

# Studies on Interaction of CO with Zeolites by Calorimetric Measurements (1)

—Migration of Cupric Ions under Adsorption 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(1)

—Cu(II)YのCO吸着過程におけるCu<sup>2+</sup>イオンの移動—

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## 1. Introduction

The behavior and catalytic activity of zeolites depend largely on the positions of the cations in the framework. Since the cations, however, in a zeolite framework are not necessarily stabilized, and their location depends on certain conditions such as thermal treatment and possibility of interacting with adsorbates, the migration or the replacement of them among the sites in the framework sometimes occurs.

The phenomenon of the migration may be divided into two types as a matter of convenience. Type 1 is due to thermal treatment and in this case the hydration state of cation is an important factor of the migration. Type 2 is due to interaction between cations compensating the excess charge of the framework and adsorbates.

There have been not a few reports that directly or indirectly deal with the first type migration in connection with the location of ion-exchanged cations in zeolites, for instance, by EPR spectrometry<sup>1-3</sup>, X-ray powder diffraction methods<sup>4, 5</sup>, single crystal and X-ray methods<sup>6</sup>, visible spectroscopic technique<sup>7</sup>, XPS<sup>8</sup>, thermogravimetry<sup>9</sup>, luminescence spectroscopic and EPR<sup>10</sup>, EPR and uv<sup>11</sup>, and ir spectroscopic technique<sup>12</sup>, or by means of magnetic susceptibility<sup>13</sup>, and catalytic activity<sup>14</sup>.

Several reports on the second type migration also have been published: under the adsorption of water<sup>2, 15-19</sup>, pyridine<sup>17, 18, 20-22</sup>, ammonia<sup>18, 20, 21, 23</sup>, butene<sup>20, 21, 24</sup>, naphthalene<sup>20, 21</sup> and benzene, cumene or cyclohexane<sup>18</sup>.

During the dehydration process by thermal treatment cations are gradually stripped of their hydration shell and

then migrate to other sites (type 1) or *vice versa* (in the case of migration under adsorption of water).

Studying the effect of sorbed molecules on the cupric ion distribution in Cu(II)Y, Gallezot and coworkers<sup>21</sup> have shown that the adsorption of a small amount of ammonia which can enter the sodalite cages produced slight but significant changes in the copper position, whereas the addition of pyridine, naphthalene or butene which cannot enter the sodalite cages induced an important migration of the cupric ions from the initial hidden sites to surface sites where they can interact with sorbed molecules (type 2).

There have been a number of investigations on the adsorption of carbon monoxide on zeolites, but as far as we know, there is only a little information about cation migration by carbon monoxide: Egerton and Stone<sup>25</sup> have pointed out that a slow adsorption, occurred during the adsorption of carbon monoxide on Cu(II)Y and Ni(II)Y, is thought to be due to a gradual increase in the number of adsorption sites caused by adsorbate-induced migration of the divalent cations.

In this study we provide a calorimetric evidence of the migration of cupric ions under the conditions of the adsorption of carbon monoxide on Cu(II)Y.

## 2. Experimental Methods

### Materials and Gas

Copper (II) ion-exchanged zeolites were prepared by repeated ion-exchange of NaY zeolite (Linde SK-40), which had been pretreated with *ca.* 1N sodium nitrate solution, in excess of 5mM copper (II) nitrate solution at room temperature for 14.3% 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 hrs at 110°C, and

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## 研 究 速 報

finally stored over saturated ammonium chloride solutions at *ca.* 25°C for at least one week before use.

The degree of exchange was calculated from the results of chemical analysis of sodium and those of atomic adsorption analysis for copper (II).

Carbon monoxide (Takachiho Chem. Co. Ltd.), which was stated to have a purity greater than 99.5% (the main impurity was air, H<sub>2</sub> and CO<sub>2</sub>), was purified by passing it through a liquid nitrogen cold trap and stored in a bulb before use.

## Apparatus

Heats of adsorption and desorption were measured with a twin conduction calorimeter (Tokyo Riko Ltd., Multipurpose Calorimeter, MPC-10 type). At the same time adsorption measurements were carried out by a volumetric adsorption system in connection with the calorimeter.

