Unique adsorption properties of organic–inorganic hybrid zeolite IEZ-1 with dimethylsilylene moieties†

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The interlayer silylation of pure silica PLS-1 with dichlorodimethylsilane gave a novel organic–inorganic hybrid zeolite IEZ-1, of which the micropores are able to adsorb benzene molecules, in contrast to its purely inorganic analogue IEZ-2.

Zeolites are microporous crystalline aluminosilicates widely used as shape-selective catalysts, ion-exchangers and adsorbents.[1] Organic functionalization of zeolites would widen the range of their applications and allow the manipulation of the surface properties that control the interaction with various organic and inorganic guest species. While zeolites with three-dimensional open framework structures are generally crystallized under hydrothermal conditions, some research groups have successfully reported the structural conversion of a layered zeolitic precursor into a zeolite by the topotactic dehydration–condensation of silanols on both sides of the interlayers.[2–8] One of the authors has recently developed the preparation of a novel titanosilicate denoted by Ti-YNU-1 from an MWW-type layered precursor.[9] Ti-YNU-1 has an expanded pore window between the crystalline MWW sheets[10] and shows a higher intrinsic catalytic activity than Ti-MWW or large-pore Ti-beta in the epoxidation of bulky alkenes with H_2O_2 as an oxidant.[9] It was supposed that a part of silica "debris" originating from the framework by acid treatment constructs monomeric silica puncheons between the MWW sheets, resulting in the formation of interlayer-expanded micropores in Ti-YNU-1.[9,10] The periodic silylation on the surface of layered silicate and the following connection between the interlayers also lead to the formation of an open framework in the interlayer space. Recently, Mochizuki *et al.*[11] and Ishii *et al.*[12] reported a stepwise bridge formation by silylation with alkoxychlorosilanes on the layered silicates.

We have developed the preparation of interlayer-expanded microporous crystals through one-step interlayer-silylation of layered zeolitic precursors using monosilane with various alkoxy and alkyl groups, and investigated their adsorptive and catalytic properties. In this paper, we focus on a layered silicate PLS-1, of formula $K_{1.3}\{(CH_3)_4NOH\}_{1.7}Si_{18}O_{34}(OH)_4$.[3] When PLS-1 was thermally treated, a zeolite denoted CDS-1, $Si_{36}O_{72}$ (IZA code:[13] CDO), was obtained as a result of dehydration–condensation of the PLS layers. The interlayer micropores of CDS-1 consist of two-dimensional straight 8-membered ring (8MR) channels along the [001] and [010] direction and their sizes are estimated at 4.7 × 3.1 and 4.5 × 3.3 Å, respectively.[3] Since such a small microporosity of CDS-1 inhibits typical organic molecules from adsorbing in their micropores, we have attempted to prepare an interlayer-expanded microporous material being capable of accommodating larger organic molecules through the interlayer silylation of pure silica PLS-1 with dichlorodimethylsilane (DCDMS), and have found remarkable adsorption properties of the organic–inorganic hybrid microporous material IEZ-1 (*I*nterlayer-*E*xpanded *Z*eolite *1*) in contrast to its purely inorganic analogue IEZ-2.‡

Fig. 1 shows XRD patterns of as-made PLS-1, calcined CDS-1, and the products after the silylation and the following calcination. The [020] reflection peak of the layered precursor PLS-1 appeared at $2\theta = 8.5°$ (Fig. 1(a)). CDS-1 obtained after direct calcination of PLS-1 gave an XRD peak at $2\theta = 9.6°$ corresponding to the [020] reflection (Fig. 1(d)), as a result of the dehydration–condensation of silanols located on the PLS-1 layers. On the other hand, the product obtained after the silylation treatment gave the [020] reflection peak at $2\theta = 7.6°$ (Fig. 1(b)). This peak shift to a lower value of 2θ implies the interlayer expansion of PLS-1 due to the intercalation of dichlorodimethylsilane molecules between the CDO layers. It is noteworthy that the interlayer-expanded

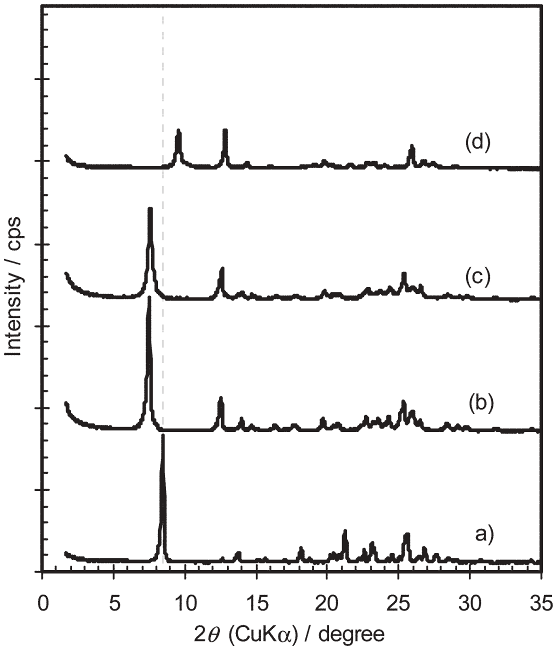

Fig. 1 XRD patterns of (a) PLS-1, (b) IEZ-1, (c) IEZ-2 and (d) CDS-1.

