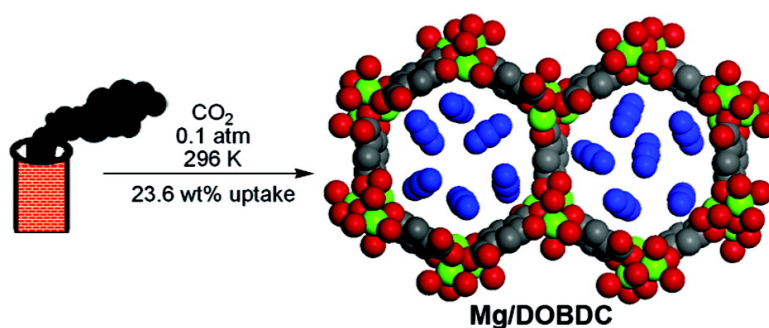


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*J. Am. Chem. Soc.*, **2008**, 130 (33), 10870-10871 • DOI: 10.1021/ja8036096 • Publication Date (Web): 29 July 2008

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## Dramatic Tuning of Carbon Dioxide Uptake via Metal Substitution in a Coordination Polymer with Cylindrical Pores

Stephen R. Caskey, Antek G. Wong-Foy, and Adam J. Matzger\*

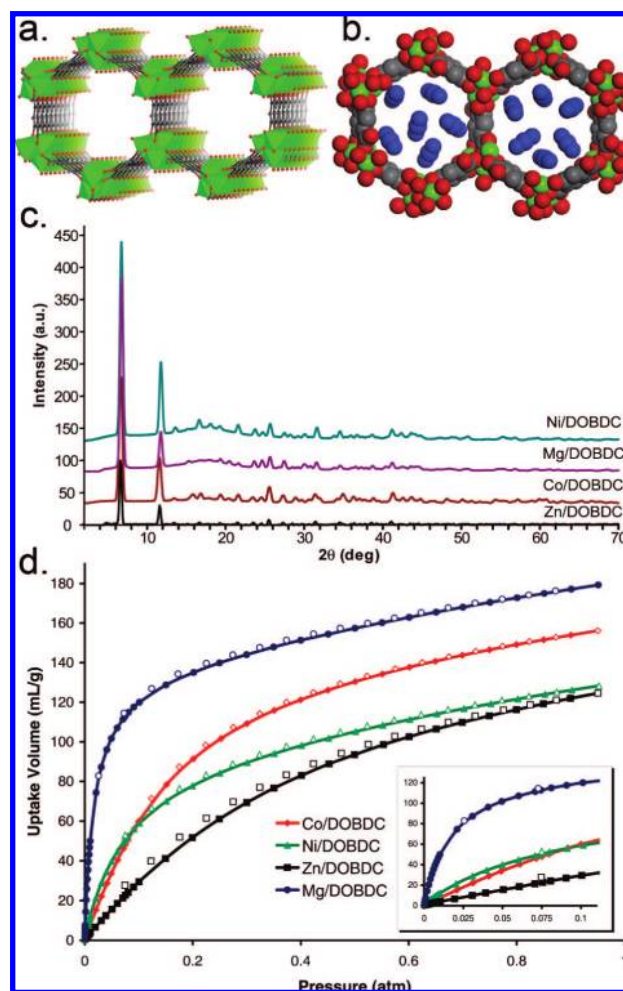
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Coal-fired power plants are the largest point sources of CO<sub>2</sub> emission and as such are attractive targets for capture technologies.<sup>1</sup> Typically these power plants produce flue gas at 1 atm with a CO<sub>2</sub> concentration of less than 15%.<sup>2,3</sup> The separation of CO<sub>2</sub> from such a low pressure stream of gases through chemisorption by amines is an effective technology for removal of CO<sub>2</sub> although amine degradation and the energy intensive nature of the regeneration process motivates alternative approaches.<sup>4</sup> These limitations have prompted significant investigation of physisorptive methods for CO<sub>2</sub> separation which require a porous material with a high uptake of CO<sub>2</sub> displaying reversible adsorption. Zeolite 13X is among the very best sorbents for CO<sub>2</sub> separation and has been reported to provide uptake of ~4.7 mmol CO<sub>2</sub>/g sorbent (20.7 wt %) at 1 atm and 298 K.<sup>5</sup>

