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Selective Adsorption of Carbon Monoxide and Complex Formation of Cuprous-Ammines in Cu(I)Y Zeolites

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Copper(I) Y zeolites can be prepared by treating copper(II) Y with carbon monoxide. The reduction process is enhanced by the presence of a small amount of ammonia. Carbon monoxide is selectively adsorbed in Cu(I)Y zeolites, the uptake being about one CO per Cu^+ ion below 100°C and at 100 Torr. The specific Cu^+–CO interaction is revealed by a strong infrared absorption band at 2160 cm^{-1} and a heat of adsorption of 14.7 kcal/mole. Diffusion of carbon monoxide into sodalite cages occurs at temperatures below 100°C. Adsorption is much smaller for carbon dioxide, nitrogen or oxygen. Cuprous ions in Y zeolite do not interact with oxygen at room temperature, but they are oxidized readily if ammonia is preadsorbed. Measurements of ammonia adsorption show that the cuprous–ammine complexes in Y zeolite are mainly $Cu(NH_3)_2^+$. At sufficiently low coverages, the isosteric heat of ammonia adsorption is 19 kcal/mole.

INTRODUCTION

Copper(II) Y zeolites have been widely studied about their structural aspects, adsorption properties and catalytic activities. Besides the acidic nature, the oxidizing property due to the presence of cupric ions (*1*) is an important factor responsible for their activities, especially in oxidation–reduction reactions. It is likely that in many situations, the lower oxidation states of copper could be present. However, little is known about the nature of copper(I) ions in zeolites. This is probably because of the apparent difficulties in preparing Cu(I) zeolites. Cuprous ions are unstable in solution and cuprous compounds are fairly readily oxidized to cupric compounds. The usual ion-exchange procedure is thus not applicable.

If Cu(II)Y zeolites are treated with carbon monoxide at temperatures above 400°C, cupric ions are reduced to cuprous ions. This has been reported by Naccache and Ben Taarit (*1*) in their study of the oxidizing and acidic properties of copper Y zeolite, by Chao and Lunsford (*2*) in their ESR investigation of Cu^+–NO interaction and by Huang and Vansant (*3*) in their measurements of ammonia adsorption. In particular, less ammonia was adsorbed in the CO-reduced sample compared to Cu(II)Y zeolite; the difference was about 1.8 NH_3 molecules/copper ion present. It was explained in terms of the difference in the number of ammonia ligands between cupric- and cuprous–ammine complexes. This paper reports the results of a recent study on the preparation of Cu(I)Y zeolites, the selective adsorption of carbon monoxide, the formation of cuprous–ammine complexes and the oxidation of cuprous ions in Y zeolites.

EXPERIMENTAL METHODS

Gases and Purifications

The use of ammonia, carbon monoxide and oxygen (*3*), and carbon dioxide (*4*) has been described elsewhere. Prepurified grade nitrogen (99.997% purity) from

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Matheson Gas Products was flowed through a liquid nitrogen cold trap and stored in a bulb before use.

Preparation of Cu(I)Y Zeolites

All Cu(I)Y zeolites were prepared *in situ* before adsorption measurements by the reduction of Cu(II)Y zeolites, whose method of preparation by ion-exchange and the extents of cation exchange are indicated in Table 1. Cu(II)Y samples were dehydrated at 400°C in a usual manner and then treated with oxygen to give light green color, as described by Huang and Vansant (*3*). Two methods were used to reduce Cu(II)Y into Cu(I)Y zeolites.

Reduction by carbon monoxide. The procedure, which was similar to that employed by Naccache and Ben Taarit (*1*) and by Chao and Lunsford (*2*), involved the treatment of the dehydrated Cu(II)Y sample with 150 Torr of carbon monoxide at 400°C, in a closed electrobalance chamber for about 36 hr. The resulting white sample was first evacuated at 400°C for 0.5 hr and was then cooled down to the adsorption temperature with continued evacuation. In a separate experiment, the reduction of Cu(II)Y zeolite was carried out in an ESR tube with frequent replacement of carbon monoxide. The extent of reduction was monitored by the ESR spectrum of cupric ions: a small amount of which was still detected after 24 hr, but not after 36 hr of CO treatment.

