Porous Materials

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Hybrid Zeolitic Imidazolate Frameworks with Catalytically Active TO_4 Building Blocks**

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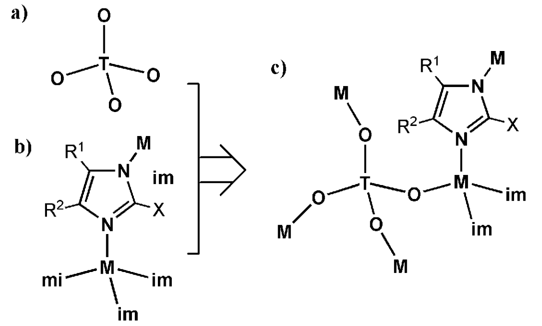
Crystalline porous materials with diverse chemical compositions (e.g., inorganic porous materials, inorganic–organic hybrid frameworks, and covalent organic frameworks) and framework topologies have been intensively studied in the past 60 years.[1] They have wide applications in fields such as heterogeneous catalysis, gas storage, and separation.[2] Moreover, some currently emerging areas related to health, energy use, and environmental conservation and remediation are still looking for the development of new porous materials.[3–5]

Zeolites are among the most well known porous materials because of their typical 4-connected open frameworks with TO_4 ($T = Si^{4+}$, Al^{3+}, or P^{5+} etc.) building blocks and outstanding catalytic or gas separation properties.[6,7] Recently, the search for new zeolite-like structures was extended to metal–organic frameworks (MOFs), and these explorations in part produced a variety of zeolitic imidazolate frameworks (ZIFs) in which the tetrahedrally coordinated divalent cations ($M^{2+} = Zn^{2+}$ or Co^{2+}) are connected by the uninegative imidazolate ligands (im^-).[8–11] The rich chemistry associated with the organic imidazolate building blocks in ZIFs leads to some exceptional properties, such as large surface area and high gas uptake capacities.[12] A question that emerges is: "Are there material with properties intermediate of those of zeolites and ZIFs?". It is true that there is a hybrid state that remains unknown to date.

In this work, we were seeking to integrate compositional and structural features of zeolites and ZIFs by combining TO_4 tetrahedra with zinc–imidazolate units. Such a combination is trusted to bear both merits of zeolites and ZIFs, for example, possession of catalytic active TO_4 sits of zeolites and high porosity of ZIFs. Herein, we report this kind of hybrid zeolitic imidazolate framework [denoted HZIFs; general formula: $M_4(im)_6TO_4$] with catalytically active TO_4 ($T = Mo^{6+}$ or W^{6+}) building blocks and high thermal stability (up to 550 °C), which presents a new class of porous materials filling the gap between zeolites and ZIFs.

The HZIFs reported herein are constructed from two kinds of tetrahedral building blocks and contain two kinds of connectivity, and combine structural features of both zeolites and ZIFs (Scheme 1). The TO_4 units used in HZIFs are not traditional SiO_4 or AlO_4 units in aluminosilicate zeolites, but catalytically active MoO_4 or WO_4 units. Each TO_4 unit forms four T–O–M bonds with other typical tetrahedral $[M(im)_3O]$ units, in which the metal center ($M = Zn^{2+}$) has three additional M–im–M bonds. Thus, the assembly of tetrahedral TO_4 and $[M(im)_3O]$ units fabricates 4-connected zeolite-type topologies with the general framework composition $M_4(im)_6TO_4$.



Scheme 1. The building blocks in a) zeolites, b) ZIFs, and c) HZIFs.

Two initial HZIFs (HZIF-1Mo and HZIF-1W) were synthesized by the self-assembly of a Zn^{2+} cation, MoO_4^{2-} or WO_4^{2-} anions, and 2-methylimidazolate (2-mim) under solvothermal conditions. Both compounds were structurally characterized by single-crystal X-ray diffraction and found to be isostructural. They crystallize in the same cubic space group $Im\bar{3}m$ and have neutral three-dimensional frameworks $Zn_4(2\text{-mim})_6TO_4{\cdot}x(\text{solvent})$ (HZIF-1Mo: T = Mo; HZIF-1W: T = W) containing structurally disordered solvent molecules. In each structure, the tetrahedral TO_4 unit bonds to four Zn centers and the tetrahedral geometry of each Zn center is completed by three 2-mim ligands (Scheme 1c). The whole framework topology is identified as the 4-connected net with symbol sdt,[13] which is still unknown in both zeolites and ZIFs.

