Mixed-Valence Ammonium Trivanadate with a Tunnel Structure Prepared by Pyrolysis of Polyoxovanadate

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(Received June 24, 1999)

The pyrolysis of a polyoxovanadate solid, $(NH_4)_{12}[V_{18}O_{42}(H_2O)]\cdot nH_2O$ ($n \approx 11$), at 300 °C in an Ar+NH_3 atmosphere gave a mixed-valence vanadium oxide, $(NH_4)_xV_3O_7$ ($x \approx 0.6$), isostructural with $Cs_{0.37}V_3O_7$. The crystal structure of $(NH_4)_xV_3O_7$ was refined by the Rietveld method (hexagonal, $P6_3/m$, a = 9.8436(6), c = 3.6165(1) Å, V = 303.47(3) Å^3, Z = 2). $(NH_4)_xV_3O_7$ comprises edge- and corner-sharing $V^{IV/V}O_5$ square-pyramids with an approximate ratio of V^{IV} : $V^V \approx 0.49$: 0.51, to form a columnar cavity along the c-axis, in which ammonium N atoms are hydrogen-bonded to apical O atoms of the $V^{IV/V}O_5$ square-pyramids. A reflux of the $(NH_4)_xV_3O_7$ powder in a 0.6 M LiOH/2-methoxyethanol solution brought about Li-insertion into the columnar cavity without any structural change in the $\{V_3O_7\}$ framework.

Mixed-valence vanadium oxides and vanadium bronzes, which consist of corner- and edge-sharing $V^{IV/V}O_5$ square-pyramids and/or distorted $V^{IV/V}O_6$ octahedra, have been investigated concerning their structures[1—4] as well as electronic and magnetic properties.[5—7] Especially, the electrochemical Li^+-intercalation/deintercalation properties on vanadium oxides with layered or tunnel-type structures have been studied, because they are candidates as cathode materials for rechargeable lithium batteries.[8—16] Many of these compounds have been prepared by solid state reactions,[4,7] pyrolyses,[2,9,17] hydrothermal reactions,[3,16] and sol–gel techniques,[5,6,8,12,14] using simple vanadium oxides such as V_2O_5, VO_2, V_2O_3, and $(NH_4)VO_3$ as starting materials. In the present study, a polyoxovanadate, $[V^{IV}_{18}O_{42}(H_2O)]^{12-}$, was used as a precursor of mixed-valence vanadium oxides. Since polyoxovanadates can be regarded as molecular fragments of vanadium oxides with infinite structures, the condensation of V^{IV}-containing polyoxovanadates by pyrolysis at low temperatures may be expected to form novel mixed-valence vanadium oxides. Figure 1 shows the structure of $[V^{IV}_{18}O_{42}(H_2O)]^{12-}$[18] used in this study, where eighteen $V^{IV}O_5$ square-pyramids are condensed with edge- and corner-sharing into a spherical $\{V_{18}O_{42}\}$ cluster encapsulating a water molecule at the center. This paper describes that the pyrolysis of the ammonium salt of $[V^{IV}_{18}O_{42}(H_2O)]^{12-}$ at 300 °C in a Ar+NH_3 flow leads to the formation of ammonium trivanadate, $(NH_4)_xV_3O_7$ ($x \approx 0.6$) possessing a tunnel-type cavity, to allow a Li^+-insertion reaction without any change in the framework structure.

Experimental

$(NH_4)_{12}[V^{IV}_{18}O_{42}(H_2O)]\cdot nH_2O$ ($n \approx 11$) (**1**) was prepared photochemically by a modification of the procedure for the potassium salt, $K_{10}[H_2V^{IV}_{18}O_{42}(H_2O)]\cdot 16H_2O$.[18] The pH level of an aqueous solution (20 ml) of $[NH_3{}^tBu]_4[V_4O_{12}]$ (0.5 g)[19] was adjusted to about 11 with aqueous ammonia. The resultant solution was mixed with methanol (2 ml), sealed in a Pyrex tube, and then exposed to light from a 500-W super-high-pressure mercury lamp without filtering for about 24 h. After exposure, the tube was kept to cool at room temperature. Dark-brown crystallines of **1** were formed within several days. The vanadium content of **1** was determined thermogravimetrically by conversion to V_2O_5 at 600 °C in air. Found: H, 3.61; N, 8.38; V, 44.4%. Calcd for $(NH_4)_{12}[V_{18}O_{42}(H_2O)]\cdot 11H_2O$: H, 3.59; N, 8.31; V, 45.36%. The V^{IV} : V^V ratio in **1** was estimated potentiometrically by direct and back titrations under a N_2 atmosphere with ammonium iron(II) sulfate and ammonium cerium(IV) sulfate solutions.[18] As a result, **1** consists of only V^{IV}. Since **1** is very air-sensitive to be oxidized, the crystalline solids should be kept in the reaction tube until the following pyrolysis.

