2019

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Disciplines
Engineering | Physical Sciences and Mathematics

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This journal article is available at Research Online: https://ro.uow.edu.au/aiimpapers/3470
Microporous materials formed via intercalation of ultrathin coordination polymers in a layered silicate

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Abstract

Development of microporous materials, like zeolites and metal-organic frameworks (MOFs), with unique and better properties, is crucially important, while yet challenging, for many energy applications. Herein, we report on a new family of microporous hybrids having well-defined permanent porosity, which is formed by pillaring a layered silicate with packed coordination polymers. This inorganic-organic hybrid material, having well-defined/two-faced micropores surrounded by the polymers and silicate walls, exhibits superior adsorption toward methanol due to co-operative interactions compared with conventional microporous materials. The material could be used as an adsorbent to selectively and effectively recover methanol from a methanol/water vapor mixture.

Keywords

Microporous material

Inorganic-organic hybrid

Layered silicate

Coordination polymer

Methanol/water separation
**Introduction**

Nowadays, microporous materials, such as zeolites and MOFs, find many important or potential applications especially in energy. Besides these well-established classes, microporous hybrids formed via pillaring layered inorganic solids with inorganic nanoparticles or organic molecules can provide unique pores surrounded by the layered materials and the pillars [1-12]; for example, pillaring of clays is a well-known route to microporous materials (so-called “pillared layered clays”) [3-7]. However, compared with zeolites and MOFs, well-defined pores still remain difficult to be formed in these microporous hybrids. And they were found only in pillared layered clays prepared from a specially synthesized clay [8] and layered metal organophosphonates, obtained by topotactic reactions between layered metal phosphates and phosphonic acids [1,2]. Pillaring of layered silicates with silica nanoparticles has also been investigated to create well-defined pores [13-15], while the pillared silicates provided only pores surrounded by silica walls.

In contrast to the pillaring with molecules, intercalation of polymers into layered inorganic solids (rather than dispersion of exfoliated layers in a polymer matrix) has long been awaited for many applications, including controlled synthesis of conjugated polymers, gene reservoirs, photonic crystals and flexible transparent gas barrier films [16-23]. Because the interlayer structure is defined by the structures of polymers (rather than host-guest interactions in the former examples using molecules), we expect that control of packing or aligning of intercalated polymers can provide well-defined pores. Surprisingly, little attention has been payed to such packing or aligning of intercalated polymers. Herein,
while paying special attention to the inherent microporosity of a certain kind of one-dimensional (1D) polymers upon packing them in a 2D fashion (Figure 1), we report on a new family of microporous inorganic-organic hybrids.

We also report on the use of the new microporous material to recover methanol from a methanol/water mixture. The separation of methanol/water mixtures has been a crucially important issue for many industrial applications. For example, large scale production of methanol from natural gas yields water as a reaction byproduct that must be separated. Because the traditional thermal processes like distillation is energy-consuming, development of more energy efficient process, like adsorbent-based separation, has been extensively investigated [24,25].

![Figure 1](image)

**Figure 1** Scheme for a design of micropores via pillaring of layered inorganic solids with coordination polymers. (a) Aligning and packing of intercalated 1D coordination polymers create well-defined micropores. The upper host layer is omitted for clarity. (b) Random distribution of intercalated 1D coordination polymers.

**Results and discussion**

The original developed strategy relies on packing 1D polymers in a 2D skeleton within layered inorganic materials. As the polymer component, we selected a typical 1D coordination polymer (CP) composed of zinc paddle-wheel units like those seen in MOFs like MOF-2 (chemical formula of Zn(bdc), where
bdc is 1,4-benzenedicarboxylate) [26]. As the layered solid component, we selected a layered silicate HUS-2 (Hiroshima University Silicate-2 (Figure S1 in Supporting Information); chemical formula of (C\textsubscript{5}H\textsubscript{14}NO\textsubscript{4}\{Si\textsubscript{20}O\textsubscript{40}(OH)\textsubscript{4}\}, where C\textsubscript{5}H\textsubscript{14}NO and OH are the interlayer choline cations and the interlayer surface silanol groups, respectively) [27]. We considered that CPs would form in the interlayer spaces of HUS-2 if zinc(II) acetylacetonate, Zn(acac), that can interact with silanol groups covering the surface of layers of HUS-2 [28,29], was intercalated in HUS-2 and the intercalated product was reacted according to the synthetic procedure of MOF-2 (with slight modification) [30].

