Journal of Materials Chemistry A

COMMUNICATION



View Article Online

View Journal | View Issue

Cite this: *J. Mater. Chem. A*, 2014, **2**, 299 Received 1st August 2013 Accepted 1st October 2013

DOI: 10.1039/c3ta12999c

www.rsc.org/MaterialsA

High propylene/propane adsorption selectivity in a copper(catecholate)-decorated porous organic polymer⁺

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A porous organic polymer decorated with high densities of copper-(catecholate) groups was prepared and characterized. Singlecomponent propylene and propane isotherms measured at ambient temperatures and ideal adsorption solution theory (IAST) calculations revealed increasing propylene/propane selectivities with increasing pressures.

The field of highly porous materials, including metal-organic frameworks (MOFs), porous organic polymers (POPs), covalent organic frameworks (COFs), and others has recently attracted much interest due to the vast numbers of functional structures that can conceivably be created. The tailorable nature of these materials has been demonstrated to be highly advantageous in a wide array of applications such as gas storage,¹⁻³ chemical separation,⁴⁻⁷ catalysis,⁸⁻¹² chemical sensing,¹³ chemical protection,¹⁴ and light harvesting.¹⁵⁻¹⁷ For many of these applications, metal centers with open coordination sites serve a crucial role as preferential binding sites, either for substrates in catalysis or for the storage and separations of gases.

In the case of gas separations, many MOFs and POPs show high selectivities in the separation of mixtures of gases with very different physical properties such as boiling points, sizes, or polarities (*e.g.*, O_2 and N_2 , or CO_2 and CH_4). However, developing materials that are capable of separating mixtures of gases with similar physical properties, such as propylene and propane, is much more challenging. To date, the production of propylene still requires costly, energy-intensive cryogenic separation from propane, a technology that is over 70 years old. Thus, adsorptive separation has been proposed as an energyand cost-effective alternative, and several MOFs have shown potential for propylene/propane separations either through a gate-opening mechanism,¹⁸ a kinetic-based mechanism,¹⁹ or an equilibrium-based mechanism.^{4,20,21} Concerning the latter, high selectivities are often observed only at very low pressures (1.88 torr) and decrease drastically with increasing pressure, which precludes the use of many of these materials in industrial settings. Thus far, only one report²⁰ has demonstrated large increases in selectivities in propylene/propane separation with increasing pressure, a phenomenon that has been attributed in MOF-74 to synergistic contributions from having both open metal sites that can bind to olefins and the proper size matching between adsorbent pores and adsorbate sizes.

Herein, we report high propylene/propane adsorption selectivities at industrially relevant pressures and temperatures for $CuA_{10}B_1$, a POP decorated with a high concentration of copper(catecholate) moieties capable of selectively binding to propylene. Single-component adsorption experiments and ideal adsorbed solution theory (IAST) calculations reveal that $CuA_{10}B_1$ exhibits a high thermodynamic propylene/propane selectivity (10.4) at 600 torr, a condition that is relevant to industrial practices.²² This selectivity can be tuned as a function of metal density and open coordination sites. In addition, the propylene/propane selectivity increases with increasing pressure, a phenomenon that has been attributed in MOF-74 to an emergent synergistic behaviour of the material:²⁰ as the pressure increases, the metal sites become saturated with propylene and the pores of the POP become more selective.

To generate our desired Cu-functionalized POP scaffold, we began with the cobalt-catalyzed acetylene trimerization of an orthoester protected 1,4-diethynyl-2,3-dihydroxybenzene (**A**) and T_d -directing tetrakis(4-ethynyl)methane (**B**) (Scheme 1). This copolymerization protocol has been previously shown to provide chemically robust amorphous polymers decorated with tuneable amounts of catechol groups by simply adjusting the ratios of monomers **A** and **B**.²³ We selected **A**₁₀**B**₁ given its high catechol group density and high metallation loadings.²³

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[†] Electronic supplementary information (ESI) available: Pore size distributions, sorption data, and IAST calculations. See DOI: 10.1039/c3ta12999c

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Scheme 1 Synthesis and metallation of A_2B_1 and $A_{10}B_1$ to generate CuA_2B_1 and $CuA_{10}B_1.$

 $CuA_{10}B_1$ was selected as the target for propylene/propane separation applications given the well-known ability of Cu^{II} to bind to olefins.

