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A New V-Based Metal–Organic Framework Synthesized from Pyrene-Based Linker

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ABSTRACT

A new vanadium based metal–organic framework (MOF), termed V-TBAPy, $V_2O_2(C_{44}H_{22}O_8)\cdot 9.5H_2O$, was designed and solvothermal synthesized. Crystal structure analysis showed that V-TBAPy is constructed from $VO(CO_2)_2$ rod-shaped SBUs (SBUs = secondary building units) and 1,3,6,8-tetrakis(p-benzoate)pyrene ($TBAPy^{4-}$) linker to adopt the ***frz*** architecture highlighted by 1D channel of 9.3 Å and 4.0 × 9.4 $Å^2$ in the structure. V-TBAPy was characterized by powder x-ray diffraction analysis (PXRD), thermal gravimetric analysis (TGA), Fourier transform infrared (FT-IR), elemental analysis (EA) and N_2 adsorption measurements at 77 K. The resulted analyses indicated the highly thermal stability and permanent porosity of V-TBAPy with the Brunauer–Emmett–Teller surface (BET) area derived from the adsorption data of V-TBAPy to be 1620 $m^2\ g^{-1}$. Furthermore, the rod-shaped morphology and the nano-size V-TBAPy were also confirmed by the scanning electron microscope (SEM) analysis suggesting the promising employment of the obtained material for adsorption and catalysis.

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1. Introduction

Metal-organic frameworks (MOFs), a new generation of highly advanced porous materials, provide the platform for solving global environmental problems.[1], [2] The beauty of MOF materials is based on the principles of reticular chemistry for which the proper selection of building blocks results in designable crystal structures owning adjustable pore sizes and shapes and tunable internal chemical environments.[3] Recently, MOFs have been employed extensively in a wide range of applications including catalysis,[4] gas storage and separation,[5] proton conduction,[6], [7] drug delivery.[8] Among the different examples, vanadium-containing MOFs are a special case with extreme stability in water and acidic environment.[9], [10] Furthermore, V-based MOFs exhibited useful in catalysis oxidation reaction though the V^{III}/V^{IV} oxidation upon thermal activation in air,[9], [11], [12] or application in photo-catalysis,[13] gas storage and separation.[14]–[16] However, only a few V-based MOFs have been reported.[10] For example, vanadium terephthalate, such as MIL-47,[17] and MIL-68,[18] or vanadium trimesate such as V-MIL-100,[11] COMOC-2,[19] COMOC-3,[20] MIL-71,[21] or the other V- based MOFs from different linkers such as MIL-59,[22] MIL-60, MIL-61,[23] and BIT-66.[13] Therefore, it makes a high demand for exploring the synthesis and application of new V-based MOFs.

We recently reported the synthesis and characterization of a new iron-based MOF, termed Fe-TBAPy. Structural analysis revealed that Fe-TBAPy is built from $[Fe(OH)(CO_2)_2]$ rod-shaped SBUs linked by $TBAPy^{4-}$ to form the *frz* topological framework. Catalysis investigations using Fe-TBAPy catalyst showed highly active for benzene hydroxylation reaction with the reaction reached 70% yield of phenol.[24] Within this trend, we would like to further investigate the synthesis and structure of vanadium-based MOFs assembled from the H_4TBAPy linker.

2. Materials and Methods

Materials. N,N-Dimethylformamide (DMF), acetic acid (CH_3COOH, 98%), dichloromethane (CH_2Cl_2, 99.9%), and anhydrous methanol (MeOH, 99.8%), were obtained from EMD Millipore Chemicals. Vanadium(III) chloride anhydrous (VCl_3, 98%) were obtained from Sigma-Aldrich. Palladium-tetrakis (triphenylphosphine) (99%). 1,3,6,8-tetrabromopyrene (purity > 98%) and methyl 4-boronobenzoate (purity > 96%) were purchased from Tokyo Chemical Industry Co. All starting materials and solvents were used without further purification. H_4TBAPy were synthesized according to the published procedures.[24]

Characterization. Thermal gravimetric analysis (TGA) was performed using a TA Q500 thermal analysis system under airflow. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vertex 70 spectrometer using the attenuated total reflectance (ATR) sampling method. N_2 adsorption measurements were performed using a Micromeritics Surface Characterization Analyzer. A liquid N_2 bath was used for the measurement at 77 K. Elemental analysis was performed using a LECO CHNS-932 analyzer. Powder X-ray Diffraction Analysis and structure solution. Powder X-ray data were collected using a Bruker D8 Advance diffractometer. The system was equipped with an anti-scattering shield that prevents incident diffuse radiation from hitting the detector.