To intercalate relatively bulky Zn(acac) molecules, choline cations of HUS-2 were first replaced with hexadecyltrimethylammonium cations (C\textsubscript{16}\textsuperscript{+}) to expand the interlayer space. The C\textsubscript{16}\textsuperscript{+}-exchanged form of HUS-2 (C\textsubscript{16}\textsuperscript{+}/HUS-2) was then reacted with Zn(acac), affording Zn/C\textsubscript{16}\textsuperscript{+}/HUS-2 bearing Zn(acac) molecules to locate in the expanded interlayer spaces possibly via hydrophobic interactions with C\textsubscript{16}\textsuperscript{+}. This was confirmed by powder X-ray diffraction (PXRD) (Figure S2), which reveals the expansion of basal spacing from 2.4 nm (C\textsubscript{16}\textsuperscript{+}/HUS-2) to 2.8 nm (Zn/C\textsubscript{16}\textsuperscript{+}/HUS-2). Then, the Zn/C\textsubscript{16}\textsuperscript{+}/HUS-2 was further reacted with the polymer precursor solution containing zinc acetate and bdc, resultantly creating the final product (named CP/HUS-2), where the basal spacing shrank to 1.8 nm and the nitrogen content substantially decreased from 2.3 wt.% in C\textsubscript{16}\textsuperscript{+}/HUS-2 to 0.4 wt.% according to the elemental analysis (Table S1).

The local structure of CP/HUS-2 was uncovered via the analysis of X-ray pair distribution function (PDF) [31] with the help of solid-state NMR data. The unit cell was determined from the Bragg
peaks of the X-ray scattering data considering the fact that the basal spacing was 1.76 nm. The PDF data showed peaks assignable to Zn-O bonds (1.96 Å) and Zn-Zn distance (3.16 Å). The Zn-Zn distance is typical for those in paddle wheel units (Figure 2a). Solid-state $^1$H NMR and $^{13}$C NMR (CP/MAS) spectra revealed the presence of acetate molecules, as well as benzenedicarboxylates (Figure 2b and Figure S3). Thus, the primary units of the CPs consisted of paddle-wheel structures of zinc, acetates and benzenedicarboxylates (the basal spacing and low nitrogen content suggest that the remaining ligand of zinc is water molecule), and thus we simulated PDF using chain structures composed of paddle-wheel zinc units connected with benzenedicarboxylates and terminated with acetate, and the PDF peaks above 8 Å can be simulated by the 2D packed chains as shown in Figure 2a, where Zn-Zn pairs between adjacent chains (~9 Å) and along the chains (~11 Å) can be simulated well. Elemental analysis indicated the molar ratio of Zn/Si in CP/HUS-2 of 0.18 (Table S1).
**Figure 2** (a) Pair distribution function (PDF) analysis of CP/HUS-2. (b) Solid-state $^1$H NMR spectrum of CP/HUS-2. Asterisks indicate peaks assignable to $^1$H in organic compounds including a solvent (N,N'-dimethylformamide) and C$_{16}^+$. (c) Solid-state $^{29}$Si NMR spectrum of CP/HUS-2 and the precursors. (d, e) Structure model of CP/HUS-2 obtained by the PDF simulation shown in the panel ‘a’. SiO$_4$ and ZnO$_4$ are shown as tetrahedra. (f) The calculated solvent accessible voids in CP/HUS-2 (Zn = gray; Si = blue; O = red; C = brown; H = white). The pores have two faces of hydrophobic (yellow) and hydrophilic (green) environments, as illustrated by a coloured ball. The dotted lines illustrate relatively strong hydrogen bonds (O-O distance within 2.6–2.9 Å) between the polymers and silicate layers.

UV-vis spectroscopy confirmed the formation of such CPs (**Figure S4**). Zn/C$_{16}^+$/HUS-2 showed an absorption centered at 300 nm assignable to the intercalated Zn(acac), while CP/HUS-2 did not show such absorption but showed an absorption at around 280 nm due to the $\pi$-$\pi^*$ excitation of the terephthalic acid linkers [32].

