

# Studies on Interaction of CO with Zeolites by Calorimetric Measurements (2)

—Adsorption Properties of CO on Cu(II)ion-Exchanged Zeolites Y—

熱測定によるゼオライトとCOの相互作用の研究(2)

—Cu(II)YのCO吸着特性—

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## 1. Introduction

It is well known that the adsorption properties and catalytic activities of zeolites are markedly affected by the nature and the distribution of cations in zeolites. By investigations of the interaction between simple gas molecules and the zeolite surface has often been obtained an important information of the nature and the distribution of these cations. Carbon monoxide is an attractive choice for such investigation<sup>1)</sup>. The CO molecule is small enough to enter the supercages of faujasite type zeolites, but too large to enter the sodalite units or hexagonal prisms. The molecule has an asymmetric charge distribution and is easily polarized; it is therefore sensitive to the strong electrostatic fields surrounding cations. It also interacts very specifically with transition metal ions, as a result of its ability to act both as a weak donor and as a  $\pi$ -acceptor, and it is well known to form chemisorption bonds on transition metal oxides.

For these reasons, a great number of studies on the adsorption of CO on various ion-exchanged zeolites has been carried out<sup>1)-18)</sup>. The adsorption of CO on multivalent cation - containing zeolites caused a specific interaction of CO molecule with the metal ions, hence the amount of CO adsorbed on these zeolites was found to be several times as much as that of adsorbed on initial Na formed zeolite<sup>3)</sup>. This specific interaction was shown to result from the formation of complexes  $\text{Me} \cdots \text{C}=\text{O}$  with an ir band at *ca.*  $2200\text{cm}^{-1}$ , which is higher than gas phase frequency<sup>2)</sup>.

The location of cations in Cu(II)-exchanged zeolites X and Y has also been exhaustively studied by several workers<sup>19)-33)</sup>. Some of them have reported that in dehydrated synthetic zeolites X and Y,  $\text{Cu}^{2+}$  strongly prefers

the sites I' in the sodalite cavities<sup>21),22),24)-29)</sup>. For instance, Gallezot and coworkers<sup>25)</sup> have made a X-ray diffraction study of two Cu(II)-exchanged Y zeolites ( $\text{Cu}_{16}\text{Na}_{24}\text{Y}$  and  $\text{Cu}_{12}\text{Na}_5\text{H}_{27}\text{Y}$ ) in the dehydrated state and reported that 11.1 and 9.9 Cu(II)-ions per unit cell occupied I' site respectively and the remaining Cu(II)-ions were in site I. While Kazanskii and coworkers<sup>19),20),26),27)</sup> have shown by the aid of EPR and uv spectroscopic studies of the coordination state and the localization sites of several cations in zeolite Y that in the dehydrated state Cu(II)-ions probably migrated to SII or SII' sites with formation of trigonal coordination. Stolyarova and coworkers<sup>10)</sup> have determined the heats of adsorption of  $\text{H}_2\text{O}$  on Cu(II)Y calorimetrically and reported the strong preference of Cu(II)-ions for SII sites. Zhavoronkov<sup>23)</sup> has calculated the priority of SII-site for a series of cations, including Cu(II), on the basis of the electrostatic and covalent parameters. Maxwell and De Boer<sup>30)</sup> have reported the results of a single-crystal X-ray analysis of dehydrated Cu(II)-exchanged natural faujasite  $\text{Cu}_{28}(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}$  (dehydrated at  $150^\circ\text{C}$ ): Cu(II)-ions were located at sites I (1.5), I' (14.2), II' (0.8), II (5.3) and III (3.3) per unit cell. Mörke and coworkers<sup>31)</sup> have reported the results of EPR spectroscopic investigation: three different location sites were distinguished; SI', SII and cluster in the supercage, the distribution of Cu(II)-ions in dehydration state (dehydrated at  $600^\circ\text{C}$ ) were in sites I' (1.6), II (0.9) and cluster (2) for  $\text{Cu}_{4.5}\text{Na}_{44.5}\text{Y}$  and I' (8.2), II (4.8) and cluster (5.5) for  $\text{Cu}_{18.5}\text{Na}_{16.5}\text{Y}$ . Schoonheydt and Velghe<sup>32)</sup> have also calculated the distribution of Cu(II)-ions from the results of the electrical conductivity: in small cages (3.4) and supercages (0) for  $\text{Cu}_{3.4}\text{Y}$ , in small cages (11.8) and supercages (0) for  $\text{Cu}_{11.6}\text{Y}$ , in small cages (11 - 14) and supercages (7 - 10) for  $\text{Cu}_{20}\text{Y}$ .

