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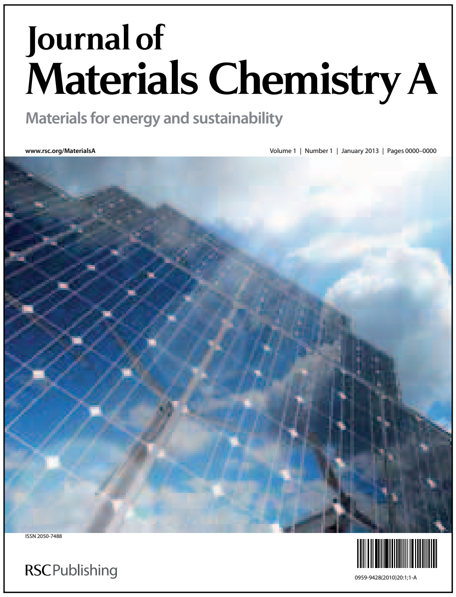

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ARTICLE TYPE

Alumina-supported cobalt-adeninate MOF membranes for CO_2/CH_4 separation

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The synthesis of continuous cobalt adeninate MOF (bio-MOF-13 (I) and bio-MOF-14 (II)) membranes supported on porous alumina tubes is demonstrated. The membranes showed high CO_2 permeabilities and low to moderate CO_2 separation selectivities for CO_2/CH_4 gas mixtures. The observed CO_2/CH_4 selectivities are attributed to preferential CO_2 adsorption within the framework.

The state-of-the-art technology for the purification of CO_2 uses amine adsorption, which is a complex, labor-intensive and costly approach. Membrane separation technology is far less expensive and requires less energy consumption. The separation of CO_2 from natural gas (NG) is of particular relevance. CO_2 needs to be removed from NG wells because it is acidic, corrosive in the presence of water, and because it significantly reduces the energetic content of NG. In principle, the use of membranes that could preferentially permeate CO_2 at high separation selectivities, can considerably reduce the cost of NG purification.[1] Polymeric membranes,[2] zeolite membranes[3] and metal-organic framework (MOF) membranes[4] can separate CO_2 from CH_4.

Recently, some of us reported a novel family of membranes composed of bio-MOF-1,[5] an adeninate-based MOF, and demonstrated their ability to separate CO_2 from CH_4.[5] Bio-MOFs 11-14,[6] which have highly desirable properties such as permanent microporosity with pore sizes close to the kinetic diameter of relevant gas molecules, high surface areas, chemical stability, and high CO_2 uptakes, are potentially ideal candidates for gas separation applications.

In this communication, we expand the scope of our earlier investigations on bio-MOF-1 membranes, to bio-MOF-13 (**I**) and bio-MOF-14 (**II**) membranes. These MOFs are stable in water (for example, **II** crystallites remain intact and retain their crystallinity and gas adsorption properties after soaking in water for 1 month), display high CO_2 adsorption capacities, and their pore sizes are close to the size of CO_2 and CH_4 molecules, making them highly appealing for CO_2/CH_4 molecular gas separation. **I**, $Co_2(ad)_2(C_3H_7CO_2)_2$, and **II**, $Co_2(ad)_2(C_4H_9CO_2)_2$, crystallize in the tetragonal space group ($I4_1/a$). **I** ($a = b = 15.79$ Å, $c = 22.33$ Å; $\alpha = \beta = \gamma = 90°$) consists of cobalt-adeninate-butyrate building blocks, while **II** ($a = b = 15.85$ Å, $c = 22.35$ Å; $\alpha = \beta = \gamma = 90°$) consists of cobalt-adeninate-valerate building blocks.[6c] The pore size of these BioMOFs depends on the conformation of the butyrate (**I**) or valerate (**II**) alkyl chains. We estimated a range of potential pore sizes for these materials by fixing the chains in one conformation or another and then performing a Connolly analysis to determine the diameter of the largest possible sphere that can travel through the pores. For **I**, the range of pore sizes determined from this analysis is 3.2-6.4 Å while that for **II** is 1.6-4 Å. It is important to mention that these are not fixed/static pore sizes. More specifically, we present the synthesis, characterization and CO_2/CH_4 gas separation performance of **I** and **II** membranes supported on porous alumina tubes.