Reduction by carbon monoxide with preadsorbed ammonia. In this method, ammonia was first adsorbed in dehydrated Cu(II)Y samples at a pressure of about 10 Torr. About 150 Torr of carbon monoxide was then introduced. Most Cu^{2+} ions in the sample could be reduced in a few hours at temperatures as low as 100°C, as was revealed from ESR observation. At 400°C, complete reduction was achieved in 1 hr. The reduced white sample was then evacuated at 400°C for a few hours before being cooled down to the adsorption temperature.

Apparatus

Adsorption was measured gravimetrically by a Cahn recording electrobalance, Model RG 2002, Ventron Instrument Corp. Pressures above 5 Torr were read from an absolute pressure gauge (Wallace & Tiernan Model FA160, 0-800 Torr range); while below 5 Torr, by a McLeod gauge (Scientific Glass Blowing Co.). The temperature measurement and details of the adsorption apparatus have been presented elsewhere (*5*).

The ESR spectra were measured by a Varian (V4502) spectrometer, with a TE_{102} mode microwave cavity and in the X-band region at 9.3 Gc/sec. The presence of Cu^{2+} ions in Y zeolites was monitored to study the effect of the CO treatment, the ammine complex formation and the oxidation–reduction of copper ions in zeolites.

Adsorbed carbon monoxide in a Cu(I)Y sample was also investigated by infrared spectroscopy. A Beckman IR 12 spectrophotometer was used. The design of the infrared cell and the preparation of zeolite pellet were the same as those described by

TABLE 1
PREPARATION OF Cu(II)Y ZEOLITES

Zeolite	Extent of exchange (%)	Copper content (mmole/g)	Exchange solution	Exchange process
Cu(II)Y (75%)	75	1.60	0.5 M $Cu(NO_3)_2$ solution with twice the stoichiometric amount of Cu^{2+}	Exchange twice at room temperature
Cu(II)Y (48%)	48	1.12	0.17 M $Cu(NO_3)_2$ solution with 50% of the stoichiometric amount of Cu^{2+}	Exchange once at room temperature

Chao and Lunsford (*6*). The pretreatment and the reduction of Cu(II)Y sample by method II followed the same procedure mentioned above. Infrared spectra were all recorded at room temperature.

RESULTS

Adsorption

Adsorption isotherms of carbon monoxide in Cu(I)Y (75%) sample between 97 and 230°C are shown in Fig. 1. At temperatures below 100°C, the adsorption, though having a rapid, initial uptake of more than 50%, reached equilibrium very slowly, as indicated in Table 2. It is interesting that the equilibrium amounts of carbon monoxide adsorbed between 0 and 100°C at 100 Torr were all close to the value corresponding to one CO per Cu^+ ion, e.g., 1.60 mmole/g for the Cu(I)Y (75%) sample. But for carbon dioxide, nitrogen and oxygen, the amounts adsorbed were much smaller (Table 3). A series of isotherms for ammonia adsorbed in Cu(I)Y (48%) zeolite between 27 and 362°C is shown in Fig. 2. Within the experimental region, adsorption was reversible and equilibrium was easily reached at higher temperatures. The sample remained white when ammonia was adsorbed; for Cu(II)Y, it turned deep blue immediately (3).

