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Ethylene Complexes in Copper(I) and Silver (I) Y Zeolites[1]

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Interactions between ethylene and Y zeolites have been studied by infrared spectroscopy. The cations that were incorporated in the zeolite framework included in one type Cu(I) and Ag(I), which have filled d orbitals and can form ethylene complexes by dπ bonding, and in the other Cu(II), Ca(II), and Zn(II), which interact with ethylene by van der Waals forces. Copper(I) Y was prepared *in situ* by the reduction of Cu(II)Y at 400°C with either carbon monoxide or a mixture of carbon monoxide and ammonia; all others were prepared by the usual ion-exchange method. Ethylene was strongly adsorbed on Cu(I)Y and Ag(I)Y at 25°C. The common feature of their ir spectra was the intense absorption band near 1430 cm^{-1} (ν_{12}), a considerable lowering of C=C stretching frequency (ν_2), and a combination band near 1930 cm^{-1} ($\nu_7 + \nu_8$). These bands remained even after the samples had been evacuated at 25°C for 1 hr. On Cu(II)Y and other cation-exchanged zeolites, the ir bands were relatively weak and they disappeared readily upon evacuation of the sample. The enhanced adsorption of ethylene amounted to a C_2H_4/Cu ratio of 1 at 25°C and above 80 Torr as Cu(II)Y was reduced to Cu(I)Y. In Ag(I)Y, ethylene strongly interacted with silver(I) ions at the hexagonal window positions (S_{II}).

INTRODUCTION

Copper(I) and silver(I) in zeolites can form complexes similar to those observed in the homogeneous phase. For instance, carbon monoxide is adsorbed in Cu(I)Y zeolite with greater uptake and higher heat than zeolites having other cations such as calcium, zinc, or manganese (*1*). The infrared spectrum for the former also shows a much stronger band with a lower C–O stretching frequency (*2*). In the presence of other ligands such as ammonia, pyridine, or ethylenediamine, the frequency is even lower. Similar interactions between carbon monoxide and Ag(I)X or Ag(I)Y zeolites were also observed (*3*). These propensities indicate that copper(I) or silver(I) carbonyls are formed in the zeolite. The specific interactions have to do with the filled 3d orbitals of copper(I) or the filled 4d orbitals of silver(I) that are capable of dπ back bonding with carbon monoxide. Thus, zeolite offers a good system for studying the coordination chemistry of copper(I) and silver(I).

Transition metal–olefin complexes in the homogeneous phase are well documented in the literature. Some of the more common ones are complexes of platinum(II), palladium(II), copper(I), and silver(I) (*4*). It is especially easy to form complexes with copper(I) and silver(I), whose salt solutions can react directly with olefins. The stability of the olefin complexes is generally attributed to the formation of a μ-bond by the overlap of a vacant outer orbital of the metal with a filled 2pπ orbital of the olefin, and the formation of

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TABLE 1

Preparation of Zeolites by Ion-Exchange

Zeolite	Exchange solution		Extent of cation exchange (%)
	Salt	Concentration (M)	
Cu(II)Y	Cupric nitrate	0.5	75
Ag(I)Y	Silver acetate	0.06	93
Ca(II)Y	Calcium chloride	0.90	77
Zn(II)Y	Zinc nitrate	0.20	74.5

a π-bond by the overlap of filled d-orbitals of the metal with a vacant $2p\pi^*$ antibonding orbital of the olefin. This is the so-called Dewar–Duncan–Chatt concept (*5*).

This paper reports the study of ethylene complexes in Y zeolites by means of infrared spectroscopy and adsorption measurement. The cations include copper(I) and silver(I) in one hand, which are capable of forming $d\pi$ back bonding, and calcium, zinc, and copper(II) on the other, which will interact with ethylene only by van der Waals forces.

EXPERIMENTAL METHODS

All zeolite samples except Cu(I)Y were prepared by ion-exchanging NaY (Linde SK-40, Lot No. 3607-381) repeatedly with appropriate salt solutions. The concentration of the exchange solution and the extent of cation exchange are indicated in Table 1. Cu(I)Y zeolite was prepared by the reduction of dehydrated Cu(II)Y with a mixture of carbon monoxide and ammonia ($CO:NH_3 = 5:1$; $P_{CO} = 200$ Torr; 1 Torr = 133.3 N m^{-2}) at 400°C. Previous study revealed that under these conditions, all copper(II) could be partially reduced to copper(I) within 1 hr (*1*).

Industrial ethylene, 98% purity, C.P. grade carbon monoxide, 99.5%, B.P. grade medical oxygen, 99.5%, high purity hydrogen, 99.995%, were supplied from Commonwealth Industrial Gases Ltd. Anhydrous ammonia, 99.7%, was supplied from I.C.I. Australia Ltd. All gases except hydrogen were each condensed in a liquid nitrogen cold trap, the middle portion of the condensate was then distilled and stored in a glass bulb. Hydrogen was passed slowly through a liquid nitrogen cold trap and into a storage bulb.

An infrared cell for the gas adsorption study in a similar design described by Peri and Hannan (*6*) was used. The windows were sodium chloride crystals. The zeolite sample was pressed into a 1.5 × 2-cm wafer with a thickness between 10 and 25 mg/cm^2. The wafer was first evacuated at 25°C and then slowly heated to 400°C. For Cu(II)Y and AgY, oxygen was admitted at a pressure of 150 Torr and the sample was heated in oxygen for at least 1 hr. Finally, the sample was evacuated at 400°C for 1 hr before being cooled to 25°C for the adsorption study. To prepare Cu(I)Y zeolite, the dehydrated Cu(II)Y sample was then reduced, as indicated above. Ethylene was adsorbed at 25°C and at pressures between 40 and 250 Torr. All infrared spectra were recorded between 1100 and 4000 cm^{-1} by an infrared spectrophotometer, Perkin-Elmer Model 577. A reference cell, which had the same path length and the same gaseous pressure as the adsorption cell, was used so that the gas phase absorption could be cancelled. Normal slit program was adopted and the resolution was 3 cm^{-1} at 3000 cm^{-1} and 1.6 cm^{-1} at 1000 cm^{-1}. An attenuator was used to adjust the transmittance at the minimum absorption of the entire recorded range to near 100%. This was usually near 2000 or 1500 cm^{-1} depending on the type of zeolite. In some instances, an ordinate expansion was used to determine the absorption frequencies of weak bands. The ordinate of the infrared spectra was expressed in percentage transmittance.

