

A Hafnium-Based Metal–Organic Framework as an Efficient and Multifunctional Catalyst for Facile CO₂ Fixation and Regioselective and Enantioselective Epoxide Activation

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Supporting Information

ABSTRACT: Porous heterogeneous catalysts play a pivotal role in the chemical industry. Herein a new Hf-based metal–organic framework (Hf-NU-1000) incorporating Hf₆ clusters is reported. It demonstrates high catalytic efficiency for the activation of epoxides, facilitating the quantitative chemical fixation of CO₂ into five-membered cyclic carbonates under ambient conditions, rendering this material an excellent catalyst. As a multifunctional catalyst, Hf-NU-1000 is also efficient for other epoxide activations, leading to the regioselective and enantioselective formation of 1,2-bifunctionalized systems via solvolytic nucleophilic ring opening.

Catalysts based on permanently porous frameworks have the potential to unify the best features of homogeneous catalysts (selectivity and ease of modification) and heterogeneous catalysts (ease of purification and recyclability). Metal–organic frameworks (MOFs) represent a special class of porous materials consisting of easily constructed organic linkers and metal clusters.¹ The modular nature and facile tunability of MOFs make them ideal heterogeneous catalysts with uniform active sites through wisely chosen building blocks. In catalysis, MOFs allow for the same level of structural refinement as molecular homogeneous catalysts, while their ultrahigh surface area, pore volume, and heterogeneous nature facilitate good catalytic activity and rapid purification.²

Catalyst-mediated reactions of CO₂ represent one potential positive contributor to climate-relevant carbon capture and storage/sequestration (CCS), albeit a far from sufficient one to satisfy this enormous challenge.³ Well-designed reactions that utilize waste CO₂ in the production of commercially relevant chemicals are much sought these days. Some of these reactions include the formation of carbonates, where the carbonyl carbon obtained from CO₂ is isohypsic with its starting material and does not require reagent-driven changes in oxidation state.⁴ The acid-catalyzed cycloaddition of CO₂ with an epoxide to form a cyclic carbonate, a functionality having various important applications,⁵ is a highly atom-economical reaction that might be catalyzed by an appropriately designed MOF. Mechanistically, this reaction is

based on an acid catalyst that activates the epoxide, which can then be attacked by a nucleophile cocatalyst to form an alkoxide. This intermediate can then react with carbon dioxide to ultimately give the cyclic carbonate.⁶ However, on account of the relatively inert nature and low reactivity of CO₂, its activation and incorporation into organic substrates still remains a formidable challenge.⁷

Although some homogeneous catalysts⁸ and several types of heterogeneous catalysts,⁹ such as zeolites,¹⁰ silica-supported salts,¹¹ metal oxides,¹² titanosilicate,¹³ a microporous polymer,¹⁴ and an organic network,¹⁵ have been utilized for the synthesis of cyclic carbonates, most of the processes demand high pressures and temperatures, thus requiring high energy and capital costs.

Recently,¹⁶ we reported a new Zr-based MOF, NU-1000, obtained via the solvothermal reaction of ZrCl₄ and 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (H₄TBAPy) with benzoic acid as a modulator. The parent-framework node consists of an octahedral Zr₆ cluster capped by eight bridging oxygen-containing ligands. The 3D NU-1000 structure can be described as 2D Kagome sheets linked by TBAPy ligands. NU-1000 shares the same topological features as MOF-545¹⁷ and PCN-222,¹⁸ comprising triangular and hexagonal channels. The presence of a high density of acidic sites, the integration of permanent porosity with ultralarge channels, the high surface area, and the extraordinary chemical stability of NU-1000 suggested that it could be an excellent catalyst platform that can overcome the above-mentioned challenges in CO₂ insertion and acid-catalyzed epoxide activation in general.