TABLE 2
SLOW ADSORPTION OF CO IN Cu(I)Y (75%) ZEOLITE

Temp (°C)	Pressure (Torr)	Time	Amount adsorbed (mmole/g)
0	100	1 min	1.43
		6.7 hr	1.77
25	100	2 min	1.26
		43 min	1.48
		24 hr	1.65
97	103	8 min	0.66
		25 min	0.96
		8.5 hr	1.49
172	50	2 min	0.52
		10 min	0.53
		20 min	0.53

Isosteric heats of adsorption q_{st} were determined from slopes of the Clausius-Clapeyron plot. Their variation with the surface coverage is shown in Table 4. Between 0.1 and 1.0 mmole/g adsorbed, the heat of adsorption of carbon monoxide was relatively constant at 14.7 kcal/mole. In the case of ammonia, the heat varied from 19.7 to 11.9 kcal/mole between the range 0.2 to 4.0 mmole/g, the latter corresponding to almost four times the total amount of Cu^+ ions in the Cu(I)Y (48%) sample. For carbon dioxide, the heat of adsorption was estimated to be 6.8 kcal/mole from a pair

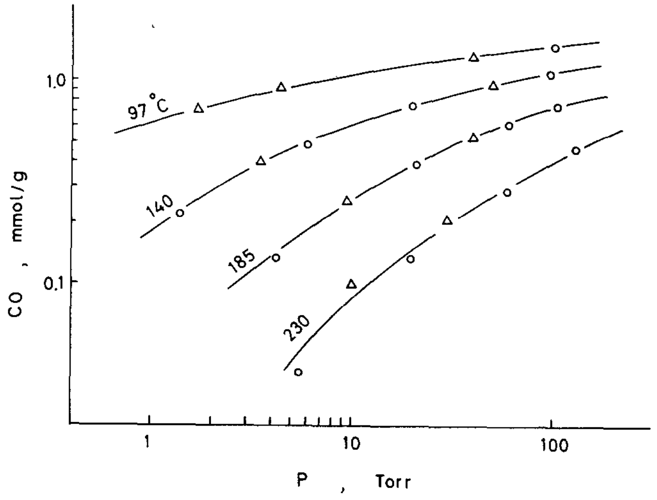

FIG. 1. Adsorption isotherms of CO in Cu(I)Y (75%) zeolite [(○) adsorption; (△) desorption].

TABLE 3
ADSORPTION OF VARIOUS GASES IN Cu(I)Y ZEOLITES

Zeolite	Gas	Temp (°C)	Pressure (Torr)	Amount adsorbed (mmole/g)
Cu(I)Y (75%)	NH_3	24	20	9.50[a]
	CO	0	101	1.77
		25	99	1.65
		95	118	1.39
		97	102.5	1.49[a]
	CO_2	27	35	0.578[a]
		100	99	0.182[a]
	N_2	0.5	99	0.044
		98	104	0.022[a]
	O_2	0.5	100	0.032
		25	106	0.024[a]
Cu(I)Y (48%)	NH_3	27	17	8.34
	CO	35	147	1.03
		100	100	0.67

[a] On samples prepared by method I. All else are on samples prepared by method II.

of isotherms. Within the same experimental region, the adsorption of nitrogen and oxygen was too small to have a significant estimate of the heat values. Infrared spectra of the adsorbed CO in Cu(I)Y (75%) are indicated in Fig. 3. A strong absorption band at 2160 cm^{-1} was observed when about 30 Torr of CO was introduced at room temperature. It persisted even after the gas phase had been pumped off to 10^{-4} Torr. Prolonged evacuation of the sample reduced the intensity slightly. After the treatment with oxygen at 400°C, the light green sample gave only a weak band with the same frequency. Presumably, this was due to a small amount of Cu^+ ions remaining in the oxidized zeolite. Adsorption measurement indicated that repeated treatments with oxygen were required to eliminate the specific CO adsorption.

TABLE 4
ISOSTERIC HEATS OF ADSORPTION, q_{st}, ON Cu(I)Y ZEOLITES

Adsorbate	Adsorbent	Coverage (mmole/g)	q_{st} (kcal/mole)
CO	Cu(I)Y (75%)	0.1	14.7
		0.2	14.8
		0.5	15.2
		0.7	14.6
		1.0	14.4
CO_2	Cu(I)Y (75%)	0.1	6.8
NH_3	Cu(I)Y (48%)	0.2	17.2
		0.5	19.1
		1.0	19.7
		1.5	19.1
		2.0	18.5
		3.0	14.2
		4.0	11.9

