Development of a site-selective copper-ion-exchanging method for HZSM-5 by vapourization of a hexafluoroacetylacetonato–copper complex

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The deposition of copper ion into a single type of ion-exchange site in HZSM-5-type zeolite is successful using bis(1,1,1,5,5,5-hexafluoroacetylacetonato)copper(II) as a volatile complex, and the sample thus prepared gives a single IR absorption band at 2158 cm^{-1} upon adsorption of CO, differing from a sample prepared by aqueous ion-exchange, which gives two bands at 2158 and 2151 cm^{-1}.

Many applications of zeolites rely on their unique surface properties that are largely determined by the concentration, distribution and nature of exchanged ions, such as protons, alkali metal and transition metal ions. Among many kinds of zeolites, the copper-ion-exchanged ZSM-5-type zeolite (Cu-ZSM-5) has become one of the most promising materials for the catalytic decomposition reaction of NO_x to N_2 and O_2.[1,2] This material has also a specific adsorption property for N_2 at room temperature; and hence it can be used as a catalyst for N_2 separation, fixation and activation.[3,4] From the viewpoints of the development of more effective catalysts, it is useful and important to obtain information on the nature of the active sites on Cu-ZSM-5 for NO_x decomposition and specific N_2 adsorption. Thus far we have investigated the state of copper ion exchanged in mordenite-type zeolites by using CO as a probe molecule and have found that there are at least two main types of sites in this substance, giving IR bands at 2160 and 2150 cm^{-1} when CO is adsorbed on each site.[5] This situation is consistent with the results obtained independently by Zecchina and coworkers[6] and by Iwamoto and Hoshino for the Cu-ZSM-5 system.[7] A great deal of effort has so far been made to analyze these exchanging sites. However, the understanding of the role of each site for NO_x decomposition reaction and N_2 fixation is still far from being complete.[8,9] The presence of a number of different ion-exchanged sites leads to complications in such studies. The most pertinent approach is to prepare site-selectively copper-ion-exchanged ZSM-5.

In the present work, we succeeded in site-selective copper-ion deposition in this zeolite and the results obtained shed light on the analysis of active sites for NO_x decomposition and N_2 adsorption.

Bis(1,1,1,5,5,5-hexafluoroacetylacetonato)copper(II), [Cu(hfac)$_2$] (Aldrich), was used as a vapourizing source in chemical vapour deposition (CVD).[10] For the measurement of IR spectra, the HZSM-5 sample (supplied from Tosoh Co.) was pressed into a pellet (5 mg) of 10 mm diameter, and it was initially treated at 300 K for 2 h under a reduced pressure of 1 mPa in the *in situ* cell. The [Cu(hfac)$_2$] complex was then vapourized onto this pellet at room temperature. The sample thus prepared was evacuated at 873 K under a reduced pressure of 1 mPa and then treated with CO at 300 K. The ion-exchanging operation of HZSM-5 with copper ions was also carried out in an aqueous solution in the same manner as described in the literature.[3]

Fig. 1 shows the transmission FTIR spectra for the HZSM-5 sample evacuated at 873 K (*a*) and for the HZSM-5 sample with modified surface by deposition of [Cu(hfac)$_2$] followed by evacuation at 873 K (*b*). The spectrum in Fig. 1(*a*) shows intense bands at 3746 and at *ca*. 3613 cm^{-1}, which are due to hydroxyl groups of free silanol and of the Brönsted acid site, respectively. At first glance, the spectrum in Fig. 1(*b*) appears to be similar to the spectrum in Fig. 1(*a*). However, the relative intensity of the 3613 cm^{-1} band to the 3746 cm^{-1} band is lower for the surface-modified HZSM-5 sample, compared with that for the original HZSM-5 sample. These data suggest ion exchange of the proton on the Brönsted acid site with copper ion in the course of the evacuation process at higher temperatures.

