Microporous Materials

DOI: 10.1002/ange.200604353

A Mesh-Adjustable Molecular Sieve for General Use in Gas Separation**

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Gas separation using molecular sieves (MSs) is a environmentally benign, energy-conserving alternative to traditional separation processes, such as distillation and absorption.[1] When using zeolite MSs,[2–4] an accurate one-on-one match between the mesh size and the separation need is essential. However, when the size disparity of the two gases to be separated is small, a MS with the optimum mesh size is not always readily available. A mismatch inevitably leads to an inefficient separation. Recently, titanosilicate was shown to possess superior flexibility over that of traditional zeolites; a few MSs with discrete mesh sizes were made based on the degree of dehydration of this material at various temperatures.[5] Nevertheless, a MS with more than one mesh size has never been made in the past. Herein, we report the design, synthesis, and application of a novel mesh-adjustable molecular sieve (MAMS-1) that possesses an infinite number of mesh sizes. MAMS-1 is based on a metal–organic framework (MOF), compounds known for their dynamic porous properties.[6] However, the concept of a MAMS has never appeared in the literature prior to the present work. MAMS-1 represents a MOF-based MS whose mesh can be adjusted continuously. The mesh range of MAMS-1 falls between 2.9 and 5.0 Å, which covers the size range of almost all commercially important gas separations. When the temperature is precisely controlled, any mesh size within this range can be accurately attained. Gas separations such as those of N_2/O_2 and N_2/CH_4, which are normally difficult to achieve, are readily attainable by using MAMS-1. In principle, by precise temperature control, any two gases with a size difference can be separated by a MAMS.

MOFs have attracted a great deal of attention because of their unique structures[6a,7] and potential applications in catalysis,[8] separation,[9] and gas storage.[10] In particular, flexible MOFs[6] have caught enormous attention lately. Numerous studies have indicated that the key to constructing a flexible MOF lies in the utilization of weak interactions, such as hydrogen bonding, π–π stacking, and hydrophobic interaction, in addition to strong covalent and coordinative bonding.[6] Flexible MOFs based on hydrogen bonding have been widely studied,[6b,c] but those originating from π–π stacking and hydrophobic interaction[11] have rarely been explored.

To make a MAMS, two factors must be taken into account: the material must have permanent porosity to hold gas molecules, and the pores must be flexible. The former usually requires strong bonds, while the latter implies weak interactions in the framework. These two seemingly irreconcilable prerequisites for a MAMS can be met simultaneously by using a graphitic structure, in which atoms in each layer are connected covalently but the layers are held together by weak interactions. One approach to such a graphitic MOF is to apply an amphiphilic ligand that consists of hydrophobic and hydrophilic ends, similar to a surfactant,[12] but with the hydrophilic end functionalized. The functional group at the hydrophilic end of the ligand will bind metal ions/clusters, and the structure will propagate into a 2D layer. Two layers of ligands will sandwich a metal-ion/cluster layer, thus giving rise to a trilayer, and these trilayers will pack through van der Waals interaction.

The ligand adopted for the aforementioned purposes is 5-*tert*-butyl-1,3-benzenedicarboxylate (bbdc), which was previously used in our laboratory to build a micelle-like cuboctahedral cage to adjust the solubility of a 24-molybdenum cluster.[13] Recently, it was also used in a zinc microporous MOF.[9e]

In fact, solvothermal reaction between H_2(bbdc) and $Ni(NO_3)_2$ in H_2O/ethylene glycol in a Teflon-lined autoclave afforded such a graphitic structure, $[Ni_8(5\text{-bbdc})_6(\mu_3\text{-OH})_4]$ (designated MAMS-1 for convenience). Desolvated MAMS-1 demonstrates temperature-induced molecular-gating effects in which the size of the gates can be tuned continuously from 2.9 to 5.0 Å for the first time. Commercially relevant gas separations, such as those of H_2/N_2, H_2/CO, N_2/O_2, N_2/CH_4, CH_4/C_2H_4, and C_2H_4/C_3H_6, can be achieved by MAMS-1. In principle, by precise temperature control, any mesh size within this range can be achieved. In fact, all the pairs of gases listed above have been separated by using MAMS-1.

