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STRUCTURE OF (VO)$_2$P$_2$O$_7$

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ABSTRACT

The crystal structure of the vanadium (IV) pyrophosphate that shows the remarkable ability to selectively catalyze the oxidation of butane to maleic anhydride has been accurately determined for the first time. This was facilitated by the growth of high quality (VO)$_2$P$_2$O$_7$ crystals under controlled oxygen fugacity. Single crystal X-ray diffraction indicated monoclinic symmetry rather than the orthorhombic symmetry assumed in earlier studies. The space group is P2$_1$ with a = 7.28 Å, b = 16.588 Å, c = 9.58 Å, β = 89.975 Å, and Z = 4. A final R of 3.1% was obtained. Typical vanadyl environments are found for all eight crystallographically distinct vanadium atoms, and normal bond angles and distances are found for the P$_2$O$_7$ groups.

MATERIALS INDEX: vanadium, phosphate, catalyst

INTRODUCTION

One of the most remarkable heterogeneous catalysts is (VO)$_2$P$_2$O$_7$. If prepared according to certain procedures, this compound can catalyze the oxidation of n-butane to maleic anhydride at selectivities exceeding 80% (1). No other compound is known to catalyze this commercially important reaction at selectivities approaching 80%. No other partial oxidation of a saturated hydrocarbon is known to be so selective. Despite the uniqueness and importance

of (VO)$_2$P$_2$O$_7$ as a catalyst, it is poorly understood. Three previous crystal structure studies *(2-4)* did not lead to a good definition of the structure.

The first single crystal X-ray diffraction study *(2)* on (VO)$_2$P$_2$O$_7$ resulted in a final R of 19.8%. A second study *(3)* yielded an R of 8.9%, but some of the interatomic distances seemed unreasonable. Both of these studies reported essentially the same structural arrangement (Fig. 1). The (VO)$_2$P$_2$O$_7$ structure has recently been redetermined by Thompson and Ebner *(4)*. They obtained good agreement factors (R = 3.4%); however, they could obtain this result only with a disordered model. Streaking effects in their diffraction patterns also indicated disorder.
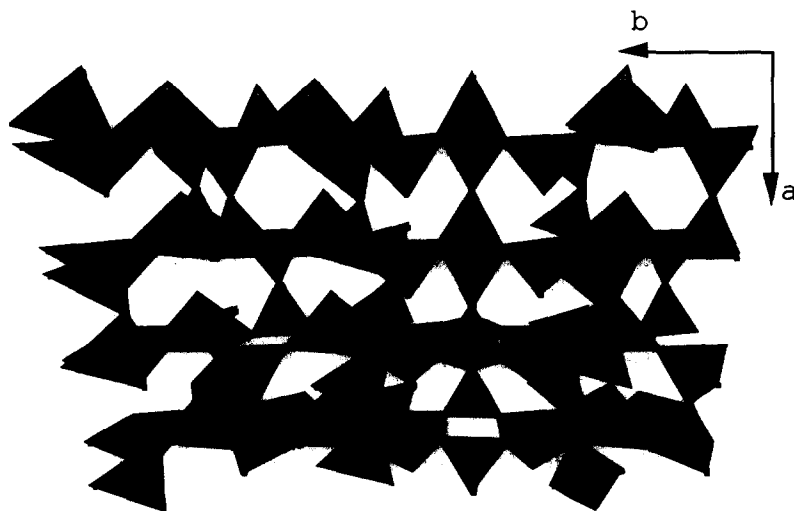

FIG 1.
The structure of (VO)$_2$P$_2$O$_7$ where the vanadyl groups are shown as square pyramids and the pyrophosphate groups are shown as a pair of corner sharing tetrahedra.

We have now obtained single crystals of (VO)$_2$P$_2$O$_7$ which give diffraction patterns free from any indications of disorder. No streaking was observed in our diffraction patterns, and a good refinement was obtained based on a fully ordered structure.

PREPARATION OF CRYSTALS

Polycrystalline $(VO)_2P_2O_7$ was prepared by dehydration of $(VO)_2P_2O_7 \cdot xH_2O$. Approximately 5 g of $(VO)_2P_2O_7$ was pressed into a 10-mm-diameter pellet. This pellet was placed in a Pt crucible and heated in a furnace where oxygen fugacity was controlled and continuously monitored. After rapid heating to 500°C, the sample was heated to 910°C at 50°/hour. After a hold period of 15 hours, the sample was cooled at 2°/hour to 890°C and then cooled at 4°/hour to 855°C. Power to the furnace was terminated, and the sample was cooled to room temperature in the furnace. This procedure was repeated at several oxygen fugacities between 0.001 atm and 0.003 atm.