To examine the possibility of the diffusion of CO into sodalite cages, adsorption was measured at −196°C. First, a sample of Cu(I)Y (75%) was cooled down slowly from 400°C to room temperature in 100 Torr of carbon monoxide, and then was cooled down to liquid nitrogen temperature. The amount of CO adsorbed at 100 Torr was 9.78 mmole/g (Fig. 4). In the second experiment, the same sample was cooled down *in vacuo* immediately to −196°C, and the isotherm was then measured. Less CO was adsorbed, the difference being 0.39 mmole/g at 100 Torr. Originally, the oxidized sample, Cu(II)Y, when cooled down *in vacuo*, adsorbed only 9.02 mmole/g of CO at −196°C. This value, which was reproducible after a reduction–oxidation cycle, is 0.76 mmole/g less than the first one. The nitrogen adsorption in the reduced form was 8.89 mmole/g. If the value of N_2 in

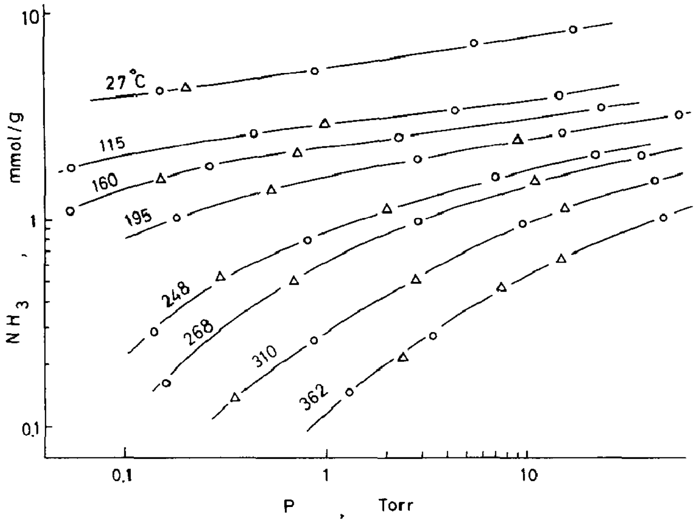

FIG. 2. Adsorption isotherms of NH_3 in Cu(I)Y (48%) zeolite [(○) adsorption; (△) desorption].

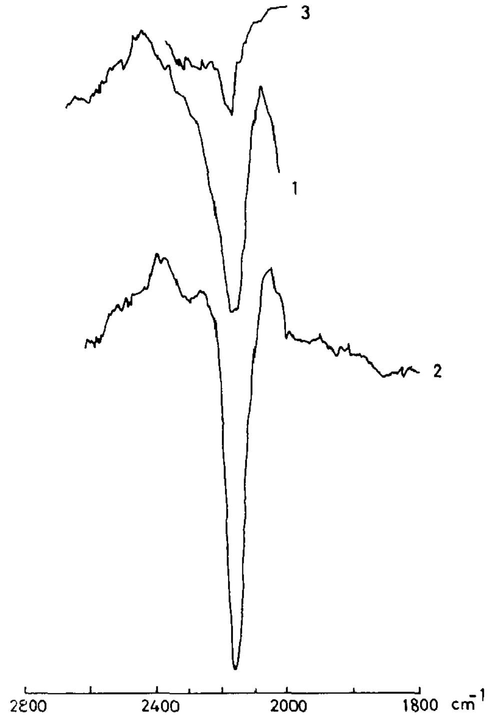

FIG. 3. Infrared spectra of adsorbed CO in Cu(I)Y (75%) zeolite recorded at 25°C. (1) 10 min after 27 Torr of CO was introduced. (2) When gas phase was pumped off 30 min after the CO adsorption. (3) 10 min after 35 Torr of CO was introduced to the sample, which had been treated with oxygen at 400°C.