Single-crystal X-ray analysis[14] revealed that MAMS-1 contains an octanickel $[Ni_8(\mu_3\text{-OH})_4]$ cluster as one of the two secondary building units (SBUs; Figure 1a), the other being the bbdc ligand. The eight octahedral Ni atoms are divided into four pairs by a twofold axis through the center of the cluster. Ni1 binds five carboxylate O atoms from four bbdc ligands and one μ_3-OH group. Ni2 is coordinated by three carboxylate O atoms and three μ_3-OH groups. Ni3 is bound to four carboxylate O atoms, one μ_3-OH group, and an aqua

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[**] The authors thank the National Science Foundation (CHE-0449634), Miami University, and the donors of the American Chemical Society Petroleum Research Fund for financial support. H.-C.Z. also acknowledges the Research Corporation for a Research Innovation Award and a Cottrell Scholar Award. The diffractometers were funded by NSF grant EAR-0003201.

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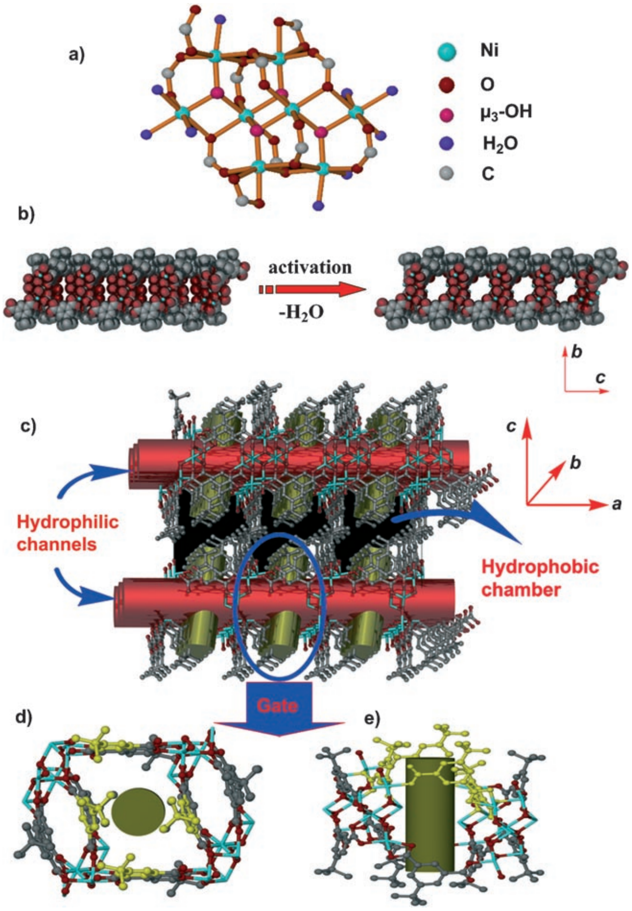

Figure 1. Crystal structure of MAMS-1. a) Structure of the octanickel cluster. b) Structures of solvated and desolvated trilayers. The desolvated trilayer displays hydrophilic channels along the *a* axis. c) Two trilayers pack along the *c* axis to form hydrophobic chambers. d) Top and e) side views of bbdc pairs.

ligand. Ni4 connects two carboxylate O atoms, one μ$_3$-OH group, and three aqua ligands.

Every octanickel cluster connects 12 bbdc ligands, and every bbdc ligand binds two octanickel clusters to afford a trilayer, with a hydrophilic cluster layer sandwiched by two hydrophobic bbdc layers (Figure 1 b). There are 1D channels along the *a* axis in the middle layer, in which guest water solvates reside. The trilayers, with their exposed hydrophobic exteriors, pack along the *c* axis through van der Waals forces (Figure 1 c), thus generating hydrophobic chambers between adjacent trilayers.

Freshly isolated MAMS-1 is not active for adsorption, which was confirmed by gas adsorption studies with CO_2 and H_2 (see the Supporting Information). MAMS-1 must be activated at an elevated temperature (Figure 1 b) as the crystal structure suggests. Thermogravimetric analysis of MAMS-1 reveals a loss of eight guest water molecules from 50 to 120 °C, and the release of eight bound aqua ligands per formula unit when heated to 250 °C (see the Supporting Information).

Gas adsorption studies at 77 K indicated that the sample evacuated at 120 °C cannot take up N_2 or H_2 (see the Supporting Information). After activation under a dynamic vacuum at 200 °C, MAMS-1 exhibits highly selective uptake of H_2 over CO, N_2, or O_2 (Figure 2 a). Such selectivity in MOFs has been reported previously in only two cases,[9b,d] but not with adjustable meshes.

