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The interaction of butenes with Cu^+ ions in CuMCM-41 studied by IR spectroscopy

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Abstract

As CuMCM-41 was found to be active in skeletal isomerisation of *n*-butenes, we followed by IR spectroscopy the interaction of but-1-ene, *cis*-but-2-ene, and *trans*-but-2-ene with Cu^+ sites in CuMCM-41. It has been revealed that Cu^+ activated strongly C=C bond, what resulted in a frequency shift of C=C stretching band by about 100 cm^{-1}. Moreover, the vibration of C–H bonds in $=CH_2$ and =C–H groups neighbouring to the double bonds was also perturbed. We suppose that the activation of C=C bond is a result of π-back donation of *d* electrons of Cu^+ to π^* antibonding orbitals of butenes. IR results evidenced also the heterogeneity of Cu^+ sites in CuMCM-41 and the presence of Cu^+ sites of various electron donor properties. But-1-ene molecules bonded to Cu^+ ions are less prone to accept protons from Brønsted acid sites than molecules bonded by hydrogen bonding to non-acidic SiOH groups, even though they are more negative than free or physisorbed molecules. The IR studies of coadsorption of CO and but-1-ene suggest that the interaction of CO with Cu^+ is much weaker if but-1-ene is present, than without butene.

Keywords: IR spectroscopy; Cu^+ cations; Butenes

1. Introduction

Isobutene is an important product in chemical industry. In most cases it is produced by a skeletal isomerisation of *n*-butenes over acidic forms of 10-member ring zeolites (mostly over ferrierite). Recently, it has been found [1,2] that Cu^+ ions in CuMCM-41 were also active in butene skeletal isomerisation: CuMCM-41 was found to be more active than HMCM-41 despite of lower acidity. This result suggests that Cu^+ ions in CuMCM-41 can activate C=C double bond in butenes, similarly as Cu^+ in CuZSM-5 activates N=O double bond in NO molecule (what results in NO dissociation). The activation of alkene molecules by Cu^+ ions in zeolites is also suggested by the fact that Cu-containing zeolites are active in several reactions of alkenes such as dimerisation [3] or oxidation [4–12].

The activation of N=O double bond by Cu^+ in zeolites was shown both in IR experiments and in DFT quantum chemical calculations. DFT calculations evidenced [13–17], that π-back donation of *d* electrons of Cu^+ ions to π^* antibonding orbitals takes place, what resulted in a distinct bond weakening. The electron donor properties of Cu^+ ions are due to the location of Cu^+ in an oxygen ring, what results in a partial neutralization of cation charge (it decreases from +1 to +0.3) and in a distinct increase of HOMO energy (from −14.115 eV for free ion to −5.170 or to −5.317 eV – depending on cluster geometry).

This study was undertaken to follow, by IR spectroscopy, the interaction of butenes (but-1-ene, *cis*-but-2-ene, and *trans*-but-2-ene) with Cu^+ cations in CuMCM-41. Our special attention was focused on the effect of Cu^+ on C=C double bond and on C–H bonds in $=CH_2$ and =C–H groups neighbouring to the double bond. Besides of CuMCM-41, HMCM-41 was also used as a "reference system" in which butenes interacted with OH groups by hydrogen bonding and silicalite in which butenes are physisorbed. Our earlier study [18] evidenced, that CuMCM-41 activated at vacuum conditions contained practically only Cu^+ cations, the Cu^{2+} content was very low. We compared

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also the properties of Cu^+ in partly amorphous CuMCM-41 and in crystalline CuZSM-5: therefore in some experiments but-1-ene was sorbed in CuZSM-5. In most cases butenes were sorbed at 250–260 K in order to avoid the isomerisation and oligomerisation which could occur in the presence of acid sites, which are always present in HMCM-41, CuMCM-41, and CuZSM-5. We studied also the coadsorption of CO and but-1-ene on Cu^+ sites in CuMCM-41. As the protonic sites play also an important role in butenes transformations we followed also their concentration by quantitative IR experiments of pyridine adsorption.

