# Site-selective Ion-exchange of CuZSM-5 Prepared by Using Aqueous Solutions of $Cu^{2+}$ with Various Kinds of Anions

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## Introduction

Copper ion-exchanged ZSM-5-type zeolite (CuZSM-5) is known to exhibit a high and stable activity in the catalytic decomposition reaction of NOx. Furthermore, we have found that CuZSM-5 exhibits an interesting property for specific $N_2$-adsorption at room temperature.[1] In both cases, it is considered that the monovalent copper-ion ($Cu^+$) species formed by heat treatment *in vacuo* acts as an active center. Therefore, the analysis of the $N_2$-adsorption property of CuZSM-5 will be helpful in analysing the catalytic activity in the decomposition reaction of NOx and in designing more effective catalysts. Recently, our group has found that the CuZSM-5 sample prepared by using a solution of $Cu(CH_3COO)_2$ is more effective adsorbent compared with the sample prepared by using a solution of $CuCl_2$ in the same copper-ion exchange level as CuZSM-5(A). However, the effect of ion-exchange method on the $N_2$-adsorption property is still not completely clarified. In the present work, we elucidate the $N_2$-adsorption property of the CuZSM-5 samples prepared by ion-exchange operation in an aqueous solution of divalent copper ion ($Cu^{2+}$) with various kinds of anions ($Cl^-$, $CH_3COO^-$, $NO_3^-$) to clarify the influence of the types of anions on the kinds of sites occupied by the copper ion.

## Results and Discussion

Figure 1 shows the Cu K-edge XANES spectra for the CuZSM-5 samples prepared by using solutions of (a) $CuCl_2$ [CuZSM-5(C)], (b) $Cu(CH_3COO)_2$ [CuZSM-5(A)], and (c) $Cu(NO_3)_2$ [CuZSM-5(N)], their copper-ion exchange levels being 121%, 121%, and 80%, respectively. The sample was first evacuated at 873 K (spectrum 1), and then treated with $N_2$ at an equilibrium pressure of 13.3 kPa (spectrum 2), and finally re-evacuated at 300 K (spectrum 3). A sharp band due to the 1s-4p transition for the $Cu^+$ species is observed at 8.983 keV, which indicates that the $Cu^{2+}$ species ion-exchanged in the CuZSM-5 samples are reduced to the monovalent state by the heat treatment at 873 K *in vacuo*. The band intensity at 8.983 keV decreased slightly when $N_2$ molecules were adsorbed on CuZSM-5(C) (Figure 1a, spectrum 2). On the other hand, for CuZSM-5(A) and CuZSM-5(N), although the band at 8.983 keV disappeared eventually (Figures 1b and 1c, spectrum 2), its original pattern can be recovered by the re-evacuation at 300 K (Figures 1b and 1c, spectrum 3). These results indicate that CuZSM-5(A) and CuZSM-5(N) are more active for the $N_2$ adsorption than CuZSM-5(C). Therefore, we can suppose that the site-selective ion-exchange takes place in the preparation process using aqueous solutions of $Cu(CH_3COO)_2$ and $Cu(NO_3)_2$.

On the basis of IR data that indicate the presence of $Cu^{2+}$-dimer species in CuZSM-5(C), the presence of acetate ion in CuZSM-5(A), and the formation of Brönsted acid-site by the heat treatment, we propose the mechanisms of ion-exchange and reduction for the CuZSM-5 samples prepared by using aqueous solutions involving $Cu^{2+}$ and different kinds of anions (Scheme 1). Thus we can conclude that the site-selective copper-ion-exchange takes place depending on the kinds of anions involved in the solutions; CuZSM-5(A) and CuZSM-5(N) exhibit superior $N_2$-adsorption property.

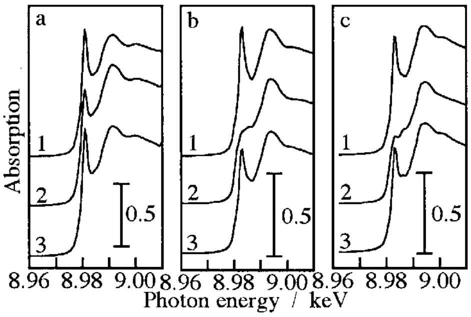
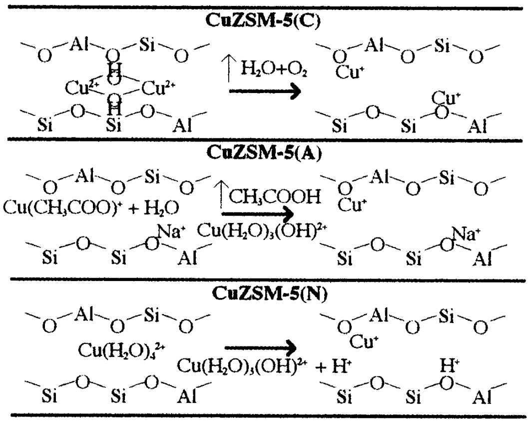


**Figure 1**

**Scheme 1**



## References

[1] Y. Kuroda, Y. Yoshikawa, S. Emura, R. Kumashiro, and M. Nagao, *J. Phys. Chem. B*, **1999**, *103*, 2155.

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