Adsorption isotherms and the amounts of ethylene remaining in Cu(II), Cu(I), and Ag(I) zeolites after evacuation were

TABLE 2

Amounts of Ethylene Adsorbed in Y Zeolites at 25°C

Zeolite	Cation content		P = 40 Torr		P = 250 Torr		After 1 hr evacuation	
	(mmol/g)	(No./unit cell)	(mmol/g)	(No. C_2H_4/unit cell)	(mmol/g)	(No. C_2H_4/unit cell)	(mmol/g)	(No. C_2H_4/unit cell)
Cu(II)Y	1.60	21	1.10	14.4	1.50	20.0	0.03	0.4
Cu(I)Y	1.60	21	2.60	34.4	3.10	40.8	0.85	11.2
Ag(I)Y	3.04	52	2.86	48.8	3.28	56.0	1.50	25.6

measured gravimetrically. Isosteric heats of adsorption were determined in the temperature range between 24 and 67°C for Cu(II)Y and between 176 and 218°C for Cu(I)Y.

To study the interaction between adsorbed ethylene and carbon monoxide on Cu(I)Y zeolite, the adsorption and desorption were measured volumetrically by the usual BET apparatus. Ethylene or carbon monoxide was preadsorbed onto the sample at 25°C at a pressure less than 10 Torr. Following a brief evacuation for 5 min, the other gas was then admitted to the adsorption cell. The adsorbates were successively removed by expanding into the gas burette. The composition of the desorbed gas was analyzed by a gas chromatograph.

RESULTS

Cu(II)Y

When ethylene was adsorbed on the dehydrated Cu(II)Y zeolite at 25°C and at 44 Torr, two infrared absorption bands of only moderate intensity were observed at 1430 and 1448 cm^{-1}, which were due to CH_2 asymmetric deformation, or ν_{12} mode according to the notation of Herzberg (7). A weak band at 1340 cm^{-1}, due to CH_2 symmetric deformation or ν_3 mode, two very weak bands at 1540 and 1560 cm^{-1}, due to C=C stretching or ν_2 mode, and two very weak bands at 2980 and 3095 cm^{-1}, due to CH stretching, were also observed. A spectrum was taken again 14 hr after the initial adsorption. All bands remained the same except that the 1430 cm^{-1} band became slightly stronger. If the ethylene pressure was increased to 180 Torr, a noticeable increase in intensity was observed only for bands at 1440, 2990, and 3080 cm^{-1}. Adsorption measurement indicated that the uptake at 250 Torr was increased by about 40% from that at 40 Torr (Table 2). Almost all adsorbed ethylene on Cu(II)Y could easily be pumped off at 25°C. The infrared spectra are shown on Fig. 1 and the adsorption isotherm at 25°C is shown on Fig. 2. At a surface coverage of 0.5 mmol/g, the isosteric heat of adsorption was 9.5 kcal/mol. At higher temperatures, the initial rapid adsorption was followed by a small amount of slow adsorption which could not be removed readily upon pumping. Presumably, copper(II) was reduced to copper(I) giving rise to stronger adsorption of ethylene.

Cu(I)Y

The infrared spectrum of Cu(I)Y had an absorption band at 2140 cm^{-1}, which was due to a trace of carbonyls occluded in the zeolite during the reduction process, two hydroxyl bands at 3550 and 3640 cm^{-1}, and a band at 1535 cm^{-1}. All except the last have been reported in a previous

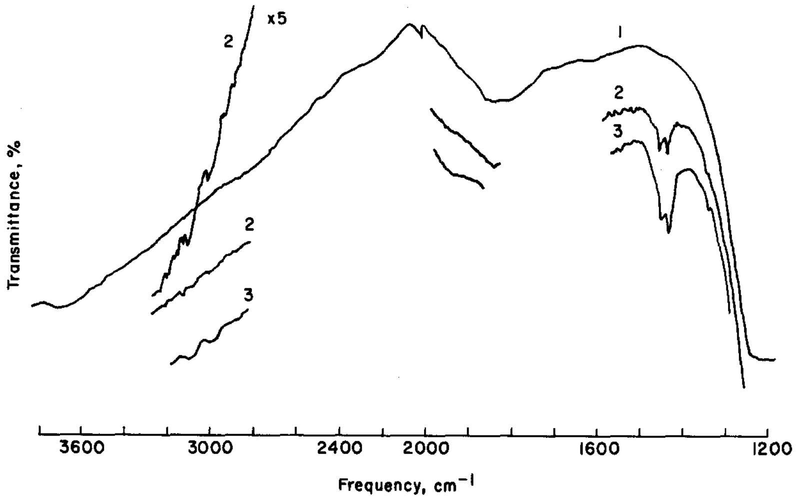
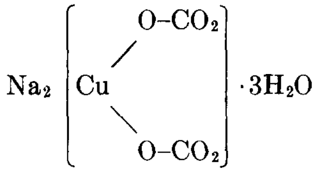


FIG. 1. Infrared spectra of adsorbed ethylene in Cu(II)Y zeolite. (1) Sample dehydrated at 450°C. (2) $P_{C_2H_4}$ = 40 Torr (× 5: five times ordinate expansion). (3) $P_{C_2H_4}$ = 250 Torr.

study (2). The band at 1535 cm^{-1}, which was observed in this study probably because of a better resolution, is in the region of asymmetric stretching of the $-O-CO_2$ group if compared with that reported in the literature for



$$Na_2\left[Cu\begin{matrix} O-CO_2 \\ O-CO_2 \end{matrix}\right]\cdot 3H_2O$$

(8). It was thus due to occluded carbonate species.

