

Energetics of Formation and Hydration of a Porous Metal Organic Nanotube

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Elemental Analysis

CHN analysis of the UMON material $((C_4H_{12}N_2)_{0.5}[(UO_2)(Hida) (H_2ida)] \cdot 1.9 H_2O)$ was determined using a Perkin/Elmer 2400 Series II Analyzer (calc, found based upon three replicates): C (19.64, 19.72 ± 0.05), N (6.87, 6.74 ± 0.07), H (3.42, 3.25 ± 0.04). Difference in the calculated versus the observed value for the H content may be due to the rapid dehydration of the material.

Surface area measurements

Surface areas of UMON were determined by argon adsorption using the Brunauer–Emmett–Teller (BET) method¹ at -186 °C. Ten-point argon adsorption isotherms were collected in a relative pressure range of $p/p^0 = 0.05–0.3$ (where, p^0 = saturation pressure) using a Micromeritics ASAP 2020 surface area and porosity analyzer. Prior to analysis, the UMON samples were degassed under vacuum at 80 °C for 4 h. The uncertainties in the BET surface area measurements were propagated by fitting a straight line to $1/[Q(p^0/p_1)]$ (Q = quantity adsorbed, mmol/g) against p/p^0 using the Micromeritics software. The surface area obtained from BET measurement using the 10 point isotherm of argon gas was $1.37 \pm 0.08 \text{ m}^2/\text{g}$. Similar values were obtained using N_2 gas and are indicative of little adsorption of the gas in the porous material.

One possible explanation for the observed poor gas adsorption could be the lack of adsorption sites due to the presence of organic molecules on the interior walls of the nanotube.

The gas adsorption properties of hybrid materials, including MOFs, MONs, and 2-D sheets, cover a range of values. For example, MOF-5 has similarly sized pore spaces (1.2 and 1.5 nm) and high uptake of Ar, N₂, H₂, and CH₄.^{2, 3} The surface adsorption sites identified in the MOF-5 structure are associated with both the zinc oxide secondary building units and the phenylene linkers. Other hybrid materials will selectively uptake gases; for example, nitrogen adsorption was not reported for the previously synthesized [Pt(en)bpy]I₄⁸⁻ MON, but Otsubo et al., did observe uptake of ethanol, methanol, and water.⁴

Selective uptake may be strongly associated with hybrid materials that contain hexavalent uranium. Hexavalent uranium forms two strong bonds with O atoms to form the nearly linear dioxo cation, UO₂²⁺. Chelation by the organic linkers occurs through the equatorial plane, which generally leaves the uranyl oxo atoms pointed toward the surface of the pore spaces. These oxo atoms are often thought of as passivated, as they only take part in weak interactions and may not be ideal gas adsorption sites. A number of porous hybrid uranyl materials have been previously reported in the literature, but only one study reported gas adsorption isotherms.⁵ Alsorook et al.⁵ reported the synthesis and characterization of a porous framework built upon uranyl cobalt phosphoacetate building units. Based upon the adsorption isotherms, the phosphoacetate compound was found to have little uptake of N₂ gas, but larger adsorption of CO₂.⁵ This suggests that there could be selective gas adsorption properties for the UMON sample that have yet to be determined.

References for Supporting Information

1. Brunauer, S.; Emmett, P. H.; Teller, E., *J. Am. Chem. Soc.* **1938**, *60*, 309-319.
2. Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M., *Science* **2013**, *341* (6149), 974-976.
3. Shekhah, O.; Liu, J.; Fischer, R. A.; Woll, C., *Chem. Soc. Rev.* **2011**, *40* (2), 1081-1106.
4. Otsubo, K.; Wakabayashi, Y.; Ohara, J.; Yamamoto, S.; Matsuzaki, H.; Okamoto, H.; Nitta, K.; Uruga, T.; Kitagawa, H., *Nature Mater.* **2011**, *10* (4), 291-295.
5. Alsobrook, A. N.; Hauser, B. G.; Hupp, J. T.; Alekseev, E. V.; Depmeier, W.; Albrecht-Schmitt, T. E., *Chem. Comm.* **2010**, *46* (48), 9167-9169.