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Adsorption in AgX and AgY Zeolites by Carbon Monoxide and Other Simple Molecules

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Carbon monoxide was strongly adsorbed in AgX and AgY zeolites to the extent of four molecules per supercage at 25°C. An intense infrared absorption band was observed at 2195 cm^{-1}, which was only slightly affected by preadsorbed ammonia. The isosteric heats of adsorption were 19.2 kcal/mole for AgX and 15.1 kcal/mole for AgY at very low coverages.

More nitrogen was adsorbed in AgX than in AgY with heat of adsorption as high as 8.2 kcal/mole at a coverage of 0.1 mmole/g. In the AgY sample, the heat was only 4.6 kcal/mole. The specific adsorption was due to higher silver content in the AgX zeolite, which also had higher heats for the adsorption of carbon monoxide and carbon dioxide. The adsorption of oxygen at 25°C in both zeolites was negligibly small. In addition to the initial reversible adsorption, a small amount of nitric oxide was slowly adsorbed in AgY. No migration of silver ions, when ammonia was adsorbed, could be inferred from adsorption measurement.

No specific adsorption of carbon monoxide in AgX and AgY and of nitrogen in AgX was observed when the samples had been treated with carbon monoxide at 350°C. Silver ions were probably reduced after this treatment.

INTRODUCTION

Formation of copper(I) carbonyls in Y zeolites has recently been reported from adsorption measurement (*1*) and from infrared spectroscopic investigation (*2*). By analogy to the coordination compounds, it is attributed to the filled 3*d* electronic configuration of the copper(I) ions. Since silver(I) ions have filled 4*d* electrons and since carbonyls have been reported on silver and on copper atoms condensing in a solid matrix of carbon monoxide at 20 K (*3*), it seems that silver ions in the zeolite framework might also bind carbon monoxide quite specifically. The results of an extensive study of the adsorption of carbon monoxide and other simple molecules such as nitrogen, oxygen, carbon dioxide, ammonia, ethylene, and nitric oxide are presented in this communication. It will be shown that the silver-exchanged zeolites have many things in common with the copper(I) zeolites concerning their adsorption behavior. There are, however, unique features that were only observed in the silver zeolites.

EXPERIMENTAL

Materials

Silver-exchanged zeolites were prepared by repeated ion-exchange of NaX (Linde 13X, Lot No. 13945000048) and NaY (Linde SK-40, Lot No. 3607-381) zeolites with 0.06 *M* silver acetate solution at 45°C. The exchanged samples were then thoroughly washed with distilled water, dried in a desiccator, and then stored in brown bottles. Analysis of the sodium content showed that the extent of cation exchange was 99% for AgX and 93% for AgY zeolites. The amount of Ag^+ ions in 1 g of the dehydrated sample and the number of Ag^+ ions in ⅛ of a unit cell are indicated in Table 1. Note that

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TABLE 1

SILVER-EXCHANGED ZEOLITES

Zeolite sample	AgX	AgY	Cu(I)Y
Extent of cation exchange, %	99	93	75[c]
Amount of Ag^+ ions, mmole/g	4.15	3.04	1.60(Cu^+)
Formular weight per unit cell	20,700[a]	17,170[b]	13,110
Number of supercages, mmole/g	0.386	0.466	0.610
Number of Ag^+ ions in ⅛ unit cell	10.75	6.53	2.62(Cu^+)

[a] Based on a Si/Al ratio of 1.23.

[b] Based on a Si/Al ratio of 2.43.

[c] Prepared by the reduction of Cu(II)Y zeolite (*1*).

there are one supercage, one sodalite cage, and two hexagonal prisms in ⅛ of a unit cell of the faujasite-type zeolite. The amount of adsorption was often expressed in molecules/cage instead of molecules per ⅛ of a unit cell, since most of the adsorbate molecules were believed to be in the supercages.

Gases

The use and the purification of carbon monoxide, nitrogen, oxygen, carbon dioxide, and ammonia have been indicated previously (*1*). Nitric oxide, technical grade with 98.5% purity, from Matheson Gas Products, was repeatedly condensed in a liquid nitrogen cold trap and distilled at about −80°C until the condensate was free of brown color. Ethylene, C. P. grade with 99.5% purity, also from Matheson Gas Products, was treated and stored similarly.