Structural analysis. The diffraction data of activated V-TBAPy were analyzed by the program Materials Studio ver. 5.5, Accelrys Software Inc (pattern indexing and Pawley refinement). The modeled framework with atomic connectivity was built using the Materials Visualizer module of Materials Studio ver. 5.5 software. Subsequently, the full profile pattern fitting (Rietveld method) was performed against the experimental powder pattern of V-TBAPy with $2\theta = 2° – 70°$.

Material synthesis. A mixture of anhydrous VCl_3 (0.050 g, 0.309 mmol) and H_4TBAPy (0.040 g, 0.058 mmol) was dissolved in 7 mL DMF. Acetic acid (200 mL) was then added and the solution was sonicated for 5 minutes before being transferred into 12 ml autoclave. Following this, the autoclave was placed in an isothermal oven at 150 °C for two days. The resulting green micro-crystalline product was collected, washed with DMF (10 mL), methanol (10 mL), and dichloromethane (10 mL) for 3 d, respectively. Finally, the product was evacuated under vacuum (10^{-3} torr) at 120 °C to yield V-TBAPy (67% yield, based on H_4TBAPy). Elemental analysis (EA) of activated sample: calcd for $V_2O_2(C_{44}H_{22}O_8)\cdot 9.5H_2O$: C, 53.69; H, 4.17; N, 0%. Found: C, 53.69; H, 3.7; N, 0.5%.

3. Results and Discussion

3.1 Synthesis and Structural Solution

A mixture of H_4TBAPy and VCl_3 was dissolved in DMF in the presence of CH_3COOH and isothermally heated at 150 °C for 48 h to yield green micro-crystalline material of V-TBAPy. The as-synthesized material was centrifuged, washed, exchanged with DMF and methanol. Subsequently, the samples were activated under dynamic vacuum at 120 °C to yield V-TBAPy. PXRD pattern of the activated V-TBAPy was collected and indexed by Material studio software. The unit cell parameters were then refined by the Pawley method against the experimental profile. Accordingly, V-TBAPy is found to crystallize in the orthorhombic space group, *Cmmm* (no. 65), with unit cell parameters, a = 30.1937; b = 6.6696; c = 15.4781 Å, which are similar to that of the parent compound $[In_2(OH)_2(TBAPy)]$.[25] As a result, we built modeled structure of V-TBAPy based on the atomic connectivity of $[In_2(OH)_2(TBAPy)]$ (Figure 1). Subsequently, the full range Rietveld refinement of the obtained model against the experimental profile was performed to optimize the atom positions and connectivity in the unit cell. The modeled structure was finally convergence with low R-values ($2\theta = 3–70$, Rp = 5.3% and Rwp = 8.76%, Figure 2). The refined structure clearly indicated that V-TBAPy adopts the ***frz*** architecture built from the connection of $[V(OH)(CO_2)_2]$ rod-shaped SBUs and $TBAPy^{4-}$ linkers. This structure is highlighted by two different channels along the Oz axis, the hexagon cross-section diameter of 9.3 Å and eclipsed cross-section diameter of 4.0 × 9.4 $Å^2$ (Figure 1).