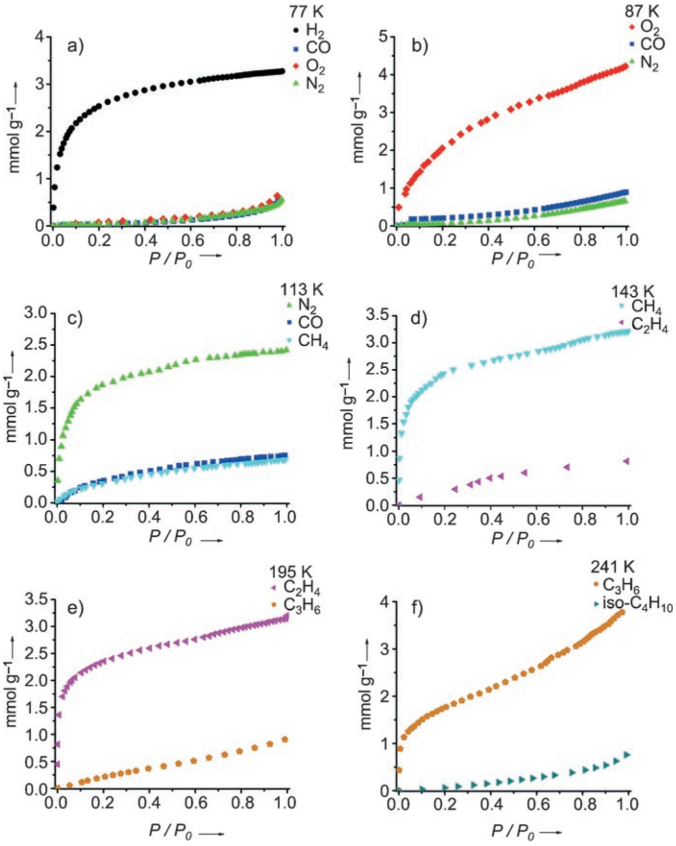

Figure 2. Gas adsorption isotherms at different temperatures: a) 77, b) 87, c) 113, d) 143, e) 195, and f) 241 K.

A close examination of the crystal structure reveals that the hydrophilic channels (atom-to-atom distance 8.0 Å; 5.0 Å when considering van der Waals radii)[15] are large enough to accommodate O_2, N_2, or CO molecules, which implies that the molecular gating effect has a different origin. In addition, the small pore volume of the hydrophilic channel is not large enough to account for the high H_2 uptake observed.

The crystal structure of MAMS-1 also shows that a hydrophobic chamber is accessible only through its hydrophobic/hydrophilic interface, on which two bbdc ligands point toward each other to form a gate based on van der Waals attraction between the two bbdc groups (Figure 1 d, e). When such gates are open the hydrophilic channels and hydrophobic chambers are all connected, thus giving rise to a 3D gas container with space continuity (Figure 1 c), which accounts for the high H_2 uptake of MAMS-1 at 77 K.

Most likely, the molecular sieving effect comes from the bbdc gates. In view of the kinetic diameters of 2.89, 3.46, 3.64, and 3.76 Å for H_2, O_2, N_2, and CO, respectively,[16] it can be inferred that the gate opening of MAMS-1 is around 3.0 to 3.4 Å. At 77 K, MAMS-1 excludes CO, N_2, and O_2 but allows H_2 to enter the hydrophobic chambers.

If this is indeed the case, the gates should open wider at higher temperatures, because the thermal vibration of the two bbdc groups can readily overcome the weak van der Waals interaction between them. The larger the amplitude of vibration, the wider the gate will open. When the temperature is raised to liquid-argon temperature (87 K, Figure 2b), gas adsorption studies reveal that only a small amount of CO or N_2 is adsorbed by MAMS-1. However, MAMS-1 can take up a significant amount of O_2. The adsorption isotherm of O_2 shows type I behavior. Dioxygen (3.46 Å) can be selectively adsorbed from a mixture with N_2 (3.64 Å) and CO (3.76 Å), which implies that at 87 K the gate opens to around 3.5 Å. With the minute size disparity between O_2 and N_2 ($\Delta\sigma = 0.18$ Å) in mind, one has to be optimistic about the application potential of MAMS-1. However, an improved version of MAMS-1 should be capable of separating O_2 and N_2 at higher temperatures and will have enormous commercial impact. The next question to ask is: can MAMS-1 selectively adsorb N_2 from a mixture with CO and CH_4? This would also address an important application in industrial ammonia synthesis.