A prominent structural feature of this sdt-type framework is to interconnect the truncated octahedral cages of $[Zn_{24}(2\text{-mim})_{36}]$ by the inorganic MoO_4 or WO_4 units (Figure 1a). The large $[Zn_{24}(2\text{-mim})_{36}]$ cage with effective diameter of 12.5 Å and pore aperture of 3.3 Å in HZIF-1W is the same as the subunit in ZIF-8, a well known framework with zeolitic sodalite (SOD) topology.[8] Interestingly, each Zn vertex of this cage is covered by another T (T = W) node through Zn–O–T connectivity (Figure 1b). Although it is surrounded by the inorganic TO_4 units, each window of the cage remains

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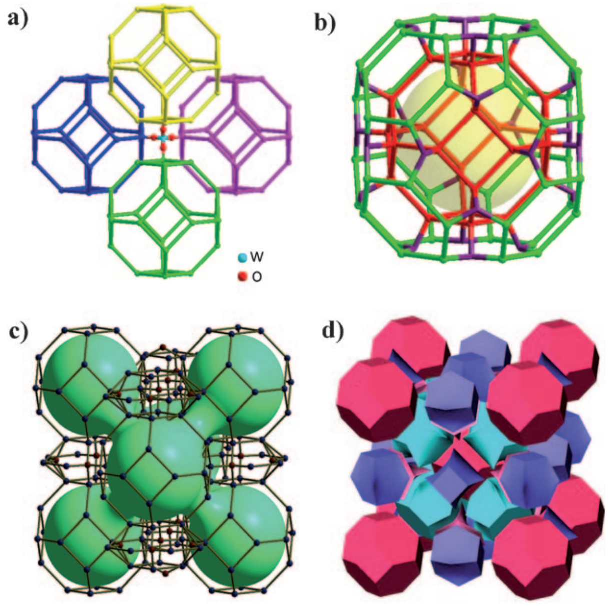

Figure 1. a) Each WO_4^{2-} ion links four truncated octahedral cages of $[Zn_{24}(2\text{-mim})_{36}]$ in the structure of HZIF-1W, and b) each cage is surrounded by the WO_4^{2-} ions. c) The resulting 3D framework with free voids (green balls) in the cages, and d) its natural tiling showing the packing of the cages (red tiles).

open and faces to next symmetry-related window of the adjacent cage. Because there are two kinds of T nodes in HZIF-1W, the nodal distance between Zn−O−W of 3.659 Å is significantly shorter than that of Zn−mim−Zn (6.005 Å), and the Zn−O−W angle of 161° is bigger than the Zn−mim−Zn angle of 146°. As a result of connectivity between inorganic TO_4 units and metal–organic cages, a microporous framework with solvent-accessible volume of 29.4 % of the crystal volume is formed (Figure 1 c).[14] The packing of the large cages can also be seen from the tiling illustration in Figure 1 d.

The free spaces in HZIF-1W are occupied by the structurally disordered *N*,*N*-dimethylformamide (DMF) molecules, equal to one and half DMF guest molecules per $Zn_4(2\text{-mim})_6TO_4$ unit, as evidenced by thermogravimetric (TG) analysis data. The TG curve of HZIF-1W shows a weight loss of 11 % from 20 to 200 °C, corresponding to the release of the DMF guest molecules (expected 11.1 %) (Figure S3 in the Supporting Information). No weight loss was observed between 200 and 550 °C, suggesting that no chemical decomposition occurred between the desolvating and ligand-releasing temperatures. The TGA curve of HZIF-1Mo is similar to that of HZIF-1W. Powder X-ray diffraction (PXRD) experiments under different temperatures were performed to investigate the thermal stability of HZIF-1W upon removal of guest molecules according to the TG analysis. The PXRD patterns below 550 °C are coincident with the corresponding patterns simulated from single-crystal XRD structures, which confirms the high structural and thermal stability (up to 550 °C) of the evacuated framework (Figure S4). The stability is significantly greater than those of ZIFs and other porous MOFs.[10]

The permanent porosity of these desolvated HZIFs was established by reversible N_2 sorption experiments at 77 K, which showed that they exhibit type I adsorption isotherm behavior typical of materials with microporosity (Figure 2 a).

