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Direct Measurement of Interaction Energy between Solids and Gases. VII. Heats of Adsorption of Carbon Monoxide on Cu(II)-exchanged Zeolites Y

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Differential heats of the adsorption of carbon monoxide on Cu(II)Y zeolites were calorimetrically determined. The heat of adsorption was larger on Cu(II)Y zeolites than on the NaY zeolite, and increased with the degree of Cu(II) ion-exchange. Repeated adsorption-desorption measurements revealed an increase in the heat of adsorption, which is considered to be due mainly to the migration of copper(II) ions from inaccessible sites for carbon monoxide to accessible ones in the process of adsorption-desorption.

The adsorption properties and catalytic activities of zeolites are markedly affected by the nature and the distribution of cations in the zeolites. Investigations of the interaction between simple gas molecules and the zeolite surface have often provided important information on the nature and the distribution of these cations. Carbon monoxide is an attractive choice for such investigations.[1]

There have been a number of investigations of the adsorption of carbon monoxide on zeolites, but, as far as we know, there is only a little information about the cation migration by carbon monoxide.[1] In this study, we have determined the heats of the adsorption of carbon monoxide on Cu(II)Y zeolites to provide calorimetric evidence for the migration of copper(II) ions under the conditions of the adsorption-desorption of carbon monoxide.

Experimental

Materials and Gas. The copper(II)-exchanged zeolites were prepared by the ion-exchange of NaY zeolite (Linde SK-40), in an excess of a 5 mM (1M=1 mol dm^{-3}) copper(II) nitrate solution at room temperature for 14.3 and 50.3% exchange, and at *ca.* 80 °C for 80.7%.

The Cu(II)-exchanged samples were then thoroughly washed with distilled water and dried for 6 h at 110 °C, and finally stored over a saturated ammonium chloride solution at *ca.* 25 °C for at least one week before use. The samples were sieved to 28—60 mesh for use.

The degree of exchange was determined from the chemical analysis of the sodium and the atomic absorption analysis for copper(II).

The carbon monoxide (Takachiho Chem. Co., Ltd.), which was stated to have a purity greater than 99.5% (the main impurities were air, H_2, and CO_2), was purified by passing it through a liquid nitrogen cold trap before storage.

Apparatus. The heats of adsorption were measured with a twin conduction calorimeter (Tokyo Riko Co., Ltd., MPC-10 type), which was connected to a volumetric adsorption system, with an error of *ca.* 5%. The ESR measurements were carried out at room temperature with an X-band 9.38 GHz spectrometer (Japan Electron Optics Laboratory Co., Ltd., JES-ME-3X). The phosphorescence spectra of CuY were taken with a Toshiba UV-D33S spectrophotometer at room temperature. The measurement of the electronic spectra was carried out with a spectrophotometer Shimazu MPS-5000 using the reflectance method.

Procedure. Each 0.5-g zeolite sample (including *ca.* 25% H_2O) in a sample cell was evacuated under a pressure of 10^{-1} Pa, heated up at a rate of 8 °C/min to 400 °C (or 100, 250 °C), and then held at that temperature for 5 h under a vacuum of 10^{-3} Pa. The sample cell was then cooled down *in vacuo* and set in a calorimeter thermostated at the desired temperature (25±0.01 °C) for measurements.

Results

Heats of Adsorption. The heats of the adsorption of carbon monoxide on NaY and three fresh Cu(II)Y (14.3, 50.3, and 80.7% exchanged) zeolites are plotted against the amounts adsorbed in Fig. 1. In the initial portion, the differential heats of the adsorption of carbon monoxide on Cu(II)Y were larger than on NaY, and they increased with the degree of copper(II) ion-exchange.

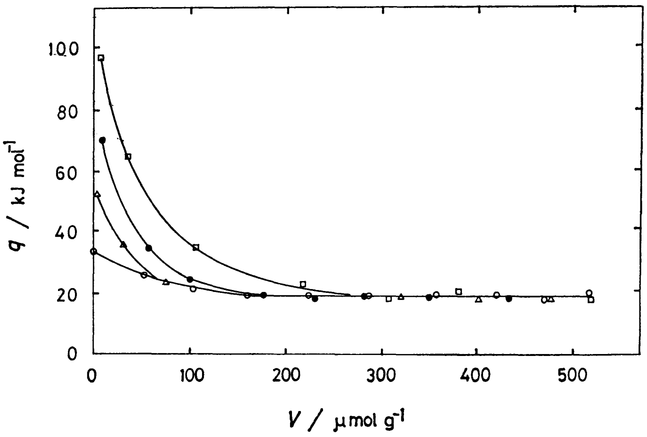

Fig. 1. Heats of adsorption of CO on Cu(II)Y and NaY.
—○—: NaY, —△—: Cu(II)Y-14.3,
—●—: Cu(II)Y-50.3, —□—: Cu(II)Y-80.7.

