

Elucidation of the coordination structure around copper ion in CuMFI associated with N₂ adsorption at room temperature

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Introduction

N₂ molecule is accepted to behave as a supercritical gas at around room temperature (r.t.) and is adsorbed on solid surfaces, only at low temperatures. We found that a copper ion-exchanged MFI (CuMFI) adsorbs N₂ molecule, even at r.t.[1]. It has so far been shown that the monovalent copper ion (Cu⁺) formed by heat treatment *in vacuo* acts as adsorption site. However, the coordination environment of the effective site for N₂ adsorption and the state of the adsorbed N₂ species on the sample are still not completely clarified. One of the solutions of these problems is to evaluate the adsorption site on CuMFI having high levels of adsorption capability for N₂ adsorption at r.t. Recently, we have demonstrated that the adsorption property of N₂ associated with CuMFI differs depending on the types of counter ion in the exchange solution and the Si/Al ratio of MFI. In this contribution, we report on the coordination structure around copper ion adsorbing an N₂ molecule, which was evaluated by using a XAFS technique. The targeted CuMFI sample (Si/Al: 19.8) was prepared *via* ion exchange using an aqueous solution of copper propionate at r.t. (ion-exchange level: 109%). Such a preparation condition, determined by us, is the optimum conditions obtainable the sample having the most efficient property for N₂ adsorption at r.t.

Results and discussion

Figure1 shows the EXAFS and XANES spectra for CuMFI under various conditions. For the 873 K-treated sample, a EXAFS band, which is ascribed to back-scattering from the nearest neighboring oxygen atom, is observed at 1.52 Å (no phase-shift correction). The coordination number of oxygen atom around copper ion ($N_{\text{Cu-O}}$) and the distance between copper ion and oxygen atom ($r_{\text{Cu-O}}$) were estimated to be respectively 2.7 and 1.98 Å by the analysis of the EXAFS datum employing the least-square method and by using Cu₂O as a reference sample. The copper ion in the sample takes the two-coordinated structure (distorted linear structure) or the three-coordinated structure (trigonal pyramidal structure). Taking account of our previous EXAFS data, for the present sample, the three-coordinated copper ion seems to be formed in higher rate. In the XANES spectrum, the band due to the 1s–4p transition of Cu⁺ is split into two bands: the bands at 8.983 keV (1s–4p_π transition) and 8.993 keV (1s–4p_σ transition). The appearance of these bands indicates the occurrence of the reduction of the exchanged divalent copper ions into the monovalent ones by evacuating the sample at 873 K and also suggests the

presence of copper ions differing in the coordination environment; the formed Cu⁺ species take a linear (two) or a planar (three) coordination structure. Noteworthy is that the 8.983 keV-band is drastically reduced in terms of intensity when the sample is exposed to an N₂ gas of about 13 kPa at r.t., and the intensity of the band is recovered after reevacuating the sample at r.t. Change in the intensity of the observed band in XANES spectrum has been interpreted as adsorption of N₂ on the three-coordinated Cu⁺ species. When the N₂ molecule is adsorbed on such a site, the Cu⁺ species take the four-coordinated arrangement analogous to the structure of the distorted tetrahedral arrangement, and by bonding with N₂ molecule, the 4p_π energy level of copper ion changes, resulting in the shift of the band toward the side with higher energy. A strong interaction between copper ion and N₂ molecule was also seen in the EXAFS spectra for the CuMFI adsorbing N₂; the band at around 1.5 Å increases in width and its intensity decreases, compared with the properties of the band for the 873 K-treated sample. By analysis of the EXAFS datum using Cu₂O and [Cu(NH₃)₂]⁺ as reference samples, a three-coordinated Cu⁺ species in the sample was found to adsorb an N₂ molecule [$N_{\text{Cu-O}} = 2.7$, $r_{\text{Cu-O}} = 1.97$; $N_{\text{Cu-N}} = 1.1$, $r_{\text{Cu-N}} = 1.91$]; the Cu⁺ species has the pseudo-tetrahedral coordination environment. In the present XAFS experiment, detailed coordination environment around copper ion before and after N₂ adsorption at r.t. was clarified for the first time.

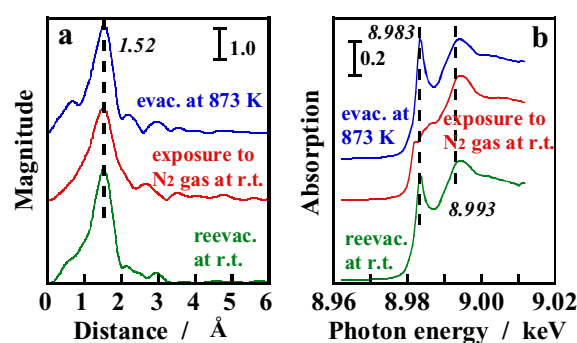


Figure1: (a) EXAFS and (b) XANES spectra for CuMFI.

Reference

[1] Y. Kuroda et al., J. Phys. Chem. B 103, 2155 (1999).

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