Inorganic–Organic Hybrid Materials

NCHU-3: A Crystalline Inorganic–Organic Hybrid Molecular Sieve with Extra-Large Cages**

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Since the discovery of aluminophosphate VPI-5,[1] the synthesis of new crystalline large-pore zeolite-analogue materials with diameters of larger than 10 Å has been an important goal because of the diverse applications of these materials as nanoreactors, biosensors, and in nanotechnology.[2–5] Considerable attention has been directed towards the associated inorganic–organic hybrid architectures that, because of the incorporation of organic functional groups within a solid state inorganic framework, promise access to an even wider range of applications, such as altering the expected shape-selective influence in molecular sieves and hydrocarbon transformations.[6–11] To date, however, relatively few examples of well-ordered crystalline solids with both large and hybrid pores are known.[12] Herein, we describe a novel nanoporous organophosphonate that contains both vanadium and gallium centers, $[Ga_2(VO)_3K_2(OH_2)_3(C_2H_4P_2O_6)_4(H_2O)_{13}]$, which we have called NCHU-3 (National Chung-Hsing University-3).

Pale-blue crystals of NCHU-3 were grown from a reaction mixture of KOH, Ga_2O_3, V_2O_5, ethylenediphosphate, and

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water in molar ratios of 1:1:2:6:2220 heated at 200 °C for 72 hrs in a 23 mL teflon-lined stainless steel autoclave. The structure of NCHU-3 was determined by single-crystal X-ray analysis (Figure 1). The orthorhombic structure has an open framework with multidimensional channels. The asymmetric unit of the framework contains one gallium-centred tetrahedron (Ga–O bond lengths: 1.800(8) (×2) and 1.805(5) Å (×2), two crystallographically distinct octahedral oxovanadyl centers ($V_1O_5(OH_2)$: 1.612(2), 1.977(8) (×2), 2.036(8) (×2), and 2.290(17) Å; $V_2O_5(OH_2)$: 1.575(15), 1.961(8) (×4), and 2.45(3) Å; the bond valence sum of vanadium is 4.0 and 4.4, respectively),[13] and two ethylenediphosphate groups. Each phosphorus atom in ethylenediphosphate is tetrahedrally coordinated, that is, the two O_3PC tetrahedron of $[O_3P–CH_2CH_2–PO_3]^{4-}$ share the carbon atoms with the ethylene groups. The secondary building blocks of NCHU-3 are described in terms of 4-, 5-, 6-, and 16-rings, which are combinations of 4, 5, 6, and 16 polyhedrons, respectively. Interestingly, NCHU-3 consists of multidimensional channels system with 6-ring apertures and 16-ring apertures, in which the pore sizes are 5 Å × 7 Å and 5 Å × 14 Å, respectively. These channels intersect at the center of a chinese-vaselike cage consisting of 63 atoms (six 6-rings and two 16-rings, Figure 1c and 1d). The cage measures 11 Å × 13 Å × 14 Å, as measured between oxygen atoms by using the positional coordinates of NCHU-3. Another important feature of the NCHU-3 structure is the hydrophobic -CH_2 moieties covering the walls of the Chinese-vaselike cages. The approximate vase-void volume is 1359 Å^3 per unit cell. Microporous materials are often compared by framework density (FD, number of density of tetrahedral atoms per 1000 Å^3).[14] The smaller the FD value, the larger is the available space in the crystal. The FD generally decreases with increasing numbers of 4-rings. NCHU-3 has eight 4-rings per cage, for which the FD is about 9.3 (tetrahedrally surrounded Ga and P atoms) and 12 (which takes into account the V atoms with octahedral coordination) compared with the very open faujasite (12.7) and cloverite (11.1).[15]

