Preparation and Characterization of Vanadyl Hydrogen Phosphate Hydrates; $VO(HPO_4)\cdot 1.5H_2O$ and $VO(HPO_4)\cdot 0.5H_2O$

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A new phase of vanadyl(IV) hydrogen phosphate sesquihydrate, $VO(HPO_4)\cdot 1.5H_2O$, has been obtained by the reduction of $VOPO_4\cdot 2H_2O$ with 1-butanol. The unit cell is the orthorhombic system with lattice constants a=7.43 Å, b=9.62 Å, and c=7.97 Å. in space group P_{mmn}.

Vanadyl pyrophosphate $(VO)_2P_2O_7$ is an active and selective catalyst for butane oxidation to maleic anhydride.The catalyst $(VO)_2P_2O_7$ is formed from its precursor, $VO(HPO_4)\cdot 0.5H_2O$, by heating at 400°C and the precursor might be formed by elimination of water from $VO(HPO_4)\cdot 4H_2O$.[1] A study of the precursor is important because it apparently controls the micro structure of the final catalyst. Described here is the structure determination of $VOHPO_4$ hydrates obtained by the reduction of $VOPO_4\cdot 2H_2O$ with 1-, 2- and iso-butanols.

$VOPO_4\cdot 2H_2O$ [2] was refluxed with stirring in butanol at 80°C for 24 hr.The resulting light-blue solid was dried for 24 hr. We refer to the products from 1- , 2- and iso-butanols as P_1 , P_2 and P_i , respectively. X-ray power diffraction patterns of the three products are shown in Figure 1. It shows that the products P_2 and P_i are the same as $VO(HPO_4)\cdot 0.5H_2O$ reported by Johnson et al..[3] The XRD pattern of the product P_1 from 1-butanol as a reducing agent, however, is neither that of $VO(HPO_4)\cdot 0.5H_2O$ nor of $VO(HPO_4)\cdot 4H_2O$. It is considered that the product P_1 formed another type of $VOHPO_4$ hydrate which has not been reported hitherto.

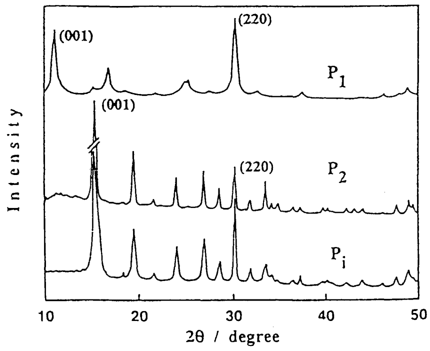

Figure 1. X-ray powder diffraction patterns of $VOHPO_4$ hydrates.

IR spectra of the products P_1,P_2 and P_i are shown in Figure 2. IR spectra of P_2 and P_i which were to be $VO(HPO_4)\cdot 0.5H_2O$ are consistent with $VO(HPO_4)\cdot$ $0.5H_2O$ spectra.[3] Bands at 3376 and 1643 cm^{-1} are assigned to coordinated water in the hydrogen compound and the prominent absorption at 900~1200 cm^{-1} range are assigned to the P-O stretching vibrations. As for the product P_1, only spectra around 3400 cm^{-1} are different from those of $VO(HPO_4)\cdot 0.5H_2O$. The envelope of O-H stretching absorptions, centered at about 3400 cm^{-1}, is composed of at least three bands at 3560, 3373 and 3040 cm^{-1}.

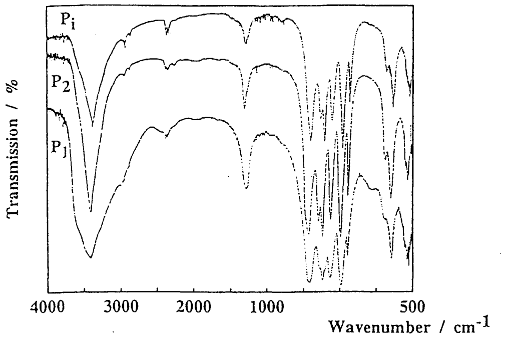

Figure 2. Infrared spectra of $VOHPO_4$ hydrates.