By comparing the dissociation enthalpies of typical Hf–O versus Zr–O bonds (802 vs 776 kJ mol⁻¹),¹⁹ we inferred that Hf is more oxophilic (i.e., has stronger M–O bonds) than Zr and should thus function as a stronger Brønsted acid. Therefore, we hypothesized that a Hf-cluster-based NU-1000 would be an even more efficient catalyst than the Zr-cluster-based NU-1000 for acid-catalyzed systems [also see the Supporting Information (SI)]. In order to test our hypothesis, we prepared the Hf-based MOF (Hf-NU-1000) with the same topology as NU-1000.²⁰ To

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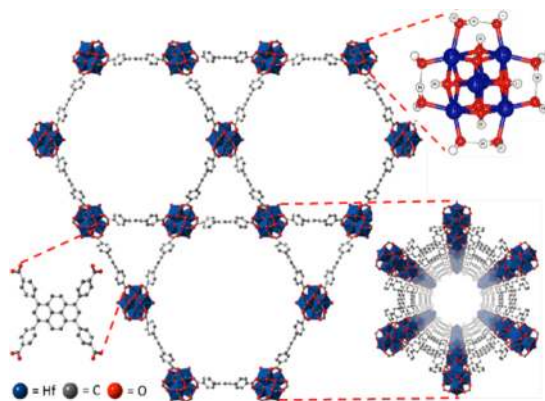


Figure 1. Relevant structural features and representations of Hf-NU-1000. For simplicity, H atoms except for the cluster are not shown. For clarity, the carboxylates have been removed from the cluster shown in the top inset.

confirm that NU-1000 and Hf-NU-1000 have the same overall crystal structure, periodic density functional theory (DFT) within the Vienna ab Initio Simulation Package (VASP)²¹ was used to optimize the ionic positions of NU-1000 starting from the validated NU-1000 X-ray diffraction (XRD) data. The Zr⁴⁺ ions were then replaced with Hf⁴⁺, and the simulated Hf-NU-1000 structure was used to optimize the ionic positions. Comparison of the experimental and simulated powder XRD (PXRD) patterns of Hf-NU-1000 and NU-1000 confirmed that the Hf and Zr versions of NU-1000 are indeed isostructural (Figure 1; also see the SI).

The porosity of Hf-NU-1000 was studied by N₂ adsorption–desorption experiments at 77 K, and the resulting isotherm (type IVc) yielded a Brunauer–Emmett–Teller (BET) surface area of 1780 m² g^{−1} and a total pore volume of 1.14 cm³ g^{−1}. DFT pore size distribution analysis revealed pore diameters of ca. 13 and 29 Å, assignable to the triangular micropores and hexagonal mesopores, respectively. Thermogravimetric analysis (TGA) of the activated sample showed no major decomposition up to 500 °C (see the SI). Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) confirmed the presence of –OH groups and H₂O molecules in the Hf₆ nodes, with peaks at 3679 cm^{−1} assigned to the non-H-bonded –OH and bridging –OH stretches, the peak at 3678 cm^{−1} assigned to the non-H-bonded H₂O stretch, and the peak at 2752 cm^{−1} assigned to the H-bonded H₂O and OH stretches (see the SI).²²

Given the high stability, porosity, and large channels of Hf-NU-1000, we decided to investigate its performance as an acid catalyst in the context of CO₂ fixation through reaction with epoxides to form cyclic carbonates under ambient conditions. Hf-NU-1000 demonstrates highly efficient catalytic activity for the quantitative cycloaddition of styrene oxide using CO₂ at 1 atm gauge pressure to form styrene carbonate at room temperature (r.t.) (Table 1, entry 1a). To the best of our knowledge, this is the mildest and the most efficient catalytic system for this type of reaction. Since the conversion of epoxide to carbonate is complete and quantitative, the pure product could be obtained after a simple aqueous extraction, without the need for laborious purification steps such as distillation, which can cause decomposition of the product and the formation of byproducts.²³ Under the same reaction conditions, NU-1000 was not as efficient as Hf-NU-1000 (entry 1b), confirming our hypothesis about their relative catalytic activities. When the same reaction conditions were employed, but in the absence of