Apparatus

Adsorption measurements were carried out by a Cahn electrobalance, Model RG 2002, and the infrared spectra were recorded by a Beckman IR 12 infrared spectrophotometer.

Procedures

Zeolite samples were evacuated at room temperature for at least 3 hrs and then were heated up at an increment of 100°C/hr to 350°C for AgX and 400°C for AgY, respectively. At the final temperatures, they were treated with 200 Torr (1 Torr = 0.1333 kN/m^2) of oxygen for more than 5 hr. The samples, which were white after the treatment, were then evacuated at the final temperatures for at least 20 min before being cooled down to the adsorption temperature.

Adsorption of carbon monoxide was measured at pressures between 0.03 and 300 Torr and at temperatures between 0 and 275°C for AgX and between 23.5 and 182°C for AgY. Adsorption of carbon dioxide was measured between 25° and 100°C, while that of nitrogen between −24° and 50°C. For oxygen, nitric oxide, ethylene, and ammonia, the adsorption was measured at room temperature only. To examine the crystallinity of zeolite samples following various, treatments, the adsorption of nitrogen, carbon monoxide, and oxygen at −196°C was measured.

The silver-exchanged zeolites were also heated in 200 Torr of carbon monoxide at 350°C for 10 hr in order to reduce the silver ions; the samples all turned black afterwards. The reduced AgX zeolite was later heated in 200 Torr of oxygen at 350 C for 10 hr. Adsorption was measured following each pretreatment.

The zeolite samples were pressed into thin pellets with thickness about 13 mg/cm^2 for the infrared study. The pretreatment of the samples followed the same procedure described above. Carbon monoxide was adsorbed at 25°C and at 50 Torr. The infrared spectra were recorded at room temperature with the use of sodium chloride windows. To study the effect of complexing agent on the carbonyl formation, ammonia was preadsorbed in AgY zeolite at 25°C and at 10 Torr, and then carbon monoxide was added. Ammonia was also partially desorbed by evacuating the sample successively at 25°, 110°, and 380°C. Carbon monoxide was added at 25°C, and the infrared spectra were taken during each interval.

TABLE 2

Adsorption in Silver-Exchanged Zeolites at 25°C and 100 Torr

Adsorbate	Sample pre-treatment[a]	Amount adsorbed, molecules/cage	
		AgX	AgY
CO	A	4.37	4.30
	B	1.47	0.17
	C	4.87	—
N_2	A	0.93	0.17
	B	0.05	0.05
	C	1.26	—
	D	0.09	—
O_2	A	0.12	0.03
	B	0.04	0.09
CO_2	A	4.17	2.24
C_2H_4	A	7.41	6.59

[a] (A) Fresh dehydrated sample. (B) Sample treated with CO at 350°C. (C) Sample treated with O_2 at 350°C after B. (D) Fresh sample preadsorbed with 1.55 CO molecules/cage (or 0.6 mmole/g).

TABLE 3

Isosteric Heat of Adsorption of Silver-Exchanged Zeolites

Adsorbate	Coverage (mmole/g)	q_{st}, kcal/mole	
		AgX	AgY
CO	0.1	19.2	15.1
	0.2	18.8	14.5
	0.5	16.0	14.8
	1.0	16.7	12.1
	1.5	13.0	10.7
	2.0	9.8	—
CO_2	0.1	11.0	7.9
	0.2	10.7	7.3
	0.5	9.9	—
	1.5	10.0	—
N_2	0.1	8.2	4.6
	0.5	6.1	—

Results

Carbon Monoxide

Substantial amounts of carbon monoxide were adsorbed at 25°C in both AgX and AgY zeolites: the uptakes at 100 Torr corresponded to 4 CO molecules per supercage (Table 2). By pumping for 1 hr, most of the adsorbed carbon monoxide could be removed from the AgY sample, but about one-third was remaining in the AgX sample. The adsorption in both zeolites was rapid compared to Cu(I)Y, in which the equilibration below 100°C was very slow (*1*). Adsorption isotherms for AgX and AgY are shown in Figs. 1 and 2, respectively. Within the experimental region, the adsorption was reversible. No significant reduction of the silver ions was noticed after the adsorption runs at higher temperatures. Isosteric heats of adsorption were determined for surface coverages between 0.1 and 2.0 mmole/g, the latter corresponding to about 5 molecules/cage. As indicated in Table 3, the heat was higher in AgX than in AgY by about 3–4 kcal/mole (1 kcal/mole = 4.184 kJ/mole).