Crystals prepared when using the lower oxygen pressure (~0.001 atm) were green, but those recovered from preparations at higher oxygen pressures were red-brown. The titration method of Nakamura et al. (5) was used to determine the oxidation state of vanadium in the crystals. The result was 4.00 for the green crystals and 4.01 for the red-brown crystals. Diffraction patterns taken on a precession camera indicated that the green crystals were of higher quality from a diffraction point of view. Therefore, only those crystals were used in further structural studies.

TABLE 1
Crystal Data and Intensity Collection for $(VO)_2P_2O_7$

Empirical formula	$V_2P_2O_9$
Formula weight (g/mol)	307.82
Space Group	$P2_1$ (no. 4)
a (Å)	7.7276(3)
b (Å)	16.5885(4)
c (Å)	9.5796(5)
β	89.975(3)
V (Å³) 1228(1)	
Z	4
Diffractometer	Rigaku AFC6R
Radiation	MoK_α (λ = 0.71069 Å) graphite-monochromated
Temperature	23°C
Maximum 2θ	70°
Data collected	-9 < h < 9, -21 < k < 21, -12 < l < 12
Scan speed (degrees/min)	16.0 in ω and 32.0 in 2θ
No. of unique data with $F_{obs} > 3\sigma$ (F_{obs})	4254
R_{merge}	3.6%
Data/parameter ratio	14.72
R	0.031
R_w	0.044

STRUCTURE DETERMINATION

Single crystal diffraction data were collected on a Rigaku AFC6R diffractometer. Despite the apparent orthorhombic symmetry, a full sphere of reflections was collected (Table 1). The intensities of three standard reflections measured every 300 reflections throughout the data collection exhibited no significant excursions. The structure was solved and refined with programs from the TEXAN software packages *(6)*. The absorption correction was performed with the DIFABS software *(7)*.

TABLE 2
Atomic and Thermal Parameters for $(VO)_2P_2O_7$

Atom	x	y	z	Beq (Å²)*	Atom	x	y	z	Beq (Å²)
V1	0.2973(2)	0.0958	0.4912(1)	0.47(5)	O11	0.4960(7)	-0.2162(3)	0.2871(4)	0.59(7)
V2	0.2039(2)	0.5960(1)	0.4909(1)	0.36(5)	O12	0.0066(8)	0.2846(3)	0.2862(5)	0.79(8)
V3	0.2087(2)	-0.09442(9)	0.5023(1)	0.33(5)	O13	0.3007(9)	0.1734(3)	0.6421(5)	1.0(1)
V4	0.2923(2)	0.4057(1)	0.5017(1)	0.25(5)	O14	0.2017(8)	0.6734(3)	0.6410(5)	0.71(9)
V5	0.2055(2)	-0.1548(1)	-0.0005(2)	0.45(6)	O15	0.2133(8)	0.1761(3)	0.3613(5)	0.44(8)
V6	0.2935(2)	0.3453(1)	-0.0002(1)	0.43(6)	O16	0.2943(9)	0.6756(3)	0.3600(5)	0.9(1)
V7	0.2081(2)	0.1561(1)	-0.0014(1)	0.34(5)	O17	0.281(1)	0.0010(4)	0.6307(6)	0.9(1)
V8	0.2914(2)	0.65607(7)	-0.0021(1)	0.33(5)	O18	0.2200(8)	0.5007(3)	0.6300(5)	0.3(1)
P1	0.2952(3)	-0.0003(1)	0.7924(2)	0.3(1)	O19	0.2221(9)	0.0017(4)	0.3639(5)	0.4(1)
P2	0.2026(4)	0.4997(2)	0.7925(2)	0.39(8)	O30	0.276(1)	0.5012(4)	0.3619(6)	0.7(1)
P3	0.1948(3)	0.0005(2)	0.2012(2)	0.3(1)	O31	0.2860(9)	-0.1795(3)	0.6294(6)	0.7(1)
P4	0.3031(4)	0.5008(1)	0.2012(2)	0.24(8)	O32	0.2117(9)	0.3207(3)	0.6287(5)	0.6(1)
P5	0.1920(4)	-0.2447(2)	0.7064(2)	0.4(1)	O33	0.199(1)	-0.1772(3)	0.3578(5)	0.8(1)
P6	0.3106(4)	0.2556(1)	0.7061(2)	0.37(9)	O34	0.298(1)	0.3230(3)	0.3572(5)	0.7(1)
P7	0.3020(3)	-0.2436(1)	0.2907(2)	0.4(1)	O35	0.2659(9)	0.0775(3)	0.1395(5)	1.0(1)
P8	0.2008(4)	0.2562(1)	0.2906(2)	0.27(8)	O36	0.2355(8)	0.5768(3)	0.1390(5)	0.67(9)
O1	0.5014(8)	0.5914(3)	0.5399(4)	0.59(8)	O37	0.2274(8)	0.0749(3)	-0.1455(5)	0.79(9)
O2	-0.0024(8)	0.0933(3)	0.5397(4)	0.76(8)	O38	0.2809(9)	0.5743(3)	-0.1465(5)	1.05(9)
O3	0.005(1)	-0.0904(3)	0.5313(5)	0.8(1)	O39	0.2727(8)	-0.0754(3)	0.1391(6)	0.6(1)
O4	0.496(1)	0.4121(3)	0.5320(4)	0.41(9)	O50	0.2329(9)	0.4247(3)	0.1390(6)	0.7(1)
O5	-0.001(1)	-0.1597(3)	0.0131(6)	0.59(8)	O51	0.2234(9)	-0.0768(3)	-0.1513(5)	0.7(1)
O6	0.500(1)	0.3435(4)	0.0115(7)	0.9(1)	O52	0.2823(9)	0.4233(3)	-0.1514(6)	0.8(1)
O7	-0.0002(9)	0.1599(3)	0.0125(6)	0.67(8)	O53	0.2510(8)	-0.2504(3)	0.1328(6)	0.3(1)
O8	0.500(1)	0.6595(3)	0.0108(6)	0.88(8)	O54	0.255(1)	0.2497(4)	0.1352(6)	0.8(1)
O9	0.4975(8)	-0.0014(3)	0.8272(6)	1.55(9)	O55	0.2496(9)	-0.2482(4)	-0.1394(6)	0.6(1)
O10	0.0044(8)	0.4983(3)	0.8252(6)	1.41(9)	O56	0.2535(9)	0.2517(4)	-0.1382(6)	0.5(1)