The PDF peaks of interatomic distances, simulated for the original silicate structure, did not match the experimental PDF peaks, except for the broad peaks at around 1.6 Å, suggesting a change of
the structure. In order to correctly identify the states of silicate in CP/HUS-2, solid-state $^{29}$Si NMR spectroscopy was carried out. Figure 2c shows that HUS-2, C$_{16}^+$/HUS-2 and Zn/C$_{16}^+$/HUS-2 have sharp signals assigned to Q$^3$ and Q$^4$ environments of silicon [33]; in contrast, CP/HUS-2 has remarkably broadened peaks, indicating the formation of a different Si compound by bonding with other elements [33] (slight Q$^3$/Q$^4$ difference is within an error again). This is also confirmed by PXRD data of CP/HUS-2, where Bragg peaks located at high angles attributed to in-plane diffractions of the original silicate (e.g. 002 and 200) layers were broadened or disappeared (Figure S5). Figure 2c indicates that the original silicate layers are disordered, as also confirmed by the PDF analysis where simulated PDF (based on the original silicate structure) does not fit the experimental data. These facts mean that the details of the silicate in this model are arbitrary, and thus the occupancy of the Si and O atoms in the silicate layers is equal to 0.78, on the basis of the elemental analysis.

The structural models, accounting for the experimental data, were comprehensively searched, and the model presented in Figure 2d and e was finally selected. As described above, CP/HUS-2 is composed of 2D-packed CP layers composed of 1D [Zn$_2$(ac)$_2$(bdc)$_2$(H$_2$O)$_2$] CP. Considering the basal spacing, which is an interlayer distance of two silicate layers, the 2D-packed CP layers and the silicate layers should be stacked alternatingly. PDF simulated for CP layers without silicate layers left broad oscillation (Figure S6), which means presence of scatter between CP layers. Thus, we added the silicate layers as shown Figure 2d and e, and the simulated curve resembled the experimental one well.

The $^1$H NMR results (indicating hydrogen bonding to the surface silanol groups; Figure 2b)
show the presence of Si-OH groups after interacting H$_2$O of [Zn$_2$(ac)$_2$(bdc)$_2$(H$_2$O)$_2$]. The integral ratio of [bdc]:[Si-OH—H$_2$O]:[ac] is 6:10:5, roughly consisting with the structural analysis. Physisorbed H$_2$O molecules, appeared at around 5 ppm, were removed prior to the measurements. Considering the distance between silicate surface and the coordinated water molecules in the paddle-wheel units, it is reasonable to suggest that the CPs are aligned along the hydrogen bonds between the coordinated water molecules and the silicate surface. These hydrogen bonds, in turn, connect different silicate layers to form a 3D [Zn$_2$(ac)$_2$(bdc)$_2$(H$_2$O)$_2$][Si$_{15}$O$_{33}$H$_6$]$_{0.77}$ structure (Figure 2f).

The sharp PDF peaks assignable to the Zn-Zn atom pairs along the CPs and between CPs (Figure 2a), with the absence of Bragg peaks assignable to these directions (Figure S2), mean that CPs are locally well ordered, though without long-range ordering, that is, the packed CPs are rather well aligned but not so perfect to become crystalline domains. This short-range order defines the packed CP structure in the range above a pore formed by bdc and acetate (>11 Å, Figure 2a), and thus is considered to be enough to exhibiting well-defined porosity. Given a fact that there is no directions in the HUS-2 where the repeating unit of the intercalated CPs can form chemical bonds with the silicate surface (Figure 2d and e), this relatively flexible 3D structure connected via hydrogen bonds seems to be very reasonable.

