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Nanoporous Metal Oxides with Tunable and Nanocrystalline Frameworks via Conversion of Metal–Organic Frameworks

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ABSTRACT: Nanoporous metal oxide materials are ubiquitous in the material sciences because of their numerous potential applications in various areas, including adsorption, catalysis, energy conversion and storage, optoelectronics, and drug delivery. While synthetic strategies for the preparation of siliceous nanoporous materials are well-established, non-siliceous metal oxide-based nanoporous materials still presents challenges. Herein, we report a novel synthetic strategy that exploits a metal-organic framework (MOF)-driven, self-templated route towards nanoporous metal oxides via thermolysis under inert atmosphere. In this approach, an aliphatic ligand-based MOF is thermally converted to nanoporous metal oxides with highly nanocrystalline frameworks, in which aliphatic ligands act as the self-templates that are afterwards evaporated to generate nanopores. We demonstrate this concept with hierarchically nanoporous magnesia (MgO) and ceria (CeO₂), which have potential applicability for adsorption, catalysis, and energy storage. The pore size of these nanoporous metal oxides can be readily tuned by simple control of experimental parameters. Significantly, nanoporous MgO exhibited exceptional CO₂ adsorption capacity (9.2 wt%) under conditions mimicking flue gas. This MOF-driven strategy can be expanded to other nanoporous monometallic and multimetallic oxides with a multitude of potential applications.

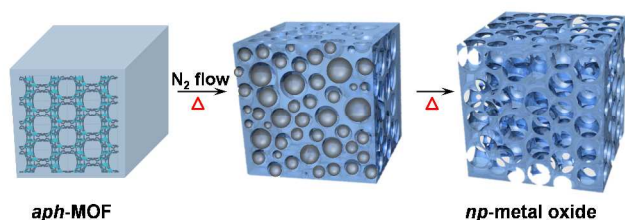
1. INTRODUCTION

Nanoporous metal oxide materials have been of pivotal importance in the material sciences, and their promise has been widely demonstrated in various areas, including adsorption, catalysis, energy conversion and storage, optoelectronics, and biological platforms.¹ Synthetic strategies for the preparation of nanoporous silicas are well-established. Soft-templating routes that rely on the synergistic self-assembly of surfactant and silicate species, followed by calcination, generate mesoporous silica materials with tunable mesostructure and pore size.²⁻⁴ In contrast, the application of a similar synthetic principle to non-siliceous compositions has rarely been successful thus far, making the preparation of non-siliceous nanoporous materials challenging.^{5,6} This difficulty predominantly stems from the uncontrollable hydrolysis and condensation of non-siliceous metal oxide precursors and the breakdown of the surfactant-metal oxide composite structure upon calcination. Even though nanoporous structures are formed via surfactant-assisted, soft-templating routes, the resulting materials are commonly composed of amorphous or semi-crystalline frameworks, rather than the nanocrystalline state which is more desirable for various applications.⁷ In order to circumvent these problems, new synthetic approaches to nanoporous non-siliceous metal oxides have been developed, including evaporation-induced self-assembly (EISA),^{8,9} nanocasting,^{5,6,10} nanoparticle self-assembly,^{11,12} and reinforced crystallization.^{7,13}

Herein, we report a novel synthetic method that exploits the thermal conversion of metal-organic frameworks (MOFs) into hierarchically nanoporous metal oxides with nanocrystalline frameworks without using structure-directing surfactants. MOFs are well-ordered crystalline solids, which are mostly composed of metal-oxygen coordinating clusters as secondary building units (SBUs) and aromatic organic linkers.^{14,15} Large surface areas and porosities as well as a high degree of tunability for both the organic and inorganic building blocks of their structures, enable the potential use of MOFs in a wide range of applications, including gas storage and separation, membranes, catalysis, sensing, and biomedical imaging.¹⁶⁻²¹ Recently, a new, burgeoning direction in the field of MOFs has been their use as ‘precursors’ of new nanostructured materials, primarily via thermolysis.²²⁻³⁵ During the thermal decomposition process, the metal ions in the MOFs can be transformed into metallic or metal oxide nanoparticles, and the organic ligands can be converted into carbonaceous structures. This MOF-driven method has been successful for preparing nanoporous carbons with controlled surface areas and porosities.²²⁻²⁷ By contrast, the preparation of nanoporous metal oxides from MOFs has not yet been successful; instead, nanoporous metal oxide nanoparticulates have been generated, presumably due to the secondary agglomeration of the metal oxide nanocrystals (NCs) during the thermolysis of the MOFs.²⁸⁻³³