When ethylene was adsorbed on Cu(I)Y at 25°C and at 39 Torr, an intense band of ν_{12} mode was recorded at 1429 cm^{-1} together with two shoulders at 1422 and 1447 cm^{-1} (Fig. 3). Two bands of moderate intensity were also observed: one at 1533 cm^{-1} due to C=C stretching (ν_2) and the other at 1925 cm^{-1} which was attributed to the combination mode of CH_2 wagging ($\nu_7 + \nu_8$). The latter was not observed on the Cu(II)Y zeolite. The band at 1305 cm^{-1} due to ν_3 mode was inconspicuous and appeared only as a shoulder. Bands due to CH stretching were all quite weak, but were observable at 2995 and 3085 cm^{-1}. The two were more evident when recorded by a five-time ordinate expansion. If gaseous ethylene was pumped off and the zeolite sample was only briefly evacuated for 5 min, the shoulder bands near 1450 cm^{-1}, the CH stretching bands near 3000 cm^{-1}, and the ν_3 band at 1305 cm^{-1} almost all diminished. Only three bands at 1430, 1533, and 1925 cm^{-1} remained unchanged. The spectrum was virtually the same when recorded after the sample had been evacuated for 1 hr. If ethylene pressure was increased to 276 Torr, only the shoulder bands of the ν_{12}

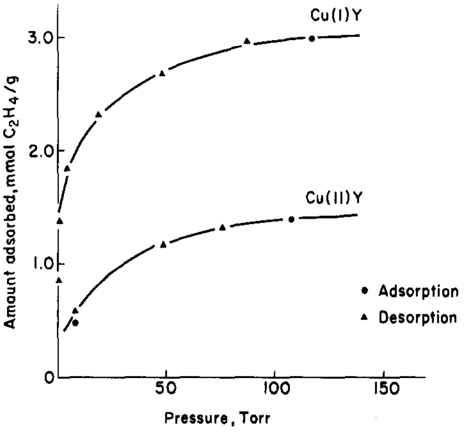


FIG. 2. Adsorption isotherms at 25°C of ethylene in CuY zeolites.

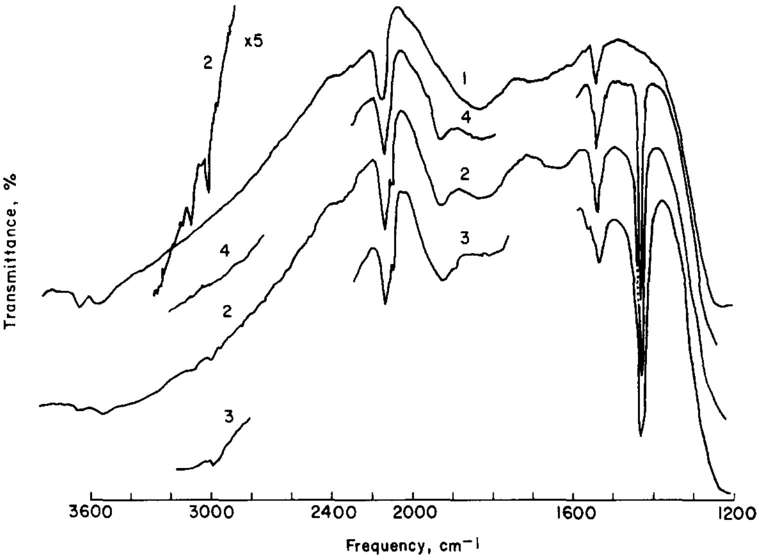


FIG. 3. Infrared spectra of adsorbed ethylene in Cu(I)Y zeolite. (1) Freshly prepared sample. (2) $P_{C_2H_4}$ = 40 Torr (× 5: five times ordinate expansion). (3) $P_{C_2H_4}$ = 250 Torr. (4) After 1 hr evacuation.

mode at 1420 and 1447 cm^{-1} increased their intensity slightly.

The carbonyl band at 2140 cm^{-1} was slightly perturbed by the adsorption of ethylene. At the shoulder of the original band, a small peak appeared at 2090 cm^{-1} which then disappeared after evacuation. This indicated that there was some interaction between the carbonyls and the ethylene complexes in the Cu(I)Y zeolite. In fact, if carbon monoxide was admitted at 25°C and at 26 Torr to the sample, which had been preadsorbed with ethylene and then briefly evacuated to remove the gas phase, a broad and intense band at 2140 cm^{-1} and a shoulder at 2090 cm^{-1} were recorded indicating the formation of carbonyls. Bands associated with the adsorbed ethylene were, however, hardly changed, as shown on Fig. 4. On the other hand, if carbon monoxide has been preadsorbed and the gas phase briefly pumped off, adsorption of ethylene at 38 Torr resulted in a noticeable change in the CO absorption band, which had then two peaks at 2090 and 2130 cm^{-1} and a shoulder at 2155 cm^{-1}. The perturbation of carbonyls by other ligands such as ammonia, pyridine, and ethylenediamine has been reported (*2*). In this case, the C–O stretching frequency is considerably lowered.

The adsorption isotherms at 25°C indicated that substantially more ethylene was held on Cu(I)Y than on Cu(II)Y zeolite (Fig. 2). The difference in uptake on the two samples in the pressure range between 40 and 250 Torr amounted to about one ethylene molecule per copper ion in the zeolite, which was equivalent to 1.6 mmol/g. The amounts of ethylene adsorbed in CuY as well as in AgY zeolites at two pressures and the amounts remaining after 1 hr evacuation of the samples are listed in Table 2. The isosteric heat of adsorption on Cu(I)Y was determined to be 16.3 kcal/mol at a surface coverage of 0.3 mmol/g and 15.5 kcal/mol at 1.0 mmol/g.

When ethylene was first adsorbed on Cu(I)Y followed by a brief evacuation, only 0.40 mmol of carbon monoxide could be adsorbed per gram of sample at 25°C and at 83 Torr. Without preadsorbed ethylene the uptake could be as high as

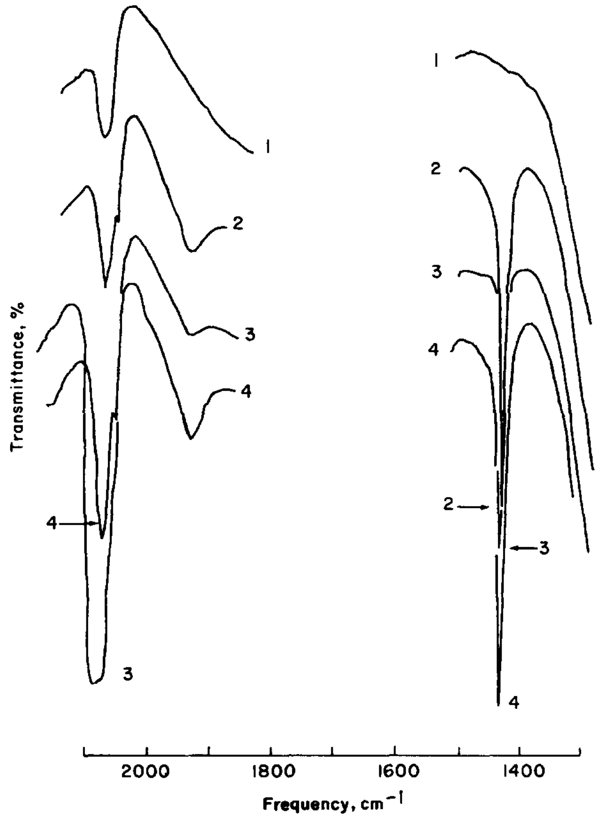


FIG. 4. Interaction between adsorbed carbon monoxide and ethylene in Cu(I)Y zeolite. (1) Freshly prepared sample. (2) C_2H_4 adsorbed at 25°C and 40 Torr. (3) CO adsorbed (25°C, 26 Torr) after gaseous C_2H_4 had been pumped off. (4) C_2H_4 adsorbed (25°C, 38 Torr) after gaseous CO had been pumped off.