Figure 2 shows the adsorption isotherms of carbon monoxide on Cu(II)Y-80.7 pretreated at 400 °C under a pressure of 10^{-3} Pa for 5 h. The adsorption measurements for the second isotherm were carried out after desorbing the adsorbed CO under a vacumm of 10^{-3} Pa for *ca.* 3 d. The third was made after the desorption of the second, and so forth. The adsorption-desorption cycle increased the amount of adsorption. However, the degree of increase in the adsorbed amount became smaller with the number of cycles, and finally no such an increase was detected between the tenth and the

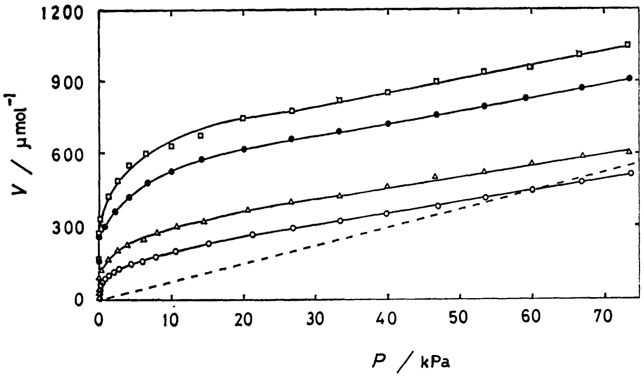

Fig. 2. Adsorption isotherms of CO on Cu(II)Y-80.7. After adsorption measurement up to *ca.* 73 kPa equilibrium pressure zeolite was evacuated at 10^{-3} Pa for *ca.* 3 d then the next run of adsorption was carried out. This procedure repeated until the isotherm practically agreed with the preceding one.
----: NaY, —○—: 1st, —△—: 3rd, —●—: 7 th, —□—: 11th run.

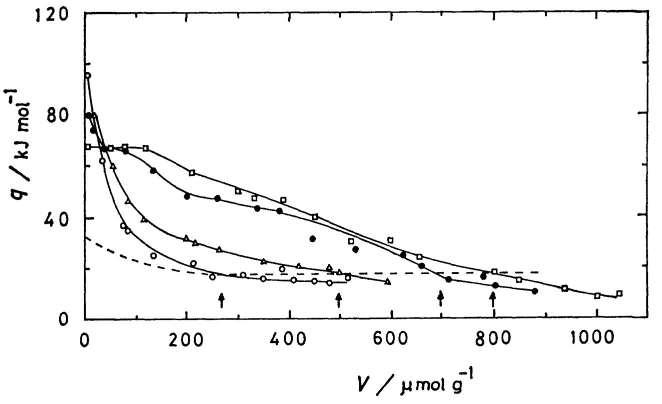

Fig. 3. Heat curves of adsorption of CO on Cu(II)Y-80.7, corresponding to Fig. 2.
----: NaY, —○—: 1st, —△—: 3rd, —●—: 7th, —□—: 11th run. Arrows show the intersection of Cu(II)Y and NaY.

eleventh isotherms.

The heat curves corresponding to the above-mentioned isotherms are shown in Fig. 3. Apart from the initial portion, the heat curves were also shifted to the higher side. The initial heats of adsorption, on the contrary, gradually decreased with the number of the run. The tenth and eleventh curves agreed with each other within experimental uncertainty.

Changes in the Heats of Adsorption in the Process of Repeated Adsorption-desorption on Cu(II)Y. Thermograms of the repeated adsorption and desorption of carbon monoxide on NaY, Cu(II)Y-14.3, and Cu(II)Y-80.7 are shown in Fig. 4. After pretreatment at 400 °C, the heats of adsorption and desorption were measured by admitting measured amounts of CO: 80 μmol g^{-1} for NaY and Cu(II)Y-14.3; 20 μmol g^{-1} for Cu(II)Y-80.7. After the first thermogram had been drawn, the first heat of desorption (Q_{d1}) was measured under evacuation up to 10^{-3} Pa; then the same procedure of adsorption and desorption was repeated several times.

