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“Twin Copper Source” Growth of Metal−Organic Framework Membrane: $Cu_3(BTC)_2$ with High Permeability and Selectivity for Recycling H_2

Hailing Guo, Guangshan Zhu,* Ian J. Hewitt, and Shilun Qiu*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China

Received September 20, 2008; E-mail: zhugs@jlu.edu.cn; sqiu@jlu.edu.cn

Metal−organic frameworks (MOFs) have emerged as a unique class of porous materials due to their potential in many applications such as gas sorption, molecular separation, storage, optics, and catalysis.[1−4] To date, research efforts have been mainly focused on the synthesis of novel structures generally by judicious selection of organic ligands and inorganic molecular building blocks (formed in situ) to construct tailored frameworks with desired properties.[5−9] However, little progress has been made to construct MOF-based films that are useful for applications in separation or sensing. Porous solid based films, namely inorganic zeolite membranes, have been shown to be efficient for gas separation.[10] Nevertheless difficulties in functionalizing the pores and thus controlling their flux properties have limited their universal application. The versatility of MOFs may allow these limitations to be overcome and provide new routes to synthesis of tunable supports for gas separation. However the preparation of thin films in this field remains an important challenge. As in the synthesis of zeolite membranes, either an in situ or a secondary-growth method can be applied.[10] If we use the in situ synthetic approach it is essential to promote the growth of crystalline material on the support rather than free growth, as shown by Fischer and Bein where an MOF crystalline surface is grown on different functionalized self-assembled monolayers (SAMs).[11] When using the secondary-growth method, it is important to fix small nanosize MOF seeds to the support surface: as demonstrated by Gascon were a $Cu_3(BTC)_2$ membrane was synthesized on α-alumina by a seeding approach.[12a] However they were unable to obtain a uniform, highly ordered, smooth membrane surface free from cracks or intercrystal gaps. Heterogeneous nucleation and crystallite intergrowth are recognized as necessary components for the formation of a continuous MOF membrane. Herein, we use a copper net to provide homogeneous nucleation sites to support a continuous MOF film growth. We chose to use the ($Cu_3(BTC)_2$) MOF ($Cu_3(C_9H_3O_6)_2(H_2O)_3 \cdot xH_2O$, HKUST-1A) due to its structural features and thermal stability as well as its sorption properties.[12b] The $Cu_3(BTC)_2$ MOF has an intersecting three-dimensional network containing large pores with a square cross section (9×9 Å^2), desirable for gas separation and purification.

The thin MOF film was prepared from a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (3.5 g) and BTC (1.68 g) dissolved in a water/ethanol solution (96 mL/96 mL).[12b] To this solution a modified copper support was introduced, and a copper net (400 mesh) cut into circular wafers (10 mm in diameter) was washed with ethanol for 30 min and then five times using water under ultrasound to clean the surface and then placed in an oven at 100 °C for oxidation, monitored by the color from yellow to green. The oxidized copper net was placed vertically in a Teflon-lined autoclave to allow crystal growth at 120 °C for 3 days. After crystallization, the membrane was washed several times with ethanol and dried at room temperature. By oxidizing the copper net before the hydrothermal synthesis, homogeneous nucleation sites are formed for the continuous film growth. The ion of Cu^{2+} both on the copper net and in the reaction solution provided a metal source for crystal growth.

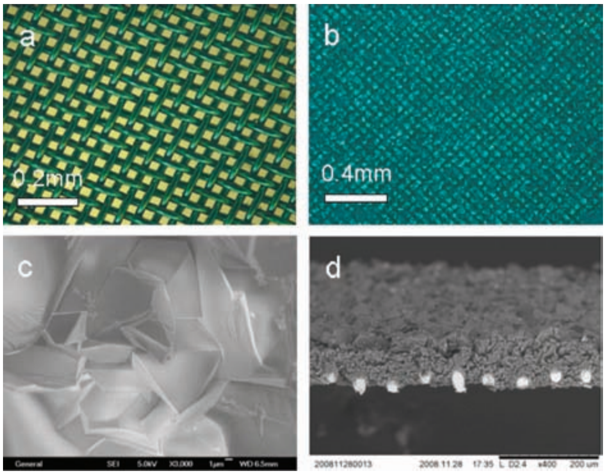

Figure 1. Optic micrographs of the (a) copper net and (b) net-supported $Cu_3(BTC)_2$ membrane; SEM image of (c) the surface and (d) cross section of the membrane.

Figure S1 shows the X-ray diffraction patterns of the $Cu_3(BTC)_2$ crystalline powder (Figure S1b) and of the copper-supported MOF membrane (Figure S1a), respectively. The XRD pattern of the membrane is similar to the $Cu_3(BTC)_2$ crystalline phase, thus indicating that the phase purity and homogeneity of the constructed crystalline membrane. The surface of the membrane was observed by both optical and scanning electron microscopy (SEM), as shown in Figure 1. Figure 1a shows the optical image of the modified copper net support with a 20 μm thread diameter and 20 μm voids in size. Figure 1b illustrates the optic micrograph of the copper net supported MOF membrane which indicates clearly that the copper net acts as a homogeneous support allowing the continuous formation of the membrane. The morphology of the membrane was observed more in detail using SEM (Figure 1c) and proven to be defect-free and that the 5−10 μm octahedral crystals merge tightly. From the cross-sectional view (Figure 1d), it can be seen that the crystals connect with the threads of the copper net compactly and uniformly and that the membrane has a thickness of nearly 60 μm, which is thinner. It is also of note that the present MOF based film contains a larger void volume compared to porous Al_2O_3 and ceramic supported materials.