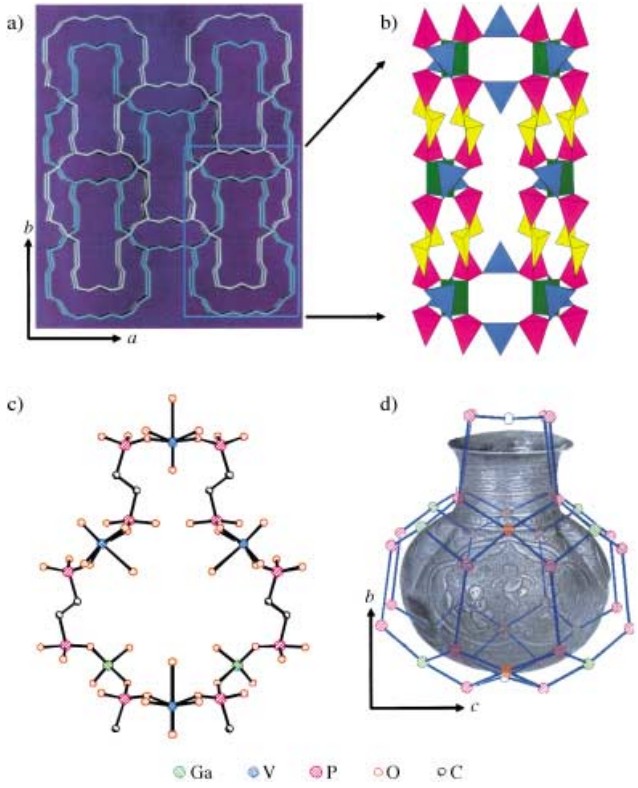

Figure 1. Molecular structure of NCHU-3. a) The framework structure of NCHU-3 view down the *c* axis showing vaselike channels in projection. b) Polyhedral view of a section of vaselike cages. (GaO_4: green tetrahedron; $VO_5(OH_2)$: blue octahedron; PO_3C: red tetrahedron; CH_2P_2: yellow tetrahedron). c) Ball-and-stick representations of the largest cavity constructed from 16-rings excluding tetrahedrally coordinated C atoms. d) Projection of vaselike cages along the *a* axis (C, H, and O atoms are omitted for clarify) showing the additional 4-, 5-, and 6-rings and Chinese vaselike void volume of 1359 Å^3.

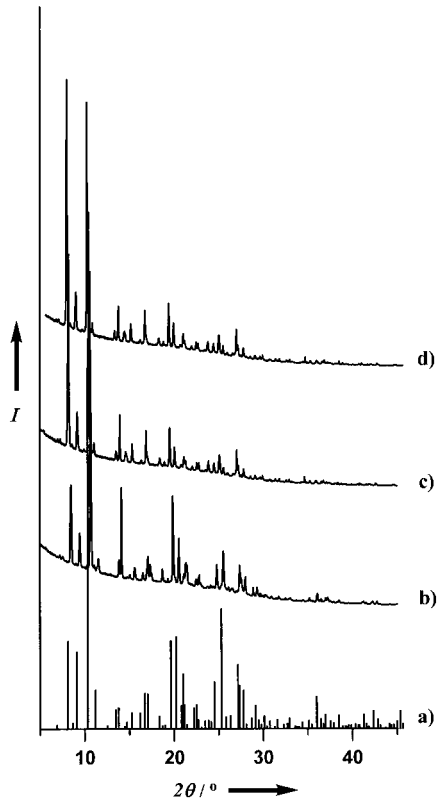

Figure 2. In situ PXRD patterns for NCHU-3 (synchrotron radiation, $\lambda = 1.32633$ Å). The sample was initially heated to 200 °C and then cooled to 40 °C in air. a) Simulated diffraction patterns on the basis of the single-crystal structure. Diffraction data recorded b) at room temperature, c) at 200 °C, and d) at 40 °C. *I* is the X-ray intensity (arbitrary units).

The key feature of NCHU-3 rests on the extra-large hydrophobic cages, which are occupied by free water molecules and highly disordered K^+ ions. Essentially, complete replacement of K^+ by NH_4^+ ions by using saturated NH_4Cl solution was easily accomplished, as confirmed by energy-dispersive X-ray fluorescence analysis. To examine the thermal and structural stability of this open framework, thermogravimetric analysis (TGA) and in situ synchrotron powder X-ray diffraction (PXRD) analysis were carried out. The TGA reveals that the water guest molecules were

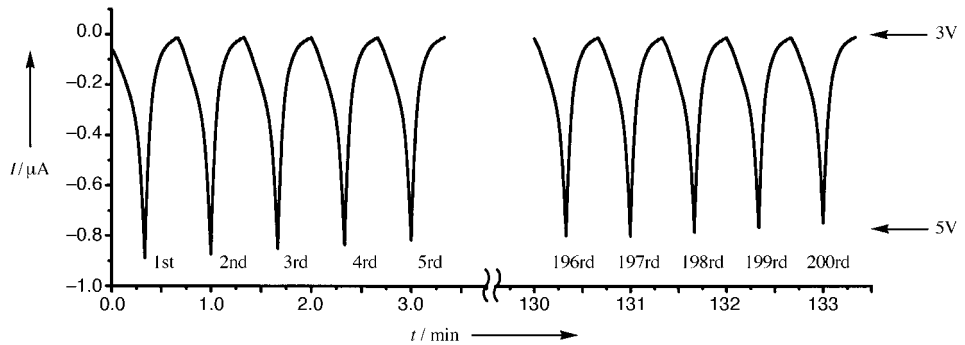

Figure 3. Current versus time plot for cyclic voltage changes in the range 3–5 V for a C/Li·NCHU-3 cell employing a 1 M $LiClO_4$ in an EC-DMC-MF electrolyte mixture ($T = 30\,°C$, scan rate 100 $mV\,s^{-1}$). The cyclability of NCHU-3 by intercalating/de-intercalating lithium ions is shown.