An infrared absorption band at 2195 cm^{-1} was observed in AgY zeolite (Fig. 3) with about the same intensity as that of the Cu(I)Y zeolite (*2*). For the AgX sample, the transmission was much smaller in the same region, although the same frequency was recorded for the adsorbed carbon monoxide

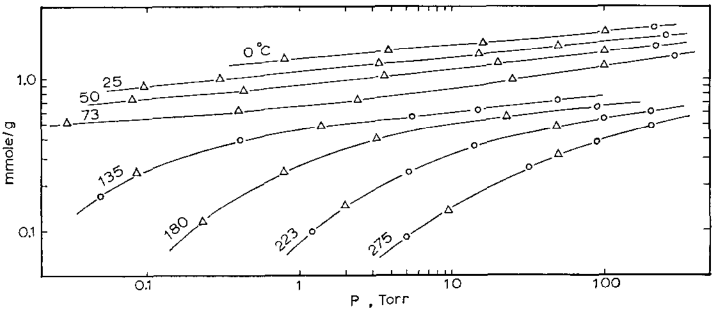

Fig. 1. Adsorption isotherms of carbon monoxide in AgX zeolite. (○, adsorption; △, desorption).

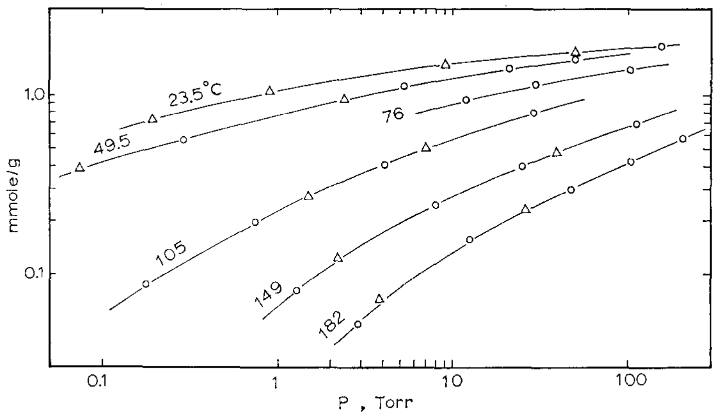

FIG. 2. Adsorption isotherms of carbon monoxide in AgY zeolite. (○, adsorption; △, desorption).

(Fig. 4). Contrary to the Cu(I)Y sample, no CO absorption band was observed when the AgY zeolite had been preadsorbed with ammonia at 10 Torr. However, if part of ammonia was desorbed by pumping at 25°C for 8 hr, a sharp band at 2170 cm^{-1} was observed (Fig. 5). The band shifted slightly to 2180 cm^{-1} after the evacuation at 110°C for 1 hr and then the addition of CO at 25°C. When all ammonia had been desorbed at 380°C, the band appeared at 2200 cm^{-1}. While ammonia was remaining in the zeolite sample, a band at 1630 cm^{-1} was always recorded.

Nitrogen and Oxygen

In general, the adsorption of nitrogen and oxygen in the silver-exchanged zeolites was much smaller compared to carbon monoxide, as indicated in Table 2. This is similar to the results of the Cu(I)Y zeolites (*1*). However, the nitrogen uptake in AgX was unusually higher compared to AgY or other X-type zeolites containing univalent cations (*4*). A series of adsorption isotherms for nitrogen in the AgX sample is shown in Fig. 6. The isosteric heat of adsorption was quite high at 0.1 mmole/g coverage: it was

