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Formation of $[Cu(\eta^2\text{-}H_2)]^+$ Species in MFI-type Zeolite and Resulting H–D Exchange Reaction with Hydrogen on Brønsted Acid Sites at 300 K

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We examined the adsorption feature of the CuMFI sample for H_2 adsorption and found a specific interaction between Cu^+ exchanged in MFI and H_2 even at 300 K, the formation of η^2-type H_2-adsorbed species in MFI-type zeolite; it caused H–D exchange reaction with hydrogen on Brønsted acid sites even at 300 K.

Zeolites are versatile materials with important applications in many fields, including catalysis, adsorption and separation, and ion exchange. The prominent features of zeolites stem from the inclusion of some aluminum atoms in the silicon oxide lattice: intrinsic ion-exchangeable properties. Of the various kinds of metal-ion-exchanged zeolites, copper-ion-exchanged MFI-type zeolite (CuMFI) has attracted wide attention since Iwamoto et al. identified excellent NO decomposition activity in an over-exchanged CuMFI sample.[1] Another interesting property of CuMFI is the prominent adsorption of N_2 molecules, even at around 300 K, although N_2 is recognized as an inert gas and is therefore adsorbed negligibly onto solid materials at around 300 K.[2] Considerable effort has been directed toward characterizing the active sites in zeolites in order to design a more effective catalyst. To this end, probe molecules offer a useful technique and many studies have been devoted to clarifying the active sites for these unique properties of CuMFI, from both experimental and theoretical viewpoints.[3–7] It would also be interesting to understand the kind of interaction that occurs between the monovalent copper ions and dihydrogen (H_2) molecules, although the interaction with H_2 is expected to be weak.[8,9] The H_2 adsorption properties of CuMFI are also very interesting from the viewpoint of dihydrogen storage.[10] In the present study, we examined the adsorption properties of CuMFI samples for H_2 molecules and identified a specific interaction between the monovalent copper ion exchanged in MFI and H_2, even at 300 K.

A sodium-type MFI zeolite with an Si:Al ratio of 11.9, supplied by the Tosoh Company, was dispersed in an aqueous solution of 0.3 M $Cu(NO_3)_2$ and treated with microwaves. The ion-exchange level of the sample was 103%. The sample is abbreviated to CuMFI(NM)-103.

The H_2 adsorption isotherms were measured at both 77 and 298 K using a volumetric adsorption apparatus. The equilibrium pressure of the gas phase was monitored using an MKS Type 310 BH Baratron pressure sensor.

IR spectra were measured using a Digilab FTS4000MXK FT-IR spectrophotometer with an MCT or a TGS detector.

Figure 1a shows the adsorption isotherms of H_2 measured at 77 K on CuMFI(NM)-103 that had been evacuated at 873 K. The second adsorption isotherm was also measured at 77 K for the sample re-evacuated at 77 K after the first adsorption measurement. These data indicate that CuMFI(NM)-103 adsorbs H_2 at 77 K. However, this point is not specific because HMFI (H^+ ion-exchanged MFI) acts as the storage material for H_2.[10] The specific feature of the present system is that there is a small and distinct difference between the first and second isotherms and this difference is almost constant in the pressure range measured. This implies a specific interaction between the CuMFI sample and the H_2 molecules at 77 K. The monolayer capacities, V_m, for the respective isotherms are evaluated and given in Figure 1.

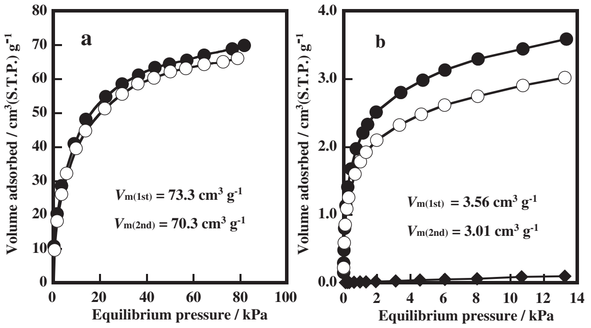

Figure 1. Adsorption isotherms of H_2 on CuMFI(NM)-103 after evacuation at 873 K. Filled and open circles represent the first and second adsorption processes, respectively. (a) Measured at 77 K; (b) Measured at 298 K. Diamond represents the isotherm of H_2 on the CuMFI(NM)-103 sample treated with CO.

