MOFs and their grafted analogues: regioselective epoxide ring-opening with Zr₆ nodes†

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Zirconium(v)-containing metal–organic framework (MOF) catalysts NU-1000 and MOF-808 were compared to analogous catalysts synthesized by grafting the nodes onto bare and functionalized silica. As-synthesized, calcined, and activated catalysts all exhibit similar selectivity in the ring-opening of 1,2-epoxyoctane with isopropanol, but MOF-808 gives exceptionally high rates and yields per gram catalyst.

Metal–organic frameworks (MOFs) have received recent attention as highly active catalysts with extraordinarily high porosity and nearly infinite synthetic tunability.1–3 The organic linker units can be catalytically active4,5 or can serve to attach or entrap molecular catalysts;6 alternately, the inorganic nodes can be catalytic.7,8 Defect sites have been recognized as critical to reactivity when the node is the catalyst.9,10 For the Zr₆-benzoate cluster-based MOFs such as NU-100012 (8-connected) and MOF-80813 (6-connected), reactivity has been implicated in the relative Brønsted acidity of Zr–OH and Zr–OH₂ protons, a property related to both node connectivity and to the presence of open (labile) Zr cation coordination sites.10 Defects must be generated and stabilized,14,15 and this is often achieved via hydrothermal treatments following MOF synthesis.16,17

Here, we demonstrate that MOF nodes can be stabilized as active sites on other materials, and that there is a correspondence between the reactivities of MOF defect sites and supported clusters with other types of oxide defect sites, such as calcined supported oxides. Supported metal oxides are essential heterogeneous catalysts for many selective oxidation reactions key to commodity and fine chemical processes, and materials investigated here offer insight into building more well-defined defect sites in MOFs.

Separately, ring-opening of epoxides is a widely studied reaction in organic synthesis, catalyzed by both Brønsted18 and Lewis acids.19,20 Electron-poor terminal epoxides are challenging substrates to activate with Lewis acids, and studying trends in alkoxylation reactivity over heterogeneous Lewis acid catalysts provides insight into routes for upgrading conventional alkoxylation processes in industry.19–23 In a few reports, homogeneous24 and clay-supported25,26 ZrIV catalysts have given high regioselectivity to the more sterically challenging β-alkoxy alcohols. Separately, some of us have reported highly regioselective and enantioretentive epoxide activation using the Hf-NU-1000 MOF catalyst (isostructural to the Zr-based NU-1000) for CO₂ fixation, methanolysis and azidolysis27 and for ring-opening with mild hydrides.28 Opportunities exist for MOFs, supported metal oxides and other Lewis acids to facilitate these selective transformations, and here we investigate the ring-opening of 1,2-epoxyoctane with isopropanol as a model reaction over various ZrO₂-based materials.

The Zr₆-benzoate cluster node,11 NU-100012 and MOF-80813 were prepared according to literature protocol previously reported by some of us and by others. Structures were

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confirmed using PXRD (Fig. S1–S3†). Zr₆ clusters were also immobilized onto SiO₂ surfaces functionalized with –PO(OH)₂ or –COOH moieties, generating catalysts “Zr₆–P–SiO₂” or “Zr₆–BA–SiO₂”, respectively (Scheme 1). Ethylphosphonic acid-modified silica (“P–SiO₂,” Sigma, 45–86 µm, 524 m² g⁻¹, 4.9 nm avg. pore dia., phosphonate loading of 0.94 mmol g⁻¹ or 1.1 nm⁻² by ICP-OES) is commercially available, whereas benzoic acid-functionalized silica (“BA–SiO₂”) was synthesized via grafting of ethyl 4-(triethoxysilyl)benzoate to mesoporous silica gel (Selecto, 32–63 µm, 569 m² g⁻¹, 5.4 nm avg. pore dia., carboxylate loading of 0.42 mmol g⁻¹ or 0.44 nm⁻² from TGA) as reported by some of us elsewhere.29,30 Functioning like a MOF linker, the supports’ acidic functional groups serve as docking points for Zr₆ clusters, which graft at >80% yield from refluxing toluene, giving final loadings of 0.5–0.8 mmol Zr g⁻¹, equivalent to surface densities of ∼0.6–0.8 Zr atoms nm⁻² (Table 1).