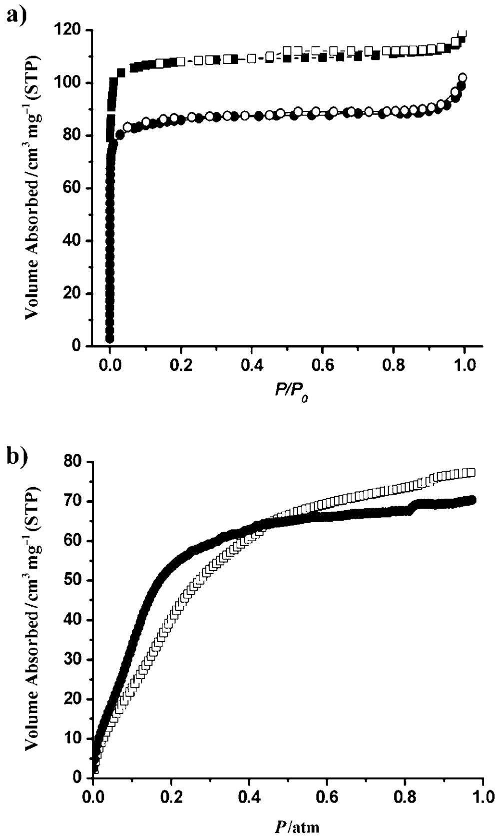

Figure 2. a) N_2 (HZIF-Mo: ■ adsorption, □ desorption; HZIF-W: ● adsorption, ○ desorption) and b) CO_2 (HZIF-Mo: □ adsorption; HZIF-W: ● adsorption) sorption isotherms. P/P_0 is the ratio of gas pressure (P) to saturation pressure (P_0), whereby $P_0 = 769$ torr.

The Langmuir surface areas were 476 and 381 $m^2 g^{-1}$ for HZIF-1Mo and HZIF-1W, respectively, demonstrating the effect of molecular weight. The BET method (Brunauer–Emmett–Teller) yields surface areas of 342 and 288 $m^2 g^{-1}$, respectively. The CO_2 uptake capacity of HZIF-1Mo reaches as high as 77.3 $cm^3 g^{-1}$ at 1 atm and 195 K, and that for HZIF-1W is 70.2 $cm^3 g^{-1}$ (Figure 2 b).

The remarkable thermal stability and the presence of catalytically active sites prompted us to examine the catalytic properties of these HZIFs. Materials based on MoO_4 or WO_4 units are useful as acid and oxidation catalysts for various reactions.[15] To determine the activity of these materials for oxidation of alcohols, both HZIF-1Mo and HZIF-1W were tested for selective oxidation of benzyl alcohol to benzaldehyde with 30 % hydrogen peroxide as the oxidant. The results show 100 % selectivity to benzaldehyde (no trace of benzoic acid) for both catalytic materials, and the conversion of benzyl alcohol are 51.4 % and 72.2 % for HZIF-1Mo and HZIF-1W, respectively, at 353 K for 6 h in aqueous solution (Figures S5 and S6). The different oxidizing abilities between the MoO_4

and WO_4 units ($MoO_4 < WO_4$) may be the reason for such different catalytic behavior.[15]

The photocatalytic activities of the desolvated samples were also investigated by spectrophotometry, the results of which demonstrate that both HZIFs have photocatalytic activity, and HZIF-1Mo possesses higher activity than HZIF-1W. The degradation of methyl orange was selected as the reference,[16] and the characteristic absorption of methyl orange at about $\lambda = 465$ nm was selected for monitoring the adsorption and photocatalytic degradation process. Figure 3 shows a comparison of photocatalytic activities of different samples. The photocatalytic activity of each sample was gradually enhanced with time increasing from 0 to 120 min. HZIF-1Mo exhibits much higher activity. After application of light for 120 min, the degradation ratio of methyl orange reaches 81.6 %. Although HZIF-1Mo and HZIF-1W possess the same topological structures, different metal ions between them lead to distinct band-gap sizes (HZIF-1Mo: E_g = 1.32 eV; HZIF-1W: E_g = 2.2 eV; Figures S8 and S9), which give rise to a discrepancy in their photocatalytic activity. Their reverse catalytic behavior in the oxidation of benzyl alcohol reaction (HZIF-1Mo < HZIF-1W) and the photocatalytic reaction (HZIF-1Mo > HZIF-1W) is related to the different catalytic mechanisms.

