H₂, N₂, CO, and CO₂ Sorption Properties of a Series of Robust Sodalite-Type Microporous Coordination Polymers

Jorge A. R. Navarro,* † Elisa Barea, † Juan M. Salas, † Norberto Masciocchi,* ‡ Simona Galli, ‡ Angelo Sironi, ‡ Conchi O. Ania, † and José B. Parra†

Departamento de Química Inorgánica, Universidad de Granada, Av. Fuentenueva S/N, 18071 Granada, Spain, Dipartimento di Scienze Chimiche e Ambientali, Università dell’Insibria, Via Valleggio 11, 22100 Como, Italy, Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano and ISTM-CNR, Via Venezian 21, 20133 Milano, Italy, and Department of Energy & Environment Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain

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H₂, N₂, CO, and CO₂ are readily incorporated in the porous, 3D sodalite frameworks of coordination polymers of the [ML₂]₆ type, with M = Pd(II) or Cu(II) and HL = 2-hydroxypyrimidine or 4-hydroxypyrimidine. The metal ion and ligand functionalization modulate their sorption properties, making these materials suitable for gas storage and separation purposes.

The optimization of the adsorption properties of porous solids is a present day challenge, boosted by industrial and environmental applications of selective gas storage, separation, and catalysis. One of the most interesting classes of porous materials comprises the open metal–organic frameworks (MOFs). These kinds of materials are extremely promising for H₂ storage applications and, although very high mass percent storage capacities (up to 3.8%) have been recently reported, the usual low density of MOFs results in a low storage capacity on a volume basis, which should be subject to improvement by employing new synthetic strategies. Besides, the formation of MOFs involves a self-assembly process of metal fragments and organic spacers, which is facilitated by the use of labile metal ions [i.e., first-row, divalent transition-metal ions, Cu(I), Ag(I), Zn(II), and Cd(II)]. Pd(II) possesses an intermediate robustness, which makes it adequate for the obtention of stable discrete polynuclear systems with cavities and voids ready for molecular recognition and catalytic processes. However, to the best of our knowledge, this metal ion has not yet been employed for the construction of crystalline porous coordination polymers.

In this Communication, we report the base-promoted polymerization of [PdCl₂(2-Hpymo)₂] (1), leading to a novel, 3D microporous sodalite network, [Pd(2-pyomo)₂]₆ (2) (Figure 1), which is thermally stable up to 330 °C in air. We also discuss the solid–gas adsorption properties of 2 and of its congeners, namely, [Cu(2-pyomo)₂]₆ (3) and [Cu(4-pyomo)₂]₆ (4).

(8) Synthesis of I. An aqueous solution of K₂PdCl₄ (4 mmol) was mixed with another one containing 2-Hpymo·HCl (8 mmol). The suspension was stirred for 1 h, and a yellow microcrystalline powder was obtained. Yield: 95%. Calcd for [Pd(C₂H₅N₂O₂Cl₂)]: C, 26.05; H, 2.18; N, 15.16. Found: C, 26.17; H, 2.26; N, 15.39. Synthesis of 2·HCl₂O. A water suspension of 1 (3 mmol in 50 mL of H₂O) was treated with a NaOH solution (1 M) until pH 6.0 was reached. The resulting suspension was refluxed for 5 days, affording a pale-yellow microcrystalline powder. Yield: 98%. Calcd for [Pd(C₂H₅N₂O₂)₂·2H₂O]: C, 27.41; H, 3.45; N, 15.98. Found: C, 27.78; H, 3.36; N, 15.53.
The structural features of the precursor 1, of the hydrated polymer [Pd(2-pymo)₂]₂·2nH₂O (2·H₂O), and of the anhydrous [Pd(2-pymo)₂]₄, form of the latter (2) have been disclosed by ab initio X-ray powder diffraction (XRPD) methods. As expected, 1 consists of discrete square-planar trans-[PdCl₂(2-Hpymo)₂] complexes (with N-monodentate centers connected through N,N-square-planar, even in the hydrated phase of the sodalite zeotype (Figure 1D). The local coordination of the Pd(II) ions is, as expected, square-planar, even in the hydrated phase 2·H₂O, where the shortest Pd···O contacts fall well above 5.0 Å. At variance, short(er) “apical” bonds of the Cu···O type [2.76(3) Å] were observed in the hydrated 4·H₂O phase, which results in a concomitant increase of ~100 °C for the dehydration temperature.