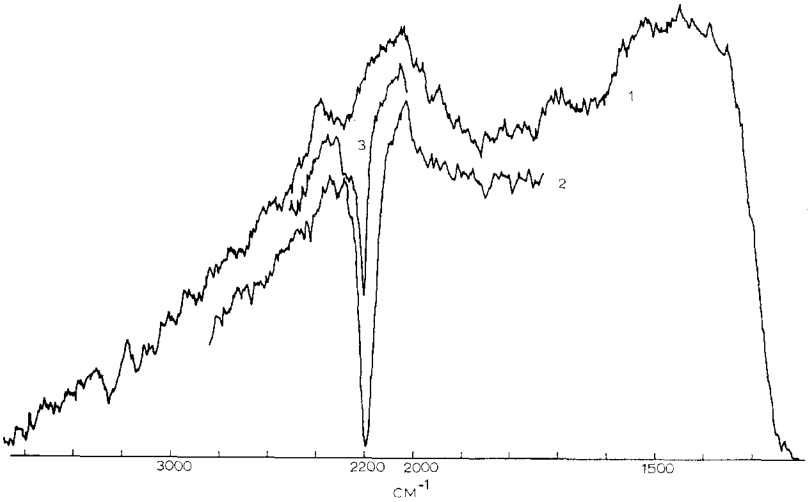

FIG. 3. Infrared spectra of AgY zeolite. (1) Dehydrated sample; (2) after adsorption of CO at 25°C and at 55 Torr; (3) after 30 min of evacuation at 25°C following (2).

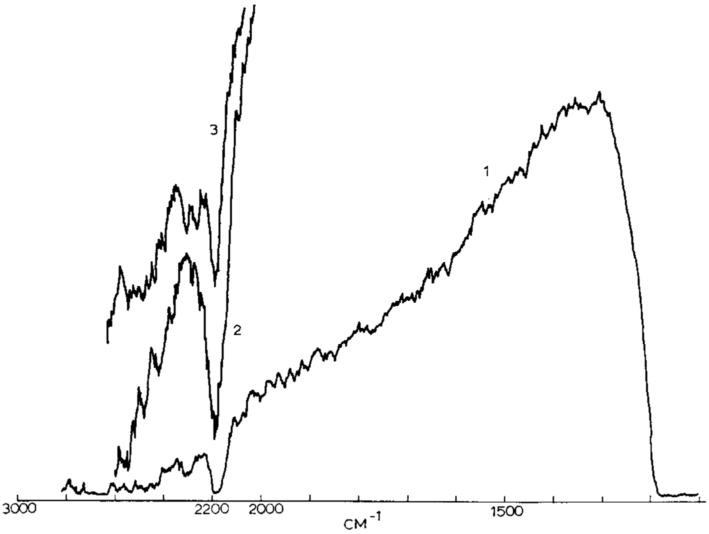

FIG. 4. Infrared spectra of AgX zeolite. (1) After adsorption of CO at 25°C and at 53 Torr; (2) same as (1), but with attenuated reference beam and slower scanning speed (40 cm^{-1}/min); (3) after 2 hr of evacuation at 25°C following (2).

8.2 kcal/mole. For AgY, it was 4.6 kcal/mole (Table 3). If the AgX sample had been preadsorbed with 0.6 mmole/g of carbon monoxide, which was not removed by pumping at 25°C for 30 min, the adsorption of nitrogen was drastically decreased (Table 2).

Carbon Dioxide

The adsorption of carbon dioxide increased steadily with pressure. While the adsorption at 25°C was quite small at low pressures, especially in AgY zeolite, it

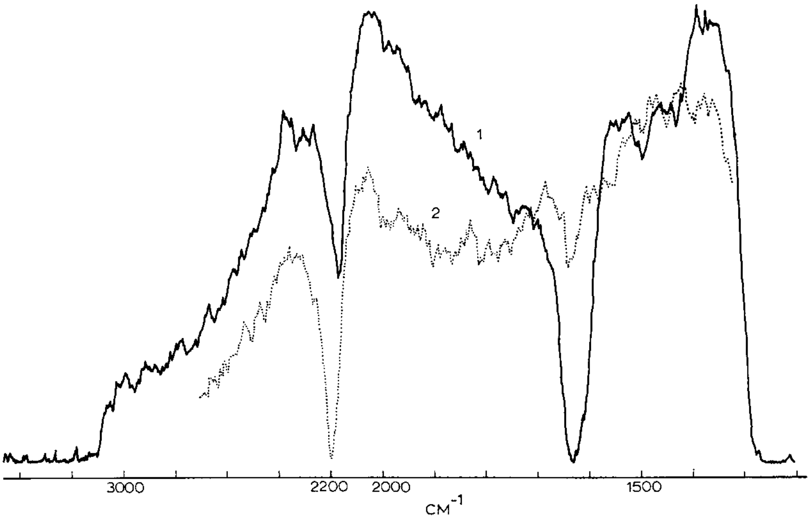

FIG. 5. Infrared spectra of AgY zeolite preadsorbed with ammonia. (1) CO adsorbed at 50 Torr after ammonia had been partially desorbed by pumping at 25°C overnight; (2) CO adsorbed at 50 Torr and at 25°C after ammonia had been desorbed at 380°C.