From this brief review described above a marked

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tendency for the location of Cu(II)-ions in Cu(II)Y would be observed. That is to say, in dehydrated state they have a strong preference for SI' or SII. But there is a discrepancy in the quantitative details. This would be due to the difference of the dehydrated state, which depends delicately not only on the dehydration conditions but also ion-exchange ones.

Rabo and coworkers<sup>3)</sup>, Egerton and Stone<sup>1)</sup> exploited the adsorption of CO as a method to determine the distribution of multivalent cations in zeolite. Haber and coworkers<sup>14)</sup> have applied this method for determination of Zn(II)-ions in zeolite X.

In this study the distribution of Cu(II)-ions in zeolites Y was determined by calorimetric measurements of the heats of adsorption of CO on Cu(II)Y zeolites.

## 2. Experimental Methods

### Materials and Gas

Copper (II) - exchanged zeolites were prepared, as described previously<sup>36)</sup>. The ion-exchange process was carried out at room temperature for Cu(II)Y-14.3 and -50.3%, while for higher exchanged -80.7% at ca. 80°C.

Carbon monoxide used was the same as in the previous work.

### Apparatus

Apparatus used for pretreatment and measurement of the heats of adsorption were also the same as in the previous work.

### Procedure

After the pretreatment under  $10^{-5}$  Torr for 5 hrs and setting the sample cell in the calorimeter as described previously, the heats of adsorption and adsorbed amounts of CO were measured at 25°C.

## 3. Results and Discussion

Rabo and coworkers<sup>3)</sup> have shown that the adsorption of CO on several bivalent-cation forms of faujasite-type zeolite can be explained in terms of a specific adsorption, attributed to the high electrostatic fields associated with the bivalent cations, together with a non-specific adsorption characteristic of the unexchanged zeolite surface of Na faujasite. The total adsorption results in the sum of the former adsorption, which is shown by the Langmuir isotherm and the latter one, which obeys Henry's law. This relationship has been confirmed by Egerton and Stone<sup>4)</sup> on CaY and also by Haber and coworkers<sup>14)</sup> on ZnX.

The adsorption isotherms of CO on NaY and three

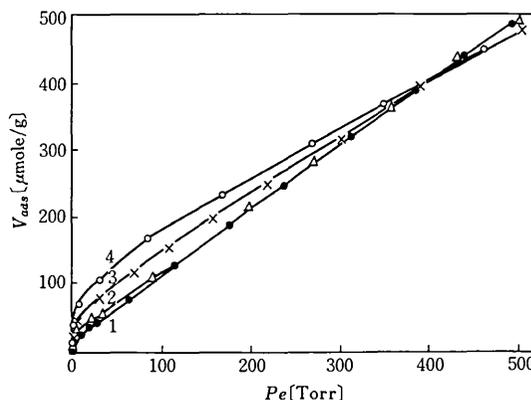


Fig. 1 Adsorption isotherms of CO on Cu(II)Y and NaY  
1 : NaY 2 : Cu(II)Y-14.3  
3 : Cu(II)Y-50.3 4 : Cu(II)Y-80.7

Cu(II)-exchanged Y (14.3, 50.3 and 80.7% exchanged) at 25°C are shown in Fig. 1. The adsorption on NaY obeys nearly Henry's law. However, the isotherms of NaY and Cu(II)-14.3 overlap above the equilibrium pressure of ca. 120 Torr, furthermore the isotherms of Cu(II)Y-50.3 and -80.7 intersect the isotherm of NaY at pressures of ca. 380 and 410 Torr, respectively. Consequently, the relationship which Rabo suggested was found to hold only in the range of relatively low equilibrium pressures, that is, at lower than ca. 30, 50 and 100 Torr, in the case of Cu(II)Y-14.3, -50.3 and -80.7, respectively. However, these results are not necessarily in contrast with the Rabo's suggestion, since in their cases the adsorption isotherms were measured at relatively low pressures.

The heats of adsorption of CO on NaY and three Cu(II)Y zeolites are plotted against the amount adsorbed in Fig. 2. In the initial stage the value of the differential heat

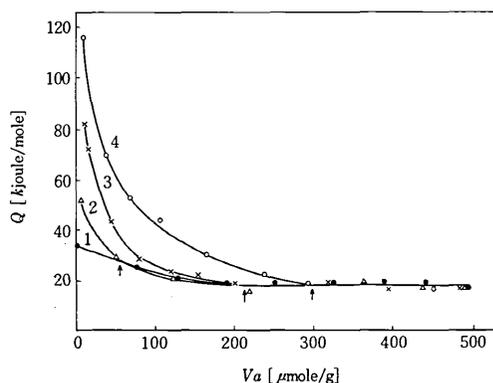


Fig. 2 Heats of adsorption of CO on Cu(II)Y and NaY  
1 : NaY 2 : Cu(II)Y-14.3  
3 : Cu(II)Y-50.3 4 : Cu(II)Y-80.7

