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Performance**

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Impact of Partial Interpenetration in a Hybrid Ultramicroporous Material on C₂H₂/C₂H₄ Separation Performance

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Phases of a 2-fold pcu Hybrid Ultramicroporous Material (HUM), SIFSIX-14-Cu-i, exhibiting 99%, 93%, 89%, and 70% partial interpenetration have been obtained. 1:99 C₂H₂/C₂H₄ gas separation studies reveal that as the proportion of interpenetrated component decreases, so does the separation performance.

The design of porous coordination networks through crystal engineering¹ and reticular chemistry² principles has yielded a rich tapestry of porous metal-organic materials, MOMs³ (e.g. porous coordination polymers,⁴ PCPs, and metal-organic frameworks,⁵ MOFs) and hybrid ultramicroporous materials, HUMs.⁶ These classes of porous materials have provided understanding about phenomena such as topology,⁷ interpenetration,⁸ post-synthetic modification,⁹ and guest-induced phase transformations in porous coordination networks.¹⁰ In effect, crystal engineering has evolved from its original focus upon design of new crystalline materials into the design of a new generation of task-specific materials for use in catalysis,¹¹ gas storage,¹² and gas separation.¹³

In the context of gas separations, major strides have recently been made with respect to the physisorptive purification of several industrially important feedstocks as new selectivity benchmarks have been set for gas mixtures such as CO₂/N₂,¹⁴ C₂H₂/C₂H₄,¹⁵ C₂H₂/CO₂,¹⁶ Xe/Kr,¹⁷ and direct air capture of CO₂¹⁸ and water.¹⁹ With respect to HUMs, the combination of ultramicropores (pore diameter < 0.7 nm) lined with inorganic walls has enabled a relatively straightforward approach to control over pore size and chemistry that can afford molecular traps for targeted gas molecules. Indeed, TIFSIX-3-Ni,^{18a} NbOFFIVE-1-Ni,^{18b} and SIFSIX-3-Zn^{14a} exhibit primitive cubic,

pcu, structures in which fluorine atoms create a binding site for CO₂ molecules. The resulting induced-dipole interactions enable benchmark performance for CO₂ capture from CO₂/CH₄ and CO₂/N₂ gas mixtures, separations that are important to natural gas processing and greenhouse gas sequestration, respectively. Similarly, the 2-fold interpenetrated HUMs SIFSIX-2-Cu-i^{15a} and SIFSIX-14-Cu-i (also termed UTSA-200),^{10a,15b} which also exhibit pcu topology, afford benchmark performance for separation of C₂H₂ from C₂H₄ gas streams, separation relevant to polyethylene production. The separation performances in these cases are the result of offset inorganic pillars that create preferential H-bonding sites for C₂H₂ that are unfavorable for C₂H₄ adsorption.

Whereas interpenetration is key to creating the tight binding sites that enable the benchmark selectivity of SIFSIX-2-Cu-i and SIFSIX-14-Cu-i, it also reduces surface area and working capacity. Given that gas separations are dependent upon both selectivity for one molecule over another and the working capacity of a material, physisorbents suited for industrial use would need to optimally balance for selectivity and working capacity. Recent reports that partial interpenetration can occur in MOMs²⁰ suggest that such an optimal balance between selectivity and working capacity might occur in a

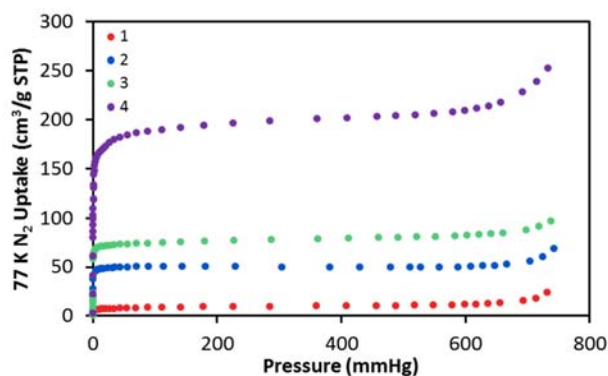


Fig. 1 77 K N₂ adsorption isotherms for phases 1, 2, 3 and 4. As the proportion of the microporous non-interpenetrated component increases vs. the ultramicroporous 2-fold interpenetrated component, so does the N₂ uptake

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porous material that is a solid solution²¹ of interpenetrated and non-interpenetrated components. This is because, in principle, such a phase could offer the best of both worlds with respect to high selectivity (interpenetration leading to ultramicropores) and working capacity (non-interpenetration leading to micropores and more uptake).^{20b} Herein, we test this hypothesis via a study of partial interpenetration and the separation properties of the recently reported 2-fold interpenetrated HUM, **SIFSIX-14-Cu-i**,^{10a,15b} the current benchmark for trace removal of C₂H₂ from C₂H₄.