2. Experimental

NaMCM-41 (Si/Al = 15) was synthesized, using the method mentioned in [19] with some modifications. Synthesis was performed at 373 K using tetradecyltrimethylammonium bromide (Aldrich) as a surfactant, sodium silicate solution (Merck) as a source of silica and sodium aluminate (Riedel–Häen) as a source of alumina. The synthesized material was washed with distilled water, dried at 383 K and calcined to remove surfactant at 813 K. The NaMCM-41 was ion-exchanged with 1 M NH_4Cl, washed with distilled water to remove chloride ions and dried at 373 K. HMCM-41 was obtained by a calcination of NH_4MCM-41 at 803 K. CuHMCM-41 was prepared by ion-exchange of HMCM-41 using copper nitrate, washed with distilled water, dried at 373 K and calcined at 773 K. Cu content of 2.3 wt.% was measured by DCP.

NaZSM-5 (Si/Al = 35) was synthesized in the Institute of Industrial Chemistry (Warsaw). It was transformed into Cu-form by the treatment with $Cu(CH_3COO)_2$ solution at 80 °C. Upon the ionic exchange, the zeolite was washed with distilled water and subsequently dried in air at 370 K. The exchange degree (Cu/Al) was 0.45. We used also a silicalite synthesized at the Department of Chemical Technology of Jagiellonian University.

But-1-ene, *cis*-but-2-ene, *trans*-but-2-ene (Fluka – 99.9% pure) as well as CO (PRAXAIR 9.5) were used in IR experiments.

For IR studies all the materials studied 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. The spectral resolution was 2 cm^{-1}.

3. Results and discussion

3.1. The concentration of protonic sites

The concentration of protonic sites in both HMCM-41 and CuMCM-41 was determined in quantitative IR studies of pyridine adsorption. The excess of pyridine (sufficient to neutralize all the acid sites) was adsorbed at 450 K, and physisorbed pyridine was removed by evacuation at the same temperature. The concentration of protonic sites was calculated from the intensity of pyridinium ions 1545 cm^{-1} band and extinction coefficient of this band (0.070 cm^2/μmol – determined in our previous study – ref. [20]). This concentration was 147 μmol H^+/g for HMCM-41 and 44 μmol H^+/g for CuMCM-41. The H^+/Cu^{2+} exchange followed by the vacuum activation and Cu^{2+} to Cu^+ reduction resulted in the loss of ca. 100 μmol/g of protonic sites. This loss is distinctly smaller than the amount of Cu introduced: 2.3%, i.e. 365 μmol/g, indicating, that most of Cu did not neutralize AlO_4^- tetrahedra.

3.2. C=C and =C–H vibrations in butenes sorbed in HMCM-41 and CuMCM-41

The spectra of but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene sorbed in silicalite, and in CuMCM-41 are presented in Fig. 1. The interaction of butenes with Si–OH groups in HMCM-41(spectra not shown) resulted in a shift of OH band by about 80 cm^{-1} and in a smaller shift of C=C stretching band (7–9 cm^{-1}) from the position of molecules physisorbed in silicalite.

The interaction of butenes and with Cu^+ cations in CuMCM-41 results in a large shift of C=C stretching band by 96 cm^{-1} for but-1-ene and by 110 cm^{-1} for *cis*-but-2-ene. For *trans*-but-2-ene, the C=C band is IR inactive in free molecule as well as in molecule bonded to Cu^+ ions. The careful analysis of the spectra shows that not only C=C band is red shifted, but also C–H bands in $=CH_2$ and =C–H groups are perturbed, and C–H stretching bands are red shifted by 7–41 cm^{-1}.

The results presented in Fig. 1 evidenced that the interaction of butenes with Cu^+ ions in CuMCM-41 resulted in a distinct weakening of C=C bond and in some perturbation of =C–H bonds neighbouring to the double bond. Similar effects were also observed if alkenes interacted with Cu^+ ions in CuX and CuY zeolites [21–23].

It is very much possible that this weakening of C=C bond is a result of π-back donation of *d* electrons of Cu^+ ions to π^* antibonding orbitals of alkenes, similarly, as the activation of NO. Electron affinity EA (i.e. the energy loss due to acceptance of electron) is a measure of ability of molecule to be electron acceptor. These values were calculated by DFT [22] as the differences between total energies of anions and neutral molecules. The values of EA of butenes (about 1.5 eV) are higher than for NO (0.5 eV), but lower than for CO and N_2 (1.9 and 2.1 eV, respectively). These results indicate that butenes are relatively good electron acceptors: better than CO and N_2, but still not as good as NO. As mentioned, the donation of electrons to π^* antibonding orbitals of butenes results in a distinct weakening of C=C bond and in some weakening of =C–H bond, neighbouring to the double bond.