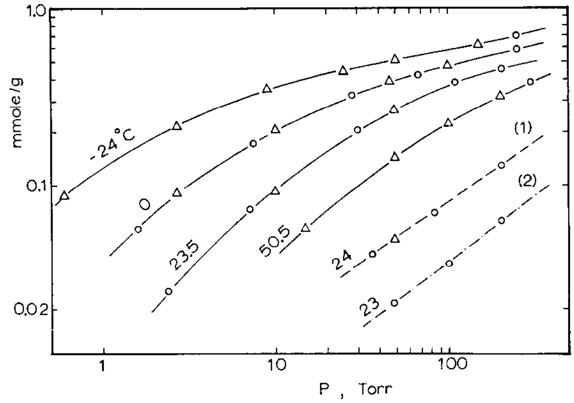

FIG. 6. Adsorption isotherms of nitrogen in AgX zeolite. (1) Adsorption isotherm of nitrogen in AgY; (2) Adsorption of nitrogen in AgX preadsorbed with 0.60 mmole/g of carbon monoxide (○, adsorption; △, desorption).

reached 4.17 molecules/cage for AgX and 2.24 molecules/cage for AgY at 100 Torr. The isotherms at 25°C for both samples are shown in Fig. 7. Again, the isosteric heat of adsorption was higher for AgX than for AgY zeolite (Table 3). In all cases, carbon dioxide could be removed rather easily by evacuation.

Ethylene

Ethylene was also specifically adsorbed in the silver-exchanged zeolites, as has been indicated by Yates (*5*). The amounts adsorbed at 25°C were as high as 2 mmole/g at a few Torrs, and then leveled off to about 3 mmole/g at higher pressures (Fig. 7). I expressed in units of molecules/cage, the adsorption at 100 Torr was 7.41 for AgX and 6.59 for AgY zeolites. Yates reported a value of 8.0 molecules/cage at 35°C and 143 Torr in AgX sample, of which 4.40 molecules/cage were not removed after evacuation for 30 min at 25°C. In the present work, the amounts remaining after evacuation for 3 hr were 3.06 and 2.88 molecules/cage, respectively, for AgX and AgY zeolites. Upon further evacuation at 100°C for 3 hr, the number of ethylene molecules remaining per cage was 1.39 for AgX and 0.57 for AgY. These figures show that about the same amount of ethylene was specifically adsorbed

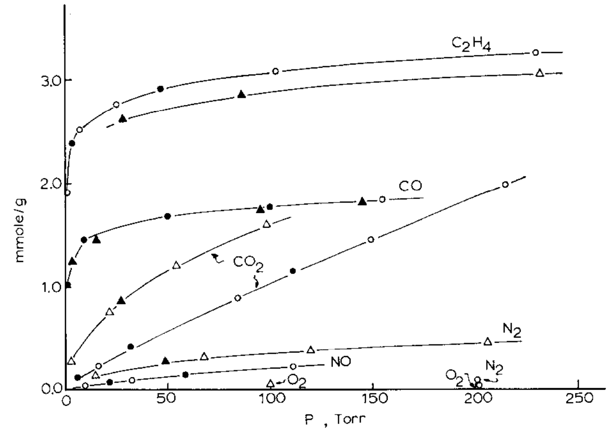

FIG. 7. Adsorption isotherms at 25°C of various gases in silver-exchanged zeolites (△, AgX; ○, AgY; open symbol, adsorption; solid symbol, desorption).

in both types regardless of the difference in cation density.

Ammonia

When expressed in terms of mmole/g, the amounts of ammonia adsorbed at 25°C in AgX and AgY zeolites were close to that of NaY sample, but smaller than those in Cu(I)Y or Cu(II)Y zeolites having high copper content (*6*). However, if expressed in molecules/cage, the values were closer to that of the Cu(I)Y zeolite. The use of this unit, which strictly should be molecules per ⅛ of a unit cell, does not preclude the possibility that ammonia may enter the sodalite cages. The nominal ammonia to cation ratios for various zeolites are indicated in Table 4. It can be seen that less ammonia was adsorbed in the silver zeolites than would have been expected by analogy with the copper zeolites concerning the complex formation.

