Realisation of truly microporous pillared clays†

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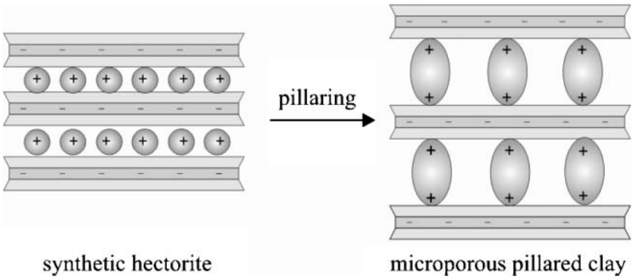
When pillaring a well crystalline synthetic hectorite using molecular pillars, we obtained a truly microporous material for the first time that displays long range order of the pillars and consequently a narrow pore size distribution.

Microporous solids, in particular zeolites, are economically important[1] in the domains of oil refining, fine chemicals, pharmaceutical, separation, environmental technologies, sensors, gas-storage and (photo-)catalysis.[2–6] During recent years, the family of microporous materials has been significantly enlarged by the advent of MOFs (metal organic frameworks).[7] Beside these well established classes, the intercalation of large complexes (pillars) in the interlayer of ionic lamellar materials provides an attractive and flexible route to microporous materials (pillared interlayered solids, Scheme 1). The potential of pillared clays (PILCs) which have been obtained applying polyoxo-cations as pillars in the field of catalysis were well studied in the past.[8–11]

While PILCs with molecular pillars as reported here, will not be able to compete with zeolites in respect to thermal stability (onset of degradation in air: 380 °C) nor with MOFs in respect to pore sizes and specific surface area, they offer several unique features: (1) the composition and thus physical properties of the host material may be easily varied by isomorphous substitution. For instance, structural transition metals may lead to magnetic ordering and electric conductivity.[12] (2) The pillars become part of the pore surface. This way, features of the pillars such as catalytic activity[13] or chirality are directly bequeathed to the microporous framework. (3) The pore volumes of PILCs may change upon incorporation of additional neutral guest molecules, a phenomenon long known as swelling.[14] It has been shown recently with MOFs that such a dynamic breathing is beneficial for gas storage purposes.[15]



Scheme 1 Schematic synthesis of pillared clays.

However, all PILCs based on natural clays, for instance montmorillonite, come with a severe flaw: a wide multimodal distribution of pore volumes ranging all the way from microporous to mesoporous. This is partially due to the nanosized and severely disordered nature of natural clays which generates wedge pores within and between tactoids. But additionally, inhomogeneities in the charge density of the silicate layers, inevitably will lead to a non-uniform distribution of pillars in the interlamellar space.[16] While for intercalation compounds of natural smectites two-dimensional long range order of pillars was never observed, we for the first time find in-plane ordering using synthetic fluorohectorite as host material.

Melt synthesis‡ of Cs-hectorite ($Cs_{0.56}Mg_{2.44}Li_{0.56}Si_4O_{10}F_2$) not only assures a homogeneous charge density, but also eliminates stacking faults resulting in a three-dimensionally ordered course grained smectite that still shows sufficient intracrystalline reactivity to be further modified by intercalation chemistry.[17] When using large organic pillars such as diprotonated DABCO molecules (2H-DABCO^{2+}; DABCO = 1,4-diazabicyclo[2.2.2]octane), PILCs are obtained where the stacking order of the parent hectorite is preserved and the microporous material obtained does not suffer from stacking faults (Fig. 1). The powder diffraction pattern (PXRD) of the PILC can be indexed with a monoclinic unit cell with symmetry *C*2/*m* (no. 12) (Fig. 1, Table 1). Surprisingly, in addition to the *hkl* reflections of the framework structure, *hk*-bands (marked with asterisks in Fig. 1) are observed. They display the typical λ-shape and can be indexed with a $3a \times b$ super-cell. Apparently, the intercalation of 2H-DABCO^{2+} affords a long range ordered, two-dimensional super-structure of the pillars in the interlamellar space.