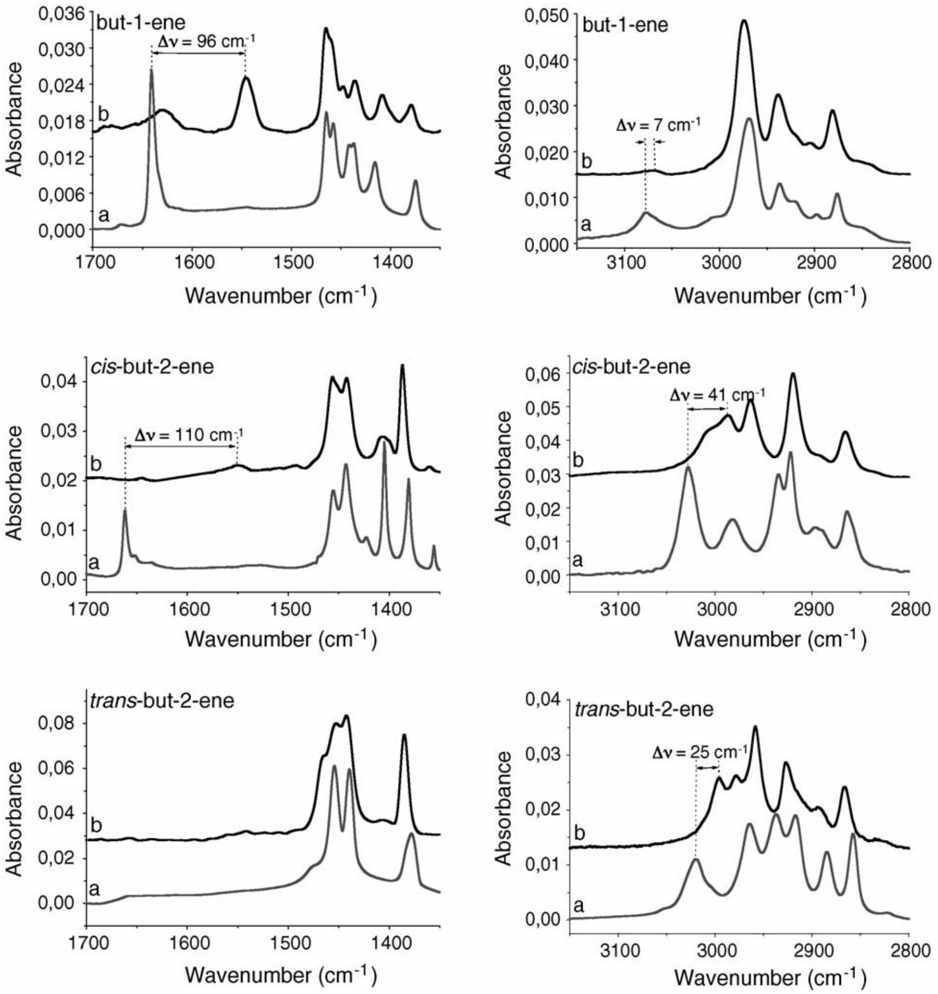

Fig. 1. IR spectra of but-1-ene, *cis*-but-2-ene, and *trans*-but-2-ene sorbed in silicalite (a) and in CuMCM-41 (b).

3.3. The activation of C=C bond by Cu^+ in CuMCM-41 and CuZSM-5

As mentioned above, the electron donor properties of Cu^+ site decide on the extend of π-back donation and on the extend of activation of alkene molecule. It was therefore interesting to compare the ability of Cu^+ ions in crystalline CuZSM-5 and in amorphous CuMCM-41 to activate but-1-ene molecules.