Nitric Oxide

Unlike other adsorbates, a slow adsorption of nitric oxide in AgY was observed following the initial rapid adsorption, whip was reversible and which had slightly greater uptake than oxygen or nitrogen at 25°C, but smaller than carbon monoxide or carbon dioxide (Fig. 7). The rate of the slow adsorption process appeared to be faster at higher pressures. For instance, the uptake increased from 0.72 mmole/g initially absorbed to 1.16 mmole/g at 625 Torr over a period of 14 hr, but it increased from 0.14 mmole/g to 0.19 mmole/g at 76 Torr over the same period and then to 0.25 mmole/g over 42 hr. After evacuation for 30 min at 25°C, 0.27 mmole/g remained for the former, but 0.10 mmole/g for the latter.

TABLE 4

Adsorption of Ammonia in Zeolites at 25°C and 100 Torr

Zeolite	Amount adsorbed: mmole/g	Amount adsorbed: molecules/cage	Nominal NH_3/cation ratio
AgX	6.3	16.3	1.52
AgY	6.9	14.8	2.27
NaY[a]	6.8	10.8	1.55
Cu(I)Y[a]	9.6	15.7	6.00
Cu(II)Y[a]	12.3	20.2	7.69

[a] From data of Huang and Vansant (*6*).

Adsorption in CO-reduced Silver Zeolites

After the AgX and AgY zeolites had been heated in 200 Torr of carbon monoxide at 350°C for 10 hr, the adsorption of carbon monoxide and nitrogen was remarkably decreased, while the adsorption of oxygen remained negligibly small (Table 2). The adsorbed carbon monoxide could also be pumped off easily at 25°C. If the reduced AgX sample was heated in 200 Torr of oxygen at 350°C for 10 hr, high uptakes of carbon monoxide and nitrogen were again measured. In fact, the values were somewhat higher than those of the fresh samples. No significant change of the zeolite structure was observed from the adsorption measurement at −196°C after these pretreatments. The change in the sample weight during these treatments was also very small. For 170 mg of the dehydrated AgX zeolite, the weight decreased only 0.2 mg after the CO treatment, and gained about 0.37 mg when re-oxized.

Adsorption at −196°C

The amounts adsorbed at 100 Torr and at −196°C of carbon monoxide, nitrogen, and oxygen in the silver zeolites as well as in other zeolites are listed in Table 5 for comparison. These values are very close to the saturation capacity of the zeolite cavities, and can be used as an index of the crystallinity of the samples. It can be seen that both AgX and AgY had high crystallinity, and that the CO-treatment only slightly reduced the adsorption capacity. When the reduced sample was treated with oxygen, the adsorption capacity returned to its original values. It also shows that oxygen had invariably higher uptakes than nitrogen or carbon monoxide in all zeolites.

Discussion

By analogy to the result of the adsorption study on Cu(I)Y zeolites, the specific adsorption of carbon monoxide in AgX and AgY zeolites is expected. The filled 4*d* electronic configuration of the silver ions indeed

TABLE 5
ADSORPTION IN ZEOLITE AT −196°C AND 100 TORR

Adsorbate	Sample pretreatment[a]	Amount adsorbed, molecules/cage				
		AgX	AgY	Cu(I)Y	HY[c]	NaX[b]
N_2	A	15.0	14.6	14.6	14.5	16.6
	B	13.4	14.4	—	—	—
	C	15.5	—	—	—	—
CO	A	15.0	14.8	16.0	14.9	—
	B	13.6	—	—	—	—
O_2	A	18.7	18.2	—	18.5	18.6
	B	17.2	18.7	—	—	—

[a] See Table 2 for meanings.
[b] From data of Barrer and Stuart (*4*).
[c] 82% decationated zeolite.

favors the carbonyl formation. The CO uptakes in the silver zeolites were close to Cu(I)Y, and were greater than those of other cations forms, univalent or multivalent. The CO to Ag^+ ratio was, however, less than one in view of higher cation contents in the silver zeolites compared to Cu(I)Y: it was 0.41 for AgX and 0.66 for AgY. For Cu(I)Y samples, the CO to Cu^+ ratio is close to one (*1*). This means that not all the silver ions were available to carbon monoxide molecules. And unlike Cu(I)Y zeolites, no slow equilibrating process was observed in the silver zeolites, which indicated that carbon monoxide did not diffuse into the sodalite cages. Silver ions in zeolites were also less stable than the Cu^+ ions as they could be reduced by carbon monoxide at 350°C. The reduced sample did not adsorb carbon monoxide specifically.