1.6 mmol/g (*1*). The desorption data, which are summarized in Table 3, showed that ethylene was held on the zeolite more strongly than carbon monoxide. While more carbon monoxide was removed at 25°C, most ethylene was desorbed only at higher temperatures. In the desorbed gas the partial pressure of ethylene relative to carbon monoxide was very low at the beginning, but increased steadily following successive removal of the adsorbates, as indicated at the last column of the table.

If carbon monoxide was preadsorbed, only as much as 0.47 mmol of ethylene could be adsorbed per gram of sample. This shows that in spite of stronger adsorption of ethylene in Cu(I)Y, preadsorbed carbon monoxide considerably hindered the adsorption of ethylene. But the desorption measurement again indicated that it was harder to remove ethylene.

No change on the infrared spectrum of adsorbed ethylene in Cu(I)Y was observed when either oxygen or hydrogen was admitted to the sample cell at 25°C and 100 Torr. Apparently, Cu(I) ions in zeolite, when complexed with ethylene, were not oxidized by oxygen under this condition, although immediate oxidation to Cu(II) ions occurred when ammonia was preadsorbed (*1*). Hydrogenation of adsorbed ethylene was reported on nickel oxide when a hydrogen–ethylene mixture was used (*9*). But this was not the case on

TABLE 3

Desorption of Ethylene and Carbon Monoxide From Cu(I)Y Zeolite

Run	Sequence	T (°C)	P (Torr)	Amount adsorbed or desorbed (mmol/g)		C_2H_4/CO
				C_2H_4	CO	
I	a. C_2H_4 preadsorbed	25	5.5	0.949	—	—
	b. Evacuation for 5 min	25	—	?	—	—
	c. CO adsorbed	25	83.0	—	0.399	—
	d. Gas removed	25	23.2	0.032	0.189	0.17
		25	11.4	0.022	0.079	0.27
		25	7.0	0.016	0.045	0.36
		240	45.0	0.310	0.056	5.50
		290	32.6	0.269	0.007	37.53
		350	20.8	0.145	0.036	4.00
	Gas removed at 25°C			0.070	0.313	
	Gas removed after heating			0.724	0.099	
	Total gas desorbed			0.794	0.412	
II	a. CO preadsorbed	25	8.6	—	0.782	—
	b. C_2H_4 adsorbed	25	47.8	0.136	—	—
	c. Gas removed	25	—	0.006	0.182	—
	d. Evacuation for 5 min	25	—	?	?	—
	e. C_2H_4 adsorbed	25	32.0	0.344	—	—
	f. Gas removed	25	13.4	0.022	0.099	0.22
		25	8.2	0.009	0.063	0.14
		230	47.5	0.179	0.207	0.86
		230	29.8	0.207	0.052	4.01
	Gas removed at 25°C			0.031	0.162	
	Gas removed after heating			0.386	0.259	
	Total gas desorbed			0.417	0.421	

Cu(I)Y zeolite. Nor was polymerization of ethylene in the zeolite observed under the experimental conditions.

AgY

A broad band due to ν_{12} mode with two peaks at 1420 and 1452 cm^{-1} was observed when ethylene was adsorbed at 25°C and at 39 Torr (Fig. 5). The latter was slightly stronger than the former. Unlike Cu(I)Y, the ν_3 band at 1318 cm^{-1} was sharp and conspicuous. Two bands due to ν_2 mode were at 1582 and 1620 cm^{-1}. Similar to Cu(I)Y, the combination band ($\nu_7 + \nu_8$) was clearly shown at 1950 cm^{-1}. Bands due to CH stretching were also observable at 2995 and 3080 cm^{-1}. The spectrum remained virtually the same when the ethylene pressure was increased to 250 Torr, in agreement with the adsorption measurement (Table 2). When the sample was evacuated for 5 min an appreciable decrease in intensity was observed only for bands at 1318 and 1452 cm^{-1}. All others were unchanged. Prolonged evacuation for 9 hr resulted in the decrease in intensity of all bands. The band at 1425 cm^{-1} had become stronger than that at 1467 cm^{-1}. The ν_2 band only appeared as a shoulder. In the region of CH stretching, a band at 3000 cm^{-1} was stronger than the other.

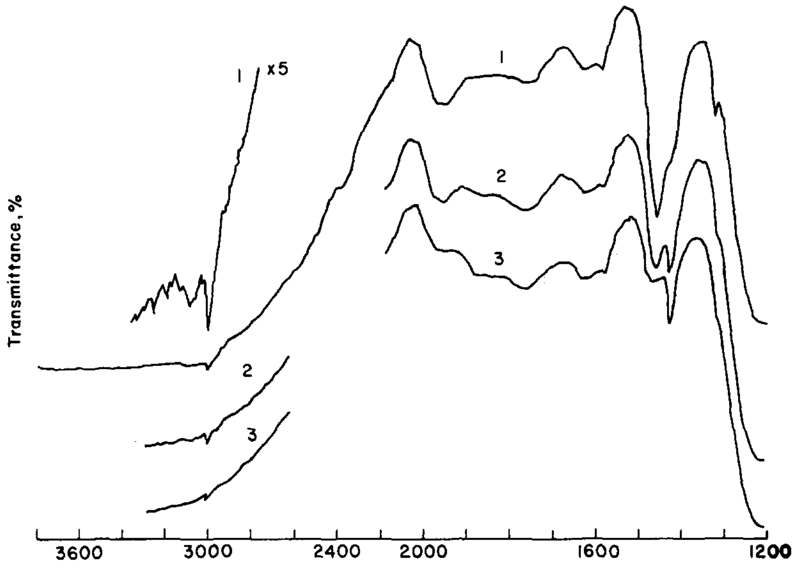


FIG. 5. Infrared spectra of adsorbed ethylene in Ag(I)Y zeolite. (1) $P_{C_2H_4}$ = 40 Torr (× 5 = five times ordinate expansion). (2) After 5 min evacuation. (3) After 9 hr evacuation.