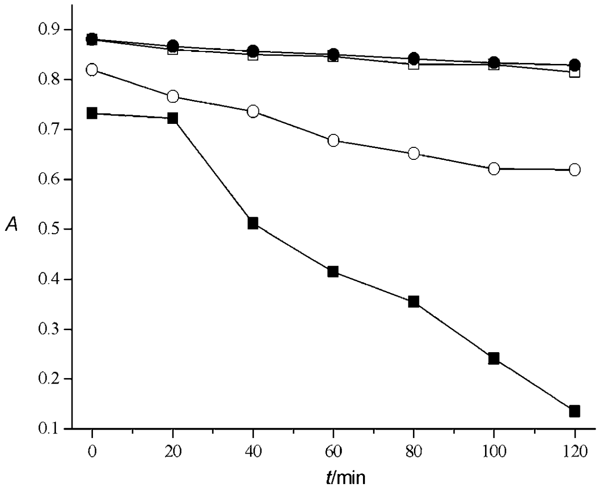

Figure 3. Plots of absorbance (*A*) versus irradiation time in the presence of methyl orange/H_2O_2 solution (●), methyl orange/H_2O_2 solution with ZIF-8 (□), methyl orange/H_2O_2 solution with HZIF-1W (○), and methyl orange/H_2O_2 solution with HZIF-1Mo (■).

HZIFs differ from ZIFs because of the additional catalytic active sites in the structures, so they can act as the heterogeneous catalysts for the selective oxidation of benzyl alcohol and the photocatalytic degradation of methyl orange. Without the MoO_4^{2-} or WO_4^{2-} ions in the synthetic reactions of above HZIFs, the obtained material ZIF-8 (E_g = 4.9 eV; Figure S11) under the similar conditions did not show any catalytic activity because of the absence of the catalytic sites in the structure and its wide band gap (Figure 3). Relative to other porous MOFs, HZIFs present notably high thermal stability and special 4-connected zeolite-like topology.

In summary, we developed a new kind of porous materials HZIFs with integrated structural features and functions of zeolites and ZIFs. These HZIFs have distinct framework topology, unusual high thermal stability, and catalytic properties, opening a new construction route toward novel zeolite-type framework materials. Further works to explore the structural diversity and new functions of HZIFs by using different imidazolate ligands and inorganic TO_4 units are in progress.

Experimental Section

Synthesis of $Zn_4(2\text{-mim})_6WO_4\cdot1.5(DMF)$ (HZIF-1W): $Zn(CH_3COO)_2\cdot2H_2O$ (0.1760 g, 0.8 mmol), 2-methylimidazole (2-mim, 0.0960 g, 1.2 mmol), tungstic acid (H_2WO_4, 0.0500 g, 0.2 mmol), and *N*,*N*-dimethylformamide (DMF, 4 mL) in a 23 mL teflon-lined air-tight reactor was heated at 160 °C for 6 days, and then cooled to room temperature. Colorless transparent polyhedral crystals were obtained as a pure phase, washed with water and ethanol, and dried at room temperature. Elemental analysis for $C_{28.5}H_{40.5}N_{13.5}Zn_4WO_{5.5}$: found (calcd): C 31.0 (30.96), H 3.88 (3.69), N 16.25 (17.1). IR (KBr pellet): $\tilde{\nu}$ = 3133m, 2927m, 1680, 1590s, 1457s, 1461s, 1309s, 1174m, 1144s, 996s, 896m, 757s, 691m cm^{-1}. A similar procedure was performed for the synthesis of $Zn_4(2\text{-mim})_6MoO_4\cdot2(DMF)$ (HZIF-1Mo) by using molybdic acid instead of tungstic acid.

Crystal data for HZIF-1W: $C_{28\cdot5}H_{40\cdot5}N_{13\cdot5}Zn_4WO_{5\cdot5}$, $M = 1105.5$, cubic, $a = 23.575(3)$ Å, $V = 13102(3)$ Å^3, $T = 293(2)$ K, space group $Im\bar{3}m$, $Z = 12$, 51 628 reflections measured, 1486 independent reflections ($R_{int} = 0.0563$). The final R_1 values were 0.0888 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2501 ($I > 2\sigma(I)$). The goodness of fit on F^2 was 1.294. Crystal data for HZIF-1Mo: $C_{30}H_{44}N_{14}Zn_4WO_{5\cdot5}$, $M = 1054.23$, cubic, $a = 23.4345(2)$ Å, $V = 12869.66(19)$ Å^3, $T = 293(2)$ K, space group $Im\bar{3}m$, $Z = 12$, 5352 reflections measured, 832 independent reflections ($R_{int} = 0.0294$). The final R_1 values were 0.0751 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2050 ($I > 2\sigma(I)$). The goodness of fit on F^2 was 0.995.

CCDC 787697 (HZIF-1Mo) and 787698 (HZIF-1W) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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