The intensity of the infrared absorption band of the adsorbed CO in AgY zeolite was equivalent to that recorded in Cu(I)Y sample. The CO stretching frequency, 2195 cm^{-1}, however, is higher than 2160 cm^{-1} observed in Cu(I)Y. Keulks and Ravi (*7*) reported a band at 2180 cm^{-1} for CO adsorbed on silica- and alumina-supported silver catalysts, which had been treated with oxygen at 150°–175°C. All these frequencies are higher than that of the gaseous CO, i.e., 2143 cm^{-1}. According to the X-ray diffraction study of the AgY zeocite (8), the distance between the silver ions at the hexagonal window and the closet oxygen of the six-membered ring is fairly short (2.32 A), compared to the sum of the Ag^+ and 0^{2-} radii, which is 2.45 A if Goldschmidt ionic radii are used or 2.66 A if Pauling's values are used. It was assumed from this information that some degree of covalent bonding was involved between the silver ions and the nearest oxide ions. Thus, the high CO stretching frequency observed in AgY zeolite could be because the π-bonding of the carbonyl structure was not effective.

It is peculiar that when ammonia had been preadsorbed in AgY, the CO stretching frequency just shifted slightly to 2170 cm^{-1}; whereas for the Cu(I)Y zeolite, a decrease of 80 cm^{-1} was observed. Conceivably, the adsorption of ammonia in AgY did not change the location of the silver ions at the hexagonal window positions so as to enable the involvement of π-bonding with the CO molecules, the effect of which was conspicuously observed in the case of Cu(I)Y zeolite. Incidently, the small ammonia to Ag^+ ratios, as shown in Table 4, revealed that the silver ions in the small cavities could not possibly migrate to the supercages to form amminecomplexes. This is contrary to that observed in CuY zeolites (*6*).

The high heat of adsorption indicates that the interaction between carbon monoxide and silver ions was quite strong. At very low coverages, the isosteric heat was as high as 19 kcal/mole for AgX and 15 kcal/mole for AgY. These are to be compared to 14.7 kcal/mole for Cu(I)Y zeolite (*1*). The magnitude of the heat and the intensity of the infrared absorption band would suggest that carbon monoxide was adsorbed on silver ions by more than physical forces. There is, however, no direct correlation between the heat of adsorption and the CO stretching frequency. While the difference in heat between AgX and AgY samples is 4 kcal/mole, both have the same CO stretching frequency. On the other hand, while there is little difference in heat between AgY and Cu(I)Y samples, the CO stretching frequency is 25 cm^{-1} apart. It seems that any correlation of this sort must be taken with caution.

Although there is little doubt that carbon monoxide was adsorbed on the silver ions, the location of the adsorption sites would have been more obvious if the adsorption data of AgY alone were considered. There are four hexagonal window positions in a supercage and the X-ray diffraction study (*8*) shows that, on the average, there are about 3.54 Ag^+ ions located at these sites. Since nearly four CO molecules per cage were adsorbed in AgY, it seems that they were held on the hexagonal window sites. It is, however, puzzling that about the same number of CO molecules was held by AgX, which has four more Ag^+ ions possibly present in the supercages, according to the assignment of Yates (*5*). Furthermore, the number of ethylene molecules adsorbed in both zeolites was also the same, which was between 6.5 and 7.5 per cage. Of these adsorbed molecules, about 3 per cage were strongly held in both samples and could not be removed by evacuation at 25°C. The adsorption and desorption data of carbon monoxide and ethylene in AgX and AgY and the location of Ag^+ ions in the zeolite lattice are summarized in Table 6. It is obvious that an assignment of the adsorption sites, which can satisfactorily describe the adsorption in both zeolites, is not easy. Should each Ag^+ ion in the supercage adsorb one CO or C_2H_4 molecule, then more would have been adsorbed in AgX than in AgY. And if C_2H_4 molecules were strongly held by Ag^+ ions on the walls of the supercage, but only weakly held by Ag^+ ions at the hexagonal windows, according to Yates, then more ethylene would have been desorbed from AgY. It seems more plausible, at least from the present result on AgY zeolite, to assume that ethylene was strongly held at the hexagonal window sites and only weakly held by Ag^+ ions in the hexagonal prisms. At any rate, an X-ray diffraction study of the dehydrated AgX zeolite would be desirable to clarify these questions.