The single-component propylene and propane isotherms for $A_{10}B_1$ and $CuA_{10}B_1$ were carried out at 298 K and up to 600 torr (Fig. 1). Prior to these measurements, both materials were activated at 200 °C under high vacuum (10^{-3} torr), activation conditions known to remove coordinated solvent/water molecules from highly hygroscopic materials such as zeolites.²⁴ Surprisingly, $CuA_{10}B_1$ has a higher propylene uptake at 600 torr (1.65 mmol g⁻¹) than the parent $A_{10}B_1$ material (1.40 mmol g⁻¹) despite its much lower specific surface area (195 vs. 617 m² g⁻¹, Fig. 1 and Table 1), smaller pore volume (0.08 and 0.25 cm³ g⁻¹ respectively, Table 1 and Fig. S1 in the ESI†), and similar dominant pore diameters (~12 Å, Fig. S3 and S4 in the ESI†). As shown in Fig. 1, the single-component isotherms of $CuA_{10}B_1$ display near saturation at ~200 torr; whereas, uptake of either propane or propylene in $A_{10}B_1$ continues to slightly increase with





increasing pressure, most likely due to its larger surface area and pore volume. We attributed much of the higher relative uptake of propylene over propane in **CuA₁₀B₁** to the coordination of the olefin to the unsaturated copper-catecholates (see below).

The single-component isotherms for $CuA_{10}B_1$ suggest a high preference for propylene uptake over propane (1.65 and 0.93 mmol g^{-1} respectively, Table 1). In contrast, the metal-free $A_{10}B_1$ has a much lower difference between propylene and propane uptakes (1.40 and 1.18 mmol g^{-1} respectively). Using the single-component isotherms as inputs, the selectivities for propylene-propane mixtures were calculated using IAST, which has been shown to accurately predict selectivities for gasmixture adsorption in many porous materials.^{25,26} While A₁₀B₁ and CuA₁₀B₁ exhibit similar selectivities (1.26 and 1.64, respectively; see Fig. 2) at low pressures (7.5 torr), the selectivities for CuA10B1 increase significantly with increasing pressure while those for $A_{10}B_1$ remain steady (10.4 and 1.7, respectively, at 600 torr; see Fig. 3). Based on previous work, this highly desirable feature can be tentatively attributed to a synergistic effect that involves the filling of pores decorated with copper-(catecholate) groups at high pressures.²⁰ These pores fill when each accessible copper(catecholate) site is occupied by a propylene molecule, which discourages further uptake.

To evaluate the aforementioned hypothesis, we attempted to verify each of the following three effects independently: (1) that the presence of a high density of copper(catecholate) sites is beneficial towards selective adsorption; (2) that coordination of propylene to the copper(catecholate) sites is a key contributor to the propylene/propane selectivity; and (3) that proper matching of the adsorbent pore size and the adsorbate size is important for the increase in selectivity as a function of increased



Fig. 2 IAST-predicted C_3H_6/C_3H_8 selectivities for equimolar mixture adsorption in $CuA_{10}B_1$ (red solid line), CuA_2B_1 (green dashed line), and $A_{10}B_1$ (blue dotted line) at 298 K as a function of pressure. These were calculated using the experimental isotherms.

Table 1 POPs	Sorption properties for $A_{10}B_1$, $CuA_{10}B_1$, and CuA_2B_1						
	Metal loading ^{<i>a</i>} theor. (exp.)	BET surface area ^b $(m^2 g^{-1})$	Total pore volume (cm ³ g ^{-1})	DPD^{c} (Å)	Uptake C_3H_6/C_3H_8 ratio ^d (mmol g ⁻¹)	Uptake C_2H_4/C_2H_6 ratio ^d (mmol g ⁻¹)	IAST-calc. C_3H_8/C_3H_6 sel. ^d (C_2H_4/C_2H_6 sel.)
A ₁₀ B ₁		617	0.25	12	1.40/1.18	1.50/1.28	1.7 (1.5)
CuA ₁₀ B ₁	24 (21)	195	0.08	12	1.65/0.93	1.77/1.25	10.4 (3.8)
CuA ₂ B ₁	15 (14)	645	0.28	12	3.91/3.00	NA	2.7 (NA)

^{*a*} wt%. ^{*b*} For nitrogen isotherms, see Fig. S1 in the ESI.† ^{*c*} DFT calc. dominant pore diameter (DPD), see Fig. S3 and S4 in the ESI.† ^{*d*} Measured at 298 K and 600 torr.

Fig. 3 $\,$ Isotherms for $CuA_{10}B_1$ (propylene, red diamonds; propane, blue triangles, dashed) measured at 298 K after exposure to 80% RH.

pressure. First, CuA_2B_1 , which has a lower density of copper-(catecholate) sites than $CuA_{10}B_1$,¹⁴ was prepared. CuA_2B_1 has higher BET surface area (645 m² g⁻¹, Table 1 and Fig. S1 in the ESI†) but similar dominant pore size (~12 Å) as the $CuA_{10}B_1$ material. While the single-component isotherms of CuA_2B_1 reveal its higher uptake capacities for both propylene and propane (3.91 and 3.00 mmol g⁻¹, respectively, Table 1 and Fig. S4 in the ESI†), its IAST-calculated selectivity for propylene (2.7 at 600 torr, see Fig. 2 and Table 1) is much lower than that for $CuA_{10}B_1$. The larger selectivity for the latter material, in spite of its lower surface area, is attributed to its higher density of copper(catecholate) sites.