Upon grafting, Zr₆ groups are irreversibly connected to the support. Diffuse reflectance UV-visible spectroscopy (DR UV-vis) gives evidence for the Zr₆ cluster in both Zr₆–P–SiO₂ and Zr₆–BA–SiO₂ based on growth of the feature at 275 nm, assigned to the ZrO₂ LMCT band (Fig. 1). Similarly, NU-1000 and MOF-808 reveal comparable LMCT features between 270–280 nm. Optical edge energies of Zr₆–P–SiO₂, Zr₆–BA–SiO₂ and MOF-808 are all ∼4.0 eV (Table 1), as determined by indirect Tauc plots,31,32 suggesting the cluster maintains structural similarity across different support environments. The optical edge of NU-1000 is due to the 1,3,6,8-tetrakis(p-tol) gives evidence for the Zr₆ cluster in both Zr₆

- **Table 1**: Summary of catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Zr precursor</th>
<th>Reference</th>
<th>BET S.A. (m² g⁻¹)</th>
<th>Zr content † (mmol g⁻¹)</th>
<th>Edge ‡ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NU-1000</td>
<td>Zr₆⁺</td>
<td>12</td>
<td>2310</td>
<td>2.74</td>
<td>2.4</td>
</tr>
<tr>
<td>MOF-808</td>
<td>Zr₆⁺</td>
<td>13</td>
<td>1940</td>
<td>4.58</td>
<td>4.0</td>
</tr>
<tr>
<td>Zr₆–P–SiO₂</td>
<td>Zr₆⁺</td>
<td>This</td>
<td>524b</td>
<td>0.54</td>
<td>3.9, 3.1†</td>
</tr>
<tr>
<td>Zr₆–BA–SiO₂</td>
<td>Zr₆⁺</td>
<td>This</td>
<td>561b</td>
<td>0.78</td>
<td>4.0</td>
</tr>
<tr>
<td>Zr₆–SiO₂</td>
<td>Zr₆⁺</td>
<td>This</td>
<td>569b</td>
<td>0.22</td>
<td>3.9</td>
</tr>
<tr>
<td>Zr–SiO₂</td>
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<td>39</td>
<td>569b</td>
<td>0.21</td>
<td>3.7</td>
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<td>41</td>
<td>95.5</td>
<td>n/a</td>
<td>7.3</td>
</tr>
</tbody>
</table>

† Zr₆-benzoate cluster Zr₆(OH)₂(OOCPh)₁₂(PrO)/(PhCOOH)₁₁. ‡ BET surface area of support prior to Zr precursor deposition. † From ICP-OES of digested catalysts. ‡ Determined from indirect Tauc plot.31,32 Σ Shoulder feature.

NU-1000 and MOF-808 are catalytically inert without activation (Table 2, entries 2–3, respectively), the former with 0.5 Maq HCl/DMSO solution at 100 °C for 18 h and the latter with supercritical CO₂ drying followed by evacuation at 150 °C for 14 h.12,13 Some of us have shown this step to be crucial in generating a preponderance of open (labile) Zr coordination site defects with greater exposed –OH and/or ligated –OH₂, responsible for strong acidity in the resulting catalysts.10 Upon activation, both NU-1000 (Table 2, entry 4) and MOF-808 (Table 2, entry 5) gives a mixture of primary and secondary alcohols similar to that of general acid catalysis (Table 2, entry 1).