The key to our approach toward hierarchically nanoporous metal oxide materials with nanocrystalline frameworks lies in the use of MOFs based on *aliphatic* carboxylate ligands, which are thermally less stable and much more labile, even under inert atmosphere, than aromatic ligands. During the thermolysis of a crystalline, aliphatic carboxylate ligand-based MOF (*aph*-MOF), the ligands were transformed into organic (or carbogenic) moieties *via* chemical decomposition, and were confined as vesicles in the solids. The organic vesicles acted as self-generated porogens, which later were converted into nanopores; they also prevented aggregation of the metal oxide nanocrystals. Finally, upon thermolysis at higher temperature, the confined organic moieties evaporated, generating highly porous nanostructures comprising nanocrystalline metal oxides (Scheme 1). We note that the control of the retention time and the evaporation rate of the organic moieties in the host solid were critical for the successful formation of nanoporous metal oxides with nanocrystalline frameworks. We demonstrate our MOF-driven approach to nanoporous metal oxides with the successful preparation of nanoporous MgO and CeO₂ with nanocrystalline frameworks. The pore sizes of these nanoporous materials could be readily tuned by simple control of experimental factors. Furthermore, we demonstrate that nanoporous MgO materials exhibit exceptionally high CO₂ absorption capacity with recyclability. Our MOF-driven method is simple yet powerful to generate nanoporous metal oxide structures. We believe that the applicability of our method to other nanoporous metal oxides as well as metals is highly viable because MOFs can be prepared with enormous structural and compositional diversities.

Scheme 1. Schematic view of the direct conversion from *aph*-MOF to *np*-metal oxide by heating under nitrogen atmosphere.



2. RESULTS AND DISCUSSION

For the preparation of an *aph*-MOF, commercially available, inexpensive adipic acid (HCOO(CH₂)₄COOH) was chosen as the aliphatic ligand. The solvothermal reaction of Mg(NO₃)₂·6H₂O and adipic acid in a mixture of *N,N*-dimethylacetamide (DMA) and methanol (MeOH) yielded colorless block-shaped crystals of [Mg₄(adipate)₄(DMA)(H₂O)]·5DMA·2MeOH·4H₂O (*Mg-aph*-MOF). Single crystal X-ray diffraction data revealed that the structure of *Mg-aph*-MOF was constructed of Mg-O chains, and

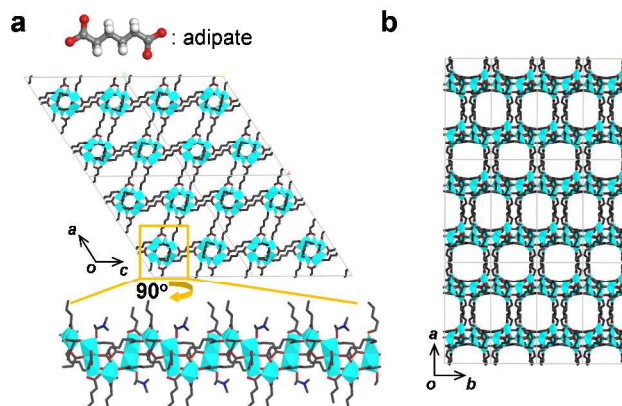


Figure 1. Single-crystal X-ray structure of *Mg-aph*-MOF. (a) 3D framework formed by association of secondary building units (SBUs) of Mg-O chain and organic ligands, adipate. The yellow rectangle indicates the (SBU) of the Mg-O chain. (b) Structure projected along the *c*-axis, showing 11 × 11 Å channels. Hydrogen atoms and guest molecules are omitted for clarity. (Color scheme: C, grey; O, red; and Mg, light blue)

adipates as the bridging ligands (Figure 1). The *Mg-aph*-MOF contained four crystallographically independent magnesium atoms in distorted octahedral coordination geometries. Of the four Mg atoms, two Mg²⁺ ions were coordinated by five oxygen atoms, among which four were provided by the adipate ligands and one was donated by a solvent molecule such as DMA or water. The other two Mg²⁺ ions were coordinated with six oxygen atoms of the adipate ligands (see the Supporting Information, Figure S1). The infinite metal-ligand coordinations generated 1D Mg-O chains as SBUs, which were bridged with four neighboring chains by adipate ligands in four different directions to construct 11 × 11 Å 3D pores containing guest solvent molecules, DMA, MeOH, and water. In the thermogravimetric analysis (TGA) trace of the as-synthesized *Mg-aph*-MOF (see the Supporting Information, Figure S2), the guest solvent molecules that occupied the void spaces of *Mg-aph*-MOF were removed during heating from room temperature to ca. 220 °C. To liberate the coordinated DMA and water molecules from Mg²⁺, the temperature required was 320 °C, and decomposition of *Mg-aph*-MOF ensued above ca. 330 °C.