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of adsorption of CO on Cu(II)Y was larger than on NaY because of its stronger electrostatic fields. The difference of the heat curves between Cu(II)Y and NaY zeolites would be mainly due to the presence of the specific adsorption, and the difference among three Cu(II)Y zeolites due to the degree of the specific interaction, that is, the specific interaction of molecules of carbon monoxide with cupric ions increases with the degree of Cu(II)-exchange. Consequently, in the region where the heat curves of Cu(II)Y agree with that of NaY only the non-specific adsorption of CO would occur, that is, the amount adsorbed at which the heat curves of Cu(II)Y begin to overlap with that of NaY would correspond to the amount of the specific adsorption. According to Smith<sup>21)</sup> and Mortier<sup>34)</sup> five kinds of cation sites are present in zeolite Y: SI, I', II', II and III'. In consideration of the structure of zeolite Y and the kinetic diameter of CO molecule, the accessible sites for CO can be determined: they are SII and III', located in the supercage, and the others are inaccessible ones.

Under the assumption that the specific adsorption is due to direct interaction of CO with accessible Cu(II)-ions on a 1 : 1 basis, the number of cupric ions occupying accessible sites for CO could be calculated.

$$N_{\text{Cu, acc}} = V_{\text{sp. ad}} \cdot 10^{-6} \cdot N_A \cdot \frac{M}{N_A} = V_{\text{sp. ad}} \cdot M \cdot 10^{-6},$$

where  $N_{\text{Cu, acc}}$ : the number of cupric ions occupying accessible sites for CO per unit cell,  $V_{\text{sp. ad}}$ : the amount adsorbed up to the completion of the specific interaction ( $\mu$  mole / g),  $N_A$ : the Avogadro number, M: molecular weight of the dehydrated Cu(II)Y.

The  $N_{\text{Cu, acc}}$  values calculated from this equation are summarized in Table 1, in which the degree of Cu(II)-exchange,  $V_{\text{sp. ad}}$  values, the number of cupric ions per unit cell ( $N_{\text{Cu, total}}$ ), and the ratio of Cu(II) occupying accessible sites to total Cu(II)-ions are also given.

These results show that *ca.* 81–83% of Cu(II)-ions should occupy inaccessible sites. But as is demonstrated in

previous work<sup>36)</sup> the adsorption of CO on Cu(II)Y induces the migration of Cu(II)-ions from inaccessible sites for CO to accessible ones; it probably takes place from SII' to SII sites. It means that the number of Cu(II)-ions occupying initially accessible sites should be somewhat less than the calculated one. Therefore these results suggest that SI' and/or SII' sites have a stronger preference for Cu(II)-ions than SII sites. The present measurements indicate that SI sites are not exclusively occupied in all three Cu(II)Y and also that contrary to the assumption of Richardson<sup>35)</sup> not all Cu(II)-ions are in the supercages. The fact that the ratios of Cu(II)-ions occupying accessible sites to total Cu(II)-ions are always *ca.* 17–19% irrespectively of the degree of exchange is possibly correlated with the Cu(II)-migration. However, persuasive interpretations for it would require further investigations determining the Cu(II)-migration quantitatively.

#### 4. Conclusion

1. Differential heats of adsorption and adsorption isotherms of carbon monoxide on Cu(II)Y zeolites were determined. The initial heat of adsorption is larger on Cu(II)Y zeolites than on NaY zeolite, and it increases with the degree of Cu(II)-exchange. Only in the range of relatively low equilibrium pressures the adsorption isotherms were described by a sum of Langmuir-type isotherm of specific adsorption and Henry-type isotherm of non-specific adsorption; lower than *ca.* 30, 50 100 Torr in the case of Cu(II)-14.3, -50.3, and 80.7, respectively.

2. Under the assumption that the number of carbon monoxide molecules adsorbed specifically could be considered as a measure of accessible cupric ions, the distribution of cupric ions in zeolite Y was determined. About 17–19% of exchanged cupric ions occupy the accessible sites on Cu(II) zeolites irrespectively of the degree of exchange in the range of 14–80%. From the heat curves the preference of SI' and/or SII' sites for Cu(II)-ions was suggested.

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Table 1 Number of Cu(II)-ions occupying accessible sites

Degree of exchange (%)	$V_{\text{sp. ad}}$ ( $\mu$ mole/g)	$N_{\text{Cu total}}$ (sites / unit cell)	$N_{\text{Cu accessible}}$	$\frac{N_{\text{Cu, acc.}}}{N_{\text{Cu, total}}} \times 100$ (%)
14.3	53	4.0	0.68	17.0
50.3	214	14.1	2.61	18.5
80.7	298	22.6	3.80	16.8

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