catalyst, no product was obtained (entry 1c). The same reaction proceeds much faster at elevated temperature (55 °C, 13 h; entry 1d). Hf-NU-1000 was compared with the reported MOFs^{9d} gea-MOF-1,^{9c} Cr-MIL-101, MOF-5, ZIF-8, Ni(salphen)-MOF, Co-MOF-74, Mg-MOF-74, [Cu(Hip)₂(Bpy)]_n[CHB(M)], ZIF-68, F-IRMOF-3, and MIL68(In)-NH₂ (Table S2, entries 1e–o), which have also been used for the preparation of styrene carbonate, and Hf-NU-1000 clearly stands out in terms of yield and milder conditions.

The industrially important epoxide divinylbenzene dioxide (DVBDO) was also examined, and biscarbonated DVBDO, which could be a useful epoxy resin monomer²⁴ candidate, was obtained quantitatively after 19 h at 55 °C (Table 1, entry 2). Hf-NU-1000 was also compared with other MOF materials for the conversion of propylene oxide (PO) to propylene carbonate (r.t., 26 h; entry 3). Hf-NU-1000 again showed shorter reaction time and higher product yield compared with the previously reported MOFs^{9d} MMCF-2,^{9a} PCN-224(Co),^{9b} gea-MOF-1,^{9c} HKUST-1, MOF-505, MMPF-9, Cr-MIL-101, MOF-5, Ni(salphen)-MOF, CHB(M), and Zn₄O(BDC)_x(ABDC)_{3−x} based on MOF-5 (MIXMOF) (Table S2, entries 3b–l). It is worth noting that PO is more studied than styrene oxide because of its higher reactivity and ease of isolation. However, its low boiling point could easily lead to mass loss, which can complicate yield calculations; thus, careful handling is required.

To confirm the heterogeneous nature of the reaction, under the same conditions as in Table 1, entry 1a, 40 h after the outset of the reaction, the catalyst was removed and the reaction was allowed to continue. As expected, no increase in the formation of carbonate was detected (see the SI). At the end of the reaction, inductively coupled plasma (ICP) analysis of the reaction mixture filtrate revealed no Hf leaching, indicating that the catalytic reaction is indeed heterogeneous in nature. Additionally, in the absence of the ammonium salt cocatalyst, no conversion was detected for the model reaction. Furthermore, the catalyst was reused five successive times without a significant decrease in the efficiency of the catalyst or structural deterioration as determined by PXRD analysis (see the SI).

After such encouraging results for the cycloaddition reaction of CO₂ with epoxides were obtained, and since mechanistically this reaction occurs via an acid-catalyzed ring-opening step,^{6,9a} we became interested in investigating the performance of Hf-NU-1000 in the activation of epoxides for the preparation of 1,2-bifunctionalized systems via acid-catalyzed nucleophilic ring

Table 1. Cycloaddition Reactions of CO₂ with Epoxides Catalyzed by Hf-NU-1000 Yielding Cyclic Carbonates

Entry	Catalyst	Subs	Prod	T [°C]	P [atm.]	t [h]	Yield [%]
1a ^[a]	Hf-NU-1000			r.t.	1	56	100 ^[c]
1b ^[a]	NU-1000			r.t.	1	56	46 ^[c]
1c ^[b]	-			r.t.	1	56	0 ^[c]
1d ^[a]	Hf-NU-1000			55	1	13	100 ^[c]
2 ^[a]	Hf-NU-1000			55	1	19	100 ^[c]
3 ^[a]	Hf-NU-1000			r.t.	1	26	100 ^[c]

^aReaction conditions: epoxide (0.2 mmol), catalyst (4.0 mol % –OH active site), and *n*Bu₄NBr (10 mol %) under CO₂ (1 atm gauge pressure). ^bThe same conditions as in footnote a, but without the catalyst. ^cDetermined by ¹H NMR analysis using 1-bromo-3,5-difluorobenzene as the internal standard.