In the literature, inter-pillar distances are usually calculated starting from the pillar density as determined by the cation

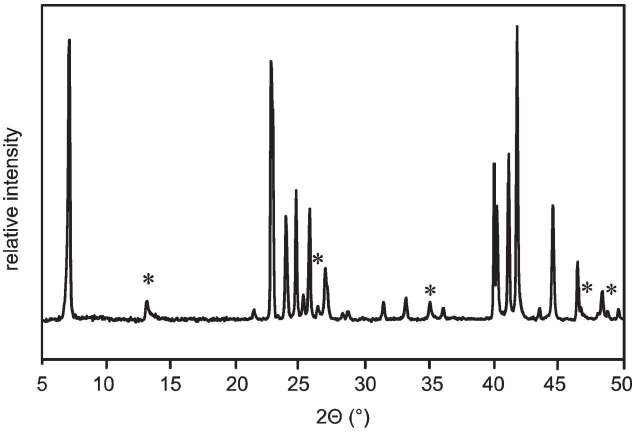


Fig. 1 PXRD of 2H-DABCO-hectorite. Asterisks (*) mark reflections due to the two-dimensional $3a \times b$ super-cell.

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† Dedicated to Professor Bernd Wrackmeyer on the occasion of his 60th birthday.

Table 1 Refined cell parameters from the X-ray powder diffraction patterns

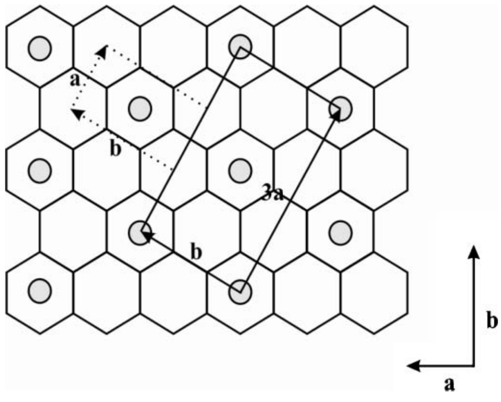
	a/Å	b/Å	c/Å	β/°
Cs-hectorite	5.249(1)	9.082(2)	14.676(4)	99.729(5)
2H-DABCO-hectorite	5.247(1)	9.083(2)	14.581(5)	96.799(5)
2D super-lattice of 2H-DABCO-hectorite	15.731(3)	9.090(2)	—	—

exchange capacity (CEC) by assuming a hexagonal distribution of pillars. This hexagonal arrangement of pillars in the interlamellar region is assumed as a consequence of strong cation–cation repulsion. Since short range pillar–pillar and host–pillar interactions are neglected in this approach the inter-pillar distance would be solely determined by the given CEC of the layered silicate. For some specific pillar densities by pure chance a pillar arrangement that is commensurate with the host structure will result, but for arbitrary CECs, the pillar arrangement would generally not be commensurate with the dimensions of the host structure.

However simulations previously published,[18,19] suggest that the host–guest-fit is amplified by the electrostatic attraction of negatively charged silicate layers and the positively charged pillars. This way, the pillar–pillar-repulsion will be overridden and in any case a pillar arrangement will be assured which is commensurate with the host structure.

With the highly ordered 2H-DABCO-hectorite these conflicting views can now be verified on an experimental basis. As mentioned earlier, the two-dimensional pillar arrangement is clearly commensurate with the host lattice. A fully occupied $3a \times b$ super-cell would require 0.33 dicationic pillars per formula unit (Scheme 2). Consequently, if this hexagonal arrangement of pillars would be commensurate with the host lattice just by chance, the layer charge of the hectorite would have to be exactly -0.66. However, the layer charge of the parent hectorite was determined to be -0.56 by microprobe analysis and additionally the pillar density was determined to be 0.27 by elemental analysis. This indicates that the $3a \times b$ super lattice of pillars is actually defective. This in turn proves that the host–pillar interaction is determining the structure of the interlamellar space which in consequence is inescapably commensurate with the host lattice regardless of the specific CEC.