Partial interpenetration in **SIFSIX-14-Cu-i** was achieved by variation of synthetic conditions and methods. We have previously found that temperature and concentration can be used to assert control over interpenetration.²² Herein, four phases were synthesized solvothermally in methanol at 120 °C; reaction duration and reaction vessel type were varied. Phase **1** was isolated after reaction in a Parr® Teflon Bomb for 1 hour. Phases **2**, **3** and **4** were prepared using variations of the originally described method;^{10a} reactions were conducted in Schott® glass bottles and heated for 1 hour, 1 day, and 1 week, respectively. The resulting solid products were repeatedly exchanged with fresh dry methanol until the solvent was clear. Phases **1-4** were at no point exposed to air, being submerged in methanol before being either dried *in-situ* or air-sealed during characterization experiments.

Laboratory powder X-ray diffraction (PXRD) experiments indicated that longer reaction times afforded additional diffraction peak consistent with the presence primitive as well as centered crystallographic symmetry (Figure S1-S10). Such a change in symmetry suggests the presence of the not yet reported non-interpenetrated polymorph, **SIFSIX-14-Cu**, which would be expected to crystallize in a primitive unit cell as was the case for **SIFSIX-1-Cu**,^{14b} **SIFSIX-2-Cu**^{14a} and [Cu(SiF₆)(1,2-bis(4-pyridyl)ethylene)]_n, **SIFSIX-7-Cu**.^{14b}

77 K N₂ gas adsorption isotherms were collected for phases **1-4** and are also consistent with partial interpenetration; **1** adsorbed only 23.5 cm³/g at 1 bar whereas **2**, **3** and **4** were observed to adsorb 68.9 cm³/g, 96.6 cm³/g, and 252.7 cm³/g, respectively (Figure 1). These values compare to uptake of N₂

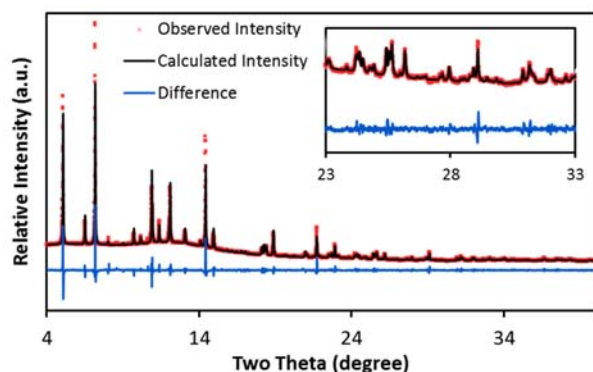


Fig. 2. Synchrotron Powder X-ray diffractogram of the partially interpenetrated phase of **SIFSIX-14-Cu-i** (phase **4**) reveals 70% 2-fold interpenetration. By varying reaction conditions, different proportions of partial interpenetration were obtained: phases **1**, **2** and **3** correspond to 99%, 93% and 89% 2-fold interpenetrated structures, respectively.

at 77 K of 643.4 cm³/g for **SIFSIX-14-Cu** (calculated) and no uptake for **SIFSIX-14-Cu-i** (experimental).^{15b} The proportions of interpenetrated and non-interpenetrated phases within each sample were estimated from quantitative phase analysis using synchrotron PXRD data. The quantitative phase analysis and N₂ adsorption data were collectively used to estimate the phase fraction for **1-4** (See Supporting Information). **1** is estimated to be the purest phase of **SIFSIX-14-Cu-i** (ca. 99% 2-fold interpenetrated content), whereas **2-4** are estimated to consist of 93%, 89%, and 70% 2-fold interpenetration, respectively (See Figure 2 and Supporting Information).