As expected, at 113 K MAMS-1 can take up a moderate amount of N_2 but relatively low quantities of CO and CH_4 (3.8 Å; Figure 2c). This finding is also consistent with the idea that the gating effect is a result of the pair of bbdc ligands, and the gate opens wider at increased temperatures. This also implies that at 113 K the gate opens to about 3.7 Å, which is wide enough to allow N_2 (3.64 Å) to enter the chambers, but molecules with larger kinetic diameters, such as CO (3.76 Å) and CH_4 (3.8 Å), will stay in the hydrophilic channels. The resolution for size discrimination is now 0.12 Å. In fact, it can be inferred from all the adsorption data obtained thus far that if temperatures can be tuned continuously and precisely, any two molecules with a size difference can be separated by MAMS-1.

With these considerations in mind, we decided to explore the possibility of using MAMS-1 in separations important to petroleum refining and the petrochemical industry. Not surprisingly, MAMS-1 can distinguish methane from ethylene at 143 K, ethylene from propylene at 195 K, and propylene from isobutane at 241 K (Figure 2d–f). Based on our data, it is certainly possible to design a temperature-swing apparatus based on MAMS-1 to perform fractional adsorption to separate a multicomponent mixture into pure fractions, just as in a distillation or absorption tower.

The mechanistic details of these unprecedented temperature-controlled gas-selective adsorption phenomena can be deduced from the crystal structure and adsorption data of MAMS-1 (Figure 3). The following are the major findings on MAMS-1:

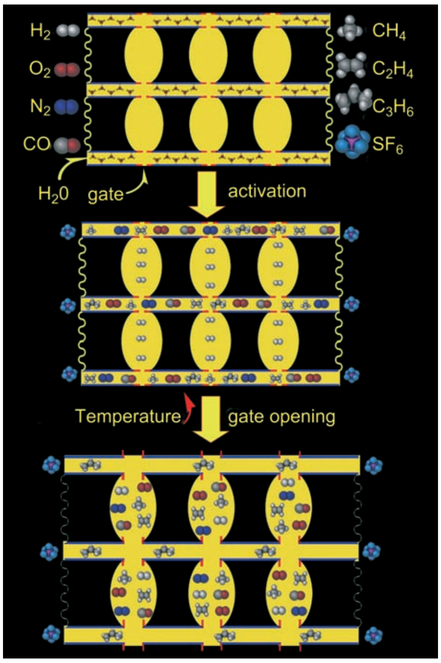

Figure 3. Schematic representation of the mechanism of the gating effect in MAMS-1.

1. The temperature-dependent molecular-gating effect does not arise from simple thermal expansion of the framework. This assessment is supported by the temperature independence of the cell parameters of MAMS-1 (see the Supporting Information).
2. The hydrophobic chambers are not accessible when the hydrophilic channels are closed, which not only can be inferred from the crystal structure but also is consistent with gas adsorption data. An inactivated sample had very low uptake of either H_2 or CO_2. A partially activated sample was inactive for gas uptake. The water guests and bound water ligands must be removed completely for MAMS-1 to be active for gas adsorption.
3. The hydrophilic channels alone are not responsible for the gas uptake. In fact, they account for only a very minor part of the adsorption. As the gas adsorption data at 77 K suggest, only H_2 can enter the hydrophobic chambers, and shows a significant uptake. At 77 K, other gas molecules stay in the hydrophilic channels, and the uptake of these gases is very low, as shown by adsorption studies.
4. Gas molecules must go through the hydrophilic channel to access the hydrophobic chambers. As previously mentioned, activation of the hydrophilic channels is a prerequisite for gas adsorption on MAMS-1. Further evidence for the hydrophilic channels being the only passage to the gas-storage chambers is provided by the observation that when the kinetic diameter of the gas molecule (for example, SF_6, 5.5 Å) exceeded the size of the hydrophilic channels (5.0 Å considering van der Waals radii), no meaningful uptake was observed in an adsorption study (see the Supporting Information). The upper limit of the channel is also consistent with an adsorption study on isobutane (5.0 Å), which is allowed to enter MAMS-1 at room temperature (see the Supporting Information).
5. Gas molecules enter the hydrophobic gas-storage chambers through the interface between the hydrophobic and hydrophilic channels, which accounts for the majority of gas uptake. The interface is controlled by a pair of bbdc ligands, which act as a gate. The opening of this gate is controlled by the amplitude of the thermal vibration. A plot of temperature versus size of the molecule allowed to enter the gate is presented in Figure 4. The data point at

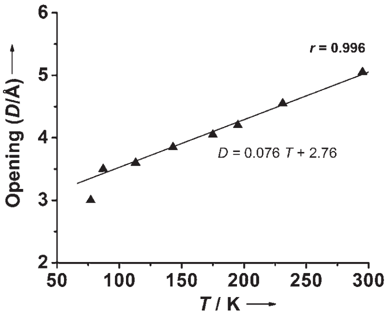

Figure 4. Temperature-dependent gate opening of MAMS-1. ▲: experimental values; ——: linear fit.