The weight loss of the three products P_1, P_2 and P_i in inert atmosphere at a heating rate of 5°C/min is displayed in Figure 3. On the P_2 and P_i, $VO(HPO_4)\cdot 0.5H_2O$,the water is lost continuously from 300 to 450°C. The weight loss corresponds approximately to the theoretical percentage of 10.46%. The weight loss curve of P_1 is interpreted in terms of two processes: loss of lattice water below about 200°C and loss of coordination water over 200°C. At the temperature from 450 to about 500°C, water is eliminated and $(VO)_2P_2O_7$ is produced. The total weight loss of water was about 18.9%. The chemical composition of the product P_1 can be written as $VPH_4O_{6.5}$.

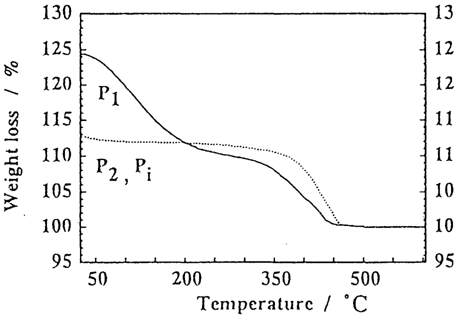

Figure 3. Thermogravimetric curves of $VOHPO_4$ hydrates.

Johnson et al.[3] reported that the crystal structure of $VO(HPO_4)\cdot 0.5H_2O$ is orthorhombic system and lattice constants a = 7.420Å, b = 9.609Å and c = 5.693Å in space group P_{mmn}-D2h. Figure 4 shows the structure of $VO(HPO_4)\cdot 0.5H_2O$ viewed in the (001) and (010) planes. $VO(HPO_4)\cdot 0.5H_2O$ consists of pairs of VO_6 octahedrons and PO_4 tetrahedrons,and it shows a layer structure parallel to the (001) plane. The vanadium coordination sphere contains one multiply bound terminal oxygen (V=O) trans to a coordinated water molecule. The coordinated water molecule bridges two vanadyl groups. The four oxygen atoms in the equatorial positions of VO_6 octahedron belong to HPO_4^{2-} groups. Each (001) layer is linked through hydrogen bonds between water molecule coordinated at vanadyl group and the neighboring P-OH group.

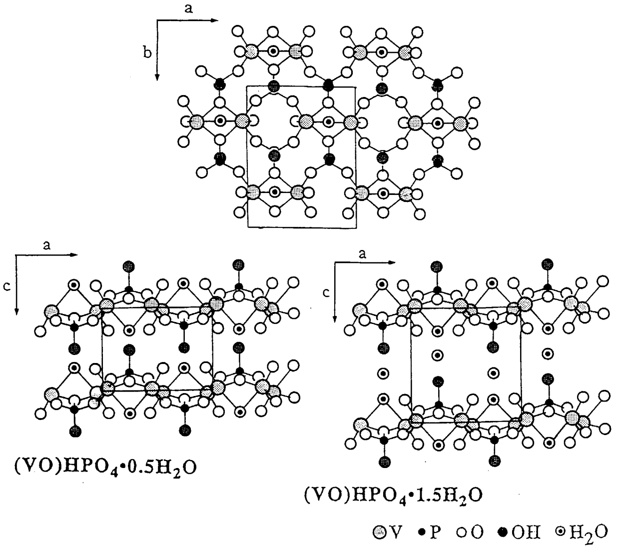

Figure 4. Crystal structures of $VO(HPO_4)•0.5H_2O$ and proposal $VO(HPO_4)•1.5H_2O$.