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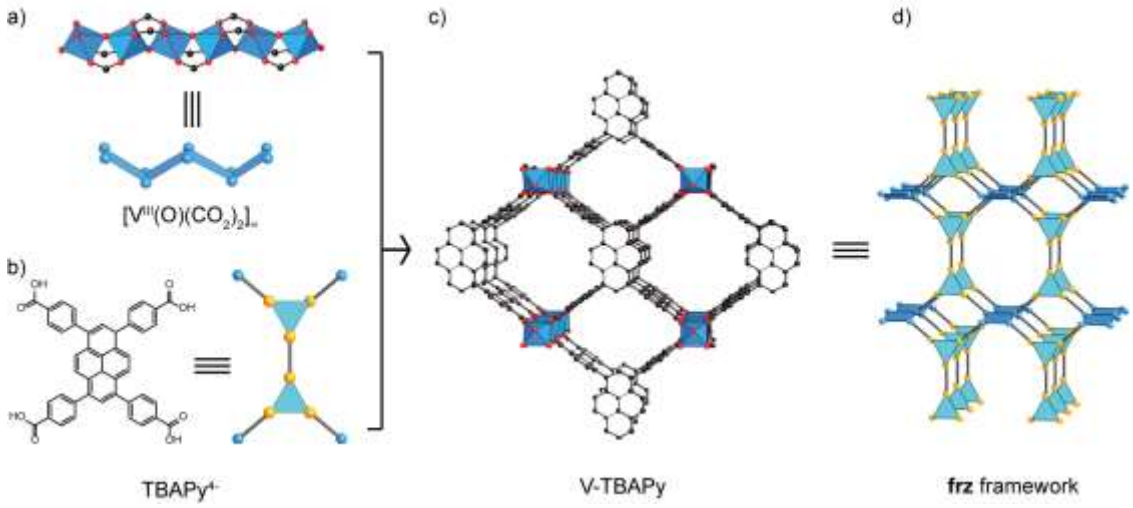

Figure 1. *V-TBAPy is built from $VO(CO_2)_2$ rod-shaped SBUs (a), linked by tetratopic $TBAPy^{4-}$ linkers (b) to form the frz-architectural framework (c and d). Atom colors: V, blue polyhedra; C, black; O, red. All hydrogen atoms are omitted for clarity.*

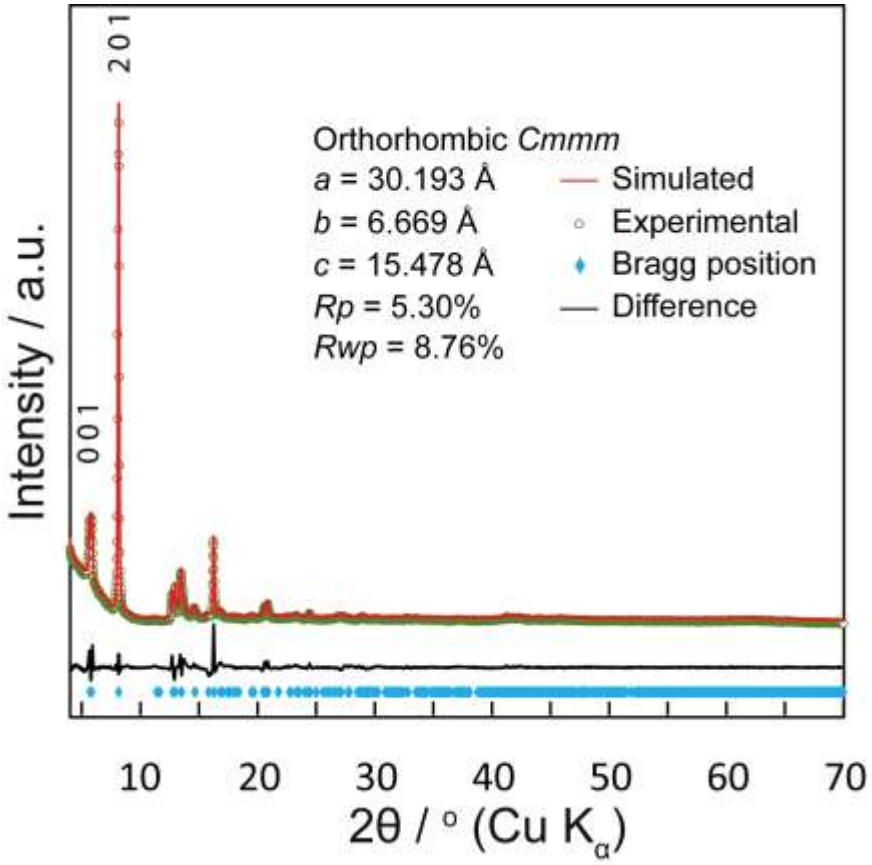

Figure 2. *Experimental (green) and refined (red) PXRD patterns of activated V-TBAPy after Rietveld refinement. The difference plot (black) and Bragg positions (blue) are also shown.*