I and **II** membranes were prepared by secondary seeded growth inside tubular porous alumina supports (0.5-μm pores, Sentro Tech Corporation). The synthesis gel preparation and composition was similar to that employed for the synthesis of the seeds.[7] The membranes were prepared by first passing a suspension of seeds in DMF through the tube to coat the interior tube walls. Some crystals (seeds) were attached at the surface of the porous support [7], serving as nucleation sites for membrane growth. These supports, with their outside wrapped with Teflon tape, were soaked in a mixed solution of cobalt salt (0.05M, 9ml) and adenine (0.05M, 27ml) in a Schlenk tube. For **I**, cobalt butyrate was used and for **II**, cobalt valerate was used as the cobalt salt. It was then vacuum sealed and heated in a oven at 130 °C for 24 h. The resulting membranes were gently washed with dry dimethylformamide. Multiple layers were applied following the same procedure. The membranes were dried and stored at 373K prior to the separation tests. The PXRD patterns of the synthesized **I** and **II** seed crystals used for the synthesis of membranes are shown in Figure 1a, and 1c respectively. The PXRD patterns reveal that the seeds are isostructural and in agreement with our previous report.[6c] Typical scanning electron microscopy (SEM) images of **I** and **II**, showing the seed crystallites, are presented in Figures 1b and 1d respectively.

Secondary seeded approach was employed to promote heterogeneous nucleation at the support surface over homogeneous nucleation in solution. The seeds provided nucleation sites for membrane growth. In principle, the addition of multiple layers helps to eliminate or at least reduce gaps between the crystals leading to the formation of a well-intergrown membrane. Table 1 shows the separation performance of alumina-supported **I** and **II** membranes. In each case, at least 5 layers were required to form a continuous membrane.

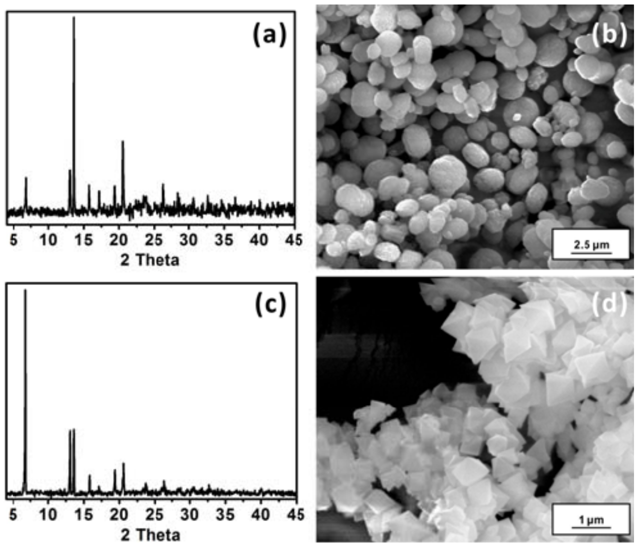

Figure 1. PXRD pattern and SEM of **I** (a,b) and **II** (c,d).These crystals were use as seeds for membrane synthesis.

Figure 2a shows a typical SEM image of the top view of a 5-layer **I** membrane. Crystallites with a size distribution in the ~2-2.5 µm range are observed. The cross section of this membrane consisted of an intergrown ~7µm layer (Figure 2b). In Figure 2c, the top view of a 5 layer **II** membrane shows ~2-4 µm crystallites. The thickness of this membrane was ~13 µm. The separation performance of **I** and **II** membranes have been included in the revisited Robeson plot [8], shown in Figure 3. A thickness of ~7 µm and ~13 µm were used to calculate the permeability of **I** and **II** in Barrers, respectively. The crystal size of the membranes is smaller than the seeds, because they were synthesized in different conditions. More specifically, membranes were synthesized under anhydrous solvents which lead to smaller crystal size. The data points for the **I** and **II** membranes are close to the present upper bound for polymeric membranes, and slightly lower than thermally rearranged [2b] polymeric membranes and most zeolite membranes.[3] Nevertheless, due to their remarkably high CO_2 permeances, a slight increase in CO_2/CH_4 separation selectivities would make these membranes attractive for CO_2 capture applications.

For **I** membranes, high CO_2 permeances in the order of ~3.1-4x10^{-6} mol/m^2 s Pa were observed with CO_2/CH_4 separation selectivities of 3.1-3.8. The reproducibility of two **I** membranes prepared independently (entries 1 and 2, Table 1) was confirmed by calculating their separation index π[3e] [π= (CO_2 permeance × (selectivity - 1)) × permeate pressure]. The calculated values were 0.88 and 0.86 respectively, indicating that these two membranes are reproducible. For the **II** membranes with the same number of layers (entry 3, Table 1), the separation indices were slightly higher (π=1.05; entry 3, Table 1; and π=1.01; entry 4, Table 1). Increasing the number of layers to 7 led to a considerable decrease in CO_2 permeance (0.75x10 $^{-6}$ mol/m^2 s Pa), and CO_2/CH_4 selectivity (1.2). The CO_2 permeance decreased most likely due to an increase in the membrane thickness. The decrease in CO_2/CH_4 selectivity as the number of layers increased, suggests an increase on the concentration of *unselective* CO_2 pathways (non-MOF pores). These unselective pores differ in size and adsorption properties from the selective pores, and therefore negatively impact the CO_2/CH_4 selectivity. The separation performance of both **I** and **II** membranes is better (at same separation conditions) than bio-MOF-1 membranes.[5]