*Beq = $(8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j a_i a_j$

Refinements were initially carried out in space groups Pcam and Pca2$_1$ because these were the space groups that earlier investigators (2-4) had considered. However, significant peaks near vanadium atoms were always found in the final difference electron density maps. Furthermore, three different crystals clearly showed reflections which violate these space groups both in precession photographs and in data collected with the diffractometer. Thirty-seven of these "forbidden" reflections had an observed intensity higher than six times sigma. The only space group consistent with the observed systematic absences is P2$_1$. Refinement in this space group was successful (Table 1), and the final difference Fourier map was featureless. The final positional parameters are given in Table 2, and the final thermal parameters are given in Table 3. Bond distances are given in Table 4, and selected bond angles are given in Table 5.

TABLE 3

Anisotropic Thermal Parameters (x 10^{-4}Å) for $(VO)_2P_2O_7$

Atom	U11	U22	U33	U12	U13	U23
V1	7(1)	59(6)	53(5)	-15(5)	16(7)	21(6)
V2	4(1)	56(6)	45(5)	10(5)	1(7)	-26(5)
V3	3(1)	60(6)	36(5)	29(5)	1(7)	-17(5)
V4	6(9)	43(6)	45(5)	-2(4)	6(7)	27(5)
V5	8(1)	40(6)	47(5)	21(5)	4(7)	-16(6)
V6	7(1)	52(6)	46(5)	-4(5)	-18(7)	32(6)
V7	6(1)	38(5)	33(5)	15(5)	12(7)	-20(5)
V8	5(1)	40(5)	37(5)	-20(5)	-6(6)	16(5)
P1	1(1)	8(1)	17(8)	8(8)	1(1)	6(6)
P2	6(1)	5(1)	33(8)	11(9)	-20(1)	-6(6)
P3	2(1)	7(1)	37(9)	-19(8)	-1(1)	-1(6)
P4	1(1)	6(1)	17(8)	14(8)	-10(9)	-4(6)
P5	9(2)	6(1)	2(1)	-26(9)	1(1)	7(6)
P6	5(1)	4(1)	48(9)	6(9)	-1(1)	5(6)
P7	6(2)	5(1)	4(1)	-4(9)	10(1)	6(6)
P8	3(1)	5(1)	23(8)	10(8)	1(1)	-11(6)