Based on the TGA results, the decomposition of *Mg-aph*-MOF was performed at 500 °C by heating with a ramping rate of 5 °C/min under a nitrogen flow of 60 cc/min (Figure 2). After maintaining the temperature at 500 °C for 12 h, the colourless crystalline *Mg-aph*-MOF was converted into an off-white solid, which was identified as single-phase cubic magnesium oxide by X-ray powder diffraction (XRPD) patterns, coincident with JCPDS file no. 89-7746 (Figure 2a). Calculation of the crystalline size of MgO, estimated by applying the Debye–Scherrer equation to the (200) reflection, indicated the formation of MgO nanocrystals of 6.3 nm in diameter. Surprisingly, the transmission electron microscopy (TEM) images of the resultant solid (Figures 2c and 2d) showed that these MgO nanocrystals comprised highly

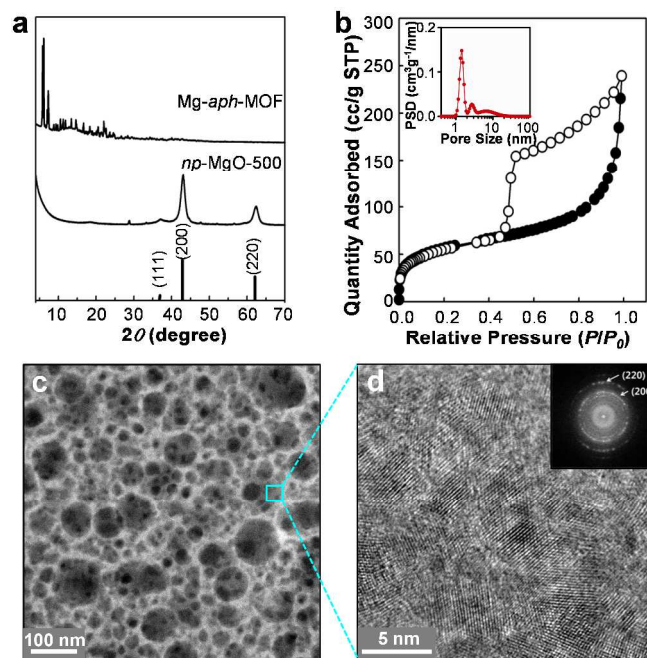


Figure 2. Characterization of *np*-MgO-500. (a) Comparison of XRPD patterns of Mg-*aph*-MOF (top) and *np*-MgO-500 (bottom). (b) N₂ sorption isotherm and NLDFT pore size distribution curve (inset) of *np*-MgO-500. (c) Dark-field TEM image of *np*-MgO-500, and (d) HR-TEM image of framework walls in *np*-MgO-500.

nanoporous structures (*np*-MgO-500). The *np*-MgO-500 had hierarchical pore structures, wherein both mesopores (a few tens of nanometers) and macropores (50 ~ 100 nm) existed. The clear lattice fringes in the high-resolution TEM image (Figure 2d) of *np*-MgO-500 as well as the corresponding selected area electron diffraction image (Figure 2d, inset) also indicated that the nanoporous solids were constructed from MgO NCs. The MgO NCs, which were interconnected in the nanoporous solid (*np*-MgO-500) wall, did not undergo larger secondary agglomeration, and coexisted with a small amount of carbon (1.79 wt%). In order to assess the porous structure of the *np*-MgO-500, a nitrogen adsorption-desorption measurement was conducted. As shown in Figure 2b, the *np*-MgO-500 showed a typical type IV isotherm with an H2 type hysteresis loop over a relative pressure range of $0.5 < P/P_0 < 0.95$, characteristic of cage-like pore structures with large mesopores and narrow channel interconnections. The pore size distribution curve of *np*-MgO-500 analyzed by the nonlocal density functional theory (NLDFT) algorithm (Figure 2b, inset) exhibited micropores centered at 1.4 nm as well as mesopores around 2.7 nm and a broad distribution from 4 to 20 nm. Hence, the *np*-MgO-500 was composed of triply hierarchical porous structures of micro-, meso-, and macropores. The Brunauer-Emmett-Teller (BET) surface area for the *np*-MgO-500 was 200 m²/g, and the total pore volume was 0.37 cc/g. Remarkably, a significant portion of the total pore volume was contributed by micropores, with their value reaching 0.13 cc/g. This synthetic method was successfully extended to the preparation of nanoporous CeO₂ (*np*-CeO₂) from Ce-*aph*-MOF (Ce₂(adipate)₃·2DEF·5H₂O; DEF = *N,N*-

diethylformamide). The resultant nanoporous CeO₂ exhibited hierarchically nanoporous structure and a crystalline framework, similar to *np*-MgO-500, and its N₂ adsorption isotherm indicated the coexistence of the micro- and mesopores, with a surface area of 100 m²/g (see the Supporting Information, Figure S3).