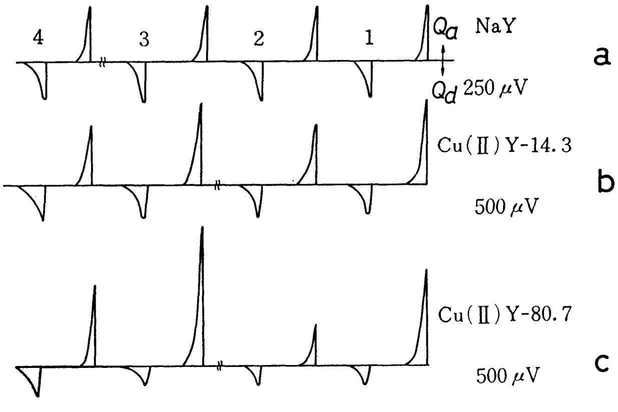

Fig. 4. Thermograms of repeated CO adsorption-desorption on NaY and Cu(II)Y, pretreated at 400 °C under a pressure of 10^{-3} Pa for 5 h. Q_a: Heat of adsorption, Q_d: heat of desorption. Admitted amount of CO: 80 μmol g^{-1} for NaY and Cu(II)Y-14.3; 20 μmol g^{-1} for Cu(II)Y-80.7. For NaY after 3 rd run and Cu(II)Y after 2 nd run the samples were evacuated overnight. 250 or 500 μV represents the full scale of the recorder response.

In the case of NaY, the heats of adsorption, Q_a, and desorption, Q_d, were practically identical at all times, not only from Q_{a1} to Q_{d3}, which were measured successively, but also at Q_{a4} and Q_{d4} which were measured after evacuation overnight under 10^{-3} Pa. In the case of Cu(II)Y-14.3, the second heat of adsorption, Q_{a2}, was smaller than the first, Q_{a1}, by 42%. This decrease occurred because of an incomplete desorption of strongly adsorbed carbon monoxide on Cu(II)Y-14.3 (Q_{d1} was smaller than Q_{a1} by 53%). However, Q_{a3}, which was measured after degassing overnight under 10^{-3} Pa, was much the same as Q_{a1}. These results showed that the carbon monoxide on Cu(II)Y-14.3 is desorbed when the sample is evacuated over a period of *ca.* 10 h (several times as long as for NaY). This was also supported by IR observation. However, when Q_{a5} (which is not shown in Fig. 4) was measured after degassing overnight under 10^{-3} Pa, an interesting phenomenon was observed: $Q_{a5} > Q_{a1}$. This phenomenon of the increase in the heat of adsorption was also, remarkably observed in the sample of higher exchanged Cu(II)Y-80.7: Q_{a2} was very much smaller than Q_{a1}, while Q_{a3}, measured after degassing overnight under 10^{-3} Pa, was *ca.* 1.5 times as large as Q_{a1}.

Figure 5 shows the changes in the thermograms with the pretreatment temperatures. The changes in the heats of adsorption markedly depended upon the pretreatment temperatures (*cf.* Fig. 4,c). In the case of the 100 °C-pretreatment in spite of the incomplete first desorption ($Q_{d1} < Q_{a1}$), the second heat of adsorption, Q_{a2}, was larger than Q_{a1}, and Q_{a3} was also larger than Q_{a2}. Furthermore, Q_{a4}, measured after evacuation overnight, was *ca.* 7.5 times as large as Q_{a1}. Intermediate behavior was observed in the case of the 250 °C-pretreatment.

The changes in the heat of adsorption, q/kJ mol^{-1}, corresponding to Figs. 4 and 5 are summarized in Table 1.

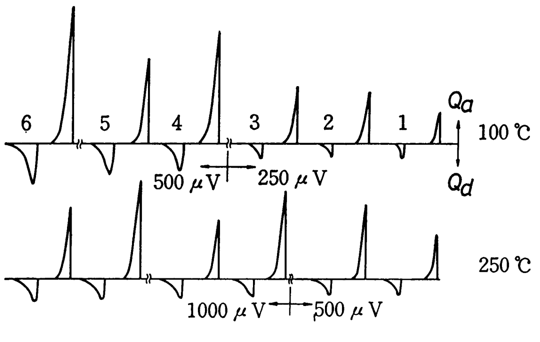

Fig. 5. Changes of thermograms of adsorption and desorption of CO on Cu(II)Y-80.7 with pretreatment temperatures 100 and 250 °C. Q_a: heat of adsorption, Q_d: heat of desorption. Admitted amount of CO: 20 μmol g^{-1}. 250, 500, or 1000 μV represents the full scale of the recorder response.