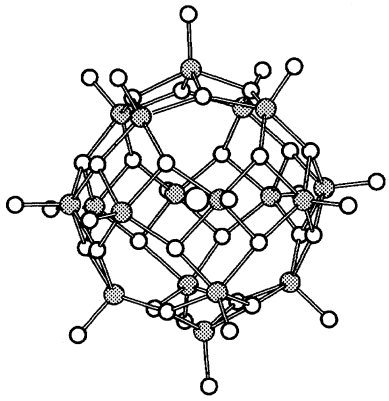

Fig. 1. Structure of $[V^{IV}_{18}O_{42}(H_2O)]^{12-}$.[18] V and O atoms are denoted by shaded and open circles, respectively. The central large open circle represents the water O atom encapsulated by the $\{V_{18}O_{42}\}$ cage.

A freshly prepared and powdered sample of **1** (0.05 g) was placed on an alumina boat in a quartz tube (diameter: 40 mm) of an electric furnace, and exposed to an Ar+NH_3 stream with a flow rate of ca. 20 ml min^{-1}. The sample was heated at 200, 250, 300, 350, and

400 °C for 2 h, and cooled to room temperature in the Ar+NH_3 flow. Powder X-ray diffraction (XRD) patterns were measured on a Rigaku RAD-1VB system. The powder pattern for Rietveld refinement[20] was collected on a Rigaku RINT-2000 diffractometer using a step scanning mode with a step width of 0.02° and a counting time of 2 s $step^{-1}$.

Results and Discussion

Pyrolysis Products. XRD patterns of the pyrolysis products are shown in Fig. 2(a)—(e). The pyrolysis of **1** at 200 and 250 °C yielded almost amorphous phases with weak unidentified peaks at 2θ = 9 and 28° (Fig. 2(a) and (b)). At 350 and 400 °C, **1** lost all NH_4^+ cations, to be converted into two VO_2 phases (Fig. 2(d) and (e)). The pyrolysis of **1** at 300 °C resulted in the formation of a new compound (**2**) (Fig. 2(c)).

Characterization of 2. The X-ray diffraction angles (Fig. 2(c)) of **2** are in accord with those (Fig. 2(f)) of $Cs_{0.37}V_3O_7$,[21] suggesting that **2** is isomorphous with $Cs_{0.37}V_3O_7$, to be formulated as $(NH_4)_xV_3O_7$. The $V^{IV}:V^V$ ratio and the total V (= $V^{IV}+V^V$) were determined by the potentiometric titrations with iron(II) and cerium(IV) solutions. The ammonium content (x) was estimated to be ca. 0.6 by elemental analysis. Found: H, 0.85; N, 3.13; V, 55.2%. Calcd for $(NH_4)_{0.6}V_3O_7$: H, 0.88; N, 3.05; V, 55.44%. To maintain electrical neutrality, the $V^{IV}:V^V$ ratio should be 0.53 : 0.47, which is close to 0.49 : 0.51 obtained by redox titration. Since all vanadium of the starting material (**1**) is V^{IV}, the pyrolysis of **1** accompanies the oxidation of V^{IV} to V^V, which was not investigated any further.

The Crystal structure of **2** was refined by the Rietveld method[20] based on the crystallographic parameters of $Cs_{0.37}V_3O_7$[21] by two different ways. In the first refinement Cs was replaced by ammonium N with the fixed site occupancy of 0.6. This refinement resulted in high convergence factors (R_{wp} = 13.85, R_p = 10.96, S = 3.27, R_I = 9.55, and R_F = 3.80) with an abnormally long V1–O2 distance (1.743(9) Å) of the $V{=}O_{terminal}$ bonds. On the other hand, in the second refinement, where a part of the V1 atom was disordered as V2 and V3 on the positions of N1 and N2, respectively, low convergence factors (R_{wp} = 11.58, R_p = 9.14, S = 2.74, R_I = 6.21, and R_F = 2.73) and a reasonable V1–O2 length (1.547(8) Å) were obtained, as shown in Tables 1 and 2. Since the numbers of equivalent positions for V1, V2, and V3 sites in a unit cell are 6, 2, and 2, respectively (Table 1), the site occupancies (Occ's) of the V1—3 atoms were refined under a constraint condition of Occ(V1) = 1 − {Occ(V2) + Occ(V3)}/3 in order to maintain the V : O = 3 : 7 ratio. Figure 3 shows the observed XRD patterns of **2** and the patterns