Physisorption measurements with Ar/Ar(I) were performed on 2H-DABCO-hectorite. The adsorption/desorption isotherm (Fig. 2) shows on the mesoporous/macroporous pressure region an almost horizontal gradient and no hysteresis. Therefore, it can be concluded that 2H-DABCO-hectorite is a purely microporous system. As determined by the BET equation, the surface area of the PILC is 115.8 m^2 g^{-1}. The pore diameter is in the range of 4–6 Å (Fig. 3). In contrast to PILCs of natural smectites, only micropores and no mesopores are observed.[20] The narrow pore size distribution is consistent with the very high degree of order and the super-lattice of pillars as seen in the PXRD. Apparently, the organic pillars cross-link the interlamellar space in a well defined way and thus preserve the three-dimensional ordering and the phase relation of consecutive silicate layers during the intercalation process.



Scheme 2 Scheme of the $3a \times b$ super lattice of pillars in 2H-DABCO-hectorite. The unit cell of the parent hectorite is shown as dotted lines.

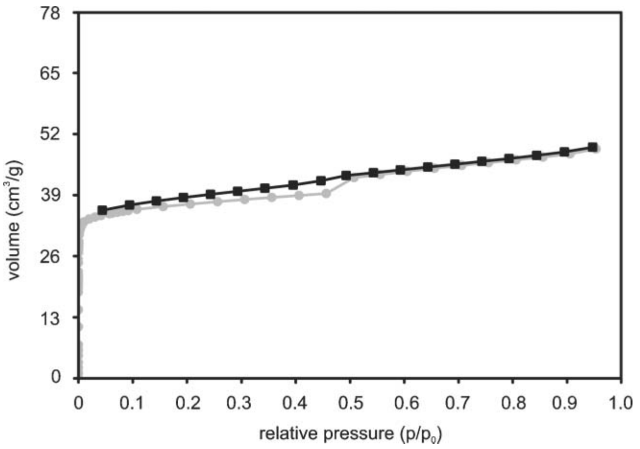


Fig. 2 Physisorption isotherm (Ar/Ar(1)) of 2H-DABCO-hectorite (● adsorption, ■ desorption).

The relatively moderate pore volume seen in Fig. 2 can be explained with the help of the ^{1}H-MAS NMR spectra of 2H-DABCO-hectorite. The lack of a *N–H*-signal in the spectrum suggests that DABCO molecules in the interlayer space are no longer protonated (Fig. 4). Apparently, upon intercalation, the acidic protons have been transferred from nitrogen to water

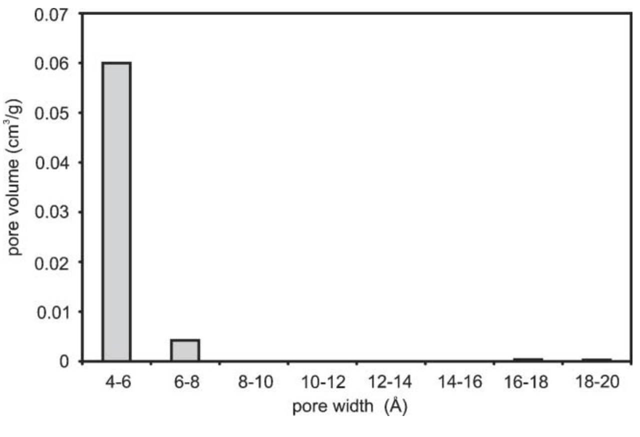


Fig. 3 Histogram of the pore width of 2H-DABCO-hectorite.

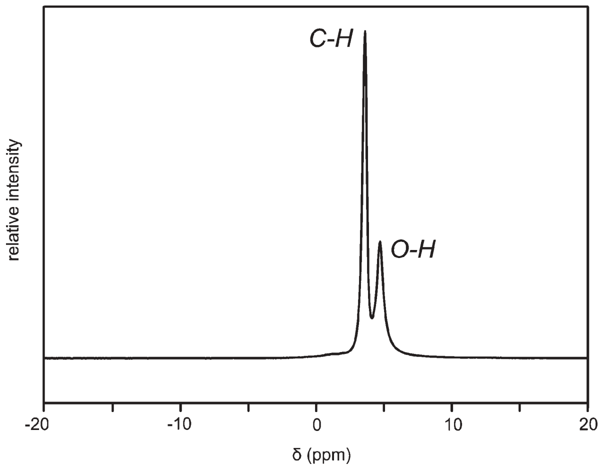


Fig. 4 ^{1}H-MAS NMR spectrum of 2H-DABCO-hectorite.

molecules present in the micropores, generating H_3O^+ between the pillars. Indeed, this pore water can not be completely removed without destroying the host structure. By NMR the ratio for interlamellar DABCO to H_3O^+ in the pores is determined to be 1.67, a value in fair agreement with the expected ratio of 2 : 1. This suggests that 2H-DABCO-hectorite is a Brønsted-acidic microporous material.