TABLE 1. CHANGES IN HEAT OF ADSORPTION (q/kJ mol^{-1}) CORRESPONDING TO FIGS. 4 AND 5

Zeolite	Cu(II) Y-14.3	Cu(II) Y-80.7	Cu(II) Y-80.7	Cu(II) Y-80.7
Pretreatment temperature/ °C	400	400	250	100
1	24.9	92.5	16.6	6.3
2	15.0	61.9	29.7	10.1
3	25.1	108.4	55.3	10.6
4	20.3	74.1	35.0	29.0
5	(26.2)		57.5	32.9
6			35.1	35.7

ESR and Phosphorescence Measurements. From the phosphorescence spectra (Fig. 6), the formation of Cu(I) was observed[2] when dehydrated Cu(II)Y-80.7 was treated with 20 kPa of CO at 400 °C for 36 h. In this case, contrary to Huang,[3] the reduction of Cu(II)Y by CO was not complete. A complete reduction was, however, achieved, as Huang[3] had reported, when NH_3 was preadsorbed in dehydrated Cu(II)Y-80.7 at a pressure of *ca.* 1.33 kPa; then the sample was treated with 20 kPa of CO at 400 °C for 1 h. However, no indication of Cu(I) formation was observed in either the sample of Cu(II)Y-80.7 evacuated at 400 °C under a pressure of 10^{-3} Pa for 5 h or, the Cu(II)Y-80.7 evacuated, followed by the adsorption of CO at room temperature. These results were in agreement with those of the ESR (Fig. 7).

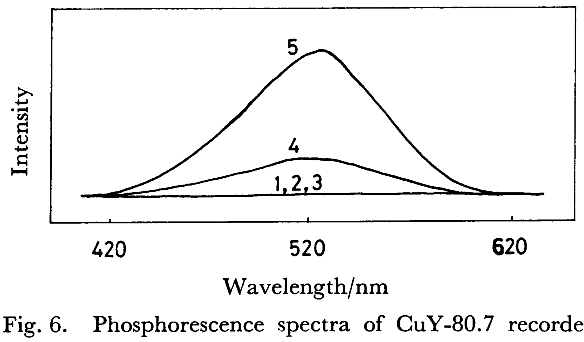

Fig. 6. Phosphorescence spectra of CuY-80.7 recorded at room temperature under the same optical conditions and nearly identical sample geometries.
(1): Cu(II)Y-80.7 untreated, (2): after evacuation of Cu(II)Y-80.7 at 400 °C under a pressure of 10^{-3} Pa for 5 h, (3): after (2) adsorption of 13.3 kPa CO at room temperature for 1 h, (4): after (2) adsorption of 20 kPa CO at 400 °C for 36 h, (5): after (2) adsorption of 1.33 kPa NH_3 at room temperature for 1 h then adsorption of 20 kPa CO at 400 °C for 1 h.

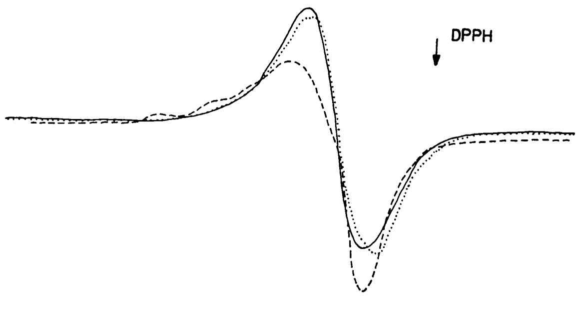

Fig. 7. ESR spectra of Cu(II)Y-80.7 recorded at room temperature.
------: (1) After evacuation at room temperature for 2 h, ——: (2) after (1) stored over saturated NH_4Cl solution at *ca.* 25 °C for 3 d, ······: (3) after evacuation at 400 °C under a pressure of 10^{-3} Pa for 5 h stored over saturated NH_4Cl solution at *ca.* 25 °C for 3 d.

Measurement of Electronic Spectra. In the near-infrared region, the Cu(II)Y-80.7 zeolites hydrated or pretreated at 100 °C showed the absorption maxima at *ca.* 1450 and 1950 nm. However, in the case of 250 or 400 °C-pretreatment these peaks were not observed. These two bands are assigned to the overtone band ($2\nu_3$) and the combination band ($\nu_2+\nu_3$) of the adsorbed water respectively.[14]