TABLE 4
Bond Distances (Å) for $(VO)_2P_2O_7$

V1	O1	1.585(6)	V8	O7	2.253(7)
	O2	2.337(6)		O8	1.619(7)
	O13	1.936(5)		O36	1.934(5)
	O15	1.935(5)		O38	1.939(5)
	O17	2.067(6)		O53	2.043(6)
	O19	2.065(6)		O55	2.088(6)
V2	O1	2.307(6)	P1	O9	1.599(7)
	O2	1.585(6)		O17	1.554(6)
	O14	1.929(5)		O37	1.478(5)
	O16	1.951(6)		O51	1.486(6)
	O18	2.071(6)	P2	O10	1.564(7)
	O30	2.075(7)		O18	1.563(5)
V3	O3	1.597(8)		O38	1.497(6)
	O4	2.307(7)		O52	1.509(6)
	O17	2.081(7)	P3	O10	1.560(7)
	O19	2.076(6)		O19	1.573(5)
	O31	1.957(6)		O35	1.510(6)
	O33	1.951(5)		O39	1.518(6)
V4	O3	2.323(8)	P4	O9	1.565(7)
	O4	1.606(7)		O30	1.554(6)
	O18	2.075(6)		O36	1.489(6)
	O30	2.079(6)		O50	1.497(6)
	O32	1.964(6)	P5	O12	1.612(6)
	O34	1.949(5)		O14	1.498(5)
V5	O5	1.602(8)		O31	1.498(6)
	O6	2.277(9)		O55	1.544(6)
	O39	1.948(6)	P6	O11	1.568(6)
	O51	1.945(5)		O13	1.497(6)
	O53	2.066(6)		O32	1.516(6)
	O55	2.070(6)		O56	1.557(6)
V6	O5	2.266(8)	P7	O11	1.567(6)
	O6	1.601(9)		O16	1.496(5)
	O50	1.932(6)		O33	1.506(6)
	O52	1.943(5)		O53	1.568(6)
	O54	2.071(6)	P8	O12	1.574(6)
	O56	2.062(6)		O15	1.495(5)
V7	O7	1.617(7)		O34	1.484(6)
	O8	2.257(7)		O54	1.549(6)
	O35	1.930(5)			
	O37	1.935(5)			
	O54	2.062(6)			
	O56	2.087(6)			