Cu(I)Y and CO in Cu(II)Y are close to the saturation capacity required to fill up the supercages, then the additional uptake of 0.76 mmole/g measured in the first experiment must be inside the sodalite cages. Evidently, the diffusion of carbon mon-

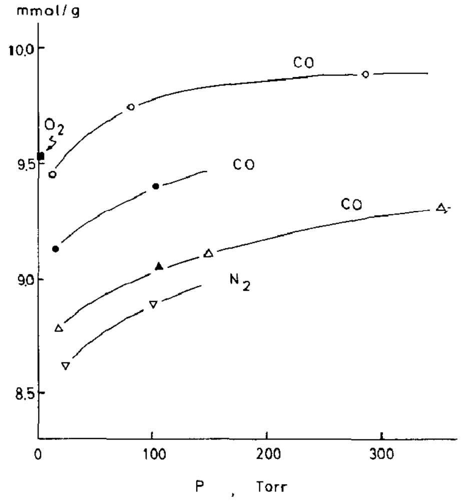

FIG. 4. Adsorption of CO in CuY (75%) sample at −196°C: (○) Cu(I)Y was cooled down from 400°C in 100 Torr of CO. (●) Cu(I)Y was cooled down *in vacuo*. (△) Cu(II)Y was cooled down *in vacuo* [(▲) after one reduction-oxidation cycle]. (▽) N_2 in Cu(I) Y; (■) O_2 in Cu(I)Y.

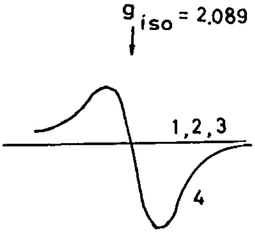

FIG. 5. ESR spectra of CuY(75%) recorded at 25°C. (1) After CO reduction treatment. (2) When O_2 was introduced at 25°C. (3) When NH_3 was adsorbed at 25°C. (4) When O_2 was added following (3).

oxide into sodalite cages occurred in Cu(I)Y zeolites.

Oxidation

To the contrary of carbon monoxide, no significant adsorption of oxygen in Cu(I)Y zeolite was measured at room temperature: the uptake was only 0.024 mmole/g at a pressure of about 100 Torr. No appearance of the ESR signal of Cu^{2+} ions was observed (Fig. 5). However, when ammonia was preadsorbed, the white sample turned deep blue immediately after oxygen was introduced. A strong, symmetrical ESR signal due to copper(II)-ammine complexes (*3*) appeared, which indicated that cuprous ions were oxidized to cupric ions in the presence of ammonia and oxygen. Another experiment showed that, when the dehydrated Cu(I)Y sample was exposed to atmosphere, it turned light blue gradually. Conceivably, the oxidation of cuprous ions took place following the adsorption of moisture from the air.

DISCUSSION

The selective adsorption of carbon monoxide in CO-reduced copper Y zeolites is evidently due to the presence of Cu^+ ions. Chao and Lunsford (*2*) have indicated in the study of NO adsorption that the characteristic ESR spectra in *X*-band and *Q*-band were due to the Cu^+–NO interaction. The possibility of a free copper atom being the paramagnetic center was ruled out, and the *g* values of the spectra were quite different from those of normal Cu^{2+} ions in Y zeolites. Furthermore, no specific CO adsorption in Cu(II)Y zeolite was observed at room temperature or lower (*3*). At 25°C and 100 Torr, less than 0.2 mmole/g of CO was adsorbed in Cu(II)Y (75%); while in the CO-reduced sample, 1.65 mmole/g was adsorbed. After treatment with oxygen of the reduced sample at 400°C, the former value was again measured.

Garner, Stone and Tiley (*7*) reported that carbon monoxide was adsorbed very rapidly on a cuprous oxide surface at room temperature, and was followed by a slow process. The initial uptake had about 90% of the equilibrium amount, which was about 30% coverage. The heat of adsorption varied from 20.8 to 18.1 kcal/mole as the coverage was increased from 9 to 26%. These heat values, though slightly greater, are fairly close to the present result of Cu(I)Y zeolite. On the cupric oxide surface, however, even larger amount of carbon monoxide was adsorbed, to the contrary of Cu(II)Y zeolite, in which the adsorption was much smaller.