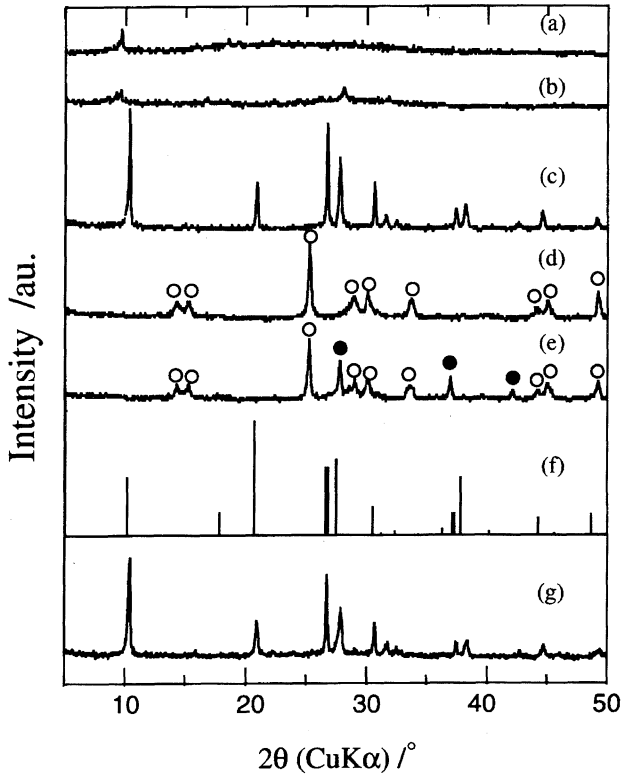

Fig. 2. The XRD patterns of the pyrolysis products of **1** treated at 200 °C (a), 250 °C (b), 300 °C (**2**) (c), 350 °C (d), and 400 °C (e). The patterns of $Cs_{0.37}V_3O_7$[21] and **2** refluxed in LiOH/2-methoxyethanol solution are shown in (f) and (g), respectively. The open (○) and filled (●) circles in (d) and (e) denote diffraction peaks of two different VO_2 phases.[25,26]

Table 1. Structural Parameters of **2** Obtained by Rietveld Refinement

Lattice type, space group: hexagonal, $P6_3/m$. Unit cell parameters: a = 9.8436(6), c = 3.6165(1) Å, V = 303.47(3) $Å^3$. R factors: R_{wp} = 11.58, R_p = 9.14, R_e = 4.23, R_F = 2.73.

Atom	x	y	z	Site[a)]	Occ[b)]	B/$Å^2$
V1	0.1218(3)	0.6227(3)	1/4	6*h*	0.917[c)]	0.33(8)[d)]
V2	0	0	1/4	2*a*	0.10(1)[c)]	0.33(8)[d)]
V3	0	0	0	2*b*	0.15(1)[c)]	0.33(8)[d)]
N1	0	0	1/4	2*a*	0.3	49(16)[e)]
N2	0	0	0	2*b*	0.3	49(16)[e)]
O1	0.0951(8)	0.5537(7)	3/4	6*h*	1.0	2.6(2)[f)]
O2	0.216(1)	0.345(1)	1/4	6*h*	1.0	2.6(2)[f)]
O3	1/3	2/3	1/4	2*c*	1.0	2.6(2)[f)]

a) Wyckoff's notation. b) Site occupancy. c) Refined under a constraint condition of Occ(V1) = 1−{Occ(V2)+Occ(V3)}/3 (see text). d) e), f) Refined as common parameters.

Table 2. V–O Bond Distances (Å) and O–V–O Bond Angles (°) in the VO_5 Square Pyramid[a)]

V1–O2^{i}	1.547(8)	V1–O3	1.905(1)
V1–O1	1.905(2)	V1–O1^{ii}	1.968(6)
O2^{i}–V1–O1	107.3(2)	O2^{i}–V1–O3	106.0(5)
O2^{i}–V1–O1^{ii}	112.5(5)	O1–V1–O1^{ii}	143.4(4)
O1–V1–O1^{ii}	78.0(2)	O3–V1–O1^{ii}	141.5(3)
O1–V1–O3	91.0(2)		

a) Symmetry codes: (i) $-x+y, 1-x, z$; (ii) $-x, 1-y, -1/2+z$.