To verify that the coordination of propylene to the copper-(catecholate) sites is a key contributor to the selectivity, we subjected a sample of activated CuA₁₀B₁ to water vapour at 80% relative humidity (Fig. S8, in the ESI[†]), which should saturate the copper(catecholate) sites with water ligands and make them inactive towards olefin binding. This is indeed the case: after mild heating to 80 °C under high vacuum (10^{-3} torr) to remove any physisorbed water molecules,27 the single-component isotherms of propylene and propane in humidity-exposed CuA₁₀B₁ (Fig. 3) revealed a drastic drop in total propylene uptake (from 1.65 to 0.91 mmol g^{-1}), while those for propane remain roughly unchanged (from 0.93 to 0.88 mmol g^{-1}). The similarity between the propylene and propane uptake values for water-treated CuA10B1 is remarkable: it clearly demonstrates that CuA10B1 cannot discriminate between propylene and propane when its copper(catecholate) sites are coordinatively saturated with water molecules.

Finally, by comparing the selectivities of $CuA_{10}B_1$ and $A_{10}B_1$ for the ethylene/ethane pair, we can elucidate the importance in proper matching of the pore size of the adsorbent and the molecule size of the adsorbates. Although the single-component adsorption isotherms of $CuA_{10}B_1$ for ethylene and ethane (Fig. S7 in the ESI†) showed greater adsorption of ethylene (1.77 *vs.* 1.25 mmol g⁻¹ for ethane, see Table 1), it is not as discriminating as in the case of propylene/propane. The corresponding IAST-predicted selectivity for an equimolar ethylene/ethane mixture (Fig. 4) corroborates this result (ethylene/ethane selectivity = 3.8 at 600 torr, Table 1). Particularly striking is the switch of the ethylene/ ethane selectivity profile into a downward trend with increasing pressures (Fig. 4), a phenomenon most often observed in equilibrium-based olefin/paraffin separations.²⁸ Together, these data provide strong evidence that it is quite important in POP-based



Fig. 4 IAST-predicted C_2H_4/C_2H_6 selectivities for equimolar mixture adsorption in $CuA_{10}B_1$ (red solid line) and $A_{10}B_1$ (blue dashed line) at 298 K as a function of pressure. These were calculated using the experimental isotherms.

gas separation to have a proper size matching of the adsorbent pores to that of the adsorbate molecules. For the metallated materials reported herein, this size-matching mechanism can become important after the first olefin binds to the metal center and reduces the accessibility of the metallated pores for subsequent molecules. Even at 600 torr when only 50% of the copper(catecholate) groups are estimated to be bound to propylene molecules, the selectivities are already several fold higher than at lower pressures.

Conclusions

In summary, we have demonstrated the excellent potential that a POP decorated with high densities of coordinatively unsaturated copper(catecholate) groups has for separating a mixture of propylene and propane at industrially relevant temperatures and pressures. Remarkably, the high selectivities observed for propylene over propane at high pressures appear to result from synergistic contributions between having open coordination sites that can bind to olefins and a suitable match in size between the pores of the adsorbent and the molecular adsorbates.

Acknowledgements

Financial support for this work is provided by DOE (Grant DE-FG02-08ER15967), the Dow Chemical Company, and NSF (Grant no. DGE-0824162). We thank Dr Yabing He and Prof. Banglin Chen at the University of Texas at San Antonio for their help with initial selectivity measurements.

Notes and references

- 1 T. A. Makal, J.-R. Li, W. Lu and H.-C. Zhou, *Chem. Soc. Rev.*, 2012, **41**, 7761–7779.
- 2 M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.*, 2012, **112**, 782–835.
- 3 Z. Guo, H. Wu, G. Srinivas, Y. Zhou, S. Xiang, Z. Chen, Y. Yang, W. Zhou, M. O'Keeffe and B. Chen, *Angew. Chem.*, *Int. Ed.*, 2011, **50**, 3178–3181.
- 4 E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny,
 C. M. Brown and J. R. Long, *Science*, 2012, 335, 1606–1610.