It is noteworthy that thermal treatments converted the Mg-*aph*-MOF into 3-dimensionally nanoporous MgO frameworks instead of discrete MgO nanoparticles embedded in a carbon matrix. We monitored the structural evolution of the Mg-*aph*-MOF with TEM images taken at each step of temperature increment (Figures 3a to 3f). As shown in Figures 3a and 3b, the crystals of Mg-*aph*-MOF did not show any changes until 160 °C, whereupon only non-coordinating guest molecules were lost. Upon heating up to 275 °C, irregular pores started to form (Figure 3c), primarily due to the evaporation of coordinating molecules (DMA and water). The pores might have been formed by the confinement of liberated coordinating guest molecules and organic ligands. These phenomena were also supported by the variable temperature XRPD patterns (see the Supporting Information, Figures S4 and S5). The XRPD pattern of as-synthesized Mg-*aph*-MOF showed strong reflections in the region 5 ~ 25°, which were commensurate with the simulated pattern from single crystal X-ray diffraction data (see the Supporting Information, Figure S4). Up to 160 °C the typical patterns of Mg-*aph*-MOF were retained, except for a slight broadening and shift of the peaks. However, above 275 °C all peaks from the crystalline Mg-*aph*-MOF disappeared, indicating that the MOF solid lost crystallinity as well as long-range orderings. When the temperature reached 350 °C, the pores were widely distributed over the solid, which implied the generation and confinement of large amounts of organic substances at the high temperature (Figure 3d). The shapes of the pores were still irregular, and the crystalline metal oxide had not yet form. However, upon further heating to 500 °C the size distribution of the spherical pores became narrower (Figure 3e), and the resultant solid started to show crystallinity (see the Supporting Information, Figure S5). Finally, after thermal treatment of Mg-*aph*-MOF at 500 °C for 12 h under inert atmosphere, highly crystalline 3D nanoporous MgO, *np*-MgO-500 was produced (Figure 3f). Comparison of the scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) results for the cross-sections of Mg-*aph*-MOF heated at 350 °C and *np*-MgO-500 also supported this evolution process; the former still possessed the organic porogens in the solid, but the latter contained a high distribution of pores and hierarchical structures (Figures 3g to 3i). To investigate the organic substances which were generated by thermolysis over each temperature range, the Mg-*aph*-MOF was analysed by pyrolysis-gas chromatography/mass spectrometry (py-GC/MS, Figure S6). As shown in Table S1, even below 300 °C the evolution of new organic species was detected, and at higher temperature, many organic substances with high boiling points were generated. This indicated that during the thermal treatment of Mg-*aph*-MOF, decomposed organic fragments reacted to yield new species, which were confined in the solid until the temperatures were high enough to evaporate them.