fitted based on the result of a second refinement, indicating that both of the pattens are quite similar. The refined Occ's of V1, V2, and V3 are 0.917, 0.10(1), and 0.15(1), respectively (Table 1), to be formulated as $(NH_4)_{0.6}(V1_{2.75})$-$(V2_{0.10})(V3_{0.15})O_7$. However, no further information on the distributions and valence states of V2 and V3 has been obtained. Such a disordering of metal cations in columnar cavities or between host layers has been found in several ternary metal oxides. For example, a columnar cavity in a modified hollandite-type $A_{2-x}V_{8+2x}O_{16+x}$ (A = K, Rb) accommodates not only A cations, but also V cations.[22] In the case of $LiFeO_2$, as another example, Fe^{3+} in $\{FeO_2\}$ layers and Li^+ between $\{FeO_2\}$ layers are partially exchanged with a disorder, to be formulated as $Li_{0.907}(Li_{0.093})_{Fe}Fe_{0.907}(Fe_{0.093})_{Li}O_2$.[23] Similarly, in a non-stoichiometric $LiNb_{1+x}O_3$ ($x = 0.008$—0.128), a part of the Li^+ cations is replaced by Nb^{5+} cations to form Li^+ vacancies as the result of charge compensation.[24]

Figure 4(a) shows the structure of **2** viewed from the *c*-axis. The $\{V_3O_7\}$ framework in the hexagonal lattice comprises edge- and corner-shared VO_5 square-pyramids, and

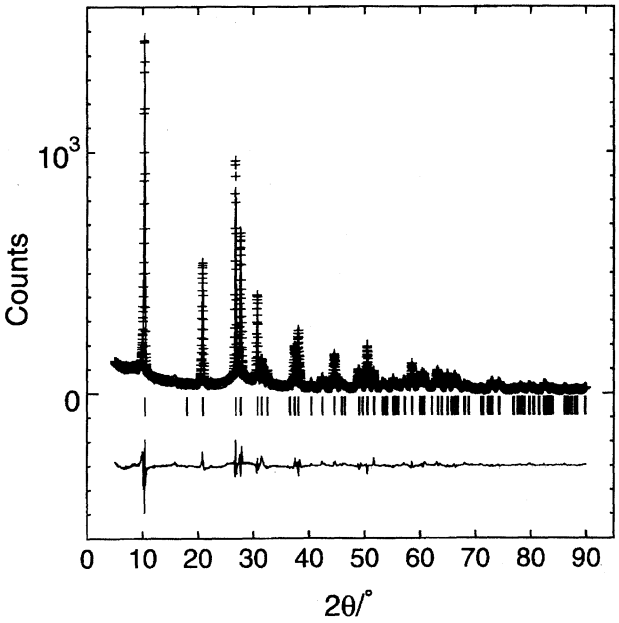

Fig. 3. Observed (+) and fitted (—) XRD patterns of **2** refined by Rietveld method.[20] The vertical bars denote calculated diffraction angles. The pattern at bottom denotes differences between observed and calculated intensities.

possesses a columnar cavity along the *c*-direction. Figure 4(b) shows a side view (perpendicular to the *c*-direction) of the $\{V_3O_7\}$ lattice, where the broken lines A, B, and C correspond to points A, B, and C in Fig. 4(a). As shown in Fig. 4(b), the O2 atom and [O1,O1′,O1″,O3] square form an apex and a basal plane of the VO_5 square-pyramid, respec-