In order to confirm that the partially interpenetrated phases are indeed solid solutions as opposed to being physical mixtures of interpenetrated and non-interpenetrated phases, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments were conducted (See Supporting Information). TGA experiments indicated that each sample had a similar onset melting point (T_m) within the range of ca. 205 °C – 220 °C. DSC experiments all showed similar endotherms between ca. 160 °C and ca. 270 °C, wherein the melt and decomposition of each sample resulted in the same peak shapes at approximately the same temperatures. Following previous work on the separation of interpenetrated and non-interpenetrated structures,²³ samples were added to an immiscible density gradient of *n*-hexane ($\rho_{\text{calc}} = 0.655$ g/cm³) and DMSO ($\rho_{\text{calc}} = 1.1$ g/cm³). The different densities of **SIFSIX-14-Cu** ($\rho_{\text{calc}} = 0.649$ g/cm³) and **SIFSIX-14-Cu-i** ($\rho_{\text{calc}} = 1.298$ g/cm³) would be expected to result in a distinct separation of a mixtures; however, all samples were found to sink to the bottom of the gradient. Given these results and the similarities in TGA and DSC data, it is reasonable to assert that each sample exists as a solid solution of **SIFSIX-14-Cu** and **SIFSIX-14-Cu-i** and not a physical mixture of the two materials.

To probe the effect of partial interpenetration on the gas separation performance of **SIFSIX-14-Cu-i**, pure gas sorption isotherms for C₂H₂ and C₂H₄ were collected on **1-4**. Low pressure 298 K adsorption isotherms indicated very similar uptake values with the average C₂H₂ uptake being 4.2±0.4 mmol/g and the average C₂H₄ uptake being 1.1±0.2 mmol/g (Figure 3). Remarkably, **1** exhibits the highest C₂H₂ loading (103.7 cm³/g) and lowest C₂H₄ loading (19.1 cm³/g) at 101.1 kPa. **2** (93% 2-fold interpenetrated) had a much lower C₂H₂ loading (85.0 cm³/g) but a slightly higher C₂H₄ loading (20.0 cm³/g) at 101.1 kPa. Increased non-interpenetration would be expected to reduce the bulk density of the material and the density of strong binding sites for C₂H₂ and is therefore consistent with lower loading of C₂H₂ at 298 K for **2** vs **1**. Conversely, the uptake capacity of C₂H₄ increases, which is consistent with increased free volume. As the proportion of non-interpenetration increases further, C₂H₂ and C₂H₄ uptakes were observed to also increase. **3** (89% two-fold interpenetrated) adsorbed 98.6 cm³/g C₂H₂ and 24.3 cm³/g C₂H₄ at 101.1 kPa, whereas **4** (70% two-fold interpenetrated) adsorbed 99.9 cm³/g C₂H₂ and 28.7 cm³/g C₂H₄ at 101.1 kPa. The uptake capacities for both C₂H₂ and C₂H₄ are consistent with the effect of lower density and increased presence of micropores vs. ultramicropores. The lower density of

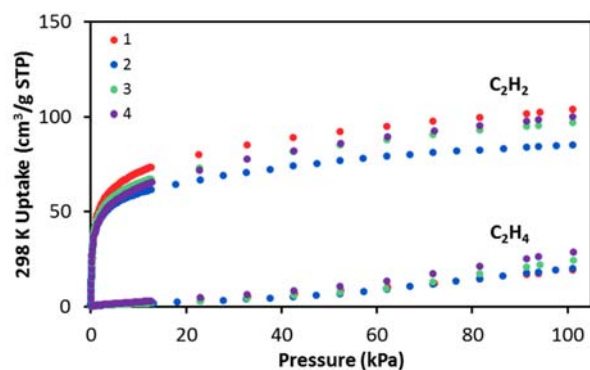


Fig. 3. 298 K C_2H_2 and C_2H_4 adsorption isotherms for **1**, **2**, **3**, and **4**.