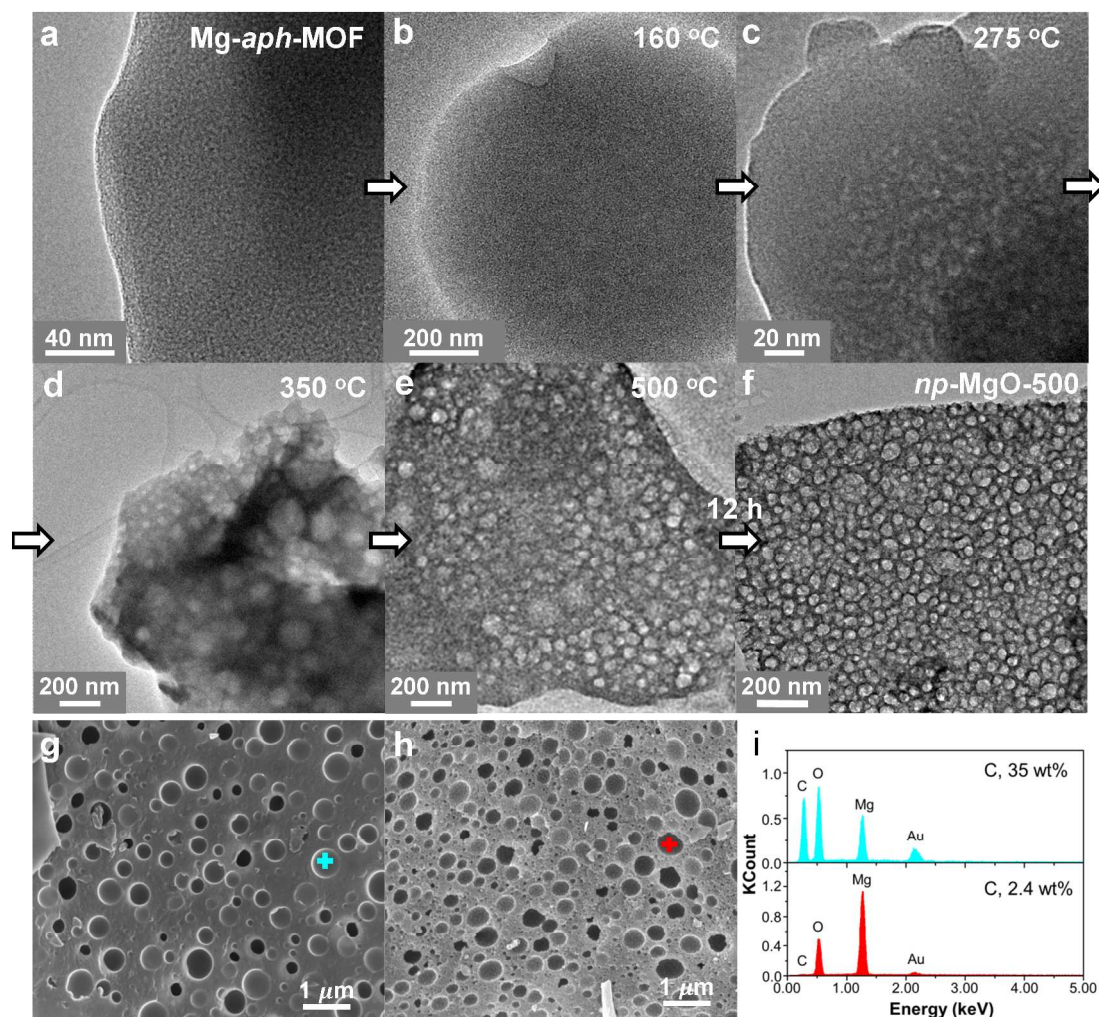


Figure 3. Temperature-dependent evolution of porous structures during conversion of Mg-aph-MOF to nanoporous MgO. High-resolution transmission electron microscopy (HR-TEM) images for Mg-aph-MOF before (a) and after heat treatment at 160 °C (b), 275 °C (c), 350 °C (d), and 500 °C (e). (f) np-MgO-500. SEM images for (g) Mg-aph-MOF after heat treatment at 350 °C, and (h) np-MgO-500. (i) EDS data for the positions, which are indicated with cross marks (+, +) in (g) and (h).

Based on the above results, we suggest that organic substances generated during the thermal decomposition of the MOF formed vesicles which acted as self-templates, and afterwards, were converted to nanopores. Meanwhile, inorganic SBUs nucleated and grew to nanocrystals at high temperature, but their growth was restricted to sizes below 10 nm due to the presence of the organic templates. Under subsequent high temperature treatment, the organic vesicles were liberated, generating numerous spherical nanopores and a nanocrystalline metal oxide framework. There has, to the our best knowledge, been no reports of the successful preparation of 3D porous structures composed of metal oxides by the thermal decomposition of MOFs. We suggest that the high thermal and chemical stabilities of conventional aromatic organic ligands, which have been used in the majority of the previous work,²²⁻³⁵ induce their preferential conversion into carbogenic structures, with the simultaneous agglomeration of the metal oxides. Therefore, MOFs composed of aromatic carboxylate ligands (*ar*-MOF) appear to be unsuitable

precursors for the preparation of porous metal oxides. To test this hypothesis, we synthesized an aromatic ligand-based MOF (Mg-*ar*-MOF), Mg₃(bpdC)₃(DMA)₄ (bpdC = biphenyl-4,4'-dicarboxylate) according to a previous report.³⁶ The thermolysis of the Mg-*ar*-MOF provided only aggregated MgO nanoparticles (Figure S7 and experimental details in the Supporting Information). Py-GC/MS results for Mg-*ar*-MOF revealed that new organic species were not formed, even at 450 °C, which means that there were no porogens to direct nanoporous structure formation during the decomposition and oxidation of the MOF (Table S2 and Figure S8).

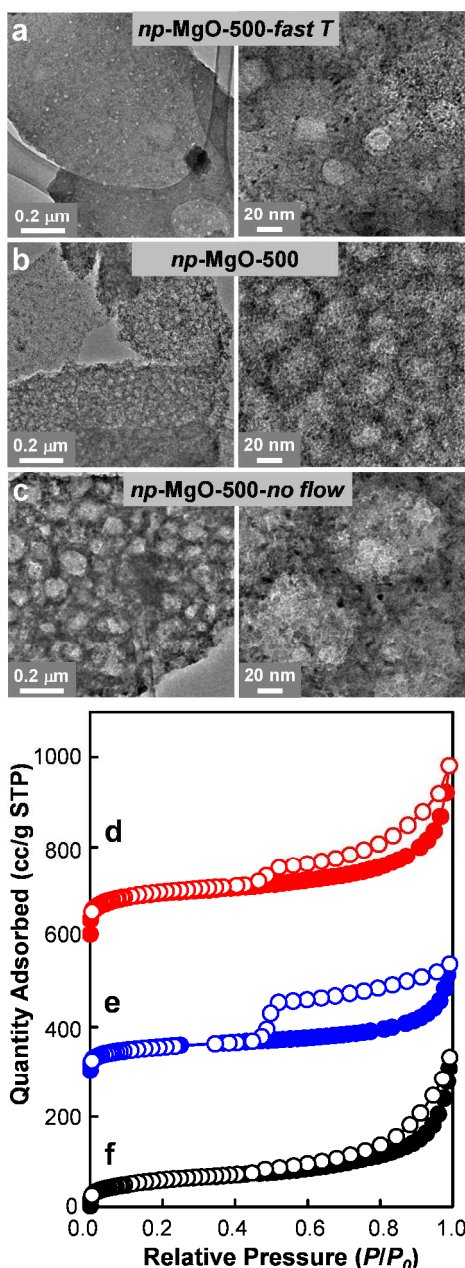


Figure 4. Pore size control of *np*-MgO under different reaction conditions. TEM images and N₂ sorption isotherms for *np*-MgO-500-*fast T* (a, d), *np*-MgO-500 (b, e), and *np*-MgO-500-*no flow* (c, f), respectively. For clarity, N₂ sorption isotherms were shifted upwards by 300, and 600 cc/g, respectively.