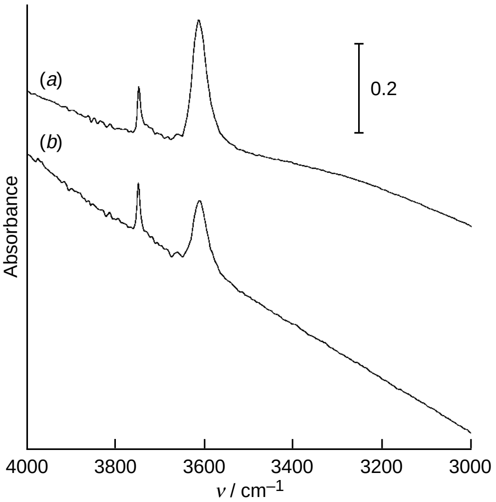

Fig. 1 IR spectra of the HZSM-5 sample evacuated at 873 K (*a*) and for the surface-modified HZSM-5 sample with Cu(hfac)$_2$ and then subsequently evacuated at 873 K (*b*)

Fig. 2 shows IR spectra for the sample prepared by deposition of [Cu(hfac)$_2$], as well as for a sample prepared by ion-exchange from aqueous solution. The spectra in Fig. 2(*b*) and (*d*) are those

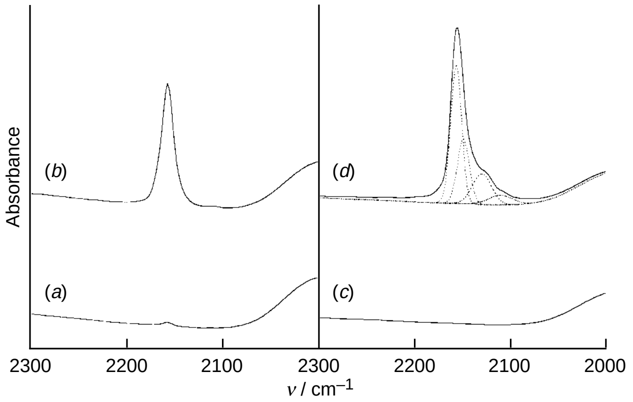

Fig. 2 IR spectra for the Cu(hfac)$_2$-deposited HZSM-5 sample (*a*) and (*b*) and for the copper-ion-exchanged HZSM-5 sample (*c*) and (*d*). These samples were pretreated in the following manner: (*a*) and (*c*), evacuated at 873 K; (*b*) and (*d*), equilibrated with CO gas at 300 K under nearly zero pressure after evacuation at 873 K. The deconvolution (dotted line) curves for spectrum (*d*) are also depicted.

for samples equilibrated with CO under nearly zero pressure, *i.e.* the chemisorption region. The spectra for both samples evacuated at 873 K after CVD [Fig. 2(*a*)] or ion-exchange from aqueous solution [Fig. 2(*c*)] are also included for comparison. As can be seen from the Fig. 2(*a*) and (*c*), scarcely any band is discernible in the 873 K treated sample in the region shown. It is clearly seen that chemisorption of CO takes place on the sample prepared by the CVD method to give a single band at 2158 cm^{-1} [Fig. 2(*b*)]. Chemisorption of CO also occurs for the sample prepared by ion-exchange from aqueous solution and the resultant CO species adsorbed give a broad IR band centred at *ca*. 2155 cm^{-1} [Fig. 2(*d*)], which is slightly but obviously tailing to the lower wavenumber side. Based on the information accumulated so far,[11–14] it is generally agreed that an absorption band at *ca*. 2150 cm^{-1} can be assigned to the C–O stretching mode of a CO species adsorbed on Cu^{I}; the copper complex was deposited on HZSM-5 by CVD and subsequent heat treatment reduced the Cu^{II} to Cu^{I}. For the ion-exchanged sample, it is apparent that heat treatment *in vacuo* reduces Cu^{II} to Cu^{I}, based on data described in previous papers.[3,5] A numerical deconvolution technique was applied to identify the bands in Fig. 2(*b*) and (*d*). For the CVD sample, only a single absorption band centred at 2158 cm^{-1} is present, *i.e.* the copper ion-exchange occurred only at one type of site. For the sample prepared by ion-exchange from aqueous solution, the observed broad band at *ca*. 2155 cm^{-1} is seen to be composed of two major components at 2158 and 2151 cm^{-1}. From the present experimental result, it is clear that for the sample prepared by ion-exchange from aqueous solution that both types of sites are occupied by copper ions. Recently, Zecchina and coworkers have reported, on the basis of EXAFS data, that two types of ion-exchanged sites exist on ZSM-5,[15] consistent with the above observations.

Taking the experimental data into consideration, it is also apparent that one of the two types of exchangeable sites in HZSM-5 is occupied selectively by copper ion in the sample prepared by CVD using [$Cu(hfac)_2$], while in the sample prepared by ion-exchange from aqueous solution both types of sites are occupied by copper ion. This new ion-exchanging method (CVD) has potential to be utilized for the analysis of the active sites in the NO_x decomposition reaction and also for the N_2 fixation reaction.

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Footnote and References

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