CaY

On the dehydrated CaY sample, a broad band at 1450 cm^{-1} and a weak band at 1678 cm^{-1} were recorded in the background spectrum. These could be due to a trace of carbonate species that was trapped in the zeolite framework during sample pretreatment. When ethylene was adsorbed at 25°C and at 46 Torr, a band of medium intensity was seen to superimpose on the 1448 cm^{-1} band of the background. This was attributed to the ν_{12} mode of the adsorbed ethylene. A weak but sharp band at 1338 cm^{-1} due to ν_3 and a very weak band at 1610 cm^{-1} due to ν_2 were also observed. Bands due to CH stretching appeared at 2980 and 3080 cm^{-1}, but were not very clear. In the spectrum taken after the sample had been evacuated at 25°C for 1.5 hr, all bands almost diminished except the one at 1636 cm^{-1}, which had become stronger and even more so after evacuation at 100°C for 1 hr. While most adsorbed ethylene was removed upon evacuation as the characteristic ir bands disappeared, some carbonaceous materials seemed to have formed and retained on the CaY sample. Two very intense bands at 1434 and 1490 cm^{-1} were observed after the sample had been heated overnight in oxygen at 400°C and 219 Torr. These bands, which remained unchanged even after prolonged evacuation at 400°C, were apparently due to unidentate carbonate species, as reported by Angell and Howell (*10*). The infrared spectra of CaY zeolite following various adsorption and desorption steps are shown on Fig. 6.

ZnY

A sharp band at 2218 cm^{-1} was observed when carbon monoxide was adsorbed on the dehydrated ZnY zeolite, similar to that reported by Angell and Schaffer (*11*). The band, unlike that observed on Cu(I)Y, disappeared after a brief evacuation of the sample. Upon adsorption of ethylene at 25°C and 51 Torr, a medium band at 1448 cm^{-1} and two small but rather conspicuous bands at 1597 and 1336 cm^{-1}

were observed. Again, the C–H stretching bands were very weak. The adsorbate could be removed rather easily by evacuation of the zeolite slightly above 25°C. The infrared spectra are shown on Fig. 7.

Infrared absorption bands of adsorbed ethylene on all zeolite samples are summarized in Table 4. The bands recorded for Zeise's salt, $KPtCl_3(C_2H_4)\cdot H_2O$, which was studied by Grogan and Nakamoto (*12*), are also listed for comparison.

DISCUSSION

Some common features of the infrared spectra were observed on the ethylene complexes of Cu(I) and Ag(I) in Y zeolites: strong absorption bands due to asymmetric CH_2 deformation (ν_{12}), substantially lower C=C stretching frequency (ν_2) than that of the gas phase, and observable combination bands due to CH_2 wagging ($\nu_7 + \nu_8$). These characteristic bands were little changed even after the zeolite samples had been evacuated at 25°C for 1 hr, thus indicating a strong interaction between ethylene and copper(I) or silver(I). On the other hand, the interaction with calcium, zinc, or copper(II) was much weaker and the above features of the infrared spectra were not generally observed. The parameters of the infrared absorption bands for various Y zeolites, such as frequency, half-width, optical density, and deviation from the gas phase frequency are summarized in Table 5.

Contrary to the above features, the bands due to CH_2 symmetric deformation (ν_3) recorded for Cu(I)Y and Ag(I)Y zeolites were weaker than those for Ca(II)Y and Zn(II)Y, and they disappeared upon evacuation of the sample. The CH stretching bands were all very weak in all zeolites. A decrease in intensity was reported when ethylene changed from the gas phase to the adsorbed state (*13*, *14*), or to the solid state (*15*). This probably has to do with the change in dipole moment of the CH species. In practice, the ν_3 band and the CH stretching bands cannot be regarded as essential to the characterization of ethylene complexes of Cu(I) and Ag(I) in zeolite.

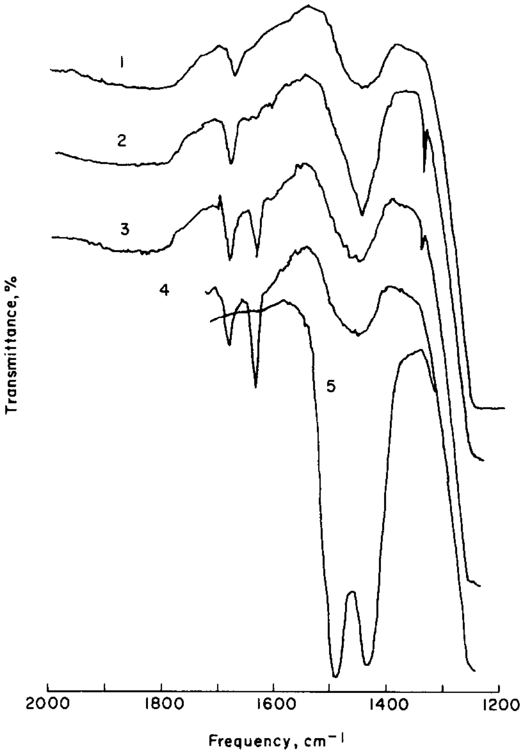


FIG. 6. Infrared spectra of adsorbed ethylene in Ca(II)Y zeolite. (1) Sample dehydrated at 450°C. (2) $P_{C_2H_4}$ = 46 Torr. (3) After 1.5 hr evacuation at 25°C. (4) After 1 hr evacuation at 100°C. (5) Heated in O_2 followed by evacuation, both at 400°C.