When CP/HUS-2 was treated with a dilute acid solution, the intercalated CPs deintercalated, while the original silicate structure was retained (Figure S7). This also supports the hydrogen bond interactions between the silicate layers and the intercalated CPs.
The location of CPs was carefully investigated via scanning electron microscopy (SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM). Scanning electron microscopy (SEM) revealed that CP/HUS-2 is shaped in the form of plate-like particles with a size of up to several µm. This is consistent with the shape of the C\textsubscript{16}\textsuperscript{+}/HUS-2 precursor, however the former is slightly more rounded and bent (Figure 3a). AFM surface profiles showed that the particle thickness and surface roughness are consistent with those of the silicate precursor (Figure 3b upper). The surface morphology was further investigated using phase images in AFM: phase contrasts between each plate and mica substrate were not clear both for C\textsubscript{16}\textsuperscript{+}/HUS-2 and CP/HUS-2 (Figure 3b lower), suggesting that viscoelasticity of CP/HUS-2 and C\textsubscript{16}\textsuperscript{+}/HUS-2 surfaces is similar to mica surface and that CP-based nanocrystals and thin films are not deposited on the CP/HUS-2 surface. TEM imaging also confirms the absence of crystals other than silicates outside CP/HUS-2 (Figure 4). And TEM-energy dispersive X-ray (EDX) elemental mapping reveals that zinc and carbon are homogeneously distributed over each CP/HUS-2 plate. All these results confirm that the packed CP layers are located in the interlayer spaces. During control synthetic tests we observed CP-based nanoparticles outside the silicate plate-like particles. These data are shown in Supporting Information along with a discussion on the formation mechanism of CP/HUS-2 (Figure S8 and Figure S9).
**Figure 3** (a) SEM and (b) tapping mode AFM images of C$_{16}$/HUS-2 and CP-HUS-2. Upper and lower panels of (b) show the topography and phase images, respectively.

**Figure 4** TEM image, EDX elemental maps and EDX spectrum of CP/HUS-2.
To evaluate the porosity of CP/HUS-2, the N$_2$ adsorption/desorption isotherms were measured after removing the remained organics such as C$_{16}$+ and dmf (nitrogen content of the recovered sample was 0.06 wt.%). As shown in Figure 5a, CP/HUS-2 exhibits microporosity with a uniform pore size, like many zeolites and MOFs. The BET area (710 m$^2$ g$^{-1}$) is considerably larger than that of pillared layered clays having well-defined pores (up to 200–300 m$^2$ g$^{-1}$) [8]. The micropore volume of CP/HUS-2 determined from the isotherm using the t-plot is 0.36 cm$^3$ g$^{-1}$, which is reasonably consistent with the solvent accessible volume of 0.45 cm$^3$ g$^{-1}$ calculated using a 1.55 Å-radius sphere as a probe by the PLATON program. These results indicate the permanent porosity [34] of CP/HUS-2. Since the interlayer 1D CPs are densely packed with each other and the parent HUS-2 scarcely shows N$_2$ adsorption (Figure 5a), the microporosity should originate from the voids bounded by the hydrophilic silicate surface having plenty of silanol groups, hydrophobic benzene rings and methyl groups of acetate (Figure 2f). We can thus expect unique material properties owing to these two-faced pores.

**Figure 5** (a) N$_2$ adsorption (filled)/desorption (open) isotherms of CP/HUS-2, HUS-2 and MOF-2. The inset shows the pore size distribution determined by MP method. (b) Adsorption isotherms of methanol vapour on CP/HUS-2, MOF-2, H/HUS-2, C$_{16}$/HUS-2, Ph/oct and zeolite. (c) Adsorption (filled)/desorption (open) isotherms of water vapour on CP/HUS-2.
We then investigated the adsorption performance of CP/HUS-2 toward methanol, which is known to be effectively adsorbed on a MOF (MOF-2) having the composition similar to the present CPs [35]. Shown in Figure 5b is the adsorption isotherms of methanol vapour on CP/HUS-2 and reference samples, MOF-2, H/HUS-2 (prepared by replacing choline cations with protons) and C_{18}/HUS-2 (prepared by grafting a part of the surface silanol groups of H/HUS-2 with octadecylsilane). CP/HUS-2 showed type II adsorption behaviour indicative of strong interactions between adsorbents and adsorbates [36]. The adsorption is as effective (or even stronger) as for MOF-2 (type V adsorption indicates weaker interactions between adsorbents and adsorbates [36]). The strong and effective adsorption can be accounted for the proposed pore structure (the PXRD pattern did not change upon the adsorption and after the desorption). In fact, C_{18}/HUS-2, having hydrophobic octadecyl groups (to form hydrophobic interaction with methyl groups) and hydrophilic silanol groups (to form hydrogen bonding with hydroxy groups) [37], adsorbs methanol more effectively (type II) than H/HUS-2 having the hydrophilic surfaces covered with silanol groups. CP/HUS-2 includes approximately 55 wt.% of silica and is heavier than MOF-2, but still it adsorbed methanol (per sample mass) more effectively than MOF-2, especially at a relatively low partial pressure. CP/HUS-2, moreover, adsorbed methanol more effectively and strongly than a typical zeolite, MFI-type zeolite (silicalite-1, Si/Al = ∞) and a state-of-the-art microporous inorganic-organic hybrid prepared by pillaring of a layered silicate (octosilicate) with phenyl groups (Ph/oct) [10]. These results show a high potential of the present material design toward a new family of
microporous hybrid materials with fascinating properties.