- 5 B. S. Ghanem, M. Hashem, K. D. M. Harris, K. J. Msayib, M. Xu,
 P. M. Budd, N. Chaukura, D. Book, S. Tedds, A. Walton and
 N. B. McKeown, *Macromolecules*, 2010, 43, 5287–5294.
- 6 M. G. Rabbani and H. M. El-Kaderi, *Chem. Mater.*, 2012, 24, 1511–1517.
- 7 X.-S. Wang, J. Liu, J. M. Bonefont, D.-Q. Yuan, P. K. Thallapally and S. Ma, *Chem. Commun.*, 2013, **49**, 1533-1535.
- 8 P. Kaur, J. T. Hupp and S. T. Nguyen, ACS Catal., 2011, 1, 819–835.
- 9 J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450–1459.
- 10 A. Corma, H. García and F. X. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606–4655.
- 11 H. J. Mackintosh, P. M. Budd and N. B. McKeown, *J. Mater. Chem.*, 2008, **18**, 573–578.
- 12 R. Palkovits, M. Antonietti, P. Kuhn, A. Thomas and F. Schüth, *Angew. Chem., Int. Ed.*, 2009, **48**, 6909–6912.
- 13 L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105–1125.
- 14 M. H. Weston, G. W. Peterson, M. A. Browe, P. Jones, O. K. Farha, J. T. Hupp and S. T. Nguyen, *Chem. Commun.*, 2013, **49**, 2995–2997.
- 15 S. Jin, H.-J. Son, O. K. Farha, G. P. Wiederrecht and J. T. Hupp, *J. Am. Chem. Soc.*, 2013, **135**, 955–958.
- 16 H.-J. Son, S. Jin, S. Patwardhan, S. J. Wezenberg, N. C. Jeong, M. So, C. E. Wilmer, A. A. Sarjeant, G. C. Schatz, R. Q. Snurr, O. K. Farha, G. P. Wiederrecht and J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **135**, 862–869.
- 17 C. A. Kent, D. Liu, L. Ma, J. M. Papanikolas, T. J. Meyer and W. Lin, J. Am. Chem. Soc., 2011, 133, 12940–12943.
- 18 J. van den Bergh, C. Gücüyener, E. A. Pidko, E. J. M. Hensen, J. Gascon and F. Kapteijn, *Chem.-Eur. J.*, 2011, 17, 8832–8840.
- 19 C. Y. Lee, Y.-S. Bae, N. C. Jeong, O. K. Farha, A. A. Sarjeant, C. L. Stern, P. Nickias, R. Q. Snurr, J. T. Hupp and S. T. Nguyen, *J. Am. Chem. Soc.*, 2011, 133, 5228–5231.

- 20 Y.-S. Bae, C. Y. Lee, K. C. Kim, O. K. Farha, P. Nickias, J. T. Hupp, S. T. Nguyen and R. Q. Snurr, *Angew. Chem.*, *Int. Ed.*, 2012, **51**, 1857–1860.
- 21 N. Lamia, M. Jorge, M. A. Granato, F. A. Almeida Paz, H. Chevreau and A. E. Rodrigues, *Chem. Eng. Sci.*, 2009, **64**, 3246–3259.
- 22 R. T. Yang, *Adsorbents: Fundamentals and Applications*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2003.
- 23 M. H. Weston, O. K. Farha, B. G. Hauser, J. T. Hupp and S. T. Nguyen, *Chem. Mater.*, 2012, 24, 1292–1296.
- 24 Mineral Adsorbents, Filter Agents and Drying Agents (Aldrich Technical Information Bulletin AL-143), Aldrich Chemical Co., Milwaukee, WI, USA, 1993, http://www.sigmaaldrich.com/ chemistry/chemical-synthesis/learning-center/technicalbulletins/al-1430/molecular-sieves.html, accessed July 27, 2013.
- 25 Y.-S. Bae, K. L. Mulfort, H. Frost, P. Ryan, S. Punnathanam,
 L. J. Broadbelt, J. T. Hupp and R. Q. Snurr, *Langmuir*, 2008,
 24, 8592–8598.
- 26 Q. Yang and C. Zhong, J. Phys. Chem. B, 2006, 110, 17776– 17783.
- 27 K. J. Crowley and G. Zografi, *J. Pharm. Sci.*, 2002, **91**, 2150–2165. We note that both physisorbed and coordinated water can be observed in the TGA profile of $CuA_{10}B_1$ that has been exposed to 80% RH (Fig. S9 in the ESI†). After activation at 80 °C under high vacuum (10⁻³ torr), this material exhibits a slightly lower BET measured surface area (165 m² g⁻¹, see Fig. S2 in the ESI†) than the fully dehydrated $CuA_{10}B_1$ while maintaining a similar pore size distribution (dominant pore size ~ 12 Å, see Fig. S5 in the ESI†).
- 28 J. W. Yoon, Y.-K. Seo, Y. K. Hwang, J.-S. Chang, H. Leclerc, S. Wuttke, P. Bazin, A. Vimont, M. Daturi, E. Bloch, P. L. Llewellyn, C. Serre, P. Horcajada, J.-M. Grenèche, A. E. Rodrigues and G. Férey, *Angew. Chem., Int. Ed.*, 2010, 49, 5804.