TABLE 5

Bond Angles (°) for $(VO)_2P_2O_7$

Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
O1-V1-O13	99.0(3)	O38-V8-O53	167.4(3)	O19-V3-O31	159.4(3)	O31-P5-O55	111.0(3)
O1-V1-O15	103.9(2)	O38-V8-O55	94.3(2)	O19-V3-O33	95.1(2)	O11-P6-O13	109.8(4)
O1-V1-O17	98.3(3)	O53-V8-O55	78.3(2)	O31-V3-O33	86.9(2)	O11-P6-O32	106.7(3)
O1-V1-O19	97.5(3)	O9-P1-O17	106.0(4)	O3-V4-O4	174.0(2)	O11-P6-O56	104.0(3)
O13-V1-O15	91.6(2)	O9-P1-O37	105.8(3)	O3-V4-O18	78.0(2)	O13-P6-O32	115.0(3)
O13-V1-O17	91.4(2)	O9-P1-O51	106.2(3)	O3-V4-O30	80.3(2)	O13-P6-O56	109.9(3)
O13-V1-O19	161.4(2)	O17-P1-O37	111.4(4)	O3-V4-O32	7.9(2)	O32-P6-O56	110.8(4)
O15-V1-O17	156.8(3)	O17-P1-O51	110.3(3)	O3-V4-O34	86.9(2)	O11-P7-O16	108.0(3)
O15-V1-O19	92.6(2)	O37-P1-O51	116.3(3)	O4-V4-O18	96.1(2)	O11-P7-O33	107.7(3)
O17-V1-O19	77.9(2)	O10-P2-O18	106.5(4)	O4-V4-O30	97.2(3)	O11-P7-O53	103.9(3)
O2-V2-O14	98.5(3)	O10-P2-O38	109.3(4)	O4-V4-O32	104.3(3)	O16-P7-O33	116.4(3)
O2-V2-O16	104.6(3)	O10-P2-O52	108.4(3)	O4-V4-O34	98.8(3)	O16-P7-O53	110.7(3)
O2-V2-O18	99.0(3)	O18-P2-O38	110.2(3)	O18-V4-O30	77.7(2)	O33-P7-O53	109.3(3)
O2-V2-O30	97.6(3)	O18-P2-O52	109.2(3)	O18-V4-O32	95.3(2)	O12-P8-O15	109.9(3)
O14-V2-O16	91.8(2)	O38-P2-O52	113.0(4)	O18-V4-O34	163.9(3)	O12-P8-O34	105.7(3)
O14-V2-O18	91.6(2)	O10-P3-O19	107.1(3)	O30-V4-O32	158.1(3)	O12-P8-O54	104.5(3)
O14-V2-O30	161.9(2)	O10-P3-O35	108.4(3)	O30-V4-O34	94.6(2)	O15-P8-O34	115.9(3)
O16-V2-O18	155.3(3)	O10-P3-O39	107.9(3)	O32-V4-O34	86.7(2)	V2-O30-P4	129.0(4)
O16-V2-O30	92.0(2)	O19-P3-O35	109.2(3)	O5-V5-O6	175.9(2)	V4-O30-P4	128.8(4)
O18-V2-O30	77.8(2)	O19-P3-O39	110.2(3)	O5-V5-O55	104.2(3)	V3-O31-P5	132.8(4)
O3-V3-O4	174.6(2)	O35-P3-O39	113.8(3)	O52-V6-O56	91.0(2)	V4-O32-P6	130.9(4)
O3-V3-O17	97.5(3)	O9-P4-O30	107.6(4)	O54-V6-O56	78.6(2)	V3-O33-P7	142.8(4)
O3-V3-O19	97.3(3)	O15-P8-O54	110.9(3)	O7-V7-O8	175.6(2)	V4-O34-P8	145.1(4)
O3-V3-O31	102.9(3)	O34-P8-O54	109.2(3)	O7-V7-O35	101.5(3)	V7-O35-P3	139.5(4)
O3-V3-O33	96.5(3)	V3-O3-V4	161.7(3)	O7-V7-O37	99.3(3)	V8-O36-P4	140.9(4)
O4-V3-O17	77.4(2)	V3-O4-V4	160.2(3)	O7-V7-O54	95.3(3)	V7-O37-P1	154.4(4)
O5-V5-O51	99.5(3)	V5-O5-V6	170.8(3)	O7-V7-O56	100.9(3)	V8-O38-P2	150.9(4)
O5-V5-O53	94.6(3)	V5-O6-V6	173.1(4)	O8-V7-O35	79.3(2)	V5-O39-P3	136.4(4)
O5-V5-O55	100.3(3)	V7-O7-V8	171.8(3)	O8-V7-O37	85.0(2)	V6-O50-P4	139.6(4)
O6-V5-O39	76.9(2)	V7-O8-V8	172.5(3)	O8-V7-O54	80.3(2)	V5-O51-P1	149.8(4)
O6-V5-O51	84.4(2)	P1-O9-P4	157.9(4)	O8-V7-O56	77.8(2)	V6-O52-P2	147.5(4)
O6-V5-O53	81.3(2)	P2-O10-P3	159.0(4)	O35-V7-O37	90.6(2)	V5-O53-V8	102.6(2)
O6-V5-O55	8.2(2)	P6-O11-P7	145.5(3)	O35-V7-O54	91.4(2)	V5-O53-P7	125.8(3)
O39-V5-O51	92.4(2)	P5-O12-P8	144.7(3)	O35-V7-O56	156.1(3)	V8-O53-P7	128.8(4)
O39-V5-O53	92.8(2)	V1-O13-P6	155.8(3)	O37-V7-O54	164.5(3)	V6-O54-V7	101.8(3)
O39-V5-O55	154.6(3)	V2-O14-P5	156.4(3)	O37-V7-O56	93.9(2)	V6-O54-P8	126.0(4)
O51-V5-O53	163.3(2)	V1-O15-P8	157.4(4)	O54-V7-O56	78.3(2)	V7-O54-P8	128.0(4)
O51-V5-O55	90.5(2)	V2-O16-P7	154.9(4)	O7-V8-O8	175.9(2)	V5-O55-V8	100.9(3)
O53-V5-O55	78.2(2)	V1-O17-V3	102.3(3)	O7-V8-O36	80.1(2)	V5-O55-P5	122.7(4)
O5-V6-O6	176.7(2)	V1-O17-P1	130.6(4)	O7-V8-O38	86.9(2)	V8-O55-P5	132.5(4)
O5-V6-O50	79.7(2)	V3-O17-P1	126.7(4)	O7-V8-O53	81.6(2)	V6-O56-V7	101.2(2)
O5-V6-O52	86.5(3)	V2-O18-V4	102.4(2)	O7-V8-O55	78.2(2)	V6-O56-P6	122.7(3)
O5-V6-O54	82.0(2)	V2-O18-P2	130.1(3)	O8-V8-O36	101.1(3)	V7-O56-P6	132.9(4)
O5-V6-O56	77.7(2)	V4-O18-P2	127.3(3)	O8-V8-O38	97.0(3)		
O6-V6-O50	101.9(3)	V1-O19-V3	102.6(2)	O8-V8-O53	94.4(3)		
O6-V6-O52	96.3(3)	V1-O19-P3	129.2(4)	O8-V8-O55	100.1(3)		
O6-V6-O54	94.9(3)	V3-O19-P3	128.1(3)	O9-P4-O50	105.5(3)		
O6-V6-O56	100.4(3)	V2-O30-V4	102.1(3)	O30-P4-O36	110.2(4)		
O50-V6-O52	92.9(2)	O4-V3-O19	79.9(2)	O30-P4-O50	110.4(3)		
O50-V6-O54	93.1(2)	O4-V3-O31	79.7(2)	O36-P4-O50	115.3(3)		
O50-V6-O56	156.8(3)	O4-V3-O33	88.4(2)	O12-P5-O14	109.9(3)		
O52-V6-O54	165.9(3)	O17-V3-O19	77.3(2)	O12-P5-O31	105.4(3)		
O36-V8-O38	90.8(2)	O17-V3-O31	95.7(2)	O12-P5-O55	104.1(3)		
O36-V8-O53	92.3(2)	O17-V3-O33	164.8(3)	O14-P5-O31	115.1(3)		
O36-V8-O55	157.3(3)			O14-P5-O55	110.6(3)		