The combination band ($\nu_7 + \nu_8$) was observed in Cu(I)Y and Ag(I)Y, and also in Zeise's salt (*12*). It is infrared active in the gas phase, and gives a rather intense band with the Q-branch centered at 1889 cm^{-1}. On CaY or ZnY zeolite, however, the band was not observed. Nor was it on various cation-exchanged X zeolites, as reported by Cater and his co-workers (*13*). By theoretical consideration they indicated that the band should be observable even if the symmetry of an ethylene molecule was changed from the D_{2h} point group in the gas phase to C_{2v} in the adsorbed state. They argued that

FIG. 7. Infrared spectra of adsorbed ethylene in Zn(II)Y zeolite. (1) Sample dehydrated at 450°C. (2) CO adsorbed at 25°C, 61 Torr. (3) C_2H_4 adsorbed at 25°C, 51 Torr. (4) After 15 min evacuation at 25°C following (3). (5) Briefly heated at 100°C following (4).

because of the ethylene–cation interaction, both ν_7 and ν_8 vibrations could be somewhat changed so that the combination band was shifted to a region where it was not observable. But why was the band recorded for Cu(I)Y and Ag(I)Y where the ethylene–cation interaction was even stronger? The discrepancy, thus, could lie in the difference of the nature of interaction.

When an ethylene molecule is adsorbed on the surface by van der Waals forces, it is more likely that the axis of C=C will be parallel to the surface. The four hydrogen atoms will usually be attracted toward the surface so that the adsorbed ethylene has a C_{2v} symmetry, as shown on Fig. 8a. Because of the change in symmetry, most vibrational modes are more or less affected. Some infrared absorption bands that do not appear in the gas phase, like the C=C stretching (ν_2) and the CH_2 symmetric deformation (ν_3), become observable. This is exemplified by the infrared spectra of adsorbed ethylene on all zeolite samples. And as a result of the change in symmetry, the $\nu_7 + \nu_8$ combination band is shifted out of the recorded range, as suggested by Carter and his co-workers.

The situation is different when ethylene is adsorbed to a cation site where dπ–pπ^* back bonding is involved, such as in the case of Cu(I)Y and Ag(I)Y. Owing to a much stronger ethylene–cation interaction, the four hydrogen atoms may instead be pushed away from the cation, as shown on Fig. 8b. In fact, neutron or X-ray diffraction studies on many metal–ethylene complexes have revealed that this is the case (*16–18*). For instance, the C–H bonds in Zeise's salt, $KPt(C_2H_4)Cl_3 \cdot H_2O$, are bent away from the central platinum atom so that the angle between the normals to the H–C–H planes, α, is 32.5° (*16*). Different angles have been reported on ethylene complexes of rhodium (*17*) and niobium (*18*), but they all indicate the same phenomenon. While there is no structural study of copper(I)–ethylene or silver(I)–ethylene complexes to indicate the α angles, it is quite likely that they would be smaller than 90°.

In zeolites, copper(I) and silver(I) are coordinated to oxide ions which may also exert weaker van der Waals forces on the molecule. These forces would tend to attract hydrogen atoms toward the cation, and hence compensate to some extent the stronger π-interactions. As a result, the C–H bonds may not bend away as much from the C=C plane. Therefore, the changes in ν_7 and ν_8 vibrational modes may be quite small such that the combination band is still in the same region as a free molecule. It was not observed on AgX by Carter *et al.* probably because the transmission was very low in the region near 1900 cm^{-1} and the band was masked (*3*). That the ν_3 band on Cu(I)Y and Ag(I)Y was weak was probably again due to the small change in the vibrational mode.

The adsorption data were in accord with the infrared spectra: ethylene was adsorbed more and stronger on Cu(I)Y than on Cu(II)Y. The difference in uptake at 25°C was 1.35 mmol/g at a pressure as low as 5 Torr and it reached 1.60 mmol/g above 80 Torr (Fig. 2). The latter is equivalent to a value of the total copper content in the Y zeolite where 75% of sodium ions have been exchanged by copper(II) ions (Table 2). Since a complete reduction of Cu(II) into Cu(I) was easily achieved according to the method described above, the adsorption data indicate that the ethylene/copper(I) ratio reached one in the zeolite framework even at subatmospheric pressures. This is rather remarkable in view of the fact that for solid cuprous chloride, much higher pressures (several atmospheres) are required to absorb ethylene to the same extent (*19*). In the acid solution or in aqueous suspension, less ethylene is adsorbed (*20*), although the C_2H_4/Cu(I) ratio in the soluble complex is also one (*21*).

There is much similarity between ethylene and carbonyl complexes in Cu(I)Y zeolite. Both give strong infrared absorp-

TABLE 4

Infrared Absorption Bands of Adsorbed Ethylene in Y Zeolites[a,b,c]

Cu(I)Y			Ag(I)Y			Cu(II)Y		Ca(II)Y		Zn(II)Y		Zeise's salt (c)	Gas phase	Assignment	Mode
A	B	C	A	B	C	A	B	A	C	A	C				
3085 W	3080 W	3090 W	3080 W	3080 VW	3085 W	3095 W	3080 W	3080 W	—	3080 W	—	3098 W	3105 VS	CH stretch	ν_9
2995 W	2995 W	2990 W	2995 M	2990 M	3000 M	2980 VW	2990 W	2980 W	—	2995 W	—	3010 W	2989 S	CH stretch	ν_{11}
1925 M	1925 M	1925 M	1950 M	1950 S	1950 M	—	—	—	—	—	—	2048 W	1889 M	Combination of CH_2 wag	$\nu_7 + \nu_8$
1533 M	1533 M	1533 M	1620 M	1630 M	1625 W	1560 W	1565 W	1610 VW	1610 VW	1597 M	1597 W	1526 W	1623 I	C=C stretch	ν_2
			1582 W	1582 M	1580 W	1540 W	1540 VW								
1447 Sh	1447 Sh	—	1452 VS	1448 VS	1458 S	1448 M	1440 S	1448 M	1448 W	1460 Sh	1462 W	1428 VS	1444 S	CH_2 asymmetric deformation	ν_{12}
1429 VS	1426 VS	1430 VS	1420 S	1420 S	1425 S	1430 M	1428 S			1448 M					
1422 Sh	1420 Sh	1422 Sh													
1305 VW	1305 VW	—	1318 M	1318 M	1315 W	1340 W	1340 W	1338 M	1340 W	1336 M	1337 W	1418 Sh	1342 I	CH_2 symmetric deformation	ν_3

[a] Adsorption condition at 25°C: A, P = 40–50 Torr; B, P = 250 Torr; C, after 1 hr evacuation.

[b] Designation of intensity: very weak (VW), weak (W), medium (M), strong (S), very strong (VS), shoulder (Sh), infrared inactive (I).

[c] From Grogan and Nakamoto (*12*).