The contrasting results from the thermolysis of Mg-*aph*-MOF and Mg-*ar*-MOF highlight the competition between the duration of the organic vesicles and the evolution of the MgO nanoporous structure. The removal of organic vesicles that is faster than the structuring of the 3D porous structure may result in the agglomeration of MgO particles. The rapid conversion of Mg²⁺ incorporate in the MOF to MgO NCs would generate large MgO particles before forming the organic vesicles. This expectation was

proven by the thermal treatment of Mg-*aph*-MOF under oxygen atmosphere instead of nitrogen gas flow. As shown in Figure S9, the product was composed of highly crystalline cubic-shaped MgO nanocrystals of ca. 50 nm in size. In addition, we carried out a control experiment to confirm the role of extended structure in the MOF for the successful generation of nanoporous structure. For this purpose, a small coordination molecule composed of Mg²⁺ and pentanoate (Mg(CH₃(CH₂)₃COO)₂) was heated at 400 °C under nitrogen for 12 h. As shown in Figure S10, while the resulting solid was single-phase cubic MgO NC (ca. 10 nm), those particles constructed a random agglomeration instead of the nanoporous structure.

Based on our understanding of the formation mechanism of the Mg-*aph*-MOF, we speculate that the thermal conversion conditions such as gas flow rate and temperature ramping rate can be critical factors for determining the size of the organic vesicles, which consequently control the nanopore size. For instance, when Mg-*aph*-MOF was thermally treated with a ten-fold faster ramping rate (50 °C/min), nanoporous MgO with a much smaller pore size (~20 nm) (*np*-MgO-500-*fast T*, Figure 4a) was obtained, which was due to the fast transport and removal of organic vesicles before they could congregate. In contrast, thermal treatment of Mg-*aph*-MOF under static nitrogen atmosphere without flow would promote the growth of the organic vesicles, thus resulting in larger pores, around 100 nm (*np*-MgO-500-*no flow*, Figure 4c). Under such a condition, the evaporation of organic vesicles to generate nanopores would be suppressed, compared to the condition where nitrogen was flowed. Consequently, the organic vesicles contained in the structure can migrate together to form enlarged organic moieties, which afterwards converted into larger pores. Nitrogen adsorption isotherm results also supported the synthesis of pore size-controlled MgO nanostructures (Figures 4d to 4f). Since the rapid escape of small organic vesicles in MgO synthesized with rapid heating rates (Figure 4a) generated high proportion of the micropores, the N₂ adsorption showed a large uptake at pressures below 0.01 atm, and the pore volume for the micropores reached 0.20 cc/g out of a total pore volume of 0.589 cc/g.

To explore the advantages of the hierarchically nanoporous MgO with a nanocrystalline framework, we studied the behavior of *np*-MgO in a carbon dioxide gas adsorbent. Chemisorbents for CO₂ removal are mostly based on alkaline earth metal oxides such as MgO and CaO, wherein abundant basic sites are capable of strongly interacting with the acidic nature of CO₂.^{37,38} However, high regeneration temperature and poor recyclability of such metal oxides during CO₂ adsorption-desorption process commonly impede their widespread use. We hypothesized that our *np*-MgO with hierarchical nanoporosity and structural robustness would be well suited for CO₂ adsorbent with high capacity and recyclability. The CO₂ gas cycling experiments were conducted using a TGA apparatus with a flow of 15% (v/v) CO₂ in N₂, which mimicked flue gas. As-prepared *np*-MgO-500 absorbed 5.2 wt% CO₂ at 27 °C (Figure 5a). After eight cycles of CO₂ adsorption/desorption over *np*-MgO-500, TEM images showed that the nanocrystalline framework became aggregated, generating secondary nanoparticles. Also, the nanopores (ca. 100 nm) in the as-prepared