With clays synthesized *via* the melt, the concept of pillaring, which is appealing to the present day for manifold reasons, may be revitalized and a new class of truly microporous materials is (re-)established. To our knowledge, the combination of first, a narrow pore size distribution, second, a two-dimensional long range order of pillars, and third, a well crystalline, non-disordered material has never been observed before for PILCs. Obviously, we will look at the possibilities to modify both host composition and pillar properties in order to explore sensor, catalytic and gas storage applications.

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Notes and references

‡ Cs-hectorite was synthesized as described previously.[17] Post synthesis, the compound was annealed for 7 days at 1175 °C in a gas-tight molybdenum crucible in order to release strain and to increase crystal size.

Complete intercalation of 2H-DABCO^{2+} can not be achieved directly because of the moderate acid lability of hectorite. Therefore, the microporous material was synthesized in a two-step process. First, the interlayer space has to be expanded by intercalation of the much less acidic H-DABCO$^+$ into Cs-hectorite at nearly neutral pH (pH = 7.5). 500 mg of annealed Cs-hectorite was refluxed ten times for 24 h with 100 ml H-DABCO$^+$Cl$^-$-solution (0.1 M), until the material was free of Cs$^+$. Consecutively, H-DABCO$^+$ cations can rapidly and readily be replaced by half as many diprotonated 2H-DABCO^{2+} molecules. For this, the H-DABCO-hectorite was treated three times for 24 h at 60 °C with 50 ml 2H-DABCO^{2+}2Cl$^-$-solution at pH = 2.5.

Quantification of the pillars was determined by elemental analysis (Elementar vario el III). In order to realize higher combustion temperatures (1150 °C) that are necessary for complete oxidation of pillars, the combustion tube was filled with tungsten(VI) oxide granules which is usually used for the *CHNS*-mode. Additionally, the combustion time in pure oxygen was increased up to 3 min by using the O_2-index 5.

The chemical composition of the Cs-hectorite was determined by wavelength dispersive X-ray spectroscopy (WDX) using an electron microprobe (Jeol JXA-8200) operated at the following settings: acceleration voltage 15 kV, initial beam current 15 nA, beam spot diameter 1 μm. Magnesium oxide (O), enstatite (Mg), andradite (Si), fluorite (F) and pollucite (Cs) were used as standards. The counting time was 20 s at the peak position and 10 s on each side of the peak position. The sample was embedded in resin on a glass slide, polished to a flat surface and coated with carbon. Due to the inability of this method to determine the Li content, the composition of the layered silicate was normalized to $Si_{4.00}$ and then further normalized to 22 negative charges to calculate the Li content of the sample.

Powder-X-ray diffraction (PXRD) data were collected in transmission geometry on a STOE Stadi P powder diffractometer with linear PSD (Ge-monochromator, Co-Kα radiation = 1.7889 Å). TREOR was applied to index and refine the PXRD trace.

The physisorption experiment with Ar/Ar(I) was performed at a Ar(I) temperature of -185.55 °C applying a Quantachrome Autosorb-1. The substance was dried for 2 days at 80 °C under high vacuum above P_2O_5. To estimate the pore diameter of 2H-DABCO-hectorite by physisorption, a non-local DFT model was used (Software Quantachrome Autosorb 1 V. 1.52, Ar on zeolite/silica, cylindrical pores, equilibrium model[21]).

The ^{1}H-MAS NMR measurements were done at room temperature with a commercial FT-NMR-spectrometer DSX 400 Advance (Bruker, Karlsruhe), with a basic frequency of $\nu_0(^1H)$ = 400.15 MHz. The chemical shift was referenced to TMS and rotation frequency was 12 kHz.

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