§3. Hydrogen Isotope Separation on Pore-Size-Controlled Mesoporous Silica

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The ability to recover tritium from tritiated water in large volume with low concentration is essential to reducing tritium emissions into the environment. Selective removal of tritium by using certain adsorbents is an attractive method because of the low cost and the ease of scaling up. Although various kinds of adsorbents such as activated carbon, amorphous silica, and zeolite have long been investigated, the tritium adsorption capacities of these adsorbents are rather low for practical application. The development of novel adsorbents is therefore still an interesting subject. We have demonstrated that Mesoporous silicas, e.g., MCM-41 and SBA-15, have several novel properties as compared to conventional microporous zeolites, and show substantially higher tritium adsorption ability and separation factor.1) This superiority might arise from the difference in surface properties, e.g., silanol groups on the surface. In this study, FT-IR measurements were performed to clarify the nature of the silanol groups and the state of HTO in mesoporous silica and microporous zeolite.

Mesoporous silica (MCM-41) was prepared as follows. A mixed aqueous solution of dodecyltrimethylammonium bromide, colloidal silica, and NaOH was hydrothermally treated at 130ºC for 24 h. The white precipitate was filtered, washed with water, and dried at 80ºC. Finally, the intended products were obtained by calcination at 550ºC for 10h. The formation of MCM-41 was confirmed by XRD measurements. The surface area (S.A.), pore diameter (Dp) and pore volume (Vp) evaluated by N_2 sorption experiments were 1109 m^2/g, 3.13 nm, and 0.79 cm^3/g, respectively (denoted MCM). As a reference, LTA(5A) zeolite was purchased from Showa Union. S.A., Dp and Vp of LTA(5A) were 417 m^2/g, 0.55 nm and 0.26 cm^3/g, respectively.

The samples for FT-IR measurements were prepared by the following procedure. The adsorbents were dehydrated at 180°C for more than 2 days, and then cooled to room temperature under a vacuum. Subsequently, D_2O was impregnated by the incipient wetness method. The sample was left standing under an Ar flow for 24 h. Then, the sample was dehydrated at 300 or 500°C for 1 h. The samples were pressed and the spectra were obtained in an N_2-purged sample holder at a resolution of 0.5 cm^{-1}. FT-IR spectra were recorded on a Spectrum 100 instrument (Perkin Elmer).

Fig. 1A(a) shows the FT-IR spectrum of MCM as prepared. The adsorption bands at about 3740, 1863, and 1626 cm^{-1} are attributed to the stretching ν(Si-OH) and ν(Si-O-Si) and the bending δ(Si-OH), respectively. The broad band at around 3725–2800 cm^{-1} is assignable to the structural hydrogen-bonded OH. D_2O impregnation and drying at 25°C, resulted in the appearance of OD-related bands at about 2660–2100 and 1424 cm^{-1}, which are assignable to structural hydrogen-bonded OD and δOD, respectively (Fig. 1A(b)). The disappearance of ν(Si-OH) and ν(Si-OD) together with the appearance of massive hydrogen-bonded OH and OD suggest hydration of MCM. Although the sample was not fully dehydrated in advance, it is obvious that some of these OD species were formed through the hydrolysis of SiO_2 and D_2O. This can be confirmed from the FT-IR spectrum measured after dehydration at 300°C (Fig. 1A(c)), in which the sharp signals assignable to ν(Si-OH) and ν(Si-OD) reappeared at 3740 and 2760 cm^{-1}, respectively.

Fig. 1B(a) shows the differential spectra of MCM after dehydration at 500°C, which was obtained by subtracting the spectra measured by using H_2O in the same manner as D_2O. The existence of ν(Si-OD) and hydrogen-bonded OD bands was clearly seen. The differential spectrum of LTA(5A), on the other hand, lacked the observable signals for ν(Si-OH) and ν(Si-OD) (Fig.1B(b)). This indicates that the LTA(5A) zeolite framework is inactive for hydrolysis. It hence follows that the MCM framework is reactive in hydrolysis. The silica surface consists mainly of siloxane bridges (Si-O-Si) and fewer silanol (Si-OH) groups. These surface siloxane bridges are hydrolyzed by adsorbed water molecules to form silanols (Si-OD), which are considered to cause the decrease in water molecule desorption, conceivably facilitating the selective adsorption of hydrogen isotopes (D or T). This finding suggests that the formation and presence of silanol is a key to the enrichment of hydrogen isotopes.

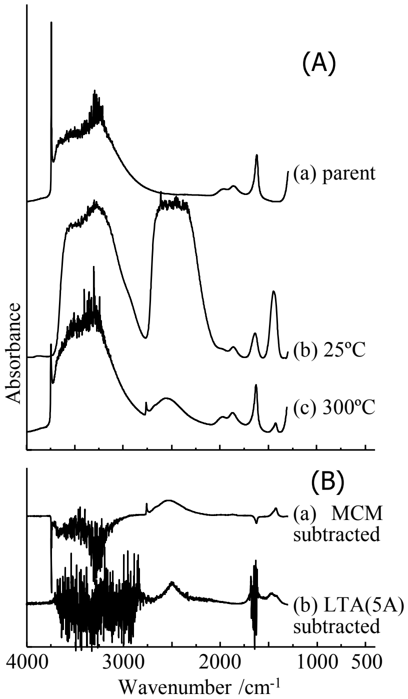

Fig. 1 (A) FT-IR spectra of MCM (a) as prepared, (b) dried at 25ºC after D_2O impregnation and (c) dried at 300ºC. (B) Differential spectra of (a) MCM and (b) LTA(5A) after drying at 500ºC.

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