It is known that cuprous ammines or chlorocuprates(I) absorb carbon monoxide quantitatively (*8*, *9*). The formation of cuprous carbonyls has been reported. An infrared study showed single peaks at 2112 and 2069 cm^{-1}, respectively, for the CO complexes formed from cuprous chloride dissolved in water or pyridine (*10*). Thus, the selective CO adsorption in Cu(I)Y zeolites could very well be due to the formation of Cu^+–CO complexes, although the infrared absorption band was at higher frequency than that of the gas phase CO. Angell and Schaffer (*11*) have observed CO absorption bands near 2200 cm^{-1} on X and Y type zeolites containing bivalent cations, which give rise to the electrostatic interaction. Bands at 2170 and 2120 cm^{-1} were also shown on all zeolite samples, presumably due to CO adsorbed on the zeolite framework. At any rate, all of these bands resulted from relatively weakly adsorbed CO; they disappeared rather quickly on pumping at room temperature. The strong absorption band observed on Cu(I)Y zeolite could not be easily removed at room temperature. And, similar to cuprous solutions, the CO/Cu^+ ratios measured in Cu(I)Y zeolites were close to one.

The nature of the Cu^+–CO interation is apparently different from the usual physical adsorption where electrostatic forces are important contributions. The latter would have the similar interaction on carbon monoxide as well as on nitrogen and carbon dioxide. In other words, if the uptake and the heat of adsorption are large for one, they would also be relatively large for the others. This has been illustrated in many adsorption studies on zeolites (*12–14*) and on amorphous silica–aluminas (*4*). However, the adsorption data of Cu(I)Y zeolites do not conform with this correlation. The adsorption was only selective to carbon monoxide, but not to nitrogen, oxygen and carbon dioxide. Heat of adsorption was as high as 14.7 kcal/mole for carbon monoxide, higher than those on most bivalent cation Y zeolites (*12*), but was as low as 6.8 kcal/mole for carbon dioxide, lower than that on NaY (*15*). Considerably large amounts of carbon monoxide were adsorbed in Cu(I)Y zeolites, but only negligible quantities were measured for nitrogen and oxygen. The strong Cu^+–CO interaction cannot be interpreted in terms of electrostatic forces; it is distinctively chemisorption.

It is strange that the oxygen uptake is small and that Cu(I)Y is stable in oxygen at room temperature. Cuprous ions in solution are known to be unstable and they can be oxidized readily when exposed to oxygen. Also remarkably different is that oxygen is adsorbed by cuprous oxide to more than one layer of coverage, giving a much higher heat of adsorption of about 55 kcal/mole (*7*). No apparent change was noticed in Cu(I)Y zeolite, even when oxygen was added after the adsorption of carbon monoxide. The unique behavior of Cu(I)Y zeolites suggests that all cuprous ions must be located inside the small cavities of the faujasite framework. They could be in the sodalite cages and were quite close to the hexagonal windows leading to the supercages, close enough to interact specifically with carbon monoxide, but not in a favorable position to adsorb oxygen or to be oxidized. The situation was different, though, when ammonia or water was present. Immediate oxidation took place because of the formation of copper(I) complexes, which were obviously located in the supercages. Just like those in the solution, Cu^+ ions would be readily oxidized when in contact with oxygen. In this wake, cupric–ammine complexes were then formed. This was indeed revealed from ESR investigation.

Without preadsorbed ammonia, Cu(I)Y zeolite can also be oxidized by oxygen, but it requires a higher temperature and a longer time. At higher temperatures, cuprous ions might have sufficient mobility or oxygen could penetrate into the sodalite cages so as to enhance the oxidation process. It could similarly be the case in the reduction process when Cu(II)Y is reduced to Cu(I)Y by carbon monoxide. As indicated previously, with preadsorbed ammonia, extensive reduction at temperatures as low as 100°C was possible, and the reduction could be completed at 400°C in a very short time. At room temperature, slight reduction was also detected.

