Inorganic–Organic Hybrid Materials

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

Ching-Yuan Cheng, Shu-Juan Fu, Chia-Jung Yang, Wei-Hung Chen, Kuan-Jiuh Lin,* Gene-Hsiang Lee, and Yu Wang

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 wellordered 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

[*] Prof. K.-J. Lin, C.-Y. Cheng, S.-J. Fu, C.-J. Yang, W.-H. Chen Department of Chemistry Nanocenter, National Chung-Hsing University Taichung 402, Taiwan (Republic of China) Fax: (+886) 4-22862547 E-mail: kjlin@dragon.nchu.edu.tw G.-H. Lee, Prof. Y. Wang Department of Chemistry National Taiwan University Taipei 106, Taiwan (Republic of China)

[**] We thank H. S. Sheu at synchrotron radiation research center for technical assistance with PXRD data. This work was supported by the National Science Council of the Republic of China (NSC 90-2113M-005-013) and the Institude of Chemistry, Academia Sinica.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Zuschriften

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 $(\times 2)$, 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 O₃PC tetrahedron of [O₃P-CH₂CH₂-PO₃]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 $5 \text{ Å} \times 7 \text{ Å}$ and $5 \text{ Å} \times 14 \text{ Å}$, respectively. These channels intersect at the center of a chinese-vaselike cage consisting of 63 atoms (six 6-rings and two 16-rings,



Figure 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. (GaO₄: green tetrahedron; VO₅(OH₂): blue octahedron; PO₃C: red tetrahedron; CH₂P₂: 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 Å³.



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).

Figure 1 c and 1 d). 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 -CH₂ moieties covering the walls of the Chinese-vaselike cages. The approximate vase-void volume is 1359 Å³ per unit cell. Microporous materials are often compared by framework density (FD, number of density of tetrahedral atoms per 1000 Å³).^[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]

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 NH₄⁺ ions by using saturated NH₄Cl solution was easily accomplished, as confirmed by energydispersive 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 LiClO₄ in an EC-DMC-MF electrolyte mixture (T=30 °C, scan rate 100 mVs⁻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 teflonlined 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_{Ka} ($\lambda = 0.71069$ Å) in the $\omega/2\theta$ scan. The structure was solved with SHELXTL PLUS and refined with SHELXL-93 on F² 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 $0.18 \times 0.06 \times 0.06 \times 0.06 \times 0.06$ 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) Å³, $Z = 4, 2\Theta_{max} =$ 55°; $R_1 = 0.101$, $wR_2(F^2) = 0.278$, and GOF = 1.113; residual electron density between -3.6 and 1.81 eÅ-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 CB21EZ, 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 LiClO₄ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and methyl formate (MF) (volume ratio 50:45:5) to give a 1M solution. Some properties of this electrolyte were reported.^[19]

Received: November 13, 2002 [Z50544]

Keywords: gallium · hydrothermal synthesis · intercalations · microporous materials · vanadium

- M. E. Davis, C. Saldarriaga, C. Montes, J. Graces, C. Crowder, *Nature* 1988, 331, 698–699.
- [2] M. E. Davis, Chem. Eur. J. 1997, 3, 1745-1750.
- [3] R. I. Walton, F. Millange, T. Loiseau, D. O'Hare, G. Ferey, Angew. Chem. 2000, 112, 4726–4729; Angew. Chem. Int. Ed. 2000, 39, 4552–4555.
- [4] X. Bu, P. Feng, G. D. Stucky, Science 1997, 278, 2080-2085.
- [5] H. Li, A. Laine, M. O'Keeffe, O. M. Yaghi, Science 1999, 283, 1145-1147.
- [6] T. Asefa, M. J. MacLachian, N. Coombs, G. A. Ozin, *Nature* 1999, 402, 867–871.
- [7] E. K. Brechin, R. A. Coxall, A. Parkin, S. Parsons, P. A. Tasker, R. E. P. Winpenny, *Angew. Chem.* 2001, *113*, 2772–2775; *Angew. Chem. Int. Ed.* 2001, *40*, 2700–2703.
- [8] D. M. Poojary, B. Zhang, A. Clearfield, J. Am. Chem. Soc. 1997, 119, 12550-12559.

Zuschriften

- [9] V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta, Angew. Chem. 1995, 107, 229–231; Angew. Chem. Int. Ed. Engl. 1995, 34, 223–226.
- [10] R. P. Hammond, J. A. Zubieta, J. Solid State Chem. 1999, 144, 442-448.
- [11] M. I. Khan, L. M. Meyer, R. C. Haushalter, A. L. Schweitzer, J. Zubieta, J. L. Dye, *Chem. Mater.* **1996**, *8*, 43–53.
- [12] a) S. Guan, S. Inagaki, T. Ohsuna, O. Terasaki, J. Am. Chem. Soc. 2000, 122, 5660-5661; b) A. Stein, B. J. Melde, R. C. Schroden, Adv. Mater. 2000, 12, 1403-1419.
- [13] At temperatures above 100 K, the susceptibility data obeys the Curie–Weiss law, and the magnetic moment ($\mu_{eff} = 3.82$ BM) is close to the expected spin-only value for two independent vanadium(IV) centers per molecule. (see Supporting Information)
- [14] G. O. Brunner, W. M. Meier, Nature 1989, 337, 146-147.
- [15] a) M. Estermann, L. B. McCusker, C. Baerlocher, A. Merrouche, H. Kessier, *Nature* 1991, 352, 320–323; b) W. M. Meier, *New Dev. Zeolite Sci. Technol. Proc. Int. Zeolite Conf.* 1986, 7, 13–22.
- [16] L. W. Huang, C. J. Yang, K. J. Lin, Chem. Eur. J. 2002, 8, 394– 400.
- [17] J.-M. Tarascon, M. Armand, Nature 2002, 414, 359-367.
- [18] Z. Gadjourova, Y. G. Andreev, D. P. Tunstall, P. G. Bruce, *Nature* 2001, 412, 520–523.
- [19] a) A. R. Armstrong, P. G. Bruce, *Nature* 1996, *381*, 499–500;
 b) S. R. P. Prabaharan, M. S. Michael, S. Radhakrishna, C. Julien, *J. Mater. Chem.* 1997, *7*, 1791–1796.