opening. As the initial step, we chose to focus on the synthesis of vicinal azidoalcohols, which are important precursors of α -amino alcohols²⁵ (known as β -blockers). Additionally, vicinal azidoalcohols are present in various bioactive natural products²⁶ and in the chemistry of carbohydrates,²⁷ nucleosides,²⁸ lactams,²⁹ and oxazolines.³⁰ Although azidoalcohols are generally synthesized from epoxides by reaction with alkali azides, this classical method is often accompanied by side reactions such as isomerization, epimerization, and rearrangement.^{27,31} To the best of our knowledge, there is no report of highly regioselective azidolysis of epoxides with a high yield and complete conversion of substrate.³² Tanabe and Cohen³³ and Song et al.³⁴ studied this reaction using a series of MOFs, but they obtained only moderate conversions and/or required stepwise postsynthetic modifications.

Under the optimized conditions, Hf-NU-1000 catalyzed the solvolytic reaction of trimethylsilyl azide (TMS-N₃) with styrene oxide with high regioselectivity for substitution at the benzylic position and complete conversion of substrate (Table S3, entry 1). The catalyst was also reused five successive times, and neither a considerable decrease in the efficiency of the catalyst nor structural deterioration as determined by PXRD analysis was observed (see the SI). In order to gain a better understanding of the origin of this unique regioselectivity, a few control reactions were conducted. First, hafnium(IV) oxychloride octahydrate was utilized as a Lewis acid catalyst to examine whether the regioselectivity originates from Hf^{IV}; the conversion decreased to 75%, and the co-occurrence of a side-product (30%) was observed (entry 2). When dehydrated Hf-NU-1000 was used, both the conversion (60%) and regioselectivity (85:15) decreased (entry 3). Additionally, aqueous HCl (an alternative homogeneous catalyst) was used to catalyze this reaction, but it showed poor conversion (48%) and the co-occurrence of a side product (26%) (entry 4).

In order to elucidate the mechanism of the reaction, we turned to computational modeling. Quantum-chemical calculations were carried out using DFT at the M06-L/def2-SVP level. The SMD continuum solvent model³⁵ was employed to account for solvation with TMS-N₃ as the solvent. Hf-NU-1000 serves as a proton donor in the ring-opening reaction because of the presence of aqua and OH ligands in the Hf₆ node. Our calculations show that styrene oxide forms an association complex with the Hf₆ node via both hydrogen-bonding and π -stacking interactions (see the SI). The main criteria defining the reaction selectivity are the difference in the activation barriers of the epoxide ring-opening step (kinetic factor) and the relative stability of the products (if the reaction operates under thermodynamic control). The optimized geometries of the transition state (TS) structures TSa (azide attack at the benzylic position) and TSb (azide attack at the less hindered side) leading to products A and B, respectively, are depicted in Figure 2. In both TS structures, the aromatic ring of styrene oxide engages in a T-shaped π -stacking interaction with the aromatic rings of the Hf₆ node linker ligands. The calculations show that for the reaction catalyzed by the Hf₆ node, the difference in activation free energies is 3.0 kcal/mol, while in the case of HCl the difference is about 2 kcal/mol. The difference in the free energies of the products [$\Delta_f G_{298}^\circ(\mathbf{b}') - \Delta_f G_{298}^\circ(\mathbf{a}')$] is 0.1 kcal/mol, while with HCl it is -2.3 kcal/mol. These numbers track the variations in the experimental ratios of the products A and B. To assess the effect of the predicted π -stacking interaction, PO was reacted with TMS-N₃ under the same conditions as mentioned in Table S3 for styrene oxide, and a dramatic decrease in regioselectivity