3.2 Characterization of V-TBAPy

We further confirmed the phase purity of V-TBAPy by powder x-ray diffraction method (Figure 3a). FT-IR analysis was also performed to characterize the activated V-TBAPy. The result showed the $\mu_{C=O}$ stretching peak of coordinated carboxylate at 1605 cm^{-1}, indicating the stability of the coordinated carboxylate bond during material activation (Figure 3b). Elemental microanalysis (EA) of V-TBAPy was carried out to gain insight into the chemical formula of V-TBAPy. The obtained analysis indicated the formula of $V_2O_2(C_{44}H_{22}O_8)\cdot 9.5H_2O$: C, 53.69; H, 4.17; N, 0%. Found: C, 53.69; H, 3.7; N, 0.5%, which confirmed the proposed chemical formula of V-TBAPy to be $V_2O_2(TBAPy)\cdot 9.5H_2O$ (the water in the formula due to the adsorption of ambient air moisture). The thermal stability were further accessed by thermogravimetric analysis (TGA) under air stream. The result indicated that V-TBAPy is stable up to 320 °C with less than 5% weight loss in the range. Enhancing temperature beyond 350 °C resulted in the rapid decomposition of V-TBAPy with the steep weight loss of 63% upon reaching 400 °C. The final residual metal oxides, ascribed to V_2O_5 was found to be 30.7% upon reaching 500 °C and in good agreement with the calculated value from the model formula (Figure 3c). N_2 adsorption isotherm of V-TBAPy was also carried to gain further insight into the structural properties of V-TBAPy. The resulted isotherms exhibit the permanent porosity of V-TBAPy with type I isotherm and the saturated uptake of 397 cm^3(STP) cm^{-3} at $P/P_0 \sim 0.95$. The BET surface area was derived from the adsorption data to reach 1620 $m^2\ g^{-1}$ (Figure 3d), which is in agreement with the theoretically predicted surface area (Materials Studio 5.5; SA = 1573 $m^2\ g^{-1}$). Furthermore, pore size distribution analysis derived from the N_2 isotherm confirmed the existence of the large 9.26 Å and small 4.0 × 9.4 $Å^2$ channel in V-TBAPy (Figure 3e).

3.3 Crystalline Morphology of V-TBAPy

We are further interested in studying the crystalline morphology of V-TBAPy by Scanning Electron Microscope (SEM) analysis. The obtained results from this analysis showed that V-TBAPy crystalline in the rod-shaped crystals. Interestingly, these crystals are shown with pretty uniform size and shape with the crystal wide and length of ~ 300 and 1000 nm, respectively. This result indicated the obtained of nano-size MOFs (Figure 3f).

4. Conclusion

In this work, a new V-based MOF, termed V-TBAPy, is synthesized and characterized. Structural analysis showed that V-TBAPy is constructed from $V(O)(CO_2)_2$ rod-shaped SBUs, which are linked by $TBAPy^{4-}$ to extend into the three-dimensional ***frz*** topological framework. The structure of V-TBAPy is highlighted by the hexagon channel of 9.3 Å and eclipsed channel of 4.0 × 9.4 $Å^2$. Remarkably, V-TBAPy crystalline in the nano-size rod-shaped crystals suggests the promising employment of the obtained material in a wide range of applications. We believe that this research will inspire the design and synthesis and application of V-based MOFs for application in gas adsorption and catalysis.