The information on the electron donor properties of Cu^+ was obtained by comparing the frequencies of CO and N_2 interacting with cations. The molecule of CO interacts with transition metal cations by both σ-donation and π-back donation. σ-donation is the interaction of an occupied σ molecular orbital with an electron acceptor adsorption site. This kind of interaction strengthens the C≡O bond, because σ molecular orbital of CO has a slight antibonding character (it overlaps π^* antibonding orbitals). The more electron donor the adsorption site is, the weaker is the σ-donation and the weaker is C≡O bond. The second type of interaction of CO with transition metal cation adsorption site is π-back donation of *d* electrons of cation to π^* antibonding orbitals of molecule, it weakens the C≡O bond. The more electron donor the adsorption site is, the stronger the π-back donation is and the weaker is C≡O bond. Therefore, the frequency of C≡O stretching vibration (similarly as of N≡N vibration) decreases as the electron donor properties of Cu^+ cation increase. The frequencies of stretching vibration of CO and N_2 interacting with Cu^+ in CuMCM-41 and CuZSM-5 (obtained in our previous study – ref. [16]) are presented in the Table 1. Both CO and N_2 frequencies for CuMCM-41 are higher than for CuZSM-5, indicating that Cu^+ ions are less electron donor in CuMCM-41.

Table 1
The electron donor properties of Cu^+ cations in CuZSM-5 and in CuMCM-41

	Electron donor properties of Cu^+		$\nu_{C=C}$
	ν_{CO}	ν_{N_2}	
CuMCM-41	2160	2300	1545
CuZSM-5	2157	2295	1538

The frequencies (in cm^{-1}) of CO and N_2 vibrations, and the frequency of C=C band in but-1-ene interacting with Cu^+.

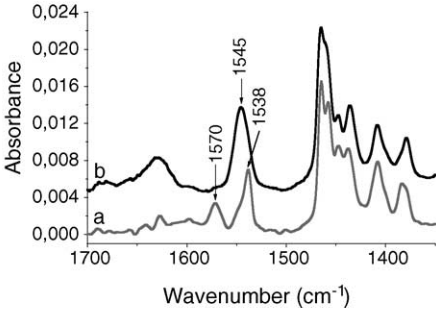

Fig. 2. IR spectra of but-1-ene sorbed in CuZSM-5 (a) and CuMCM-41 (b).

The spectra of but-1-ene sorbed in both CuMCM-41 and CuZSM-5 are shown in Fig. 2. In both cases the band at about 1540 cm^{-1} of C=C interacting with Cu^+ is present. Moreover, in CuZSM-5 a second band at 1570 cm^{-1}, the assignment of which will be discussed in the next chapter, is also seen. The frequency of the C=C band, in the case of CuMCM-41, is higher than in CuZSM-5 (1545 and 1538 cm^{-1}, respectively), indicating weaker C=C bond activation in CuMCM-41. This is due to weaker electron donor properties of Cu^+ ions and weaker π-back donation effect.

In the case of CuMCM-41, the C=C band is broader than in CuZSM-5 suggesting a heterogeneity of Cu^+ sites in CuMCM-41 and the presence of Cu^+ ions of various electron donor properties. It may be due to the presence of Cu^+ ions in various environment in amorphous MCM-41. DFT quantum chemical calculations evidenced [16] that the electron donor properties of Cu^+ depend on the number of oxygen atoms surrounding the cation. In amorphous aluminosilicate there may be Cu^+ cations of various number of oxygen atoms surrounding the cation.

3.4. Various loading of but-1-ene in CuMCM-41

The spectra recorded upon the sorption of increasing amount of but-1-ene in CuMCM-41 are presented in Fig. 3. At relatively low but-1-ene loading only the bands of but-1-ene interacting with Cu^+ ions are present – the most characteristic one is that at 1545 cm^{-1}. At higher loading the band of but-1-ene hydrogen bonded to Si–OH groups (1634 cm^{-1}) appears together with the new band at 1570 cm^{-1}. The band at 1570 cm^{-1} can arise from [21] the interaction of two but-1-ene molecules with one Cu^+ cation. All these results indicate that butene molecules react preferentially with Cu^+ ions, but at higher loading they form hydrogen bonding with Si–OH groups, and also complexes in which one Cu^+ ion bonds two but-1-ene molecules.