Discussion

The synthetic Y zeolites have two sets of cavities. The larger cavities, called supercages, have a diameter of *ca.* 13 Å. The entrances to the supercages have a free diameter of approximately 9 Å. The smaller cavities, called sodalite cages, have a free diameter of 7 Å and are connected to the supercages by openings with a free diameter of 2.5 Å. The sodalite cages are joined to each other by 2.4 Å free-diameter hexagonal prisms.[4,5] The kinetic diameter of the carbon monoxide molecule is *ca.* 3.8 Å,[6] and so it must be unable to pass through these small openings. According to Smith[7] and Mortier,[8] there are five kinds of cation sites in Y zeolite; *i.e.*, SI, at the center of a hexagonal prism; SI′, displaced from a shared hexagonal face into the sodalite cage; SII′, displaced from an unshared hexagonal face into the sodalite cage; SII, slightly displaced into the supercage, and SIII′, in the supercage, formed by two O_1 and O_4 oxygens. Thus, carbon monoxide would possibly be chemisorbed, with a relatively strong interaction, on Cu(II) at the SII or SIII′ sites. The Cu(II) ions at the SI, SI′, or SII′ sites may not be accessible to carbon monoxide, as is supported by the work of Egerton and Ston.[1] They showed by experiments on a sample of synthetic sodalite that CO was not adsorbed at temperatures below 200 °C. Also, they pointed out that a slow adsorption of CO occurring on Cu(II)Y and Ni(II)Y zeolites was to be ascribed to a gradual increase in the number of adsorption sites caused by the adsorption-induced migration of the divalent cations.

The present results and those formerly reported by other workers can well be interpreted in terms of the model to be discussed below. The difference between the adsorption properties of NaY and Cu(II)Y is primarily to be ascribed to the existence of the accessibility of Cu(II) to the visiting CO. The higher values of q in the initial portion of q *vs.* V curves are attributable to the adsorption on exchangeable cations. The curves in Fig. 1 show that Cu(II) adsorbs CO with a stronger interaction than does Na, and that the quantity of Cu(II) accessible to CO increases with the increase in the content of Cu(II). When the adsorbed amount increases, the q-value converges to 20 kJ mol^{-1} for all the samples studied. It is known that, in such a region, CO is adsorbed on the framework oxygen. Thus, the amount of the accessible Cu(II) can easily be estimated from Fig. 1; it is found to increase with the number of the adsorption-desorption cycles, as is shown in Fig. 3 and Table 2. This can be explained as follows. The Cu(II) ions at the SI, SI′, and/or SII′ sites migrate, in the course of the cycle, to the SII and/or SIII′ sites, which are accessible to the visiting CO. Though there are many possibilities, the most plausible one is that a predominant part of the Cu(II) migration occurs from the SII′ to the SII site. This change corresponds to a small displacement from one side of the 6-membered oxygen ring to the other side, and may take place with a small activation energy.

TABLE 2. INCREASE IN THE NUMBER OF ACCESSIBLE Cu(II) IONS WITH THE ADSORPTION-DESORPTION RUN

Number of run	$V_{\mathrm{sp.ad}}$ / μmol g^{-1}		Ratio of accessible Cu(II) ions compared with 1st run	
	a	b	a	b
I	270	170	1	1
III	500	280	1.9	1.6
VII	700	510	2.6	3.0
XI	800	620	3.0	3.6

a) The amount of specific adsorption was determined from the amount adsorbed where the heat curves of Cu(II)Y intersect with that of NaY. b) The amount of specific adsorption was determined by the extrapolation of the lines in the high-pressure region of the isotherms in Fig. 2 to 0 pressure.

The above discussions are based on the assumption that no reduction of Cu(II) to Cu(I) occurred; this assumption was supported by the ESR and phosphorescence studies. The ESR signal ascribed to the Cu(II) ion did not change in repeated adsorption-desorption cycles. It should have decreased if any reduction of Cu(II) had occurred. The phosphorescence spectrum in Fig. 6 shows that Cu(I) was not produced in the present treatments.

The extent of cation migration depends upon also the quantity of residual water molecules.[9-13] The present electronic spectral data show that the samples pretreated at 250 or 400 °C are considered to be dehydrated ones, and that at 100 °C, partially hydrated. This is compatible with the electronic spectral data reported by De Wilde *et al.*[15] The increase in the heat of adsorption (q) shown in Table 1 may be ascribed to another reason besides the above-mentioned migration of Cu(II): that is, the release of coordinated H_2O (or OH group). Since the samples pretreated at 250 or 400 °C are considered to be dehydrated, the phenomenon is ascribed to the Cu(II) migration, whereas in the sample pretreated at 100 °C the second reason cannot be neglected.

In conclusion, the observed results can consistently be explained by the proposed model that Cu(II) at the SII and/or SIII′ sites strongly adsorb CO, and that the number of such Cu(II) cations increases with the adsorption-desorption cycles as a result of the Cu(II) migration from the inaccessible sites to the accessible ones. In the case of partially hydrated Cu(II)Y, the replacement of coordinated H_2O (or OH group) by CO may also occur.

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