## Procedure

Each sample of 0.5g zeolite (including *ca.* 25% H<sub>2</sub>O) in a sample cell was evacuated under 10<sup>-3</sup> Torr and then heated up at an increment of 8°C/min to 400°C (or 100°, 250°C, according to the experimental conditions), followed by an evacuation for 1 hr at this temperature evacuated under 10<sup>-5</sup> Torr for 5 hrs.

The sample cell was then cooled down *in vacuo* and set in the calorimeter thermostated at the desired temperature (25 ± 0.01°C) for measurements.

Heats of adsorption of CO were measured under a certain initial pressure of CO. After the first thermogram had been drawn the first heat of desorption of CO was measured under evacuation under 10<sup>-5</sup> Torr, then the same procedure of adsorption and desorption was repeated continuously several times.

## 3. Results and Discussion

Thermograms of CO adsorption and desorption on NaY, Cu(II)Y-14.3 and Cu(II)Y-80.7 are shown in Fig. 1. In the case of NaY the heats of adsorption,  $q_a$ , and desorption,  $q_d$ , were practically identical in all times, not only  $q_{a1}-q_{d3}$ , which were measured continuously, but also  $q_{a4}$  and  $q_{d4}$  measured after evacuation under 10<sup>-5</sup> Torr overnight, therefore the adsorption of CO on NaY can be regarded as reversible. While 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 value was not equal to that of a monotonous decrease of the differential heat of adsorption with respect to the coverage<sup>37</sup>. However it was always observed that the quanti-

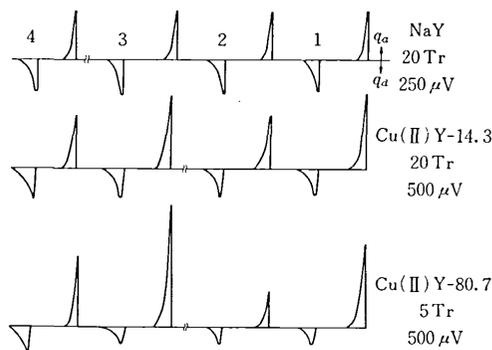


Fig.1 Thermograms of CO adsorption and desorption on NaY and Cu(II)Y

ty of  $q_a$  or  $q_d$  corresponded to the amount adsorbed or desorbed. This decrease occurred owing to the incomplete desorption ( $q_{d1}$  was smaller than  $q_{a1}$  by 53%), *i.e.* irreversible adsorption of CO on Cu(II)Y-14.3. However,  $q_{a3}$ , which was measured after degassing overnight under 10<sup>-5</sup> Torr was much the same to  $q_{a1}$ . These results show that the adsorption of CO on Cu(II)Y-14.3 also can be considered reversible when the desorption is carried out over a period of *ca.* 10 hrs (as much several times as in the case of NaY), and also show that the adsorption or desorption equilibrium is not yet established even when it is regarded to be reached calorimetrically. But when  $q_{a5}$  was measured after degassing overnight under 10<sup>-5</sup> Torr an interesting phenomenon was observed:  $q_{a5} > q_{a1}$ . This phenomenon was remarkably observed as shown below on the sample of higher exchanged zeolite.

In the case of higher exchanged Cu(II)Y-80.7,  $q_{a2}$  was extremely smaller than  $q_{a1}$ , while  $q_{a3}$ , measured after degassing overnight under 10<sup>-5</sup> Torr, was *ca.* 1.5 times larger than  $q_{a1}$ , and  $q_{a5}$  was equal to  $q_{a3}$ .

