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Immobilization of Sodium Ions on the Pore Surface of a Porous Coordination Polymer

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Modification of chemical properties of porous coordination polymers (PCPs) is an ongoing challenge in the area of material chemistry.[1] Especially, PCPs with functional groups, such as open metal sites or metal-free organic groups in the pores, are currently the focus of heterogeneous catalysts or selective guest adsorbents.[2]

In addition to transition metal ions, alkali cations are intriguing because of their various coordination modes, low polarizability, and unique affinity for basic molecules ranging from a strong base, NH_3, to a weak one, acetone. For instance, alkali cations in zeolites are well-known to be catalytic sites for hydrocarbon transformation and also serve as guest recognition sites in biological systems.[3] From this viewpoint, a PCP whose pore surfaces immobilize regularly ordered and available alkali cations is one of the challenges toward materials with high performance pores. For this purpose, alkali cations should not sit at connector sites of a framework but at linker sites, which mainly afford the guest-accessible pore interiors. Therefore, we designed a heterometallic PCP containing transition metal ions as connectors of a framework and alkali metal ions as affinity sites on the pore surface. In this report, we synthesized a thermally stable Cd(II) PCP framework with immobilization of the sodium cations into the pore surface by employing a bifunctional carboxylate/sulfonate ligand. The carboxylate group favors transition metal ions in coordination, whereas the sulfonate group can easily coordinate to alkali metal ions.[4] We also estimated the affinity of alkali metal sites for guests and their adsorption properties by solid-state NMR and adsorption measurements.

Heterometallic microporous coordination polymer, $\{[\mathrm{CdNa(2\text{-}stp)(dabco)_{0.5}(H_2O)]\cdot 2H_2O}\}_n$ (2-stp = 2-sulfonylterephthalate, dabco = 1,4-diazabicyclo[2,2,2]octane) ($\mathbf{1{\supset}3H_2O}$), was prepared by the reaction of $Cd(NO_3)_2\cdot 4H_2O$ with 2-stpNa and dabco in H_2O/EtOH media under basic conditions using NaOH. The crystal structure of $\mathbf{1{\supset}3H_2O}$ was determined by single-crystal X-ray crystallography,[5] and Figure 1a shows the structure around the Cd(II) and Na(I) ions at 223 K. The asymmetric unit contains each one of Cd(II), Na(I), 2-stp, one coordinated and two guest water molecules, and 0.5 dabco ligands. The Cd(II) atoms are heptacoordinated to four O atoms from the two bidentate carboxylate groups and two O atoms from monodentate sulfonate groups of 2-stp and one dabco nitrogen atom. Na(I) cations have hexacoordination environments and are bound to two O atoms of the sulfonate group, three O atoms of the monodentate carboxylate groups, and one water molecule. All the benzene rings of 2-stp are parallel to the *ac* planes, and the sulfonate group of 2-stp links Cd(II) centers along the *b* axis. As a consequence, the neutral 2D layers that consist of Cd(II), Na(I), and 2-stp sit on the *ab* plane, and the dabco ligands connect each of the layers to build a rigid 3D pillared-layer-type porous structure (Figure 1b). This compound possesses straight 1D channels along the *b* axis with a cross-section of approximately 4.9 × 4.9 Å^2, and the sodium cations are immobilized on the pore surfaces with one coordinated water molecule. The total void volume, V_{void}, within the crystal of $\mathbf{1{\supset}H_2O}$ without water guests is 20.6% per unit volume determined by PLATON.[6] The thermogravimetric analysis (TGA) performed on as-synthesized $\mathbf{1{\supset}3H_2O}$ (Figure S1) shows the first weight loss of 11.5%, from 25 to 150 °C. This corresponds to the loss of the three water molecules per formula unit: one water coordinated to Na(I) and the other to the guests (calculated 11.1%). After simultaneous removal of the guest and coordinated water molecules, no obvious weight loss steps occurred below 330 °C, indicating that the anhydrous porous structure of **1** is highly stable up to 300 °C. The thermal stability was also confirmed by XRPD measurement (Figure S2). Figure 2a shows the coordination atmosphere of the pentacoordinated sodium ions with their sixth site open for a guest, which are regularly embedded in the 1D pore wall. Consequently, the V_{void} of **1** is 25.7%. The cross-section of the 1D channel of **1** running parallel to the *b* axis is represented in Figure 2b. The interatomic distance between the adjacent Na(I) along the *b* axis is 7.08 Å, resulting in a high density of Na(I) in the porous structure (2.3 mmol/g). In a few minutes of exposure of **1** to open air, this rapidly changed to $\mathbf{1{\supset}H_2O}$, and a long time exposure (over 1 day) provides the further water sorption to $\mathbf{1{\supset}3H_2O}$.

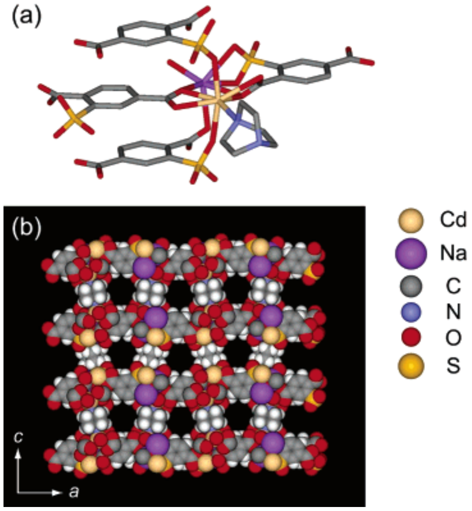

Figure 1. (a) Crystallographic environment around Cd(II) and Na(I) centers (H atoms are omitted). (b) Three-dimensional assembled structure of $\mathbf{1{\supset}H_2O}$. Guests are omitted.