molecular traps would be expected to on average result in weaker sorbent-sorbate interactions²⁴ and affect both selectivity and working capacity. At 101.1 kPa, ideal adsorbed solution theory (IAST) calculations revealed C_2H_2 over C_2H_4 selectivity as follows (S_{AE} , 1/99): **2** exhibits a $S_{AE} = 347$, whereas S_{AE} for **1**, **3**, and **4** are calculated to be 323, 301, and 216, respectively. These calculations suggest that a small proportion of **SIFSIX-14-Cu** vs. **SIFSIX-14-Cu-i** could offer slightly improved C_2H_2/C_2H_4 separation performance whereas a larger proportion would decrease performance. To evaluate whether these pure gas isotherms and IAST calculations transfer to separation performance, we conducted 1:99 C_2H_2/C_2H_4 dynamic gas breakthrough measurements at room temperature. Samples of **1** – **4** were in turn exposed to a 5 ml/min flow rate of a 1:99 C_2H_2/C_2H_4 (v/v) gas mixture. Near-spontaneous breakthrough of C_2H_4 was observed for each sample, while breakthrough times for C_2H_2 were found to occur at 507 min/g, 475 min/g, 476 min/g, and 420 min/g for **1** – **4**, respectively (Figure 4). These breakthrough times correspond to 1.12 mmol/g, 1.06 mmol/g, 1.06 mmol/g, and 0.96 mmol/g, respectively, of adsorbed C_2H_2 . Further, effluent production of >99.9999% C_2H_4 for phases **1** – **4** corresponds to 111.94 mmol/g, 104.91 mmol/g, 105.22 mmol/g, and 92.73 mmol/g. That there is a decrease in the density of binding sites as the proportion of non-interpenetrated content increases can explain the breakthrough performances. Indeed, given that phases with a higher proportion of non-interpenetration have a lower density and higher free volume, the difference in volumetric C_2H_4 production in **1** – **4** is even more pronounced if volumetric measures are used. Nonetheless, each sample was capable of adsorbing comparatively large quantities of C_2H_2 and the separation performance of each sample is competitive with that of current benchmarks.¹⁰

Hydrolytic stability of hybrid pillared square grids and HUMs has been addressed by us;^{18c, 18d} **1-4** were evaluated by PXRD after exposure to laboratory atmosphere for 24 hours. Transformation to a non-porous two-fold interpenetrated **sql-c*** topology phase, $\{[Cu(1,2-bis(4-pyridyl)diazene)_2(H_2O)_2] \cdot SiF_6 \cdot xH_2O\}_n$, was confirmed.^{10a}

We have prepared four partially interpenetrated solid solutions of **SIFSIX-14-Cu-i** and **SIFSIX-14-Cu** in which the concentration of **SIFSIX-14-Cu-i** varies from ca. 99% to 70%. The composition of these four phases was determined by

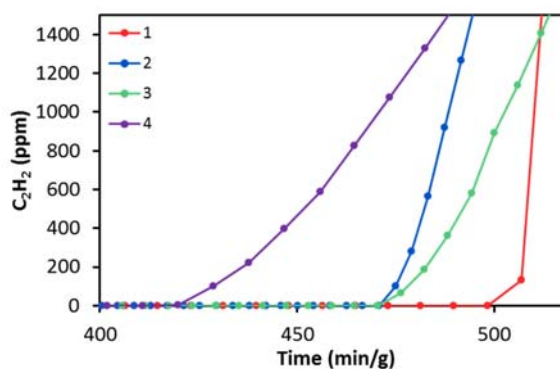


Fig. 4. Breakthrough profiles of C_2H_2 in **1**, **2**, **3**, and **4** at 5 ml/min and 298 K. C_2H_2 levels of < 1 ppm were measured in effluent gas before breakthrough occurred.

PXRD, 77 K N_2 adsorption, TGA and DSC experiments. 298 K C_2H_2 and C_2H_4 sorption experiments and IAST calculations suggest that these partially interpenetrated phases may exhibit slightly better separation performances with higher working capacities. However, dynamic breakthrough experiments conducted upon 1:99 C_2H_2/C_2H_4 gas mixtures indicate that as the proportion of non-interpenetrated content increases, the separation performance decreases. We attribute this reduced performance to the fact that there must be a decrease in the density of strong C_2H_2 binding sites in ultramicroporous materials such as **SIFSIX-14-Cu-i**, i.e. a material in which the strong binding site(s) is a consequence of interpenetration. This study suggests that whereas crystal engineering of partially interpenetrated HUMs can be achieved systematically, optimal separation performance lies with fully interpenetrated variants. However, we cannot extrapolate this conclusion to microporous materials where other factors will impact sorbent-sorbate interactions.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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