In addition to its excellent adsorption, CP/HUS-2 shows superb moisture stability. Even when exposed to a water vapour in a helium atmosphere (15 g m$^{-3}$ of water vapour corresponds to 50% relative humidity), CP/HUS-2 hardly revealed any traces of structural deterioration, as confirmed by the PXRD pattern and the N$_2$ adsorption isotherm (Figure S10). Such enhanced stability is assignable to the robust structure of the silicate layers [38] or suppressed water adsorption within the interlayer space. The latter is more reasonable considering the fact that CP-HUS-2 scarcely adsorbed water vapour (Figure 5c).

The thermal stability of CP/HUS-2 during thermogravimetric analysis was confirmed up to 350 °C, which is close to its decomposition temperature of ca. 400 °C, where the oxidation of bdc and ac took place revealing a weight loss of ca. 25% (Figure S11). The mechanical stability was also investigated via compaction of the powder using a pellet-forming die under varied forces, revealing that CP/HUS-2 was stable up to 10 tons.

**Figure 6** Time course adsorption of methanol vapour on CP/HUS-2 from (●) methanol/water vapour mixture and (○) methanol vapour at 298 K.

Based on the above adsorption properties, we expected that CP/HUS-2 could be used as an
adsorbent to recover methanol from a methanol/water mixture. Figure 6 shows time course adsorption of methanol from a mixture of methanol and water vapors at 298 K (saturated vapors for each). CP/HUS-2 rapidly adsorbed methanol with a maximum adsorption amount of more than 6 mmol g⁻¹, consisted with adsorption isotherm data (Figure 5b). Importantly, the adsorption profile was almost identical to that measured without water vapor. This means that CP/HUS-2 can adsorb methanol in a high selectivity and has a potential as a material for industrial methanol/water separation processes.

Conclusions

We created a new microporous inorganic-organic hybrid material by pillaring a layered silicate with 1D CPs that were packed in 2D microporous layers. This inorganic-organic hybrid material had open micropores surrounded by the hydrophobic polymers wall and hydrophilic silicate wall, exhibiting cooperative adsorption for methanol. This microporous material showed a potential as an adsorbent to separate methanol/water mixtures in an energy efficient fashion. The packing and arrainment of 1D CPs in the present material suggested that building-unit-thick ultrathin 2D MOF-like structure molded by the narrow 2D interlayer spaces became available. Although the syntheses of 2D MOF structures, via exfoliation or bottom-up approaches, on substrates and in free-standing forms, has recently attracted increased attention with respect to the development of exotic properties different from those of the bulk [39-41], dimensional control of inherently 3D MOF crystals (e.g. MOF-5 and HKUS-1) into 2D arrangements has remained a big challenge. Since a variety of 1D coordination polymers (or MOF
structures) and layered materials with different reactivities (e.g. surface functionality and degree of interlayer expansion) is available [12], the presently designed novel synthetic procedure, in addition to enriching a family of microporous materials with unique properties, can be also utilized to precisely construct new and diverse 2D MOF structures.