Because the adsorption behavior of H_2 on the CuMFI(NM)-103 sample suggests a different mechanism from the simple physisorption seen in HMFI,[10] it is expected that H_2 adsorption would occur even at higher temperatures. Figure 1b shows the first and second adsorption isotherms of H_2 at 298 K for a CuMFI(NM)-103 sample that had been evacuated at 873 K. The amount of H_2 adsorbed increased steeply along the ordinate in the lower pressure region and then gradually increased to reach saturation, indicating a strong interaction between the H_2 molecules and the CuMFI(NM)-103 sample, even at 298 K; the ratio of H_2/Cu^+ is estimated to be 0.6. This tendency was also observed for the second adsorption process. The monolayer capacities are comparable to those obtained for the difference between the first and second adsorption isotherms measured at 77 K for the CuMFI(NM)-103 sample. The adsorption behavior of H_2 on CuMFI is particularly surprising in view of the fact that H_2 adsorption occurs at around room temperature, because the temperature of 298 K is much higher than the critical temperature of H_2 33.2 K. The other noteworthy feature of the present system is the distinct difference in the amounts of H_2 adsorbed between the first and second adsorptions (measured after re-evacuation at 298 K), i.e., 0.55 $cm^3\,g^{-1}$; some H_2 was irreversibly restored in CuMFI even at 298 K. It is important to clarify the species acting in H_2 adsorption. CO is known as the titrant of the monovalent copper ion. Therefore, we used it as a probe molecule to examine the site of adsorption of H_2 molecules. First, CO was adsorbed onto an 873 K-treated sample at 298 K under the pressure of 13 kPa, and then evacuated at 298 K, followed by H_2 adsorption measurement at 298 K. This treatment blocks the active sites of monovalent ions, whereas the other sites remain unchanged. The amount adsorbed decreased dramatically with this treatment, as is apparent from the data shown in Figure 1b. It was thus demonstrated that the monovalent copper ion plays a pivotal role in H_2 adsorption. These properties are also very interesting from the standpoint of the storage of H_2.

Figure 2 shows the infrared (IR) spectra of CuMFI, which was evacuated at 873 K, followed by the introduction of H_2 or D_2 gas. There are no absorption bands for CuMFI(NM)-103, except the OH stretching vibrational bands due to the surface silanol and Brønsted acid sites in the region depicted in Figure 2a. After the introduction of H_2 gas to CuMFI at 300 K, a prominent feature was observed; a new and weak band was visible at around 3080 cm^{-1}, although neither the positions nor intensities of the bands due to OH groups had changed appreciably. The difference spectrum in the presence and absence of H_2 is shown in the inserted figure for clarity. Considering the adsorption data described above and shown in Figure 1, this new band is attributable to the stretching vibrations of H_2 species adsorbed onto the monovalent copper ions exchanged in MFI. The interaction of H_2 at lower temperatures with various kinds of cations has been reported so far, and the shift is at most about 200 cm^{-1}, which is mainly due to the electrostatic interaction.[11] An example of the strong interactions observed between the monovalent copper ions and H_2 molecule in copper complexes was investigated by H. S. Plitt et al. and P. R. Kemper et al., who reported that the stretching vibrational band was observed at around 3000 or 3700 cm^{-1}.[12,13] The bonding state is a side-on type in both cases; therefore, we infer that the adsorption of H_2 onto CuMFI is a side-on type, the formation of an η^2-type interaction.

Another interesting feature was also observed in this system. Exposing the sample to D_2 of ca. 9 kPa at 300 K resulted in the situation shown in Figure 2b. A new and weak band appeared at 2663 cm^{-1}, accompanied by a reduction in the intensity of the OH stretching vibrational band observed at 3614 cm^{-1} due to the Brønsted acid site. This indicates that a H–D exchange occurred even at 300 K on this sample. With an increase in the reaction temperature, this reaction proceeded and a H–D exchange at the Brønsted acid site was almost complete at a temperature of 523 K. On the other hand, the H–D exchange on the silanol groups was scarcely observed at 300 K and only slightly at the higher temperature of 523 K. These phenomena indicate that the H–D exchange reaction occurs preferentially at the Brønsted acid site. To examine the effects of different kinds of metal ions exchanged in MFI, similar experiments were performed in the MgMFI-82– and HMFI–D_2 systems (not shown). On these surfaces, the H–D exchange reaction was scarcely detected at 473 K. The reaction on these surfaces was initiated at above 523 K and was not complete even at 673 K. Moreover, the exchange reaction was observed at both silanol and Brønsted acid sites, and the extent of the exchange was similar at both sites. From these data, it is clear that a specific interaction occurs between the monovalent copper ion and dihydrogen molecule, when CuMFI is exposed to D_2 of ca. 10 kPa at 300 K.

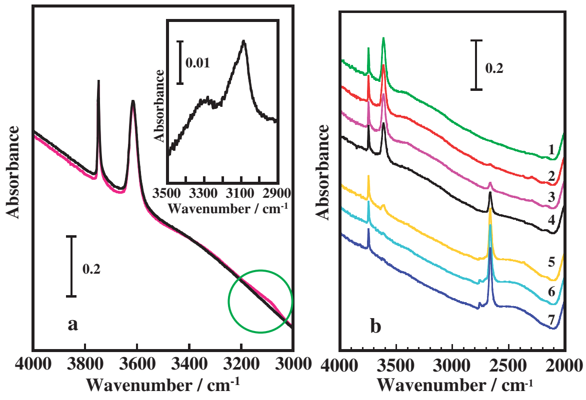

Figure 2. (a) IR spectra of CuMFI(NM)-103 at 300 K: (Black line) evacuated at 873 K; (Red line) H_2 adsorption at 300 K under a pressure of 13.5 kPa. The difference spectrum is also shown in the inserted figure. (b) IR spectra during H–D exchange reaction on the CuMFI(NM)-103 sample at various temperatures: (1) evacuated at 873 K, followed by treatment with D_2 gas under the pressure of 9.2 kPa at (2) 300, (3) 323, (4) 373, (5) 423, (6) 473, and (7) 523 K.

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