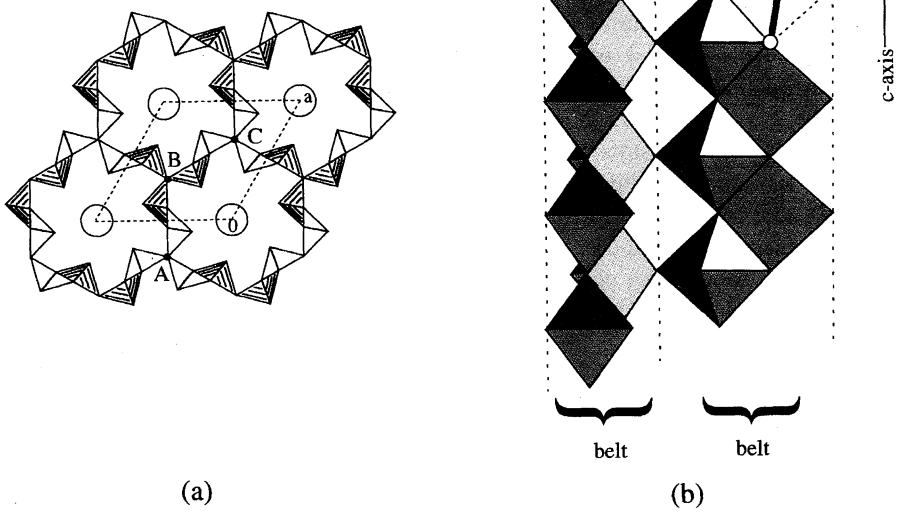

Fig. 4. Polyhedral representation of the crystal structure of **2** viewed parallel (a) and perpendicular (b) to the *c*-axis. Two of the VO_5 square-pyramids in (b) are drawn by ball and stick model. The points A, B, and C in (a) correspond to the dashed lines A, B, and C in (b), respectively.

tively. The VO_5 polyhedra are connected by edge-sharing along the *c*-direction to form a belt structure (Fig. 4(b)). One columnar cavity is made up of six belts by corner-sharing through O3 atoms with a hexagonal configuration (Fig. 4(a)). It is noteworthy that the same belt structure can be found in layer-structural V_2O_5 and $M_xV_2O_5$ (M = alkaline or alkaline earth metals) bonzes.[1] Table 2 summarizes the bond distances and angles for the VO_5 square-pyramid, which are similar to those for isostructural $Cs_{0.37}V_3O_7$.[21] The ammonium N atoms in the columnar cavities are hydrogen-bonded to the terminal O2 atoms at N···O distances of 2.980(9)—3.114(8) Å.

There have been several methods for the preparation of vanadium oxides and vanadium bronzes by pyrolysis of NH_4VO_3 in a reducing or inert gas atmosphere. For example, the decomposition of NH_4VO_3 solids in H_2 flow at 230 °C yields β-$(NH_4)_xV_2O_5$ ($x \approx 0.38$) consisting of host $\{V_2^{IV/V}O_5\}$ layers and NH_4^+ cations.[17] VO_2 with a tunnel-structure has been prepared by the pyrolysis of NH_4VO_3 at 330 °C in NH_3 stream.[9] Also, NH_4VO_3 was converted to layer-structural V_6O_{13-y} by decomposition at 500—550 °C in an Ar stream.[15] The pyrolyses of $NH_4V^VO_3$ or $V^{IV}OSO_4$ at 200—400 °C under Ar+NH_3 atmosphere exhibited no formation of **2**, suggesting that the formation of **2** is characteristic of the pyrolysis of **1**. This renders the fact that both the VO_5 square-pyramids and the ratio of V : O = 3 : 7 are common to the anion frameworks of $\{V_{18}O_{42}\}$ in **1** and $\{V_3O_7\}$ in **2**. We are actively pursuing the pyrolysis of the polyoxovanadates with other structures and compositions to address a preparative novel vanadium oxides.

Li Insertion into 2. The insertion of Li^+ into a columnar cavity occurred by the reflux of **1** (0.15 g) in 0.6 M LiOH/2-methoxyethanol (1 M = 1 mol dm^{-3}) solutions (20 ml) for 2 h. The product was collected by filtration, washed with 2-methoxyethanol, and dried in air. An elemental analysis showed the V/Li ratio to be ca. 2.9 (observed; H, 1.40; Li, 2.30; N, 1.91; V, 48.1%). The V^{IV} : V^V ratio (ca. 0.45 : 0.55) was nearly the same as that (0.49 : 0.51) for **2**. The XRD pattern is shown in Fig. 2(g), which is similar to the pattern of **2** (Fig. 1(c)), indicating that the $\{V_3O_7\}$ framework is retained through the Li-insertion reaction. The a (= b) axis was ca. 0.05 Å less than for **2**, probably due to the small size of Li^+ compared to NH_4^+. These results suggest the approximate formula of the Li-insertion product to be Li-$(OH)(H_2O)(NH_4)_{0.4}V_3O_7$ (Calcd for: H, 1.48; Li, 2.21; N, 1.78; V, 48.67%). The existence of OH^- and/or H_2O was also suggested by IR absorption bands (data not shown) at ca. 1600 and ca. 3400 cm^{-1}, which are assigned to ν(OH) and δ(HOH) vibrations, respectively.[27]

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (No. 260) from the Ministry of Education, Science, Sport and Culture. The authors express their thanks to Professor M. Wakihara and Dr. H. Ikuta for providing facilities for X-ray powder diffraction measurement.

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