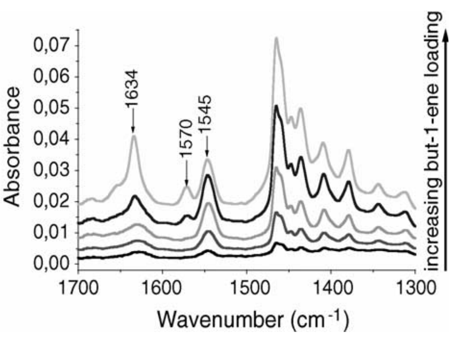

Fig. 3. The spectra of increasing amount of but-1-ene sorbed in CuMCM-41.

3.5. Proton addition to but-1-ene bonded to Cu^+ in CuMCM-41

As mentioned in Section 1, CuMCM-41 is an active catalyst in *n*-butene skeletal isomerisation to isobutene. One of the proposals in the literature on the skeletal isomerisation of alkenes comprises of several steps: the first one is proton addition to alkene and secondary carbocation formation, what is followed by a skeletal isomerisation of secondary carbocation to tertiary carbocation. Finally, tertiary carbocation gives off the proton forming neutral isobutene molecule.

It was interesting to know, if the fact that *n*-butenes sorbed in CuMCM-41 are bonded to Cu^+ ions facilities the proton acceptance by butene or makes it more difficult. In order to answer this question, we followed by IR spectroscopy the isomerisation of but-1-ene sorbed in CuMCM-41 to but-2-enes. According to a Whitemore mechanism, the double bond migration in but-1-ene composes of two main steps: proton addition and secondary carbocation formation, followed by proton abstraction from a carbon neighbouring to positively charged carbon, and but-2-enes formation (*cis*- and *trans*-). The rate of but-1-ene isomerisation to but-2-enes may be taken as the measure of ability of Brønsted site to be proton donor and ability of but-1-ene molecule to be proton acceptor (which is our main subject of interest). CuMCM-41, similarly as Cu-containing zeolites (besides of Cu^+ cations), contains also Brønsted sites being Si–OH–Al groups, the protons of which were produced by a hydrolysis during the activation at vacuum at high temperature, or may originate from not complete H^+ to Cu^{2+} exchange.

But-1-ene isomerisation is accompanied by a decrease of the IR band of C=C– vinyl group stretching and in the appearance of a much weaker 1645 cm^{-1} band of –C=C– stretching in vinylidene group in *cis*-but-2-ene (this vibration in *trans*-but-2-ene is IR inactive).

But-1-ene sorbed at 250 K in CuMCM-41 (Fig. 4 spectrum a) shows the bands of molecules bonded to Cu^+ cations (1545 and 1570 cm^{-1}), as well as the band of but-1-ene bonded to non-acidic Si–OH groups by hydrogen bonding at 1634 cm^{-1}. The heating to 260 K and subsequently to 265 K results in a distinct decrease of 1634 cm^{-1} band of hydrogen bonded but-1-ene without a distinct variation of 1545 and 1570 cm^{-1} bands (only the proportion between the intensities of these two bands changes). At room temperature (Fig. 4, spectrum d) the band of hydrogen bonded but-1-ene is absent but the bands of but-1-ene

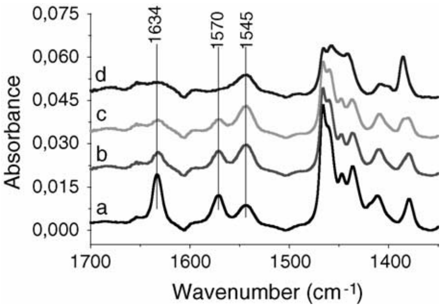

Fig. 4. The spectra of but-1-ene sorbed at 250 K (a) and upon heating to 260 (b), 265 K (c) and room temperature (d).

bonded to Cu$^+$ at 1545 and 1570 cm^{-1} are still present, but their intensity is lower then immediately upon the sorption (spectrum a). These results indicate that but-1-ene bonded to Cu$^+$ isomerises more slowly than but-1-ene hydrogen bonded. It suggests that but-1-ene bonded to Cu$^+$ is less prone to accept proton than but-1-ene hydrogen bonded.

It is possible, that the resistance to accept protons may be the fact that the carbon atom in –C=C fragment bonded to Cu$^+$ may have higher coordination number than in free or weakly bonded molecule.