Microporous coordination polymers (MCPs), extended networks composed of metal ions or clusters connected by multifunctional ligands that act as linkers, have received significant attention of late as sorbents for the separation of gases. However, despite record setting surface areas coupled with high free volumes, physisorptive materials have yet to significantly surpass liquid amines as effective sorbents in the low pressure region (0 to 1 atm) for CO<sub>2</sub> uptake. This is clearly not a problem of ultimate capacity because high uptakes (>100 wt %) have been reported well above atmospheric pressure for a variety of MCPs.<sup>6</sup> This situation provides an interesting comparison to cryogenic hydrogen storage in MCPs, where capacity at 1 atm for all known materials is also inadequate and therefore the high pressure region is of considerably more interest.<sup>7</sup> Because the pressure region of interest for CO<sub>2</sub> separation is much lower and the attractive interactions are much greater it seemed likely that materials performing well for hydrogen storage at low temperature and pressure could serve as promising CO<sub>2</sub> hosts. The MCP MOF-74 is particularly promising in this regard with remarkably strong affinity for H<sub>2</sub> at 77 K and low pressure,<sup>8</sup> coordinatively unsaturated metal sites and the presence of small cylindrical pores are believed to be key structural features.<sup>7-9</sup>

Significant work is ongoing by several groups involving the 2,5-dihydroxyterephthalic acid linker. This linker is known to form MCPs based on both the tetraanionic form 2,5-dioxido-1,4-benzene-dicarboxylate (DOBDC), where both the aryloxy and carboxylate moieties act as ligands to the metal and the dianionic form 2,5-dihydroxy-1,4-benzene-dicarboxylate (DHBDC), where only the carboxylate moieties act as ligands to the metal and the alcohol remains protonated. Yaghi and co-workers first reported MOF-74,<sup>10</sup> also known as CPO-27-Zn<sup>11</sup> (hereafter **Zn/DOBDC**). Immediately following the report of **Zn/DOBDC**, Dietzel and co-workers prepared CPO-27-Co<sup>12</sup> (hereafter **Co/DOBDC**) and later CPO-27-Ni<sup>13</sup> (hereafter **Ni/DOBDC**) which are isostructural to **Zn/DOBDC**. Each of these materials is composed of M<sup>II</sup> ions generating linear, infinite-rod secondary building units (SBUs) bound by DOBDC resulting in a hexagonal, 1D pore structure (Figure 1a). The pores



**Figure 1.** (a) View of 1D channels present in the M/DOBDC structure (solvent omitted). (b) Space-filling model of the pore structure of 1 unit cell of **Mg/DOBDC** (Mg atoms, green; C atoms, gray; O atoms, red; H atoms and solvent molecules removed for clarity) occupied by 12 molecules of CO<sub>2</sub> (blue) which represents the sorption at 0.1 atm and 296 K. (c) PXRD data for M/DOBDC series depicting the isostructural relationship. (d) CO<sub>2</sub> sorption isotherm (296 K, 0 to 1 atm) comparing M/DOBDC series, along with an inset of the low pressure region from 0 to 0.1 atm (filled markers represent adsorption points; open markers represent desorption points).

of the as-synthesized material are lined with solvent molecules, typically H<sub>2</sub>O or DMF, that complete the coordination sphere of the M<sup>II</sup> ions and are removed upon evacuation to generate coordinately unsaturated metal sites.<sup>11</sup> Sorbent materials are thus provided with a characteristic honeycomb structure composed of 1D channels. As demonstrated below, **Zn/DOBDC** and isostructural analogues are high affinity sorbent materials for CO<sub>2</sub>.

In striving for a diversity of metals in the M/DOBDC series, we sought a lighter, harder metal as a contrast to the late transition metals.<sup>14</sup> Synthesis of **Mg/DOBDC** was carried out under solvothermal conditions in a DMF/ethanol/H<sub>2</sub>O mixture at 125 °C. The material was then activated by immersion of the yellow microcrystalline product in methanol to extract high boiling solvents from the pores, followed by evacuation at 250 °C for 5 h. Comparison of the PXRD patterns (Figure 1c) to the data previously reported for M/DOBDC<sup>10,12,13</sup> reveals the isostructural nature of this series. **Mg/DOBDC** indexes in a trigonal cell with  $a = 26.02(1)$  Å and  $c = 6.721(4)$  Å.