In view of the fact that silver ions are univalent with rather small polarizing power, i.e., the charge to radius ratio, it is striking that the heat of nitrogen adsorption in AgX

TABLE 6

THE ADSORPTION SITES IN SILVER-EXCHANGED ZEOLITES

Location of Ag^+ ions	AgX	AgY
Reference	Yates (*5*)	Eulenberger *et al.* (*8*)
Inside the hexagonal prisms	2	2
Inside the sodalite cages	0	1.34
In the supercages		
On the wall	4.75	0
At the hexagonal window	4	3.54
Total	10.75	6.88
No. of CO molecules		
Adsorbed at 25°C and 100 Torr	4.37	4.30
After evacuation at 25°C	1.43	0.37
No. of C_2H_4 molecules		
Adsorbed at 25°C and 100 Torr	7.41 (8.0)[a]	6.59
After evacuation at 25°C for 3 hr	3.06 (4.40)[b]	2.88

[a] From the work of Yates (*5*), at 35°C and 143 Torr.

[b] From the work of Yates (*5*), after evacuation at 25°C for ½ hr.

was as high as 8.2 kcal/mole while that for AgY was only 4.6 kcal/mole. The heat values reported on X and Y type zeolites are usually between 3.5 and 6 kcal/mole (*4*, *9*). Values as high as 7 kcal/mole have been determined in LiX (*4*) and CaY (*10*); both cations are considered to have large polarizing powers. Also, potassium ions have about the same ionic radius as silver ions, but the heat of nitrogen adsorption in KX zeolite is only 4.4 kcal/mole (*4*). Apparently, the difference in heat between AgX and AgY must be due to the difference in cation distribution in the supercage. Some Ag^+ ions in AgX might be so located as to contribute more electrostatic interaction with the adsorbate molecules. As indicated in Table 3, the heats for carbon monoxide and carbon dioxide were also higher for AgX than for AgY zeolite. Barrer and Coughlan (*11*) have pointed out that the higher cation density in the supercages of NaX may explain the higher heat of CO_2 adsorption compared to the NaY sample.

The number of the specific sites, which adsorbed nitrogen rather strongly and which were only present in AgX zeolite, was about one per supercage. When these sites were occupied by carbon monoxide, which could not be pumped off at 25°C, the specific adsorption of nitrogen was diminished. Moreover, these sites became inactive if the sample had been treated with carbon monoxide at 350°C, but could be recovered by treating with oxygen at the same temperature.

It is worth mentioning that, in the absence of X-ray diffraction technique, the crystallinity of the faujasite structure may be examined by the adsorption of small molecules like nitrogen, carbon monoxide or oxygen at liquid nitrogen temperature. In fact, the gas adsorption measurement is sometimes more reliable for observing the change in the surface area of zeolite than the X-ray method, as was pointed out by Yates (*12*). A comparison of the adsorption capacity in various cation exchanged zeolites revealed that both AgX and AgY samples had retained their crystallinity even after various pretreatments.

The slow adsorption of nitric oxide in AgY zeolite has also been observed from ESR investigation by Chao and Lunsford (*13*). A detailed structure of the Ag(I)-NO complexes has been studied. The adsorption measurement indicated that the amount of NO adsorbed in AgY was small compared to those of CO and CO_2. No high heat of adsorption of nitric oxide would be expected for the reversible portion of the adsorption.

CONCLUSION

The present study has indicated that carbon monoxide is strongly adsorbed on silver ions in both the X and Y type zeolites with about four molecules per supercage. The additional sites of Ag^+ ions in AgX zeolite are responsible for higher heats of adsorption of nitrogen, carbon monoxide and carbon dioxide, as compared to AgY zeolite. No migration of silver ions, when ammonia is adsorbed, can be inferred from adsorption measurement; the presence of ammonia ligands has little effect on the CO stretching frequency of the adsorbed carbon monoxide.

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