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Highly Selective Sorption of Small Polar Molecules by a Nonporous Ionic Crystal of a Lacunary Keggin-type Heteropoly Anion and Alkali Metal Cations

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Cesium–potassium salt of the lacunary phosphotungstate $Cs_{6.1}K_{0.9}[PW_{11}O_{39}]$, which is a nonporous ionic solid, absorbed only water and methanol, whereas larger alcohols ($C \geq 2$) and hydrocarbons were completely excluded. $Cs_{6.1}K_{0.9}[PW_{11}O_{39}]$ selectively removed water from water–ethanol mixed gas and was reusable by vacuum treatment at room temperature.

Nanostructured materials that sorb particular molecules can be used in a variety of applications, such as gas storage,[1] separation,[2] and heterogeneous catalysis.[3] Aluminosilicate zeolites and their inorganic analogues, like aluminophosphate, are examples of such materials.[3–5] Zeolites have well-defined molecular-sized pores, in which shape-selective adsorption and catalysis can occur.[3–11] Recently, there is great interest in organic zeolites constructed with organic and organometallic building blocks because they can have flexible channels when appropriate organic functional groups are used, leading to unique selective inclusion properties.[1,2,12]

Ionic crystals of polyoxometalates are nanostructured materials that are capable of selectively absorbing molecules.[13–22] These polyoxometalates can absorb molecules into the solid bulk via strong interactions between the absorbed molecules and constituent cations and/or anions. Acid-type polyoxometalate compounds, like $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, absorb polar molecules in the bulk, but the absorption is nonselective.[23–25] On the other hand, nonacidic ionic crystals formed with Keggin-type polyoxometalates ($[\alpha\text{-}XW_{12}O_{40}]^{n-}$), macrocations including $[Cr_3O(OOCR)_6Y_3]^+$ ($R = H$, C_nH_m and $Y = H_2O$, pyridine), and alkali metal cations exhibit selective sorption properties; that is, they discriminate the molecules depending on the size, polarity, and hydrophobicity/hydrophilicity.[13–20] The absorption properties are finely controlled by adjusting the charge of the polyoxometalates and the organic moiety of the macrocations. For example, $K_3[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-}SiW_{12}O_{40}]$ absorbs polar organic molecules up to C2,[13] whereas $Cs_5[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-}CoW_{12}O_{40}]$ absorbs only water.[13] $A_2[Cr_3O(OOCC_2H_5)_6(H_2O)_3]_2[\alpha\text{-}SiW_{12}O_{40}]$ ($A = K$, Rb, Cs, and NH_4) has both hydrophilic and hydrophobic channels in the crystal lattice and shows amphiphilic sorption abilities.[18,19] Herein we report the highly selective absorption of small polar molecules, including water and methanol, by a macrocation-free, completely inorganic ionic crystal of a lacunary Keggin-type heteropoly anion ($[\alpha\text{-}PW_{11}O_{39}]^{7-}$) and alkaline cations: $Cs_{6.1}K_{0.9}[PW_{11}O_{39}]$ (**1**).[26]

1 was synthesized as follows: $K_7PW_{11}O_{39}\cdot nH_2O$ (5.00 g) was dissolved in water (100 mL). An aqueous solution of CsCl, which was prepared by dissolving CsCl (1.89 g, 11.2 mmol) in water (20 mL), was added to the $K_7PW_{11}O_{39}$ solution with vigorous stirring. The resulting solution was allowed to stand for 1 day at room temperature, during which time a white solid precipitated. The white solid ($Cs_{6.1}K_{0.9}PW_{11}O_{39}\cdot 9.3H_2O$, **2**) was separated via filtration and dried at 333 K overnight. **2** was treated in a vacuum or under N_2 flow at 473 K for 2 h to afford **1**.

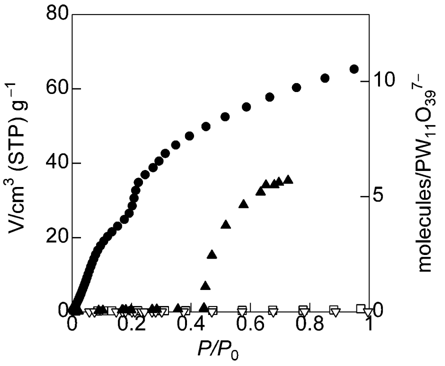

Figure 1. Sorption isotherms for $Cs_{6.1}K_{0.9}PW_{11}O_{39}$ (**1**) at 298 K. (●) Water, $P_0 = 3.17$ kPa, (▲) methanol, $P_0 = 16.9$ kPa, (□) ethanol, $P_0 = 7.87$ kPa, and (▽) 1-propanol, $P_0 = 2.98$ kPa.