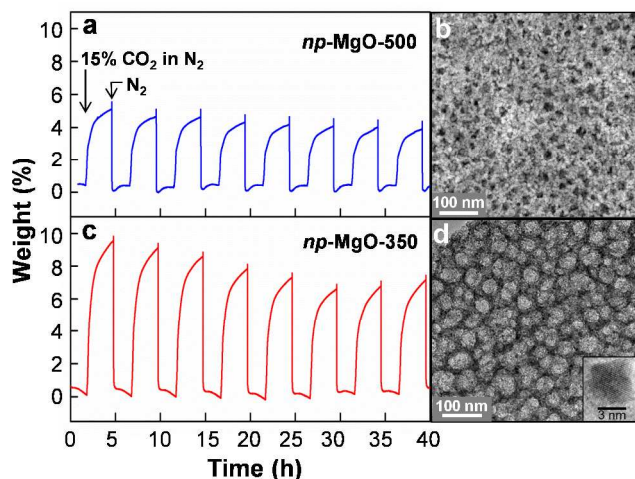


Figure 5. Studies of *np*-MgO upon carbon dioxide gas cycling experiment. (a) and (c) Gas cycling result, and (b) and (d) TEM image after the cycles for *np*-MgO-500 and *np*-MgO-350, respectively.

were reduced to around 20 nm in size (Figure 5b). The small carbon content (1.76 wt%) in *np*-MgO-500 was inadequate to sustain the hierarchically nanoporous MgO structure during the several cycles of adsorption/desorption, because *np*-MgO-500 suffers from significant changes in the crystal systems between MgO (cubic) and MgCO₃ (trigonal). To increase the carbon content as an adhesive and protectant, but to still provide the hierarchical structure, the thermal treatment of *Mg-aph*-MOF was conducted at a lower temperature, 350 °C, for 12 h under inert atmosphere. The resultant solid, designated as *np*-MgO-350, was a nanoporous, dark brown solid with a carbon content of 10 wt%. The BET surface area was 160 m²/g (see the Supporting Information, Figure S11). As shown in Figure 5c, the CO₂ uptake capacity of *np*-MgO-350 at 27 °C was much higher than *np*-MgO-500 at 9.2 wt%, which was the highest recorded value for MgO nanomaterials under similar conditions,³⁹⁻⁴¹ and was 12 times better than commercially available 50 nm-sized-MgO powder (0.76 wt%) (Table S3 and S4, and Figure S12 in the Supporting Information). This capacity is also comparable with the result from the Mg-based MOF, Mg₂(dobpdc) (dobpdc⁴⁻ = 4,4'-dioxido-3,3'-biphenyldicarboxylate), which showed 2.52 mmol/g and 9.9 wt% upon exposure to flowing 15% CO₂ in N₂ at 40 °C.⁴² More importantly, even after eight cycles of CO₂ adsorption/desorption, the hierarchically nanoporous structures of *np*-MgO-350 remained intact, as evidenced by TEM (Figure 5d). Since acidic CO₂ molecules are adsorbed at low-coordinated and basic O²⁻-Mg²⁺ sites on MgO, a high surface area which provides many edge- and corner-located oxygen atoms is critical to the CO₂ capacity of MgO adsorbents.^{37,38} Therefore, in the present work, hierarchically porous MgO prepared by our MOF-driven method assured superior performance associated with facile mass transport and recyclability. In addition, the large population of surface defect sites on the MgO nanocrystals comprising the framework wall may allow for a low regeneration temperature of 300 °C (Figure S13), which affords a definite advantage for practical application.

3. CONCLUSIONS

In conclusion, we have developed a novel, simple method to synthesize hierarchically nanoporous frameworks of nanocrystalline metal oxides such as magnesia and ceria by the thermal conversion of well-designed MOFs. The introduction of aliphatic ligands to MOFs as an organic building block was the key to controlling the thermal stability and inducing the self-templating effect. By controlling the thermolysis conditions such as temperature, rate of temperature increase, and carrier gas flow rate, we could readily engineer the pore sizes of MgO as well as the carbon support content. In addition, because of the high surface area and hierarchically porous structure of the nanoporous MgO, it performed exceptionally in the uptake of CO₂ gas under mimicked flue gas conditions. Therefore, this approach to aliphatic ligand-based MOF decomposition can be expanded to other nanoporous monometallic and multimetallic oxides with a multitude of potential applications, especially for energy-related materials.

4. MATERIALS AND METHODS

All chemicals and solvents were of reagent grade and used without further purification. Infrared spectra were recorded with a ThermoFisher Scientific iS10 FT-IR spectrometer. Elemental analyses were performed at the UNIST Central Research Facilities Center (UCRF) in Ulsan National Institute of Science and Technology (UNIST). Thermogravimetric analyses (TGA) were performed under N₂(g) at a scan rate of 5 °C min⁻¹, using a TGA Q50 from TA instruments. X-ray photoelectron spectroscopy (XPS) was performed on a K-alpha from Thermo Fisher. The chemical composition of MgO was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, PerkinElmer, ELAN DRC-e). X-ray powder diffraction data were recorded on a Bruker D8 advance diffractometer at 40 kV and 40 mA for Cu Kα (λ = 1.54050 Å), with a step size of 0.02° in 2θ. High-resolution transmission electron microscopy (HR-TEM) images and energy dispersive X-ray spectra (EDS) were obtained on JEOL JEM-2100 microscope.