Surface area analysis by N<sub>2</sub> sorption was performed on evacuated **Mg/DOBDC** and a value of 1495 m<sup>2</sup>/g was estimated by the BET method (Langmuir 1905 m<sup>2</sup>/g). To our knowledge this is the highest surface area for a magnesium MCP. Because surface area is reported as an area per given mass, this value for **Mg/DOBDC** is consistent with the trend toward higher surface area for the lighter metal in a series of isostructural materials, where **Co/DOBDC** (1080 m<sup>2</sup>/g, measured here), **Ni/DOBDC** (1070 m<sup>2</sup>/g),<sup>13</sup> and **Zn/DOBDC** (816 m<sup>2</sup>/g)<sup>6</sup> are each composed of heavier transition metals and therefore provide lower surface areas. This point is well illustrated when the saturation uptake of the Mg, Co, and Ni materials is converted to the number of N<sub>2</sub> molecules per unit cell (UC); the difference is minimal at 35–38 molecules per UC indicating that the surface area differences arise from variation in the weight of the asymmetric unit and not any specific interaction between the metal and the adsorbed gas. **Zn/DOBDC** is somewhat lower at 26 molecules per UC suggesting incomplete activation, pore blockage, or partial collapse of the structure upon evacuation.

CO<sub>2</sub> sorption isotherms were measured at 296 K to elucidate the effect of metal identity on the uptake in this isostructural series of materials (Figure 1d). Measurement of **Zn/DOBDC** provided an uptake of 5.8 wt % at 0.1 atm and 24.4 wt % at 1 atm (for comparison MOF-5 is <5% at 1 atm<sup>6</sup>). For **Ni/DOBDC**, an uptake of 11.6 wt % at 0.1 atm and 25.6 wt % at 1 atm was observed. For **Co/DOBDC**, a very similar uptake of 11.7 wt % at 0.1 atm was observed yet the uptake at 1 atm was somewhat higher at 30.6 wt %. Finally, **Mg/DOBDC** was found to provide an uptake of 23.6 wt % at 0.1 atm and 35.2 wt % at 1 atm. The value for **Mg/DOBDC** is double the value for any of the other materials in the M/DOBDC series at 0.1 atm. Conversion of these uptake values at 0.1 atm to the number of molecules per UC, thus eliminating the weight effect of each metal, reinforces that this is not simply an effect of the weight of the incorporated metal on surface area. Hence, **Mg/DOBDC** hosts ~12 molecules of CO<sub>2</sub> per UC at 0.1 atm (Figure 1b) whereas **Co/DOBDC** and **Ni/DOBDC** each takes up ~7 molecules/UC and **Zn/DOBDC** is somewhat lower at 4 molecules/UC.

Heat of adsorption measurements (Supporting Information) show that **Mg/DOBDC** has an initial affinity of 47 kJ/mol whereas **Ni/DOBDC** and **Co/DOBDC** have initial affinities of 41 and 37 kJ/mol, respectively. These values then fall slightly as the highest affinity sites are filled. The values for **Ni/DOBDC** and **Co/DOBDC** are in the range of previously reported values for zeolite 13X at 40 kJ/mol<sup>15</sup> but all are somewhat lower than **Mg/DOBDC**.<sup>16</sup>

The exceptional uptake of **Mg/DOBDC** for CO<sub>2</sub> may be attributed to the increased ionic character of the Mg–O bond. In CO<sub>2</sub> sequestration chemistry, MgO is well-known to exothermically

chemisorb CO<sub>2</sub> to form MgCO<sub>3</sub>.<sup>17</sup> In this case, while **Mg/DOBDC** does not chemisorb CO<sub>2</sub>, presumably because of the rigid nature of the framework that prevents insertion into the Mg–O bonds, the increased ionic character of this bond imparts additional uptake of the material for CO<sub>2</sub> beyond simple weight effects while maintaining the reversibility of adsorption.

This study provides a systematic evaluation of the effects of metal identity on surface area and CO<sub>2</sub> uptake. **Mg/DOBDC** in particular was found to significantly outperform all other physisorptive materials in low pressure physisorption of CO<sub>2</sub> and is synthesized in one-step from commercially available starting materials. The exceptional uptake of the Mg-based material for CO<sub>2</sub> at ambient temperature and pressure demonstrates that physisorptive materials can achieve affinities and capacities competitive with amine sorbents.

**Acknowledgment.** This work is supported by Grant #454 of the 21st Century Jobs Trust Fund received through the SEIC Board from the State of Michigan.

**Supporting Information Available:** Complete ref 1c; synthetic procedures, TGA data, powder X-ray diffraction data, and sorption data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA8036096