With sufficient ammonia concentrations, $Cu(NH_3)_4^{2+}$ complexes are formed in cupric solution, while $Cu(NH_3)_2^+$ complexes are present in cuprous solution. Adsorption measurement has demonstrated that cupric–ammine complexes formed in Cu(II)Y zeolites are mainly $Cu(NH_3)_4^{2+}$ (*3*). The ammonia uptake was considerably decreased when the sample was reduced by carbon monoxide. Adsorption isotherms of ammonia at room temperature in both Cu(II)Y and Cu(I)Y zeolites are shown in Fig. 6. If the uptakes at 20 Torr are taken for comparison, then the difference between Cu(II)Y (75%) and Cu(II)Y (48%) is 2.1 mmole/g or 4.4 NH_3/Cu^{2+}, but it is 1.0 mmole/g or 2.1 NH_3/Cu^+ between Cu(I)Y (75%) and Cu(I)Y (48%). To compare the oxidized with the reduced forms, the difference between Cu(II)Y (75%) and Cu(I)Y (75%) is 2.8 mmole/g or 1.75 NH_3/Cu(total), and is 1.7 mmole/g or 1.52 NH_3/Cu(total) between Cu(II)Y (48%) and Cu(I)Y (48%). These figures indicate that the cuprous–

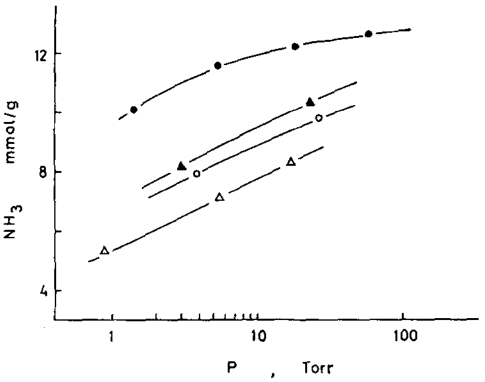

FIG. 6. Adsorption isotherms of NH_3 at 25°C. (●) Cu(II)Y (75%); (○) Cu(I)Y (75%); (▲) Cu(II)Y (48%); (△) Cu(I)Y (48%).

ammine complexes in Y zeolites are mainly $Cu(NH_3)_2^+$.

Reproducible results even after repeated adsorption measurements and oxidation–reduction cycles show that higher exchanged Cu(I)Y zeolites were quite stable in that further reduction of Cu^+ ions into metallic copper did not occur. Had Cu^0 formed, the sample would have appeared pink (*1*) and the agglomeration of copper atoms would have prevented the reversible oxidation–reduction cycle. The heat of adsorption of ammonia was thus determined for the Cu(I)Y (48%) sample at sufficiently low surface coverages. Up to a coverage of 2 mmole/g the heat was relatively constant at about 19 kcal/mole. This value could represent the NH_3–Cu^+ interaction in Y zeolite, even with the consideration that Lewis acid sites should exist as suggested by Naccache and Ben Taarit (*1*).

The slow adsorption of carbon monoxide in Cu(I)Y zeolites following a large portion of rapid, initial uptake is rather striking. It shows that carbon monoxide could possibly penetrate into the sodalite cages below 100°C. This was not observed in synthetic sodalite and other Y type zeolites, even at a temperature as high as 200°C (*12*). Adsorption measurements at −196°C indicated that more carbon monoxide was adsorbed when the Cu(I)Y sample was cooled down from 400°C in the presence of carbon monoxide. The uptake was substantially greater than the saturation capacity of nitrogen. It can be concluded that the diffusion of carbon monoxide occurs at low temperatures.

In this connection, the adsorption of oxygen in Cu(I)Y (75%) was also measured at −196°C. At 1 Torr pressure, the uptake was 9.35 mmole/g, which is about 1 mmole/g more than the nitrogen value. Possibly, some oxygen molecules entered the sodalite cages, like that observed in A type zeolite (*16*). However, when the sample was warmed up to room temperature in the presence of oxygen, no apparent oxidation was observed. All adsorbed oxygen could be pumped off right away.

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