The porous framework of 2 is defined by the sodalitic β cages (Figure 1D), with an interior diameter of ca. 9 Å, interconnected by hexagonal windows. It should be noted that there are two kinds of hexagonal windows: one narrower (4.8 Å) and hydrophobic (Figure 1C) and the other wider (8.8 Å) and hydrophilic (Figure 1B) and the available volume for the inclusion is ca. 1800 Å³ per unit cell, i.e. 42% of the crystal volume (see Table 1).

Table 1. Unit Cell and Pore Volumes for the Hydrated and Anhydrous Forms of 2–4. BET Surfaces (m² g⁻¹); Calculated from the N₂ Adsorption Isotherms at 77 K, and Sorption Properties toward H₂ [Weight Percentage and Storage Density, ρ(H₂), at 77 K and 900 Torr]

<table>
<thead>
<tr>
<th>Form</th>
<th>Cell volume: empty space;</th>
<th>Space group; % void</th>
<th>SA, m² g⁻¹</th>
<th>H₂, wt %</th>
<th>ρ(H₂), kg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT hydrated</td>
<td>130 °C anhydrous</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4315; 1808; Pm3n; 41.9</td>
<td>4364; 1801; Pm3n; 41.3</td>
<td>600</td>
<td>1.29</td>
<td>0.018</td>
</tr>
<tr>
<td>3</td>
<td>3852; 1257 (3 x); R3m; 32.6</td>
<td>3422; 953; Pm3m; 27.8</td>
<td>350</td>
<td>0.86</td>
<td>0.013</td>
</tr>
<tr>
<td>4</td>
<td>3910; 1240; P4₁2₁2₁ 31.7</td>
<td>3512; 1033; P4₁2₁2₁ 24.4</td>
<td>65</td>
<td>0.03</td>
<td>0.0004</td>
</tr>
</tbody>
</table>

* Idealized ordered model.

To evaluate the open porosity of the open framework 2–4 and to estimate their possible use in catalysis and for gas separation or storage application purposes, we have studied the sorption isotherms of H₂, N₂, and CO at 77 K and of CO₂ at 293 K (see Figures 2 and 3). The N₂ and CO isotherms are of type I and reversible in all cases, except 3 (see note ref 12 and Table 1), indicative of materials with pores in the nanometer range. Indeed, density functional theory (DFT) and Horváth–Kawazoe analysis of the N₂ isotherms for 2 and 3 account for adsorption taking place in very narrow pores (~11 Å width), in agreement with the...
values obtained for the sodalitic β cages by our crystal structure analysis (ca. 9 Å; see above). The results are also in agreement with strong adsorbate-adsorbent interactions, with the micropores being filled by N\textsubscript{2} and CO guest molecules at very low pressures. In addition, 2 and 3 show a relatively high capacity for CO\textsubscript{2} storage, viz. ca. 3 and 1.5 CO\textsubscript{2} molecules per β cage,\textsuperscript{15} respectively, at room temperature and low relative pressures (Figure 3).

2 and 3 also show fully reversible type I H\textsubscript{2} sorption isotherms, indicative of the filling of the micropores only. It is worth noting that the two species possess a relevant capacity of H\textsubscript{2} storage at 77 K and 900 Torr: ca. 1.3% and 0.86% weight percentage, i.e., 11.6 and 6.6 H\textsubscript{2} molecules per β cage, respectively. This results in high storage volumetric densities, viz., 0.018 kg of H\textsubscript{2}/L for 2 and 0.013 kg of H\textsubscript{2}/L for 3. Thus, 2 overcomes the highest known values observed for MOF-type materials at similar experimental conditions, namely, 0.017 kg of H\textsubscript{2}/L for MOF-505 [Cu\textsubscript{2}(bptc)]\textsuperscript{4–b} which shows the maximum known value of H\textsubscript{2} weight percentage uptake (2.47% at 77 K and 760 Torr).