The synthetic zeolites Y 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 having a free diameter of 2.5 Å. Sodalite cages are jointed to each other by 2.4 Å free diameter hexagonal prisms<sup>27, 28</sup>. While the kinetic diameter of CO molecule is *ca.* 3.8 Å<sup>29</sup>. The cation sites of synthetic zeolites Y are shown in Fig. 2: SI, at the center of a hexagonal prism, SI', displaced from a shared hexagonal face into the sodalite

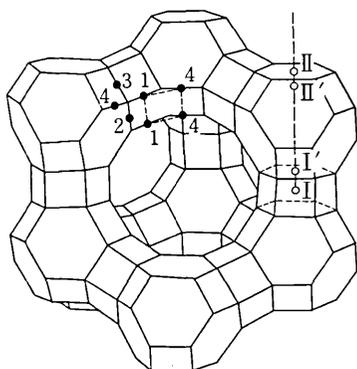


Fig.2 Faujasite framework and cation site indication

case, SII', displaced from an unshared hexagonal face into the sodelite cage, SII, slightly displaced into the supercage, and SIII', in the supercage, formed by two O<sub>1</sub> and O<sub>4</sub> oxygens<sup>16, 26</sup>

From the fact that the phenomenon above-mentioned leads to an increase in the amount of CO adsorbed, it must be reasonable to presume the following causes responsible for this phenomenon on the basis of the structure and the position of sites above-mentioned: (1) by the adsorption of CO the coordinated H<sub>2</sub>O or hydroxyl groups on Cu(II)-ions in the supercages were released, which should result in an increase of the number of adsorption sites after the desorption of CO; (2) penetration of CO into the small cavities increased the amount of CO adsorbed; (3) migration of Cu(II) - ions from inaccessible sites to accessible ones increased the amount of CO adsorbed. However, the coordinated H<sub>2</sub>O or hydroxyl groups remained on Cu(II)-ions after thermo-evacuation can not probably be released during the adsorption and desorption of CO at 25°C. Egerton and Stone<sup>24</sup> has shown by the experiments on a sample of synthetic sodalite that CO was not adsorbed at temperatures less than 200°C and that even at 250°C the adsorption was very slow. Thus, it is unlikely that CO would be able to penetrate into the small cavities at 25°C. In conclusion, this phenomenon is thought to be due to the migration of Cu(II)-ions from inaccessible sites for CO to accessible ones. From the consideration of the location of sites and the relative size of CO and cavities the migration probably takes place from SII' to SII (Fig. 3).

The result that  $q_{a5}$  was equal to  $q_{a3}$  in the case of Cu(II)Y-80.7 can be interpreted by the completion of the migration under these conditions. When the initial pressure of CO increased to 50 Torr after these experiments the

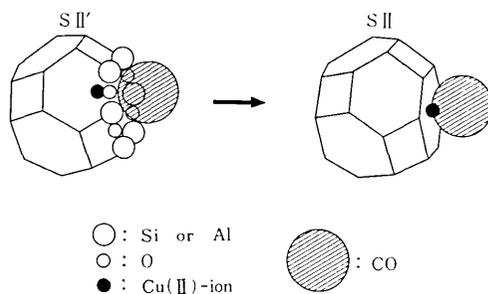


Fig.3 Schematic drawing of cation migration

migration occurred again and completed after several doses. This phenomenon was also observed at the initial pressure of 100 Torr of CO.

As the location of ion-exchanged cations in zeolite is closely related to the residual water content or the degree of dehydration of zeolite<sup>30-34</sup>, pretreatment conditions, in particular, heat-treatment temperature might be an important factor for the site selectivity of ion-exchanged cations. Therefore, adsorption and desorption measurements were carried out after heat-treatment at different temperatures in order to clarify the relation between the migration and heat-treatment temperature. In the case of the pretreatment at 100°C as shown in Fig. 4, the behavior of heats of adsorption and desorption is considerably different from that at 400°C (Fig. 1). In spite of the incomplete first desorption ( $q_{d1} < q_{a1}$ ) the second heat of adsorption,  $q_{a2}$ , was larger than  $q_{a1}$ , and  $q_{a3}$  also larger than  $q_{a2}$ . Even this behavior shows a larger probability of migration than that in the case of the 400°C-pretreatment and  $q_{a4}$  measured after evacuation overnight supports this large probability ( $q_{a4} \approx 7.5 \times q_{a1}$ ). The same behavior was observed in the case of the 250°C-pretreatment. But the migration rate was not so large as in the case of the 100°C-pretreatment.