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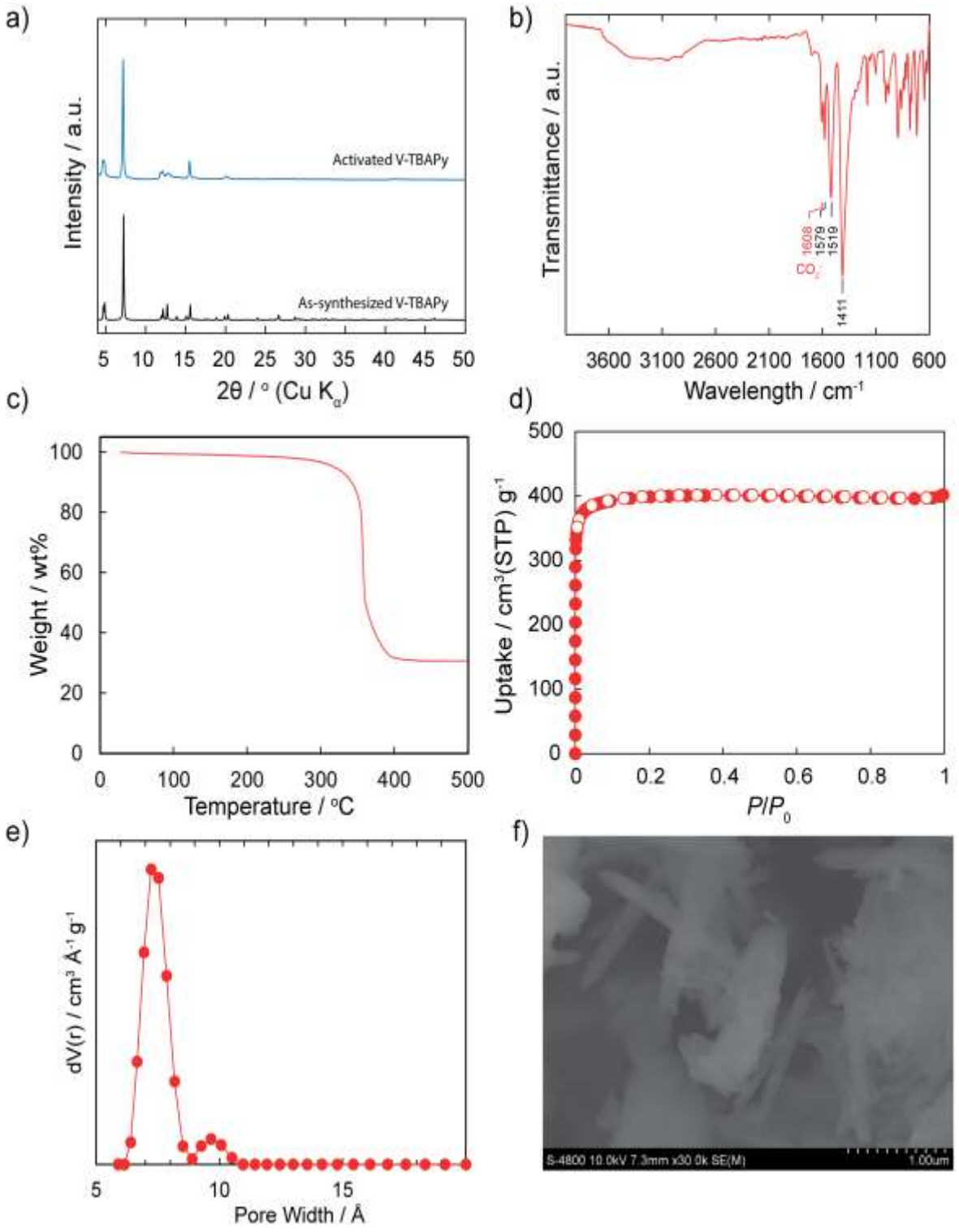

Figure 3. *Characterization of V-TBAPy: a) Powder X-ray diffraction patterns of as-synthesized sample in comparison with the calculated pattern from the modeled structure; b) FT-IR spectra of activated V-TBAPy; c) TGA analysis of V-TBAPy under airflow; d) 77 K N_2 adsorption isotherm of V-TBAPy; e) Pore size distribution of V-TBAPy calculated from the N2 adsorption isotherm using DFT method; f) SEM image of V-TBAPy nano-crystals.*

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