Figure 1 shows sorption isotherms of water, methanol, ethanol, and 1-propanol for **1** at 298 K. The isotherms showed that ethanol and 1-propanol were completely excluded. In addition, *n*-hexane and benzene were completely excluded (data not shown). They were excluded because **1** has a low Brunauer–Emmett–Teller (BET) surface area ($0.9\ m^2\ g^{-1}$), which was calculated from the adsorption isotherm of N_2 at 77 K (Figure S1[27]). In contrast, the amount of sorbed water increased with an increase in P/P_0 and reached ca. $65\ cm^3\ g^{-1}$ at $P/P_0 = 0.95$, which corresponds to a $H_2O/PW_{11}O_{39}{}^{7-}$ ratio of 10.5. The amount of saturated water was basically equal to that of lattice water in **2**. Since the possible amount of water adsorbed on the outer surface calculated from the BET surface area ($0.9\ m^2\ g^{-1}$) of **1** was $0.27\ cm^3\ g^{-1}$, which is much smaller than the actual amount of sorbed water (ca. $65\ cm^3\ g^{-1}$); **1** absorbs water molecules into its bulk. In the absorption isotherm of water, the amount of sorbed water increased in a stepwise manner: the amount sharply increased up to $H_2O/PW_{11}O_{39}{}^{7-} = 4$ from $P/P_0 = 0.02$ to 0.18 and then sharply increased again to $H_2O/PW_{11}O_{39}{}^{7-} = 6$ from $P/P_0 = 0.20$ to 0.28, followed by a gradual increase to $H_2O/PW_{11}O_{39}{}^{7-} = 10.5$. This result indicates that at least two or more water adsorption sites are present in the bulk of **1**. In addition, the amount of water at the second step ($P/P_0 = 0.28$) was $H_2O/PW_{11}O_{39}{}^{7-} = 6$, which corresponded to the amount of Cs^+ in

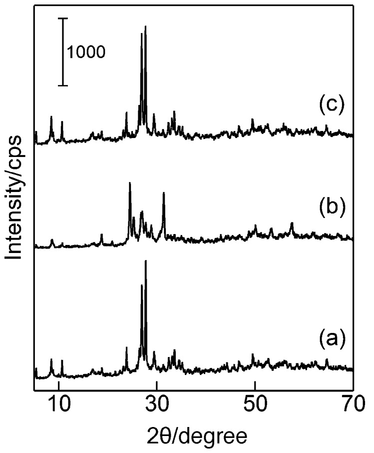

Figure 2. Powder XRD patterns of (a) **2**, (b) **1**, and (c) the material obtained by exposing **1** to saturated water vapor at 298 K for 24 h.

1, suggesting that water molecules interact mainly with Cs^+, not with heteropoly anion. The absorption of water could be repeated at least five times by vacuum treatment at 473 K for 3 h (Figure S2[27]) or at 298 K overnight (Figure S3[27]).

Powder X-ray diffraction (XRD) patterns of **2** gave sharp diffraction lines (Figure 2). When **2** was transformed into **1** by treating it in a vacuum at 473 K for 2 h, the XRD pattern changed dramatically. However, the material obtained by exposing **1** to saturated water vapor at 298 K for 24 h gave essentially the same pattern as that for initial **2**, meaning that water absorption was reversible.

The amount of sorbed methanol was small at low pressures, but a sudden uptake occurred around $P/P_0 = 0.44$. At $P/P_0 = 0.6$, the $CH_3OH/PW_{11}O_{39}{}^{7-}$ ratio saturated at ca. 6. When **1** absorbed methanol, its crystal lattice expanded, similar to when water molecules were absorbed. Since **1** excluded molecules like methane and argon, the cross-sectional areas of which are smaller than that of methanol, at 298 K only a small amount of acetonitrile was absorbed into **1** (data not shown), the interaction between the OH group of methanol and Cs^+ controls the absorption. Namely, interactions between water and methanol and Cs^+, like dipole–ion interactions, can overcome the energy needed for expanding the lattice of **1**. Since ethanol and 1-propanol require a larger lattice expansion in order to be absorbed into the bulk of **1** due to the large-sized molecule, they were excluded because there was not enough energy to overcome that needed to expand the lattice. Glendening and Feller[28] and Lee et al.[29] demonstrated by ab initio molecular orbital calculations that the interaction energy between Cs^+ and water was not so large, comparing with those in the case of other alkali metal cations including Li^+, Na^+, K^+, and Rb^+. In other words, such weak interaction between Cs^+ and water as well as methanol resulted in the selective sorption property of **1**.

