Copper(I)–Ethylene Complexes in Y Zeolite

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Summary Ethylene formed a stable complex with copper (I) in Y zeolite to the extent of one molecule per copper ion, with characteristic i.r. absorption bands at 1428, 1533 and 1920 cm^{-1}.

COPPER(I) ions catalyse many reactions both in the homogeneous and heterogeneous phase and play an important rôle in some biological systems. An increasing number of studies of copper(I) co-ordination compounds can be found in the literature and recently, it has been pointed out that copper(I) ions can be easily produced within a zeolite framework,[1] permitting the study of isolated copper(I) ions in the solid state. For example, the formation of carbonyl and ammine complexes has been observed by adsorption measurements and i.r. spectroscopy.[1,2]

FIGURE. I.r. spectra of copper(I)–ethylene complex in Y zeolites at 25°.

(1) $Cu^{II}Y$, $P(C_2H_4)$ = 30 Torr.
(2) $Cu^{I}Y$, $P(C_2H_4)$ = 30 Torr.
(3) Evacuation at 25° for 1 h following (2).

Ethylene is known to form complexes with silver and cuprous ions in solution and in solid compounds.[3,4] and the strong interaction between ethylene and AgX zeolite has been noted.[5] We now report the formation of stable copper(I)–ethylene complexes in Y type zeolite together with the stoicheiometry and i.r. spectrum.

TABLE. Adsorption of ethylene at 25° in CuY Zeolites[a]

Cation	Amount adsorbed/mmol g^{-1} 10 *Torr*	100 *Torr*	After 1 h evacuation
Cu^{I}	2·04	2·97	0·85
Cu^{II}	0·64	1·38	<0·03
Cu^{I} – Cu^{II}	1·40	1·59	0·82

[a] Copper content = 1·60 mmol g^{-1}.[2]

$Cu^{I}Y$ was prepared by the reduction with carbon monoxide of a $Cu^{II}Y$ sample, which was ion exchanged from NaY zeolite.[2] The exchanged sample had a copper content of 1·60 mmol g^{-1}. The adsorption of ethylene in both zeolites was measured gravimetrically. The uptake at 25° and at two pressures and the amount remaining after evacuation are indicated in the Table. More ethylene molecules are adsorbed in the reduced Cu^{I} sample, the difference reaching a limiting value of one ethylene per copper(I) ion at about 100 Torr. Since no complexes are expected in the $Cu^{II}Y$ sample, the lower uptake of ethylene is due to weak physical adsorption on the zeolite. In fact, all the ethylene adsorbed in $Cu^{II}Y$ could be pumped off easily, but nearly half the ethylene was strongly held by $Cu^{I}Y$ and could not be removed at 25°.

While only weak i.r. bands were observed when ethylene was adsorbed in $Cu^{II}Y$, an intense band at 1428 cm^{-1} appeared in the $Cu^{I}Y$ sample (Figure). This band is due to the asymmetric CH_2 deformation or ν_{12}, according to the notation of Herzberg.[6] The other bands at 1442, 1533, 1890, 1920, and 2992 cm^{-1}, were all relatively weak. Upon pumping of the sample at 25°, only the bands at 1428, 1533, and 1920 cm^{-1} remained. These bands can be regarded as characteristic of the copper(I)–ethylene complex formed.

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