After de-gas treatment at 140 °C for 10 h under low pressure, the adsorption isotherm of CO_2 on **1** at 195 K was measured (Figure

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10.1021/ja0606879 CCC: $33.50 © 2006 American Chemical Society

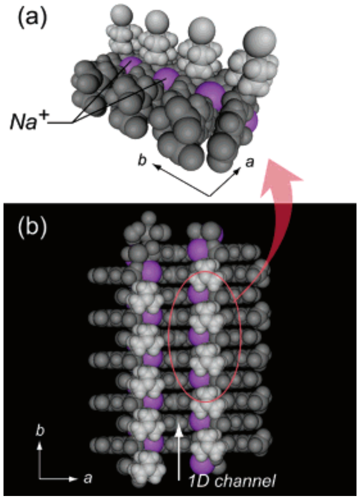

Figure 2. (a) View of the coordination environment around Na(I). (b) A cross-section of 1D channel of **1** along the *b* axis. Purple, dark gray, and light gray represent Na(I), 2D sheet, and pillar ligand systems, respectively.

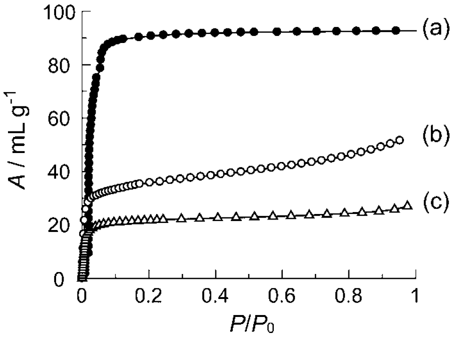

Figure 3. Adsorption isotherms of (a) CO_2 (195 K), (b) acetone (298 K), and (c) benzene (298 K) for **1**.

3a). This adsorption isotherm is a Type I as defined by the IUPAC classification, confirming the presence of uniform micropores inside the framework. The saturated adsorbed amount of CO_2 is about 92.6 mL/g at $P/P_0 = 0.95$ and 1.8 molecules per Na(I) ion. To assess the Lewis acid strength of the Na(I) sites, we employed acetone as a guest. Acetone is a good probe to determine the Brønsted/Lewis acid strength of porous media with NMR technique.[7,8] First we measured the adsorption isotherm of acetone at 298 K shown in Figure 3b. This also shows Type I uptake, and the amount of acetone at $P/P_0 = 0.95$ is consistent with 1.0 molecule per Na(I) ion. Taking the size of acetone (6.60 × 4.13 × 5.23 Å^3)[9] and pore dimension into account, the guests are expected to be confined and located around the Na(I) ions. The solid-state ^{13}C CPMAS NMR of **1⊃acetone** was measured (Figure S3). The chemical shift of acetone-2-^{13}C resonance appears at 212.1 ppm, and this shows downfield shift from its normal resonance position at 206 ppm.[7,10] The Na(I) ions of **1** operate as an electron-withdrawing site for the O atom of acetone, and the only one sharp peak indicates that all the adsorbed acetone molecules interact with Na(I) ions. This NMR spectrum represents that **1** has Lewis acidic pores, whose acidity strength is slightly smaller than that of HX zeolite. To obtain the characteristic adsorption energy (βE_0) of acetone on **1**, which is related to the energetics of the adsorbate/adsorbent system, the DR equation was used to fit the experimental adsorption isotherm.[11] From the linear plot at high P/P_0 region, $\beta E_0 = 18.8$ kJ/mol is obtained. This value is greater than that of physisorbed acetone in microporous activated carbons (∼14 kJ/mol),[12] indicative of the attractive effect of the sodium ions.

In the case of benzene as a guest, the isotherm at 298 K also shows adsorption from low P/P_0 and the saturated amount is 26 mL/g (0.5 molecules) per Na(I). To determine the adsorption behavior of benzene in **1**, we performed a solid-state ^{2}H NMR measurement for full loading of $\mathbf{1{\supset}C_6D_6}$, and the fast rotation of benzene around its C_6 axis is observed at below 233 K (Figure S4). This anisotropic motion has also been observed in several zeolites with alkali cations,[13] where benzene molecules are confined through Lewis acid attractive interaction of the sodium cations. The design for PCPs could provide a series of acidic pore surfaces by tuning pillar ligands or alkali cations.

In summary, we have first demonstrated the synthesis of the heterometallic PCP containing 1D channels with ordered usable Na(I) cations with the aid of a carboxylate/sulfonate bifunctional ligand. The stable framework of **1** showed Lewis acidic property with the anisotropic confinement of basic guests around Na(I) sites. This result paves the way for the development of high performance PCPs toward porous material chemistry.

Acknowledgment. This work was supported by Grant-In-Aid for Science Research in a Priority Area "Chemistry of Coordination Space" (No. 464) from the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: Synthesis, crystallographic data, NMR spectra, XRPD patterns, and TGA curve for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) Crystal data for $\mathbf{1{\supset}3H_2O}$: $C_{11}H_9NO_{10}NaSCd$, fw = 482.64, orthorhombic, space group *Pbcn*, $a = 20.720(3)$ Å, $b = 7.0822(10)$ Å, $c = 22.878(3)$ Å, $V = 3357.2(8)$ Å^3, $Z = 8$, $T = 223$ K, $D_c = 1.910$ g/cm^3; $R_1 = 0.0744$, $wR_2 = 0.2001$, GOF = 1.098.
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JA0606879