In contrast, grafted Zr₆ supported on modified SiO₂ is active as-synthesized. The same ‘activation’ with HCl actually reduces the catalytic activity, presumably by cleaving Zr₆ from the surface. Zr₆–P–SiO₂ (Table 2, entry 6) and Zr₆–BA–SiO₂ (Table 2, entry 7) give very similar selectivity to the MOF catalysts. Importantly, immobilization onto a support or within a framework plays a crucial role in the resulting reactivity, as the Zr₆ cluster itself is inactive as a homogeneous catalyst (Table 2, entry 10). Even though all are mildly acidic (Table S1†), no significant reaction occurs on the supports alone (Table 2, entries 11–12).
Next we sought to compare these materials to a calcined, supported Zr oxide. For one material, the Zr_6 cluster was deposited onto bare SiO_2 via wetness impregnation in toluene (“Zr_6-SiO_2”) at 0.22 mmol Zr g^{-1} (0.23 Zr atoms nm^{-2}). After solvent evaporation, the material was calcined in static air at 550 °C for 6 h. Separately, a dimethoxyxal[b]arene-Zr-Cl_2 (“dmCxB-Zr_6”) complex was grafted to SiO_2 at a nearly identical surface density, which upon calcination yields a material with highly dispersed, undercoordinated Zr oxide sites (“Zr-SiO_2”), recently reported by some of us for alkene epoxidation.39 DR UV-vis of the calcined oxides display optical edges of 3.9 and 3.7 eV, respectively, similar to the grafted clusters and MOF-808, and in agreement with the absence of nanocrystallites of ZrO_2.39-41 For ring-opening of 1,2-epoxyoctane, Zr_6-SiO_2 and Zr-SiO_2 (Table 2, entries 8–9, respectively) both give nearly identical initial rates and similar 24 h yields, at ~70% regioselectivity to the secondary alcohol product, marginally lower than the selectivity shown by the MOFs and their grafted analogues. Bulk ZrO_2 (Table 2, entry 13) is seen to be completely inactive.

All catalysts in this study have selectivity independent of conversion (Fig. S7) and are stable to leaching and loss of crystallinity (for MOF catalysts) (Fig. S8, Table S2). Differences in rate and conversion are therefore attributed to the availability of Zr atoms in each material to participate in catalysis. On a per-Zr atom basis, the initial rates (TOF) follow the trend of Zr-SiO_2 ~ Zr_6-SiO_2 > activated MOF-808 > Zr_6-P-SiO_2 > Zr_6-BA-SiO_2 ~ activated NU-1000. The calcined, pure oxide catalysts are expected to have a preponderance of highly dispersed, acidic Zr^{IV} sites, consistent with their high initial TOF and ultimate TON. The other catalysts are organic-inorganic hybrids and, by inference, have fewer defects that generate acid sites. Indeed, NU-1000 is known as a particularly stable MOF,12,17 consistent with its low TOF. Alternate activation methods may increase its per-Zr reactivity.41 Likewise, Zr_6-BA-SiO_2 is structurally similar to the defect-free and inactive Zr_6 cluster. MOF-808 is unique in that it has a moderate initial TOF, due to its inherently defective nodes,13,42 but also a high final TON unlike, for example Zr_6-P-SiO_2, indicating that the MOF structure maintains active site accessibility even with extended reaction time.

The prior comparisons have been made on the basis of turnover numbers, per Zr atom. However, on mass basis, the MOF catalysts have much higher activity and final productivity than any of the grafted or calcined catalysts. In particular, MOF-808 has an extremely high loading of Zr_6 sites, giving it a 6-fold higher initial rate and a 20-fold higher final productivity than those of the reference Zr-SiO_2 or Zr_6-SiO_2 catalysts.

Conclusions

In summary, this study demonstrates the correspondences among acid catalysis carried out by the defects at ZrO_2 nodes in MOFs, amorphous chemical analogues synthesized by grafting the ZrO_2 nodes to appropriately decorated silica surfaces, and classical ZrO_2-SiO_2 supported oxides. In the MOFs and grafted materials, the incorporation of the Zr_6 node into...
the solid material generates catalytically active defect sites from the otherwise inert Zr₆ node. One significant advantage of MOF catalysis is the very high density (mmol g⁻¹) of active sites that can be generated upon activation, resulting in excellent yields per g total catalyst. As a corollary, the high permetal reactivity of conventional supported oxides should serve as an inspiration for building new generations of more selective and well-defined site architectures at high total loadings within MOFs.

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Notes and references

‡ Reaction protocol: 6.9 mmol 1,2-epoxyoctane was added to a 4 mL screw-top vial with a magnetic stirbar containing 0.069 mmol Zr catalyst, 28 mmol iso-propanol and 7.0 mmol mesitylene (internal standard). The reaction vial was sealed, shaken at 700 rpm at 55 °C in a Glas-Col heated vortexer to initiate the reaction. Aliquots (50 µL) were withdrawn at specified time intervals using a syringe with a glass microfilter to remove suspended catalyst, diluted with 1.5 mL THF and analyzed using an Agilent HP 6890 GC-FID equipped with a Zebron ZB-624 capillary column (30 m × 0.25 mm × 1.4 µm) and quantified using calibrated standards. Mass balances >92%. See ESI.