**Experimental**

**Materials Synthesis:** C$_{16}^+$-HUS-2 was prepared from HUS-2 according to the reported method [26]. Zn/C$_{16}^+$-HUS-2 was synthesized by mixing C$_{16}^+$-HUS-2 (250 mg) with a solution of Zn(acac) (260 mg) in a mixture (50 mL) of ethanol and hexane (3: 17 in volume) at 60 °C for 3 days, after which the solvent was evaporated. Zn/C$_{16}^+$-HUS-2 (150 mg) was dispersed in DMF (25 mL) containing zinc acetate dehydrate (150 mg), and this dispersion was dropped to a solution of terephthalic acid (75 mg) and trimethylamine (10 μL) in DMF (25 mL) under stirring. The solid product was separated by centrifugation, washed with chloroform and purified by decantation with chloroform, finally yielding CP/HUS-2. MOF-2 were prepared along with the reported method [30]. H/HUS-2 was produced by dispersing C$_{16}^+$-HUS-2 (500 mg) in 0.1M hydrogen chloride (20 mL) for 6 h at room temperature followed by washing with water. C18/HUS-2 was fabricated as follows: a dispersion of C$_{16}^+$-HUS-2 (200 mg) and dehydrated toluene (50 mL) containing octadecyltrimethoxysilane (50 μL) was heated at 60 °C for 1 day, after this the product was separated by evaporation of the solvent and washed with a
mixture (20 mL) of 0.1M hydrogen chloride and ethanol (1:1 in volume), and then with acetone. Ph/oct was prepared according to the literature using 1,4-bis(dichloromethylsilyl)benzene [10].

**Materials Characterization:** PXRD patterns were taken using a Rigaku RADIB diffractometer. UV-vis diffuse reflectance spectra of the samples were recorded on a UV-vis spectrometer (JASCO V-570) with BaSO$_4$ as a reference. Solid-state NMR spectra were recorded at 119.17 MHz on a Varian 600PS solid NMR spectrometer using a 6 mm-diameter zirconia rotor. For solid-state $^1$H NMR, prior to the measurements, the sample was heated at 100 °C under a nitrogen flow to remove physisorbed water molecules. Inductively coupled plasma-atomic emission spectrometry was performed using a Spectro Ciros Ccd instrument. Thermogravimetric analysis was carried out using a Rigaku Thermo plus TG8120 apparatus. SEM and AFM images were recorded with a Hitachi S-4800 SEM and Shimadzu SPM-9700 microscopes, respectively. TEM images were obtained using a JEOL JEM-3199FEF with an EDX analyzer. Adsorption or adsorption/desorption isotherms were recorded using a MicrotrakBel Belmax. Prior to the measurements, CP/HUS-2, MOF-2, silicalite-1 and the others were evacuated at 300 °C for 12 h, 140 °C for 16 h, 200 °C for 3 h and 120 °C for 3 h, respectively. Hydrostability tests were performed on a MicrotrakBel Belflow apparatus. The mechanical stability of CP/HUS-2 was evaluated through compaction of the pure powder using a pellet-forming die. A force of 4, 7 or 10 tons was applied for 40 min, forming the pellet. The pellet was grounded and analysed by PXRD and N$_2$ adsorption/desorption.

**PDF analysis:** X-ray total scattering data for obtaining pair distribution functions (PDFs) were collected on a Rigaku R-AXIS imaging plate detector at the BL04B2 beamline of SPring-8 at a beam energy of
61.32 keV ($\lambda = 0.20220$ Å). The samples were sealed in Lindeman glass capillaries (inner diameter: 0.48 mm; outer diameter: 0.5 mm; Hilgenberg). The 2D scattering data were converted into 1D patterns using the program Fit2D [31]. Corrections were made for background, absorption, fluorescence, X-ray polarization, double scattering and Compton scattering. These corrected intensities were normalized by the Faber-Ziman type scattering form factors calculated using atomic scattering factors [42] to obtain structure functions, $S(Q)$ [43]. The $S(Q)$ ($Q_{\text{max}} = 19.1$ Å$^{-1}$) was treated with a revised Lorch function ($\Delta = 0.98$) [44], and then converted into reduced PDF, $G(r)$, where $r$ is the interatomic distance.