DISCUSSION

The vanadium atoms in $(VO_2)P_2O_7$ show a typical vanadyl arrangement (Table 4): four nearly coplanar V-O bonds of about 2 Å, one short V-O bond of about 1.6 Å opposite a long V-O bond of about 2.3 Å. Likewise, the P_2O_7 groups show normal bond lengths and angles (Tables 4 and 5). The P-O-P angles lie within the normal range of 130° to 160°. The structure we find (Fig. 1) for $(VO)_2P_2O_7$ is basically the same as that found in previous studies (2-4). There are no differences in the way in which the vanadyl and pyrophosphate groups are connected.

We conclude that much of the problem with earlier single crystal studies (2-4) of $(VO_2)P_2O_7$ was due to the use of an incorrect space group. The deviation from orthorhombic symmetry is small but significant. Another difference between our study and the previous studies is the quality of our crystals. None of the streaking effects reported in the previous studies (2-4) were evident in the diffraction pattern of our green crystals. It is likely that the better quality of our crystals can be attributed to our control oxygen fugacity during crystal growth. Ebner and Thompson (4) also reported both green and red-brown crystals, and they also indicated that the red-brown crystals were of poorer quality. They did not, however, show that the red-brown crystals have an average vanadium oxidation state higher than four.

Bond valence calculations (8) based on our structure for $(VO)_2P_2O_7$ show a range of 4.02 to 4.18 for the eight vanadium atoms and a range of 4.76 to 4.97 for the eight phosphorous atoms. These are well within the range expected for V^{4+} and P^{5+}, and this indicates that all vanadium atoms and all phosphorous atoms are essentially equivalent chemically. The bond valences calculated (9) based on the best previously available structural data give a range of 3.69 to 4.44 for vanadium. These values are smaller and larger, respectively, than expected for V^{4+}, and this confirms the fact that our structure is considerably more accurate.

The $(VO)_2P_2O_7$ structure presented here should not be regarded as the structure of the real vanadyl pyrophosphate catalyst. The real catalyst gives an X-ray diffraction pattern similar to that generated from parameters determined in this study. However, there are peak shifts and broadening effects due to extended defects (10). These defects can account for the observation that the real catalysts always have an average vanadium oxidation state significantly higher than four (e.g., ~4.1). These same defects can also account for the streaking effects observed by Ebner and Thompson (4) in single crystal X-ray studies and by Bordes and Courtine (11) in electron diffraction studies. One of the most significant conclusions of our work is that it is in fact possible to obtain $(VO)_2P_2O_7$ crystals which are relatively free of both extended and point defects.

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