Another implication of the gas sorption performances of 2 and 3 is the relative surface coverage of H\textsubscript{2} molecules\textsuperscript{16} (83 and 94%, respectively), which are among the highest known values, i.e., Mn(HCOO)\textsubscript{2} (150%),\textsuperscript{17} Cu\textsubscript{3}(Co(CN)\textsubscript{6})\textsubscript{2} (94%),\textsuperscript{18} [Cu\textsubscript{2}(bptc)] (52%),\textsuperscript{19} zeolite HSSZ-13\textsuperscript{19} (76%), and highly activated porous carbon materials (38%).\textsuperscript{1b} The steep slope of the hydrogen sorption isotherms of 2 and 3 in the low-pressure range is also indicative of the strong interaction of the hydrogen molecules with the pore walls. It is noteworthy that 2, based on the heavier Pd, outperforms the behavior of 3 and 4, thanks to the significantly longer M-N bonds in 2, leading to a higher pore surface (see below and Table 1). It is also interesting to note that the much steeper slope of the N\textsubscript{2}/CO isotherms than the H\textsubscript{2} ones in the low-pressure range clearly points to a N\textsubscript{2}/CO selectivity of 2 and 3 over H\textsubscript{2}.

In addition, it should be noted that 3 and 4, although sharing nearly equal cell parameters and empty volumes, have different sorption performances. Indeed, they mainly differ in the distinct decoration of the metallicacic[c]arene motives: in 3, the internal surface of these pores is covered by hydrogen atoms, while some of them (one out of three) are substituted by oxygen atoms in 4. Presumably, the oxygen atoms in 4, pointing away from the Cu atoms into the open cavities, hinder the diffusion of adsorbate molecules through the pores, thus accounting for the dramatic lowering of its affinity for guest molecules.

Another interesting feature of 3 is the marked effect of the activation temperature on its adsorption selectivity. Thus, it is worth noting that the two species possess a relevant capacity of H\textsubscript{2} storage at 77 K and 900 Torr: ca. 1.3% and 0.86% weight percentage, i.e., 11.6 and 6.6 H\textsubscript{2} molecules per β cage, respectively. This results in high storage volumetric densities, viz., 0.018 kg of H\textsubscript{2}/L for 2 and 0.013 kg of H\textsubscript{2}/L for 3.

From the analysis of the unit cell volumes of the hydrated and anhydrous species (see Table 1), a structural interpretation of the sorption behavior can be derived. Indeed, (i) given the actual site symmetry of the metal ions, the size of the unit cell strictly depends on the M-N bond distances, which control the X-pyomo-bridged M···M contacts (i.e., the edges of the sodalitic framework): longer M-N values [e.g., for Pd(II)] thus cooperatively result in a much larger empty volume and higher surface area (as observed in 2); (ii) the copper species 3 and 4 (reversibly) deflate (by as much as 430 Å\textsuperscript{3} per unit cell, or 11%) to their evacuated analogues upon loss of water molecules because Cu-N bonds shrink with the lowering of the Cu(II) coordination number in the anhydrous phase;\textsuperscript{7} (iii) such an effect is not observed on passing from 2-H\textsubscript{2}O to 2, probably because the low tendency of Pd(II) ions to coordination numbers higher than 4 forces the water molecules to cluster in the sodalitic cages.\textsuperscript{20}

As far as the sorption of hydrogen is concerned, the performance of 2 closely approaches those of the best MOFs reported up to date\textsuperscript{3a,4} on a volume basis. This is related to the empty volume actually available for inclusion and to the stability of the framework.

In light of possible practical applications, another remarkable feature of 2 and 3 is the reversibility of their sorption isotherms; moreover, their ability for adsorption of molecules other than H\textsubscript{2} (i.e., H\textsubscript{2}O, CO, and CO\textsubscript{2}) should also be emphasized because the removal of small amounts of contaminant gases from H\textsubscript{2} is still an open challenge for the real use of hydrogen as a fuel.\textsuperscript{21}


Supporting Information Available: XRPD and thermodiffractometric results, thermogravimetry, and sorption isotherms. This material is available free of charge via the Internet at http://pubs.acs.org.

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