It should be noted that the alkaline cations present in the ionic crystals strongly affect their absorption properties. As shown in Figure S4,[27] $K_7PW_{11}O_{39}$, which was obtained by treating $K_7PW_{11}O_{39}\cdot nH_2O$ in vacuum at 473 K, absorbed water and excluded methanol. On the other hand, $Cs_7PW_{11}O_{39}$ absorbed methanol as well as water at low pressures (Figure S5[27]), which is quite different from the absorption behavior of **1**. Differences in the energies of the interactions between methanol and Cs^+ and K^+ likely cause the differences in the absorption properties. However, further investigations are needed to understand the effects of the cations.

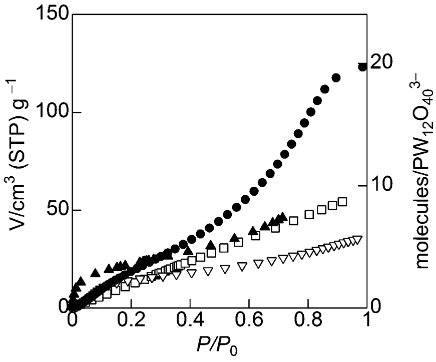

Figure 3. Sorption isotherms for $Cs_3PW_{12}O_{40}$ at 298 K. (●) Water, $P_0 = 3.17$ kPa, (▲) methanol, $P_0 = 16.9$ kPa, (□) ethanol, $P_0 = 7.87$ kPa, and (▽) 1-propanol, $P_0 = 2.80$ kPa.

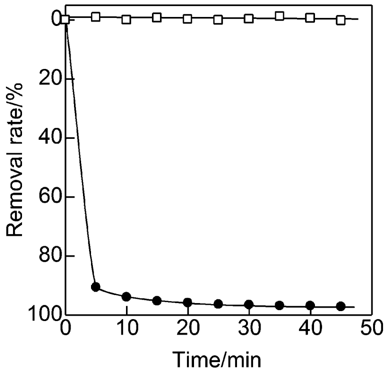

Figure 4. Selective removal of water from water–ethanol mixed gas over **1** at 298 K. (●) Water and (□) ethanol. The experiment was carried out in a closed gas-circulation system with an online gas chromatograph. Initial amounts of water and ethanol were 7.2 and 25.4 μmol, respectively and weight of **1** was 0.2 g.

For comparison, sorption isotherms were obtained for an ionic crystal of a consummate Keggin-type heteropoly anion and Cs^+, $Cs_3PW_{12}O_{40}$, at 298 K (Figure 3), whose BET surface area was calculated to be $130\,m^2\,g^{-1}$ from a N_2 adsorption isotherm at 77 K (Figure S6[27]). Unlike **1**, large amounts of ethanol and 1-propanol, as well as water and methanol, were sorbed on $Cs_3PW_{12}O_{40}$ due to its large surface area. In other words, the sorptions were not selective. The BET surface areas calculated from the isotherms of water, ethanol, and 1-propanol in the P/P_0 range of 0.1–0.3 were 81, 95, and $75\,m^2\,g^{-1}$, respectively. Since the surface areas are consistent with that calculated from the N_2 adsorption isotherm at 77 K, $Cs_3PW_{12}O_{40}$ adsorbs only on the surface, similar to normal solid materials.

The characteristic absorption behavior of **1**, that is, only water molecules can be absorbed into it at low pressure, can be applied to the selective removal of water from lower alcohols. In fact, it was demonstrated that **1** sorbed only water in water–ethanol mixed gas at 298 K (Figure 4) and was reusable only by vacuum treatment at 298 K (Figure S7[27]). In contrast, only a small amount of water was removed over Na_2SO_4, and both ethanol and water were included over molecular sieves 3A (Figure S8[27]), which are well-known and frequently utilized dehydrating agents. Therefore, we concluded that **1** is a new molecular sieve for small polar molecules and is especially useful as a dehydrating agent.

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26 Elemental analysis for $Cs_{6.1}K_{0.9}PW_{11}O_{39}\cdot 9.3H_2O$ (**2**): calculated: Cs, 23.2; K, 0.52; P, 0.83; W, 54.2%; found: Cs, 23.1; K, 1.03; P, 0.88; W, 53.8%. IR spectra of **2** (KBr), which was exposed to water under ambient conditions, gave bands at 1085 and 1040 cm^{-1} (ν_{as} P–O), 950 cm^{-1} (ν W–O_d), 900 and 860 cm^{-1} (ν W–O_b–W), and 810 and 725 cm^{-1} (ν W–O_c–W). ^{31}P MAS NMR spectrum of **2** gave a peak at −10.7 ppm. The weight loss of **2** on TG profile under He flow up to 473 K was 4.6 wt%, which corresponds to $H_2O/PW_{11}O_{40}{}^{7-} = 9.3$.
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