TABLE 5

Characteristics of Infrared Bands of Adsorbed Ethylene in Y Zeolites

Y Zeolite	Ethylene adsorbed at $P = 40$ Torr					After brief evacuation at 25°C				
	Cu(I)	Ag(I)		Ca(II)	Zn(II)	Cu(I)	Ag(I)		Ca(II)	Zn(II)
ν_3 Band										
Frequency (cm^{-1})	1305	1318	—	1338	1336	—	—	—	1340	1337
Half-width (cm^{-1})	3	10	—	3	4	—	—	—	3	3
OD[a]	0.024	0.068	—	0.068	0.145	—	—	—	0.021	0.093
$\Delta\nu$[b] (cm^{-1})	−37	−24	—	−4	−6	—	—	—	−2	−5
ν_{12} Band										
Frequency (cm^{-1})	1429	1420	1452	1448	1448	1430	1425	1458	1448	1462
Half-width (cm^{-1})	13	38	38	40	45	8	35	40	25	20
OD	0.814	0.252	0.433	0.124	0.078	0.684	0.207	0.211	0.044	0.022
$\Delta\nu$ (cm^{-1})	−15	−24	4	4	4	−14	−9	14	4	18
ν_2 Band										
Frequency (cm^{-1})	1533	1582	1620	1610	1597	1533	1580	1625	1610	1597
Half-width (cm^{-1})	10	15	35	5	7	10	9	30	5	6
OD	0.066	0.019	0.005	0.010	0.054	0.079	0.023	0.014	0.006	0.038
$\Delta\nu$ (cm^{-1})	−90	−41	−3	−13	−26	−90	−43	−3	−13	−26
$\nu_7 + \nu_8$ Band										
Frequency (cm^{-1})	1925	1950	—	—	—	1925	1950	—	—	—
Half-width (cm^{-1})	40	60	—	—	—	30	48	—	—	—
OD	0.051	0.061	—	—	—	0.047	0.034	—	—	—
$\Delta\nu$ (cm^{-1})	36	61	—	—	—	36	63	—	—	—

[a] OD: Optical density $A = \log (I_0/I)$, where I_0 is the intensity at baseline and I is the intensity at the peak.

[b] $\Delta\nu$ = Shift from gas phase frequency.

tion bands, and both have high heats of adsorption. In both cases, the ligand to metal ratio approaches one at 25°C and at very low pressures. This would imply that essentially all copper(I) ions in zeolite are coordinated to the adsorbate molecules. It is assumed that no more than one carbon monoxide or ethylene molecule can be associated with one copper(I) ion, and there is no indication that this may be so even in the homogeneous phase.

The distribution of copper(I) in Y zeolite is not known as there is no X-ray diffraction study reported in the literature. There are various sites in the zeolite at which these cations are likely located: S_I at the center of the hexagonal prism; $S_{I'}$ inside the sodalite cage but close to the hexagonal prism; S_{II} at the center of the six-membered ring between a sodalite cage and a supercage; and $S_{II'}$, near S_{II} but retracting into the sodalite cage. In fact, the X-ray study (*22*) of a dehydrated, 57% exchanged Cu(II)Y zeolite showed that copper(II) ions were distributed between $S_{I'}$ and S_I sites, preferably at $S_{I'}$. Similar sites may be occupied when copper(II) ions are reduced to copper(I) ions. Among the four types of sites, S_{II} and $S_{II'}$, sites are more accessible to coordinate with the adsorbing molecules. Copper(I) ions in S_I and $S_{I'}$ sites, however, are rather remote from the supercages. Unless the adsorbate molecules can enter the sodalite cages, these cations have to move to other sites more accessible for the coordination. Relocation of cations does happen in zeolite when strong ligands are present (*2*).

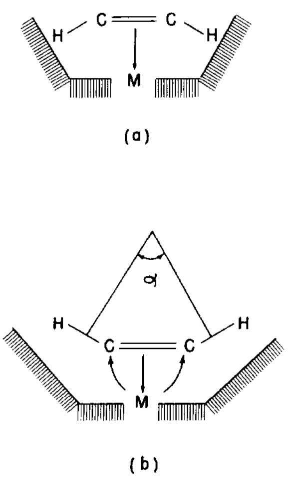


FIG. 8. Schematic view of ethylene–cation interaction in zeolites. (a) Cations capable of van der Waals interaction. (b) Cations capable of π interaction.

When carbon monoxide was adsorbed in Cu(I)Y between 0 and 100°C, a slow equilibrating process was observed which followed a rapid and large initial uptake (*1*). If carbon monoxide was first exposed to the adsorbent at 400°C and the system was cooled slowly to −196°C, then the total uptake was 0.4 mmol/g more than when carbon monoxide was directly introduced to Cu(I)Y at −196°C. The two observations reveal that carbon monoxide was entering the sodalite cages. This is rather surprising since carbon monoxide has a van der Waals diameter of 3.12 Å which is larger than the free opening of the hexagonal window (2.2 Å). In fact, the diffusion process does not occur in synthetic sodalite or other cation-exchanged Y zeolites even at a temperature as high as 200°C (*23*). However, in view of the strong Cu(I)–CO interaction, the shape of a carbon monoxide molecule could be somewhat changed. This, coupled with a slight vibrational enlargement of the hexagonal window at higher temperatures, would enable carbon monoxide to enter the sodalite cages.

Ethylene molecules are too big to enter the sodalite cages. All must be in the supercages. Indeed, unlike carbon monoxide, no slow adsorption was observed for the ethylene–copper(I)Y system. The coordination sites would thus be at the six-membered rings (S_{II} or $S_{II'}$).

Copper(I) ions at S_I and $S_{I'}$ sites have to migrate to nearby $S_{II'}$ (or even S_{II}) to coordinate with ethylene. In the infrared spectrum, no two or more distinct absorption bands were observed for the ν_{12} mode or any other mode to show that there were two or more distinctly different coordination sites. It is most likely that all the Cu(I)–C_2H_4 complexes were near the six-membered rings where they had the least hinderance from the oxide ions. In the faujasite type zeolite, there are four six-membered rings in a supercage. If all of the Cu(I)–C_2H_4 complexs were at this location, they would, on the average, amount to 2.62 per supercage or 21 per unit cell, as indicated in Table 2. Certainly, an ethylene to copper(I) ratio of one could be reached, just as in the case of carbon monoxide.