The structure was analyzed using the PDFfit2 program [45]: first, initial structure models were selected on the basis of the results of primary analysis, solid-state NMR, powder X-ray diffraction, and PDF data. The structures of the materials, except for H atoms, were further analyzed by the real-space Reverse Monte Carlo method (or simulated annealing) [46]. For this analysis, we modified the PDFfit2 program via adding a code to minimize the weighted $R$-value through iterative runs of the PDFfit2 calculation for a configuration where one randomly chosen atom or molecule (as a rigid body) was moved or rotate freely under the restraints and constraints: bond length restraints ($\pm 0.05$ Å to the initial values), bond angle restraints ($\pm 5^\circ$ to the initial values), rigid body constraints ($\pm 0.3^\circ$ of rotation using its centroid as the rotation center, and $\pm 0.2$ Å translation along the $a$, $b$ and $c$ axes) to the aromatic rings and SiO$_4$. This process reproduced the slightly disordered structure of the silicate, as discussed in the main text. After reaching $R_{\text{w}} < 0.25$, the silicate atoms were fixed and all other atom coordinates in the coordination polymer were refined without any restraints and rigid bodies (maximum moves were 0.01
Å along all axes). The hydrogen atoms were added using the Materials Studio program at the structurally reasonable positions.

**Separation of methanol/water vapours:** Saturated methanol vapour or a mixture of saturated methanol and water vapours (298 K) was injected to a closed stainless-steel container in which CP/HUS-2 was placed. The temperature of the container was kept at 298 K. The amount of methanol in the head space of the container was quantified by GC-FID for a given time.

**Acknowledgement**

The authors acknowledge K. Ebihara and K. Kurashima (NIMS) for a support during TEM measurements. This work was supported in part by JSPS KAKENHI Grant Number 26708027. D.G. is grateful to the Australian Research Council for granting a Laureate Fellowship. The synchrotron radiation experiments were performed at the BL04B2 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2015B1084 and 2016A1841).

**References**


A microporous material, formed by pillaring a layered silicate with packed 1D coordination polymers, has well-defined, two-faced micropores surrounded by the polymers and silicate walls and exhibits cooperative effects on methanol/water separation.
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Yusuke Ide received his bachelor’s degree (2001), master’s degree (2003), and Ph.D. degree (2007) from Waseda University under the supervision of Prof. Makoto Ogawa. After working as a research associate at his laboratory, in 2010, he moved to Hiroshima University to work as an assistant professor in the laboratory of Prof. Tsuneji Sano. In 2012, he moved to MANA of NIMS to work as a senior researcher in the research group of Prof. Y. Bando. Since 2017, he has been a Group Leader (acting). His research interests focus on the material design of layered inorganic solids for adsorption, photocatalysis, etc.
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Dmitri Golberg

Dmitri Golberg is an Australian Laureate Fellow, Professor and a Leader of “Inorganic Nanomaterials” Laboratory at Queensland University of Technology (QUT), Australia, and “Nanotube” Group at the National Institute for Materials Science (NIMS), Japan. His research focuses on the synthesis, microscopic analysis, and property measurements of inorganic nanomaterials. With more than 700 published articles, 43,000 citations and Hirsh factor of 111, he is placed within top 300 most-cited world materials scientists.
Control synthetic experiments. To shed a light on the formation mechanism of CP/HUS-2, control synthetic experiments were conducted. We used two other silicate precursors, C$_{16}^+$/HUS-2 (without Zn(acac) molecules) and Zn$^{2+}$/HUS-2, prepared by replacing the interlayer choline cations of HUS-2 quantitatively with zinc cations (Zn$^{2+}$/HUS-2 was prepared by dispersing HUS-2 (100 mg) in an aqueous zing nitride solution (100 mL, 0.5 mmol L$^{-1}$) for 3 days at room temperature followed by washing with water). The C$_{16}^+$ and zinc cations are located in the interlayer space via electrostatic interactions with deprotonated surface silanol groups, Si-O$^-$, respectively, and are not immobilized on the interlayer surface. When C$_{16}^+$/HUS-2 and Zn$^{2+}$/HUS-2 were reacted under the identical conditions, rod-shaped aggregated particles formed outside HUS-2 plates (SEM image of the product from Zn$^{2+}$/HUS-2 is shown in Figure S7a as a typical example). Tapping mode AFM revealed that such particles were quite different from mica in viscoelasticity (Figure S7b), indicating the formation of MOF-2 and/or MOF-5 outside HUS-2 particles, considering the PXRD data. The adsorption isotherm of bdc on C$_{16}^+$/HUS-2 from a DMF solution (Figure S8), moreover, revealed that C$_{16}^+$/HUS-2 could adsorb a significant amount, much larger than the cation exchange capacity of HUS-2, of bulky bdc molecules from relatively high concentration solution of bdc, like the present precursor solution. These results indicate the importance of both the expanded interlayer space and zinc(II) that can be immobilized on the interlayer surface, like Zn(acac), to effectively
intercalate the precursors (zinc, bdc and ac) and then to deposit and immobilize the CPs in HUS-2.