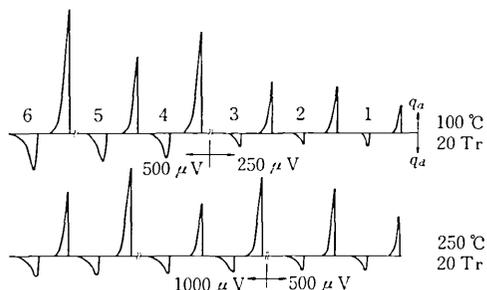


Fig.4 Changes of thermograms with pretreatment temperatures

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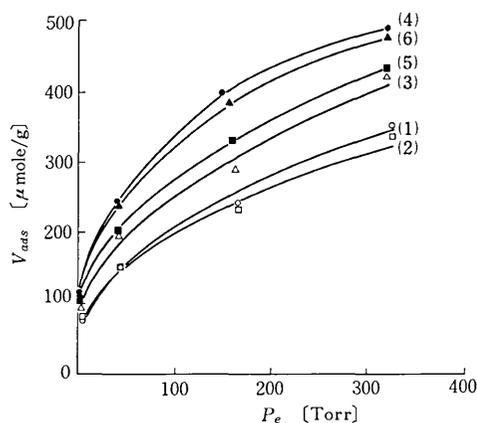


Fig.5 Adsorption isotherms of CO on Cu(II)Y-80.7

- (1): after pretreatment under  $10^{-5}$  Torr at  $400^{\circ}\text{C}$  for 5 hrs
- (2): after (1), outgassing at  $25^{\circ}\text{C}$  for 15 hrs and re-adsorption of CO
- (3): after (2), outgassing at  $25^{\circ}\text{C}$  for 40 hrs and re-adsorption of CO
- (4): after (3), outgassing at  $25^{\circ}\text{C}$  for 15 hrs furthermore at  $400^{\circ}\text{C}$  for 5 hrs and re-adsorption of CO
- (5): after (4), outgassing at  $25^{\circ}\text{C}$  for 15 hrs and re-adsorption of CO
- (6): after (5), outgassing at  $25^{\circ}\text{C}$  for 40 hrs and re-adsorption of CO

It is interesting to know whether the migrated Cu(II)-ions might come back to the initial sites under the same thermal conditions as at the pretreatment or not. Recently Michelena and coworkers<sup>35</sup> have reported that the first adsorption isotherm of CO on CaA zeolite after a dehydration at  $450^{\circ}\text{C}$  and the second one obtained after evacuation at  $450^{\circ}\text{C}$  for 14 hrs of the first sample-adsorbate system are identical. This suggests that the adsorption isotherms should be always identical in the absence of irreversible adsorption. In Fig. 5 the isotherm (2) is situated lower than (1), but (3) is higher than (1). The former difference is due to the incomplete desorption of CO and the latter would be another support of the migration of Cu(II)-ions. While the isotherm (4), whose sample was undergone the same thermal treatment as at the initial pretreatment, is higher than the initial one (1). This increase in adsorption amount was probably taken place by the partial reduction under the existence of small amount of undesorbed CO of Cu(II)Y to Cu(I)Y, which has extremely higher adsorptive ability<sup>36</sup>. A decrease in adsorption of (5) or (6) than (4) is explained by the irreversible adsorption of CO on Cu(I)Y<sup>32</sup>. Owing to the decrease in the amount of Cu(II)-ions, even after migration of Cu(II)-ions the isotherm (6) does not exceed (4) in the amount of CO adsorbed.

## 4. Conclusions

Repeated adsorption-desorption measurements revealed the migration of cupric-ions from inaccessible sites for CO to accessible ones under the adsorption of CO on Cu(II)Y, and it probably took place from SII' to SII. The migration becomes significant with increases in the degree of Cu(II)-exchange and in the amount of CO adsorbed. Furthermore, the migration depends on the pretreatment conditions, particularly heat-treatment temperature. They affect the hydration state of Cu(II)-ions or the amount of residual water, which is a determining factor of the steric conformation or the mobility of Cu(II)-ions.

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