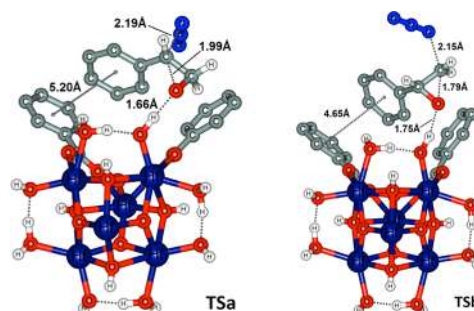


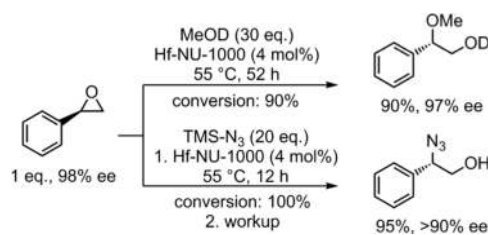
Figure 2. Optimized geometries of the TS structures TSa and TSb for the epoxide ring-opening steps leading to the products A and B, respectively. H atoms of the phenyl rings have been removed for clarity.

was detected. In this case, a 25:75 ratio of the two regioisomers was observed, with the major product resulting from azide attack at the less hindered side (see the SI).

Encouraged by the above results, we employed Hf-NU-1000 to catalyze alcoholytic epoxide ring opening. The opening of epoxides with alcohols is an important transformation in the synthesis of β -alkoxy alcohols.³⁶ However, the application of such reactions generally is limited because of the poor nucleophilicity of alcohols, which requires harsh and/or strongly acidic conditions, usually leading to the formation of a mixture of regioisomers and polymerization.³⁷ Therefore, the regioselective alcoholysis of epoxides has been the subject of extensive studies.³⁸ On the basis of the above optimized geometries of the transition states, we speculated that the approach of methanol to hydrogen-bonded epoxide would show good stereoselection. Therefore, under our optimized conditions, (+)-(*R*)-styrene epoxide was reacted with methanol in the presence of Hf-NU-1000 (4.0 mol % of $-\text{OH}$ active sites). The regioisomer corresponding to attack at the benzylic position with inversion of the epoxide stereogenic center was obtained selectively and in an enantioselective fashion (Scheme 1, top). Additionally, (+)-(*R*)-styrene epoxide was also reacted with TMS-N₃ in the presence of Hf-NU-1000 (4.0 mol % of $-\text{OH}$ active sites). Again, the preferred regioisomer was obtained with inversion of the epoxide stereogenic center in an enantioselective fashion (Scheme 1, bottom). These selective inversions of the stereogenic center indicate an S_N2-type mechanism in which the carbocation is not formed as an intermediate. Hf-NU-1000, an achiral catalyst, yielded the enantiomerically pure product, which makes it a promising catalyst in asymmetric catalysis on account of its simple design.

In summary, a new polyoxohafnium-cluster-based MOF isostructural with Zr-based NU-1000 has been prepared and characterized. It demonstrates excellent performance in the context of chemical fixation of CO₂ as an inexpensive,

Scheme 1. Regioselective and Enantioselective Methanolysis (top) and Azidolysis (bottom) of Styrene Oxide Catalyzed by Hf-NU-1000 To Give β -Methoxy- and β -Azido Alcohols



environmentally benign, ubiquitous, and sustainable carbon source for the preparation of cyclic carbonates under ambient conditions. In addition, this multifunctional catalyst is efficient for solvolytic reactions and activates epoxides for the regioselective and enantioselective synthesis of 1,2-bifunctionalized systems. We have further shown that the catalyst can be recycled and reused for multiple successive runs without considerable loss of activity or structural deterioration. We speculate that this catalyst will be useful for the fixation of CO₂, the regioselective synthesis of enantiomerically enriched β -azidoalcohols and β -alkoxy alcohols, and related reactions of epoxides with suppressed formation of byproducts while adhering well to the principles of green chemistry and atom economy.

■ ASSOCIATED CONTENT

Supporting Information

Syntheses, characterization data, and experimental methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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