915.
- (27) Hübner, G.; Roduner, E. Zeolites and mesoporous materials at the dawn of the 21st century. In *Studies in surface science and catalysis*, electronic ed.; Galarneau, A., Di Renzo, F., Fajula, F., Vedrine, J., Eds.; Elsevier: 2001; 135, 12P09.
- (28) Hübner, G.; Rauhut, G.; Stoll, H.; Roduner, E.; *Phys. Chem. Chem. Phys.* **2002**, 4, 1073.
- (29) Datka, J.; Kozyra, P.; Kukulska-Zajac, E.; Szutiak, M.; Kumar, N. *Proc. 14th International Zeolite Conference Cape Town*, electronic ed.; van Steen, E. W. J., Callanan, L. H., Clayes, M., O'Connor, C. T., Eds.; 2004; p 1655.
- (30) Hübner, G.; Rauhut, G.; Stoll, H.; Roduner, E.; *J. Phys. Chem.* **2003**, 107, 8568.
- (31) Palomino, G. T.; Bordiga, S.; Zecchina, A.; Marra, G. L.; Lamberti, C. *J. Phys. Chem. B* **2000**, 104, 8641.
- (32) Howard, J.; Nicol, J. M. *Zeolites* **1988**, 8, 142.
- (33) Borovkov, V. Yu.; Karge, H. G. *J. Chem. Soc., Faraday Trans.* **1995**, 191, 2035.
- (34) Borgard, G. D.; Molvik, S.; Balarman, P.; Root, T.; Dumestic, J. A. *Langmuir* **1995**, 11, 2065.
- (35) Borovkov, V. Yu.; Jiang, M.; Fu, Y. *J. Phys. Chem. B* **1999**, 103, 5010.
- (36) Wichterlova, B.; Sobalik, Z.; Dedecek, J. *Catal. Today* **1997**, 30, 199.

- (37) Bordiga, S.; Paze, C.; Berlier, G.; Scarano, D.; Spoto, G.; Zecchina, A.; Lamberti, C. *Catal. Today* **2001**, 70, 91.
- (38) Hadjiivanov, K. I.; Kantcheva, M. M.; Klissurski, D. G. *J. Chem. Soc., Faraday Trans.* **1996**, 92, 4595.
- (39) Zecchina, A.; Bordiga, S.; Salvalaggio, M.; Spoto, G.; Scarano, D.; Lamberti, C. *J. Catal.* **1998**, 101, 344.
- (40) Datka, J.; Gil, B.; Kawalek, M.; Staudte, B. *J. Mol. Struct.* **1999**, 511–512, 133.
- (41) Sarkany, J.; Sachtler, W. M. H. Catalysis by Microporous Materials. In *Studies in Surface Science and Catalysis*; Beyer, H. K., Karge, H. G., Nagy, J. B., Eds.; Elsevier: 1995; 94, 649.
- (42) Lei, G. D.; Adelman, B. J.; Sarkany, J.; Sachtler, W. M. H. *Appl. Catal. B* **1995**, 5, 245.
- (43) Sarkany, J. *J. Mol. Struct.* **1997**, 410–411, 95.
- (44) Sarkany, J. *J. Mol. Struct.* **1997**, 410–411, 137.
- (45) Sarkany, J. *J. Mol. Struct.* **1997**, 410–411, 145.
- (46) Sobalik, Z.; Tvaruzkova, Z.; Wichterlova, B. *J. Phys. Chem. B* **1998**, 102, 1077.
- (47) Sobalik, Z.; Tvaruzkova, Z.; Wichterlova, B. In *Proceedings of 12th IZC Conference*; Treacy, M. M. J., Marcus, B. K., Higgins, M. E., Eds.; Materials Research Society, Baltimore, MD, 1998; p 2339.
- (48) Sobalik, Z.; Dedeczek, J. Z.; Wichterlova, B. *Microporous Mesoporous Mater.* **1998**, 525.
- (49) Broclawik, E.; Datka, J.; Gil, B.; Kozyra, P. *Phys. Chem., Chem. Phys.* **2000**, 2, 401.