The cation distribution in Ag(I)Y is somewhat different. More silver(I) ions were ion-exchanged into the zeolite. There are on the average 52 silver(I) ions in a unit cell, which has 8 supercages and 16 hexagonal prisms. According to an X-ray diffraction study, the hexagonal prisms (S_I) are almost fully occupied by the silver ions (*24*). The remaining cations are then distributed in S_{II} and other sites inside the sodalite cages. Unlike copper(II) or copper(I), silver(I) ions in Y zeolite are rather immobile, as revealed by adsorption measurement and infrared study (*3*). Despite a higher cation content, less ammonia was adsorbed in Ag(I)Y than in Cu(I)Y. On the infrared spectrum of adsorbed carbon monoxide, there was no substantial lowering of the C–O stretching frequency when Ag(I)Y was preadsorbed with ammonia. Thus, the presence of ammonia did not seem to cause silver(I) ions to migrate into the supercages, as it did to copper(I) ions.

The adsorption of carbon monoxide in Ag(I)Y was rapid at 25°C and it was not followed by a slow equilibrating process as in the case of Cu(I)Y. At 100 Torr, the carbon monoxide to silver(I) ratio was only 0.66. This indicates that carbon monoxide did not enter the sodalite cages and that not all silver(I) ions in the zeolite were coordinated with carbon monoxide.

Though more ethylene was adsorbed in Ag(I)Y, not all silver(I) ions were accessible for coordination. Only those that were exposed to the supercages could interact with ethylene. With 52 silver(I) ions per unit cell, it is possible to have a full occupancy of the 32 S_{II} sites once all of the 16 S_I sites are taken. The remainder may then be located in the sodalite cages. From Table 2 the ethylene uptake in Ag(I)Y at 25°C and 40 Torr amounted to 49 molecules in one unit cell; at 250 Torr, it increased slightly to 56 molecules. Some of them would be adsorbed on the zeolite surface even in the absence of specific cation interactions. In fact, about 14 molecules were held on Cu(II)Y at 25°C and 40 Torr, and about 20 molecules at 250 Torr. These molecules were only weakly held and could easily be pumped off, as indicated by adsorption measurement and by infrared investigation. Assuming that the same number of ethylene molecules were adsorbed in Ag(I)Y that were not cation-specific, then the numbers that were associated with accessible silver(I) ions would be 34 and 36, respectively, at 40 and 250 Torr. These numbers are remarkably close to the number of S_{II} sites in a unit cell. We may thus conclude that, like carbon monoxide, ethylene was coordinated to silver(I) ions at all S_{II} sites. The presence of other silver(I) ions in the sodalite cages might have some influence on some of these sites as there were two rather strong ir bands due to ν_{12} mode.

Stronger adsorption for gas molecules are generally observed on zeolites with divalent than with univalent cations. The difference is often attributed to greater electrostatic interactions associated with the divalent cations. For instance, the isosteric heat of adsorption of carbon monoxide on a 76% exchanged CaY zeolite is 10.2 kcal/mol, but on NaY it is only 5.8 kcal/mol (*23*). For ethylene, the heat

TABLE 6

Heats of Adsorption of Carbon Monoxide and Ethylene in Zeolites

Cation	Na(I)		Ca(II)		Cu(II)	Cu(I)	Zn(II)	Ag(I)		Cd(II)
Zeolite type	X	Y	X	Y[a]	Y	Y	Y[b]	X	Y	X
Carbon monoxide										
$-\Delta H_{ad}$ (kcal/mol)	6.4	5.8	—	10.2	—	14.6	17.0	16.0	14.8	—
Coverage (mmol/g)	0.4	0.2	—	0.4	—	0.7	?	0.5	0.5	—
Reference	(25)	(23)	—	(23)	—	(1)	(26)	(3)	(3)	—
Ethylene										
$-\Delta H_{ad}$ (kcal/mol)	8.6	7.6	9.1	—	9.5	15.9	—	18.1	—	14.9
Coverage (mmol/g)	0.06–0.5	?	0.06–0.5	—	0.5	0.5	—	0.06–0.5	—	0.06–0.5
Reference	(13)	(26)	(13)	—	Present work	Present work	—	(13)	—	(13)

[a] 76% exchanged sample.

[b] 62% exchanged sample.

is 9.1 kcal/mol on CaX and 8.6 kcal/mol on NaX (*13*). The interaction is, however, even stronger when the cations are capable of forming dπ back bonding with the adsorbate molecules. Such is the case when carbon monoxide or ethylene is adsorbed on copper(I) or silver(I) zeolites. The heats of adsorption, which are summarized in Table 6, are all greater than 14 kcal/mol. Obviously, mere van der Waals forces associated with univalent cations cannot be accounted for these high values. Zinc(II) and cadmium(II) are isoelectronic with copper(I) and silver(I), respectively, but they do not form π complexes with carbon monoxide or ethylene. Their interaction with these molecules should be similar to calcium or other divalent cations. The unusually high heats of adsorption for CO on ZnY (*26*) and for C_2H_4 on CdX (*13*) must be due to high cation density in the zeolite which gives rise to greater electrostatic interactions. We have shown in this work that the infrared bands for carbon monoxide and ethylene were much weaker in ZnY than in Cu(I)Y or Ag(I)Y zeolite.

The strength of the coordinate bond of ethylene is, in most cases, revealed by the shift to a lower frequency of the carbon double bond stretch. It is lowered by 90 cm^{-1} for Cu(I)Y and 41 cm^{-1} for AgY. Other reported values are: 52 cm^{-1} for AgX (*13*) and 97 cm^{-1} for Zeise's salt (*12*). Carter *et al.* (*13*) illustrated the cation specificity of ethylene adsorption in X zeolites by correlating the double bond shift with the heat of adsorption. However, in view of the different nature of various cation–ethylene interactions, the correlation must be taken with caution. It lacks consistency even when comparison is made between Cu(I) and Ag(I), both of which are known to form π-complexes. For example, adsorbed ethylene in Cu(I)Y has a greater double bond frequency shift and yet gives a smaller heat. The same is also observed in the case of carbonyl complexes (*1*, *3*). While both have virtually the same heat of adsorption, much greater shift in the C–O stretching frequency is observed on Cu(I)Y. Nevertheless, adsorption measurement in conjunction with infrared spectroscopy should provide a good method for characterizing the specific interactions in zeolites. The study on Cu(I)Y and Ag(I)Y is one good example.

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