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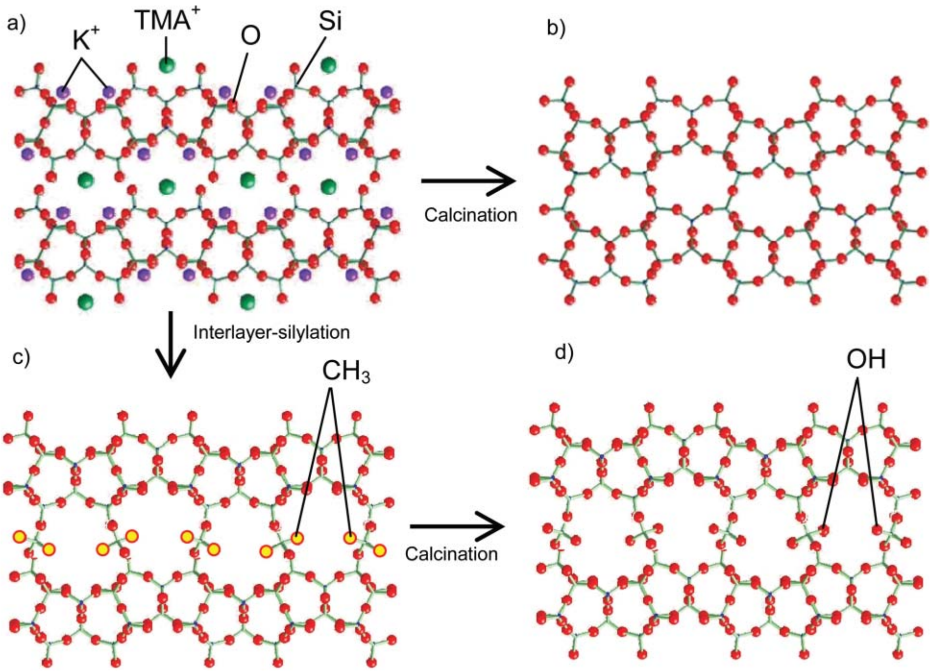

Fig. 2 Possible schemes for the formation of interlayer-expanded structure by the intercalation of DCDMS molecules: (a) PLS-1, (b) CDS-1, (c) IEZ-1 and (d) IEZ-2.

structure was retained after calcination in air at 500 °C (Fig. 1(c)). We have named the interlayer-expanded structures obtained by the interlayer silylation and the following calcination at 500 °C IEZ-1 and IEZ-2, respectively. The interlayer silylation of PLS-1 caused an increase in the *d*-spacing value along the *b* axis by 1.2 Å, from 10.4 Å (PLS-1) to 11.6 Å (IEZ-1). The crystalline structure within the CDO layers is highly stable and rigid; both samples showed similar spacing values for reflections along the *a* and *c* axes in the XRD patterns.

While the ^{29}Si MAS NMR spectrum of PLS-1 showed Q^3 and Q^4 peaks in almost equal intensities, that of IEZ-1 demonstrated the conspicuously decreased intensity of the Q^3 peak and an appreciable D^2 peak at around −12 ppm (see ESI 1†), implying the presence of the $Si(CH_3)_2(OSi)_2$ moiety between the CDO layers. The calcination of IEZ-1 caused the combustion of methyl groups attached to the interlayer silicon atoms to convert them into hydroxyl groups, as evidenced by the appearance of a Q^2 peak at around −90 ppm at the expense of the D^2 peak in the ^{29}Si NMR spectrum of IEZ-2. This Q^2 peak was hardly observed in the ^{29}Si NMR spectrum of CDS-1. Combined with the XRD data, ^{29}Si NMR spectra indicate that the interlayer-expanded structure in IEZ-1 was formed due to the construction of monomeric silica puncheons between the CDO layers.

IEZ-1 as well as CDS-1 gave a type-I nitrogen adsorption isotherm (see ESI 2†). Structural expansion of CDO layers led to an enlarged specific surface area and micropore volume for IEZ-1 (376 $m^2\ g^{-1}$ and 0.095 $cm^3\ g^{-1}$) in comparison with CDS-1 (292 $m^2\ g^{-1}$ and 0.063 $cm^3\ g^{-1}$). IEZ-2 also gave high specific surface area and micropore volume (442 $m^2\ g^{-1}$ and 0.130 $cm^3\ g^{-1}$).