As compared to HMCM-41 high activity of CuMCM-41 in skeletal isomerisation of *n*-butenes may be due to a lower activation energy of another reaction steps, such as branching of secondary carbocation to tertiary one, or to abstraction of proton from tertiary carbocation what results in the formation of neutral isobutene molecule.

3.6. Coadsorption of but-1-ene and CO in CuMCM-41

As mentioned above, CO may be used as a probe molecule to follow the properties of Cu$^+$ adsorption site (or of other adsorption sites). The CO stretching frequency decreases as electron donor properties of adsorption site increase and the CO frequency may be taken as the measure of electron donor properties of the sites.

In this study we followed also a coadsorption of CO and but-1-ene on Cu$^+$ sites in CuMCM-41. The spectrum of CO sorbed in CuMCM-41 is presented in Fig. 5 (spectrum a) and shows an intensive band at 2160 cm^{-1}. CO is relatively strongly bonded to Cu$^+$, because the evacuation at room temperature decreases only slightly CO band (Fig. 5, spectrum b). If CO is sorbed in CuMCM-41 with preadsorbed but-1-ene (Fig. 5, spectrum c) the CO band appears at 2147 cm^{-1}. The bonding of CO with Cu$^+$ in the presence of but-1-ene is much weaker than without butene: a short evacuation at room temperature results in a distinct decrease of 2147 cm^{-1} band (Fig. 5, spectrum d) The red shift of C–O band from 2160 to 2147 cm^{-1}, i.e. towards the position of physisorbed CO (ca. 2140 cm^{-1}), and the fact, that CO is very weakly bonded to Cu$^+$ suggests, that in the presence of but-1-ene CO is in larger distance from Cu$^+$ and is very weakly bonded.

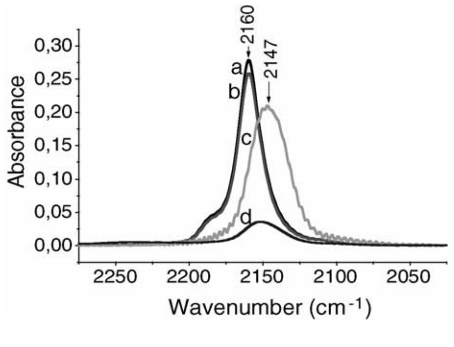

Fig. 5. The spectrum of CO sorbed at room temperature in CuMCM-41 (a) and upon 60 s evacuation (b). The spectra of CO sorbed in CuMCM-41 with preadsorbed but-1-ene (c) and upon 60 s evacuation (d).

4. Conclusions

Performed IR study evidenced a strong activation of C=C bond in butenes. IR band of C=C stretching vibrations shifted by about 100 cm^{-1} in the case of but-1-ene and *cis*-but-2-ene (in *trans*-but-2-ene C=C stretching is IR inactive), and the bands of C–H stretching in =CH$_2$ and =C–H groups neighbouring to the double bond shifted by 7–41 cm^{-1}. This activation may be the result of π-back donation of *d* electrons of Cu$^+$ to π^* antibonding orbitals of butenes.

In the case of CuMCM-41, the effect of π-back donation is weaker than for CuZSM-5, as suggested by smaller C=C frequency shift. This is due to weaker electron donor properties of Cu$^+$ in CuMCM-41 than in CuZSM-5 (as evidenced by IR studies of CO and N$_2$ sorption).

In CuMCM-41 Cu$^+$ sites are heterogeneous, there are sites of various electron donor properties, which may be explained by the presence of Cu$^+$ in various environment. The heterogeneity of Cu$^+$ sites in CuMCM-41 is higher than in CuZSM-5.

But-1-ene molecules bonded to Cu$^+$ in CuMCM-41 are less prone to accept protons from Brønsted acid sites, than but-1-ene bonded by hydrogen bonding to Si–OH groups (even though it is more negative because of π-back donation). It is possible that the resistance to accept protons may be due to the fact that carbon atom in –C=C fragment bonded to Cu$^+$ may have higher coordination number than for free or weakly bonded molecule.

IR experiments of coadsorption of CO and but-1-ene on Cu$^+$ sites in CuMCM-41 suggest that in the presence of but-1-ene CO is very weakly bonded with Cu$^+$.

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