**Thermal stability.** We checked the effect of evacuation temperature (for 3h) of CP/HUS-2 on the microporous structure. This revealed that the N$_2$ adsorption/desorption isotherm shapes were hardly changed and the BET surface area increased by up to 350 °C, consisting with TG-DTA data (**Figure S10**). Such high thermal stability, even after the dehydration of the coordinated water molecules from [Zn$_2$(ac)$_2$(bdc)$_2$(H$_2$O)$_2$], suggests that the paddle-wheel units can link to the silicate layers via stronger interactions between zinc and silanol groups (SiO$^-$/SiOH) to retain micropores, as reported for the evacuation of MOF-2 [1].
Supplementary Table and Figures

Table S1. Composition of C$_{16}$+/HUS-2 and CP/HUS-2.

<table>
<thead>
<tr>
<th></th>
<th>N / wt.%$^a$</th>
<th>Zn / wt.%$^b$</th>
<th>Si / wt.%$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{16}$+/HUS-2</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CP/HUS-2</td>
<td>0.4</td>
<td>10.7</td>
<td>26.2</td>
</tr>
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</table>

$^a$ Determined by CHN analysis. $^b$ Determined by ICP of the dissolved sample.
Figure S1. Structure of HUS-2 (Si = blue; O = red; N = purple; C = brown; H = pink).
Figure S2. Powder X-ray diffraction patterns of HUS-2, C_{16}^+/HUS-2, Zn/C_{16}^+/HUS-2 and CP/HUS-2. Triangle and diamond symbols indicate peaks assignable to (010) reflection of the CP-non-intercalated phase and (040) reflection of a slightly expanded CP/HUS-2, possibly due to water uptake during X-ray diffraction measurement.
Figure S3. Solid-state $^{13}$C NMR (CP/MAS) spectrum of CP/HUS-2.
Figure S4. UV-Vis spectra of C$_{16}^{+}$/HUS-2, Zn/C$_{16}^{+}$/HUS-2 and CP/HUS-2.
Figure S5. Powder X-ray diffraction patterns at a higher 2θ region of HUS-2, C$_{16}^+$/HUS-2, Zn/C$_{16}^+$/HUS-2 and CP/HUS-2.
Figure S6. PDF revealing that coordination polymers, composed of paddle wheel units, [Zn₂(ac)₂(bdc)₂(H₂O)₂], are aligned between silicate layers.
Figure S7. a, Powder X-ray diffraction patterns CP/HUS-2 before and after the treatment with a dilute HCl solution (pH = 4.8). The peak due to in-plane diffractions of the original silicate layers (001) was still observed after the acid treatment. b, (left) typical ED patterns of CP/HUS-2. (right) ED patterns showing relatively strong reflections. (Inset) red, blue and green circles are simulated ED patterns of HUS-2 and disordered HUS-2. During the observation, we could hardly get images showing reflections (left), consisted with the fact that the original silicate structure was distorted. Although we could rarely get images showing strong reflections (right), all the spots were assignable to HUS-2 layers. This is reasonable given the fact that MOF-5, composed of elements and molecules similar to those comprising the present CPs, are unstable under the electron beam [2,3].
Figure S8. a, SEM images of C16+/HUS-2, CP/HUS-2 and the product prepared from Zn2+/HUS-2. b, Tapping mode AFM images of C16+/HUS-2, CP/HUS-2 and the product prepared from Zn2+/HUS-2. The upper and lower panels are topography and phase images, respectively.
Figure S9. Adsorption isotherm of bdc on C\textsubscript{16}+/HUS-2 form dmf solution. Horizontal dashed line indicates cation exchange capacity of HUS-2.
Figure S10. N\textsubscript{2} adsorption isotherms of CP/HUS-2 before and after exposure to a helium gas containing different amounts of water vapour.
Figure S11. Thermogravimetric-differential thermal analysis curves of CP/HUS-2.
References