Following the successful construction of the MOF based membrane, gas separation studies were investigated. The copper net supported $Cu_3(BTC)_2$ membrane was fixed in a gas separation setup (Figure S2) and then used for separation studies of H_2/CO_2, H_2/N_2, and H_2/CH_4 mixtures. The determined permeation and separation

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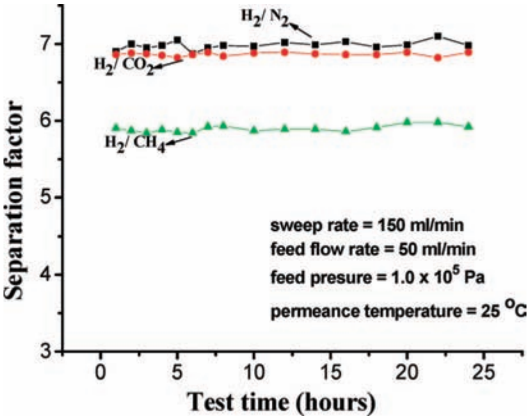

Figure 2. Plot of H_2/N_2, H_2/CH_4, and H_2/CO_2 separation factor of the copper net supported $Cu_3(BTC)_2$ membrane with change in test time.

factors are summarized in Table S1. The permeation flux of H_2 ($\sim 1 \times 10^{-1}$ mol·m^{-2}·s^{-1}) is much higher than those of other gases in the mixture systems showing that the membrane has a higher size selectivity preference for H_2. It can be explained that the small H_2 molecule goes through the HKUST-1 membrane more easily compared to the strong adsorbing sorbates (CO_2, N_2, and CH_4). It is also worth mentioning (as illustrated in Figure S3) that the sorption capacity of CO_2, CH_4, and N_2 is much higher than that of H_2. The reduced sorption of H_2 compared to the other sorbates is correlated to the structural and chemical futures of the present MOF favoring stronger interactions of CO_2, CH_4, and N_2. In Table S1, it is also noted that the separation factors of the H_2/N_2 and H_2/CO_2 mixture gas is higher than the ideal separation factors. However, we find that the H_2 and CH_4 ideal selectivity was higher than the separation selectivity, which can be explained by the slower-diffusing CH_4 prohibiting the diffusion of the faster-diffusing H_2, and accordingly the stronger sorbed CH_4 inhibits H_2 sorption in the mixture. The model also indicates that the CH_4 flux should be higher in the mixture than for the single gas because H_2 increases the CH_4 diffusion. We also find the separation factor of the mixture gas is still larger than the value of the Knudsen diffusion coefficient, which shows that the membrane is suitable for gas separation. Furthermore, compared with literature data on gas permeation properties of those material membranes, the HKUST-1 membrane from this study showed a better gas permeation performance, as shown in Table S2. The presently studied MOF has large channels permitting a much larger permeation flux of H_2 compared to other membranes reported in the open literature.[13] This unique property, high flux, is of great industrial importance for gas separation applications and is observed in our reported MOF membrane.

To assess the thermal stability of the $Cu_3(BTC)_2$ membrane, the separation temperature was increased from 273 to 343 K. It was found that the H_2 permeation flux increased from 0.54×10^{-1} to 1.3×10^{-1} mol·m^{-2}·s^{-1} (Figure S4a, S4b) and that the separation selectivity was reduced. Interestingly, the H_2/N_2 separation factor of the $Cu_3(BTC)_2$ membrane is optimal at 298 K ($\sim$7.04), whereas the H_2/CO_2 separation factor is observed to be enhanced at 313 K. The reproducibility and durability of the membrane performances were also examined. As shown in Figure 2, the $Cu_3(BTC)_2$ membrane retains its separation factors and permeations over a 24 h period. The membrane can be used repeatedly over a long period of time (evaluated for 6 months in the present study), which supports the finding that the copper net supported $Cu_3(BTC)_2$ membrane has significant stability and recyclability.

In summary, the copper net supported $Cu_3(BTC)_2$ membrane has been successfully synthesized by means of a "twin copper source" technique. Compared with the conventional zeolite membranes, the copper net supported $Cu_3(BTC)_2$ membrane exhibits a higher permeation flux and excellent permeation selectivity for H_2. Such characteristics of the copper net supported $Cu_3(BTC)_2$ membrane offer great potential toward applications such as separating, recycling, and reusing H_2 exhausted from steam reforming natural gas.

Work is in progress to extend this approach to other potential MOF families as well as exploring their utilization in separating and purifying mixture gases of special interest.

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Supporting Information Available: Table of gas permeation and separation factors. Drawing of the gas separation setup. Figures for the permeance and separation factor of membrane vs the permeation temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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