77 K gives an underestimation of the gate opening, because a gas molecule with a size between 2.89 Å (H_2) and 3.40 Å (Ar) is not available for gas adsorption studies. Ignoring the point at 77 K, the gate opening D and temperature T can be related by a linear equation, $D = 0.0076\,T + 2.76$, with a correlation coefficient of 0.996 (Figure 4). This equation can be used to predict whether a gas molecule will be allowed to enter the gate at a certain temperature. It can also be used to find the best temperature for the separation of a mixture.

In summary, by using an amphiphilic ligand (bbdc) in a solvothermal reaction with $Ni(NO_3)_2$, we obtained a graphitic MOF structure (MAMS-1) generated by packing of trilayers through van der Waals interactions. In each trilayer, a hydrophilic octanickel cluster layer is sandwiched by two hydrophobic bbdc layers. Packing of the trilayers generates hydrophobic gas-storage chambers, which are not accessible without activation. There are channels in the hydrophilic layer that can be desolvated at 200 °C under a dynamic vacuum, which activates MAMS-1 for gas storage. Gas molecules enter the hydrophobic gas-storage chambers through the hydrophilic channels and gates in the hydrophobic/hydrophilic interface. A gate is formed by a pair of bbdc groups held in close proximity through van der Waals interaction, which is readily weakened by thermal vibration. As the temperature increases the gates of MAMS-1 open linearly, thus giving rise to an unprecedented molecular sieve with an adjustable mesh that can separate any two gases with kinetic diameters in the range of 2.9 to 5.0 Å, which corresponds to the size limits of most commercially relevant gases. In addition, a linear relationship between mesh size and temperature, $D = D_0 + a\,T$ (D = mesh size (in Å) at temperature T (in K), D_0 = mesh size at 0 K, and a = constant), has also been discovered. Mechanistic studies of the molecular gating effect of MAMS-1 suggest that D_0 can be tuned by ligand design, which implies the possibility of a MAMS that will be omnipotent in gas separation even at ambient temperatures.

Experimental Section

Synthesis of MAMS-1: 5-*tert*-Butyl-1,3-benzenedicarboxylic acid (H_2(bbdc); 0.075 g, 0.34 mmol) and $Ni(NO_3)_2{\cdot}6\,H_2O$ (0.15 g, 0.51 mmol) in H_2O/ethylene glycol (4:1 v/v, 7.5 mL) were placed in a 20-mL Teflon container and sealed in an autoclave. The autoclave was heated to 210 °C (heating rate 2 °C min^{-1}) in a programmable oven, and this temperature was maintained for 24 h before the autoclave was cooled to room temperature (cooling rate 0.5 °C min^{-1}). The light-green needlelike crystals obtained were washed with distilled water and methanol to give pure MAMS-1 with the formula $[Ni_8(C_{12}H_{12}O_4)_6(H_2O)_8(\mu_3\text{-}OH)_4]{\cdot}8\,H_2O$ (55 % yield based on H_2-(bbdc)). Elemental analysis (%) calcd: C 40.28, H 5.07, O 32.79; found: C 40.69, H 5.07, O 33.05. IR: $\tilde{\nu}$ = 3305 (w, br), 2960 (m), 1620 (m), 1571 (m), 1419 (m), 1347 (vs), 1275 (m), 1098 (m), 1033 (s), 865 (s), 785 cm^{-1} (m).

Received: October 24, 2006
Revised: November 20, 2006

Keywords: amphiphiles · gas separation · layered compounds · microporous materials · molecular sieves

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[14] Crystal structure determination of MAMS-1, $C_{36}H_{52}Ni_4O_{21}$: $M_r = 1055.62$, green block, $0.23 \times 0.08 \times 0.08$ mm, $T = 213(2)$ K, $\lambda(\mathrm{Mo}_{K\alpha}) = 0.71073$ Å, monoclinic, space group $P21/c$, $a = 10.9685(2)$, $b = 11.308(2)$, $c = 38.405(7)$ Å, $\beta = 96.781(3)°$, $V = 4730.1(14)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.482\ \mathrm{g\,cm^{-3}}$; R_1 $(I > 2\sigma(I)) = 0.0609$, wR_2 (all data) $= 0.1456$, GOF $= 1.021$. CCDC-617998 (MAMS-1) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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