Fig. 2 illustrates the scheme for the formation of IEZ-1 and IEZ-2. Since IEZ-1 contains the monomeric silica puncheons composed of the dimethylsilylene moiety, IEZ-1 is classified as an organic–inorganic hybrid microporous material. The structural characteristic of IEZ-1 and 2 is that the methyl/hydroxyl groups attached to the interlayer silicon atoms overhang their 10MR apertures. Based on the ^{29}Si MAS NMR and CHN analysis, we have estimated that IEZ-1 and 2 have the empirical formulae $Si_{36+4x}O_{68+8x}(OH)_{8-8x}(CH_3)_{8x}$ (x = 0.6–0.8) and $Si_{36+4y}O_{68+8y}(OH)_8$ (y = 0.3–0.5), respectively.

It is noteworthy that benzene molecules adsorbed only into the expanded micropores of IEZ-1, as evidenced by the considerable benzene uptake below a relative pressure of 0.1 (Fig. 3(a)). As shown in Fig. 3(b), however, the micropores of IEZ-2 hardly

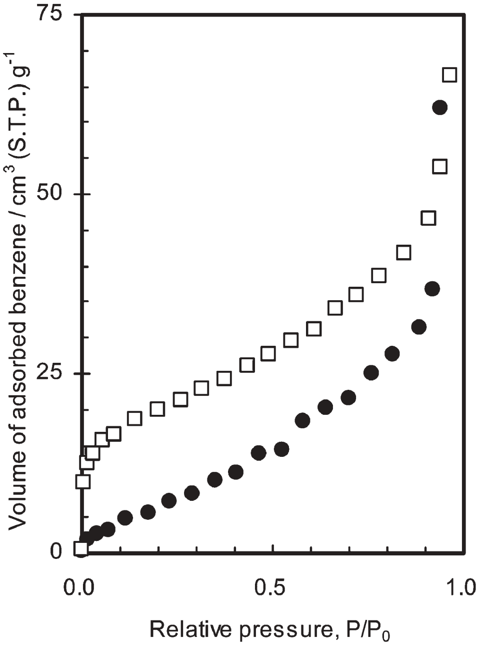

Fig. 3 Benzene adsorption isotherms of (a) IEZ-1 (□) and (b) IEZ-2 (●).

adsorbed benzene molecules. On the other hand, in the liquid phase adsorption of phenol, the micropores of IEZ-2 adsorbed 0.4 mmol g^{-1} of phenol (*cf.* 0.3 mmol g^{-1} for IEZ-1), although it possesses the same cross-sectional size as benzene. These results imply that the selectivity in adsorption of aromatic molecules in the micropores of IEZ-1 and 2 is not controlled by the pore size limitation but by the affinity of the methyl/hydroxyl groups, which overhang the 10MR apertures, for each aromatic molecule penetrating into 10MR windows. However, *n*-hexane truly adsorbed in IEZ-2, because it is small enough to make its way through the 10MR apertures without being interfered with by hydroxyl groups overhanging the 10MR apertures.

In conclusion, the novel interlayer-expanded structure IEZ-1 was prepared by the interlayer-silylation of PLS-1. The methyl groups derived from silylating agents, such as dichlorodimethylsilane, were retained in the interlayer micropores of IEZ-1. Particularly noteworthy is that benzene molecules were adsorbed into the micropores of IEZ-1, whereas calcined product, IEZ-2, hardly adsorbed benzene.

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Notes and references

‡ PLS-1 was hydrothermally synthesized following a previous report.[3] Hydrothermal silylation of PLS-1 was performed at 170 °C for 24 h in an autoclave under static conditions. Typically, PLS-1, 0.5 g, was added to a mixture of 0.10 g of dichlorodimethylsilane (DCDMS) and 30 ml of 0.3 M hydrochloric acid solution. After silylation, IEZ-1 was recovered by filtration and then dried at 100 °C. The silylated products were calcined in air at 500 °C for 12 h (ramping rate = 5 °C min^{-1}) to give IEZ-2.

The products were identified by an X-ray diffractometer (XRD, Rint-Ultima III, Rigaku) using Cu-Kα radiation at 40 kV and 20 mA. The CHN analysis was conducted by using a PE-2400-II (Perkin Elmer). The solid-state ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) measurements of the products were carried out using an ECA-400 (JEOL) at a magnetic field of 9.4 T. ^{29}Si MAS NMR spectra for the products were recorded at 79.2 MHz with a pulse width of 7.0 μs, a relaxation delay of 60 s, and a spinning rate of about 5 kHz. The textural properties of the products were determined using nitrogen adsorption at −196 °C on an Autosorb-1 (Quantachrome Instrument). The vapor-phase adsorption measurements of organic molecules on the products were performed at 25 °C on a BELSORP-18 (Bel Japan Inc.). Prior to the each adsorption measurement, the sample was evacuated at 200 °C for 6 h. The liquid-phase adsorption of phenol was performed as follows; the sample was evacuated at 200 °C for 1 h, phenol dissolved in 1,3,5-triisopropylbenzene was added to the dried sample, and the temperature of the mixture was then held at 25 °C for 24 h. The amount of phenol remaining in the liquid phase was determined by using GC.

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