liberated below 200 °C, which corresponds to a weight loss of 14 %. No weight loss was observed in the temperature range of 200–550 °C. The simulated diffraction pattern based on the analysis of a single-crystal X-ray structure (Figure 2a) is in good agreement with the PXRD pattern obtained for NCHU-3 (Figure 2b), which indicates that NCHU-3 is a pure phase. The NCHU-3 sample was initially heated to 200 °C (Figure 2c) and then cooled to 40 °C (Figure 2d), both diffraction patterns show that the positions of the most intense lines remain unchanged relative to the unheated sample of NCHU-3. The good agreement between PXRD patterns demonstrates that the open-framework was retained even after the loss of water molecules. Given the thermal and structural stability of the open framework, the presence of vacant cages in NCHU-3 affords a natural affinity to absorb aliphatic and aromatic molecules reversibly. A TGA study reveals a reversible aniline sorption cycle in the pores of NCHU-3 (see Supporting Information). The framework, which features redox oxovanadyl centers, provides an intercalation host for lithium ions.[16] Some preliminary reversible cycling data are presented in Figure 3. The cyclability of the cell was over 200 cycles between 3 and 5 V, which indicates that lithium ions and electrons can be removed and reinserted into the NCHU-3 host. This result demonstrates that NCHU-3 is scientifically interesting and potentially attractive as a new cathode material for rechargeable lithium batteries.[17–19] Further measurements of capacity are in progress.

In conclusion, we present the synthesis and structure of the first multidimensional, intersecting, large-pore hybrid organo-phosphonate molecular sieve. NCHU-3 is novel not only in the unusual shape of its cages with hydrophobic walls, but also in its framework featuring redox-active oxovanadyl centers. The above results may provide new developments in separation, catalytic, and nanoelectronic applications.

Experimental Section

NCHU-3: A reaction mixture of V_2O_5 (0.0909 g, 0.5 mmole), ethylenediphosphate (0.2850 g, 1.5 mmole), Ga_2O_3(0.0468 g, 0.25 mmole), KOH (0.25 mL, 10 M), and H_2O (10 mL) was sealed in a 23 mL teflon-lined stainless autoclave, heated at 200 °C for 72 h, then cooled to 70 °C at 9 $K\,h^{-1}$. The resulting blue crystals were isolated by filtration, and washed with deionized water. Yield 0.046 g (34 % based on Ga_2O_5), and the synthesis was highly reproducible. Crystallography: The X-ray diffraction low-temperature (120 K) data were collected on a CCD Bruker AXS SMART-1000 diffractometer with monochromated $Mo_{K\alpha}$ ($\lambda = 0.71069$ Å) in the $\omega/2\theta$ scan. The structure was solved with SHELXTL PLUS and refined with SHELXL-93 on F^2 by full-matrix least-squares methods. The highly disordered potassium ions and water molecules could not be completely located in the structure analysis. The induction-coupled plasma-mass spectrometry and energy dispersive X-ray analysis both showed the compound contained K, Ga, V, and P in approximately constant proportions. $Ga_2(VO)_3K_2(OH_2)_3(C_2H_4P_2O_6)_4(H_2O)_{13}$, Crystal size $0.18 \times 0.06 \times 0.06$ mm, Orthorhombic system, space group *Cmcm*, $a = 16.6870(2)$, $b = 14.7395(3)$, $c = 17.5737(3)$ Å, $V = 4322.4(1)$ $Å^3$, $Z = 4$, $2\Theta_{max} = 55°$; $R_1 = 0.101$, $wR_2(F^2) = 0.278$, and GOF = 1.113; residual electron density between −3.6 and 1.81 e $Å^{-3}$. CCDC-195599 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

The lithium-ion intercalation of NCHU-3 was prepared according to our previous procedures.[16] The cathode was fabricated by compressing powdered Li·NCHU-3 (85 %), black carbon (10 %) and PTFE (5 %) on an aluminum disk. The pellet was then dried at 120 °C in air. The electrolyte was prepared by dissolving $LiClO_4$ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and methyl formate (MF) (volume ratio 50:45:5) to give a 1 M solution. Some properties of this electrolyte were reported.[19]

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