Preparation of *Mg-aph*-MOF ({[Mg₄(adipate)₄(DMA)(H₂O)]·5DMA·2MeOH·4H₂O}).

Adipic acid (0.053 g, 0.36 mmol) was dissolved in DMA (4 mL), and mixed with an MeOH (2 mL) solution of Mg(NO₃)₂·6H₂O (0.084 g, 0.33 mmol). The solution was heated in a Teflon vessel in an autoclave at 120 °C for 24 h, and then cooled to room temperature. Colorless rod-shaped crystals formed, which were filtered, and washed briefly with the mother liquor. Yield: 44 mg (38%). Anal. Calcd for Mg₄C₅₀H₁₀₄N₆O₂₉: C, 44.46; H, 7.76; N, 6.22. Found: C, 44.45; H, 7.03; N, 6.17. FT-IR (Nujol mull): ν_{OH}, 3374 (m, br); ν_{C=O}, 1651 (br); ν_{O-C=O}, 1605, 1560 (s) cm⁻¹.

Preparation of *np*-MgO-350 and *np*-MgO-500. Solid *Mg-aph*-MOF was ground into a powder and then heated at 5 °C/min under a nitrogen flow of 60 mL/min. After reaching the target temperature (350 °C and 500 °C, respectively), the material was maintained at the temperature for 12 h and then cooled to room temperature. The resultant solid, *np*-MgO-350, was black, whereas *np*-MgO-500 was obtained as a white powder.

Preparation of *Ce-aph*-MOF ({Ce₂(adipate)₃·2DEF·5H₂O}).

Adipic acid (0.022 g, 0.15 mmol) was dissolved in *N,N*-diethylformamide (DEF, 2.5 mL), and mixed with a DEF (2.5

mL) solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.044 g, 0.10 mmol). The solution was sealed in a glass jar, heated at 110 °C for 24 h, and then cooled to room temperature. Pale yellow needle-shaped crystals formed, which were filtered and washed briefly with the mother liquor. Yield: 22 mg (44%). Anal. Calcd for $\text{Ce}_2\text{C}_{48}\text{H}_{96}\text{O}_{21}\text{N}_6$: C, 41.97; H, 7.04; N, 6.12. Found: C, 42.10; H, 6.88; N, 6.07. FT-IR (Nujol mull): ν_{OH} , 3444 (m, br); $\nu_{\text{C-O}}$ (non-coordinating DEF), 1680 (s); $\nu_{\text{C=O}}$ (coordinating DEF), 1650 (s); $\nu_{\text{O-C=O}}$, 1570 (s) cm^{-1} .

Preparation of *np*-CeO₂. Solid Ce-*aph*-MOF was ground into a powder and then heated at 5 °C/min under a nitrogen flow of 60 mL/min. After reaching the target temperature of 500 °C, the material was maintained at that temperature for 12 h and then cooled to room temperature. The resultant black solid was ground into a powder. The powder was heated 1 °C/min to 300 °C under an oxygen flow of 100 mL/min. After the material was maintained at this temperature for 2 h and then cooled to room temperature, pale yellow *np*-CeO₂ was obtained.

Preparation of *ar*-MgO. $\text{Mg}_3(\text{bpd})_3(\text{DMA})_4$ (Mg-*ar*-MOF) was heated at 5 °C/min to 600 °C under a nitrogen flow of 60 mL/min. The material was maintained at this temperature for 12 h and then cooled to room temperature.

Gas Sorption Study. The nitrogen adsorption-desorption isotherms were measured at 77 K on a BELsorp-MAX adsorption analyzer. Prior to adsorption measurement the samples were evacuated at 200 °C under vacuum ($p < 10^{-5}$ mbar) for 12 h. The specific surface area was determined from the linear part of the BET equation, and the total pore volume was calculated from the amount adsorbed at a relative pressure of about 0.99. The results were summarized in Table S5.

Single-Crystal X-ray Crystallography. A single-crystal of **1** was mounted on the top of a capillary with Paratone oil. Diffraction data were collected at 173 K using a Rigaku R-axis Rapid II diffractometer (Mo $K\alpha$, $\lambda = 0.71073$ Å), which was equipped with an X-ray diffraction camera system with an imaging plate. Full sphere data were collected for all the crystals, and the raw data were processed and scaled using the RapidAuto software suite.⁴⁴ The crystal structures were solved by direct methods⁴⁵ and refined by full-matrix least-squares refinement using the SHELXL-97 computer program.⁴⁴ The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were positioned geometrically using a riding model. For **1**, the electron density of the disordered guest molecules was flattened using the ‘SQUEEZE’ option of the program PLATON.⁴⁶ The crystallographic data and selected bond lengths and angles of **1** are summarized in Tables S6 and S7.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data as a CIF file, Table S1-7, Figures S1–13, and related references. 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 interests.

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