In particular the CO_2/CH_4 separation selectivities were higher for **I** and **II** membranes as compared to bio-MOF-1, in part because of the higher CO_2 isosteric heats of adsorption of the former (~40.5 kJ/mol, 273 K)[6c] vs 21.9 kJ/mol at 273 K for bio-MOF-1.[6d] The low to moderate CO_2/CH_4 separation selectivities for **I** and **II** membranes suggest that the principal mechanism of separation is preferential CO_2 adsorption. While at this stage we do not know the specific nature of the framework-CO_2 interactions, computational modeling of the ground state structure of CO_2 in bio-MOF-12, $Co_2(ad)_2(C_2H_5CO_2)_2$, indicates that the closest interactions are between Lewis acidic sites on the framework and the Lewis basic oxygen atoms on CO_2. [6c]

Table 1. CO_2/CH_4 separation performance of **I** and **II** membranes. Pressure drop =138 KPa, Temp. 295K

Membrane*	Permeance mol/m^2·s·Pa (x10^{-6})		CO_2/CH_4 separation selectivity
	CO_2	CH_4	
I	3.10	0.82	3.8
I	4.06	1.31	3.1
II	4.16	1.18	3.5
II	4.55	1.41	3.2

*For all membranes the number of layers was five

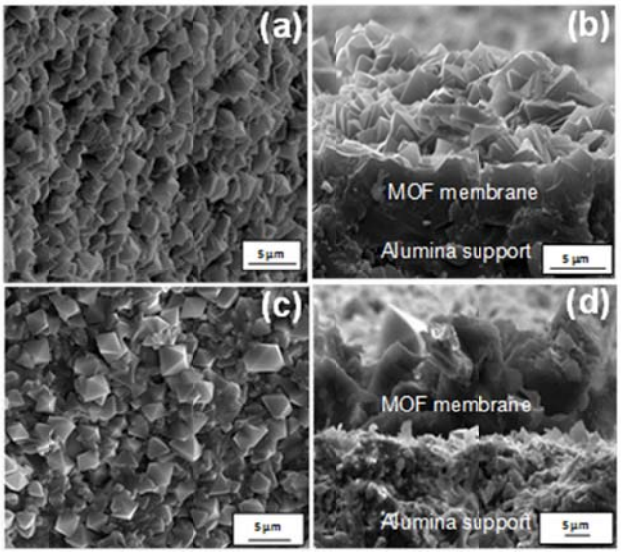

Figure 2. Top view and cross-sectional view of a **I** membrane (a,b) and a **II** membrane (c,d) supported on alumina porous tubes.

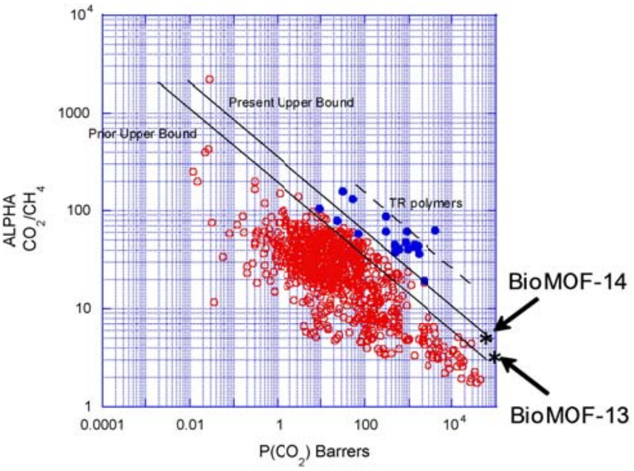

Figure 3. Revisited Robeson plot for CO_2/CH_4 mixtures.[8] The separation performance for **I** and **II** membranes is included in the plot.

Conclusions

In summary, we have demonstrated the preparation of continuous **I** and **II** membranes by secondary seeded growth on tubular alumina porous support for CO_2/CH_4 gas separation. These membranes displayed CO_2 permeances as high as ~4 × 10^{-6} mol / m^2 s Pa with CO_2/CH_4 separation selectivities in the 3-4 range at 295 K. Preferential adsorption of CO_2 is suggested as the potential separation mechanism. The presence of basic linkers in **I** and **II** may be associated with this enhanced CO_2 adsorption, although at this stage the specific nature of the CO_2/framework interactions is unclear. These and other adeninate-MOF membrane compositions may find applications in other relevant molecular gas separations.

Notes and references

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