As the XRD patterns in Figure 1 shows clearly, the product P_1 has a different pattern from that of $VO(HPO_4)•0.5H_2O$. However, IR spectra in Figure 2 do not give different bands between P_1 and $VO(HPO_4)•0.5H_2O$ except bands around 3400 cm^{-1} which are from O-H stretching vibration. The prominent P-O stretching vibration at 900~1200 cm^{-1} are the same. The result indicates that the (001) plane of P_1 might be topologically similar to that of $VO(HPO_4)•0.5H_2O$. The (220) line ($2θ=30.1°$) in the XRD pattern of $VO(HPO_4)•0.5H_2O$ is also observed in the P_1 as shown in Figure 1. Considering that the product P_1 has the same (001) plane as that of $VO(HPO_4)•0.5H_2O$, using the lattice constants a = 7.43Å and b = 9.62Å of $VO(HPO_4)•0.5H_2O$ for the lattice constants a and b of P_1, regarding a strong line $2θ=11.8°$ (d=7.97Å) as the lattice constant c of P_1, the d value of each lattice plane of P_1 was calculated and listed in Table 1. The calculated d values were consistent with the observed values of the product P_1. From the TGA results in Figure 3 it was found out that the experimental formula of P_1 is $VPH_4O_{6.5}$, and that the heating up to 500 °C eliminates two water molecules. Therefore, it can be written that the chemical formula of P_1 is $VO(HPO_4)•1.5H_2O$. The unit cell is orthorhombic with lattice constants a = 7.43Å, b = 9.62Å and c=7.97Å.

Vanadyl hydrogen phosphate sesquihydrate, $VOHPO_4•1.5H_2O$, is produced in the reduction of $VOPO_4•2H_2O$ with 1-butanol. The structural analogies between the (001) planes of $VO(HPO_4)•0.5H_2O$ and $VO(HPO_4)•1.5H_2O$ are established. The main differences is that one water molecule as lattice water resides in the layer space parallel to the (001) plane of $VO(HPO_4)•1.5H_2O$. Figure 4 shows the proposal $VO(HPO_4)•1.5H_2O$ structure viewed in the (010) plane. $VOHPO_4$ hydrates obtained by the reduction of $VOPO_4•2H_2O$ with 1-,2- and iso-butanols were activated in a mixture of 2% butane in air (SV=2400 $ml•g^{-1}•h^{-1}$) at 480°C. After this treatment, the catalytic activity of butane oxidation was measured. The result is shown in Table 2. The activity of $(VO)_2P_2O_7$ is higher with the catalyst prepared from the precursor $VO(HPO_4)•1.5H_2O$ than that from the precursor $VO(HPO_4)•0.5H_2O$.

Table 1. X-ray powder diffraction data for proposal $VO(HPO_4)•1.5H_2O$ compared $VO(HPO_4)•0.5H_2O$

	$VO(HPO_4)•0.5H_2O$			$VO(HPO_4)•1.5H_2O$		
hkl	d_{calcd}	d_{obsd}	I_{obsd}	d_{calcd}	d_{obsd}	I_{obsd}
110	5.88			5.88		
001	5.70	5.75	100.0	7.97	7.97	85.1
020	4.81	4.85	2.7	4.81	4.81	1.0
101	4.52	4.55	33.3	5.43	5.28	51.7
111	4.09	4.11	6.5	4.73		
021	3.68	3.69	19.5	4.12		
121	3.30	3.31	24.0	3.60	3.59	14.9
201	3.11	3.12	12.6	3.37	3.39	1.0
220	2.94	2.95	31.1	2.94	2.94	100.0
031	2.79	2.81	8.7	2.98		
102	2.66	2.67	15.3	3.51	3.55	13.9
131	2.62	2.62	6.0	2.76	2.75	11.5
112	2.56	2.57	3.8	3.30	3.27	9.5
022	2.45	2.46	3.8	3.07		
040	2.41	2.41	4.4	2.41	2.40	16.1
202	2.26	2.27	2.2	2.72		
231	2.23	2.24	3.3	2.32		
311	2.21	2.21	1.6	2.30		
032	2.13	2.14	2.7	2.50		
321	2.05	2.05	3.3	2.12		
330	1.96	1.96	1.6	1.96	1.96	7.0
241	1.90	1.91	6.0	1.96		
150	1.862	1.86	7.7	1.86	1.87	16.1
331	1.85	1.84	6.0	1.90	1.90	8.0

Table 2. Catalytic activity for butane oxidation to maleic anhydride at 400 °C

Catalyst	S.A. ($m^2 g^{-1}$)	C_4H_{10} Conv. (%)	MA Select. (%)	MA Yield (%)
from P_1	22.6	56.0	87.3	48.9
P_2	9.8	31.4	94.0	29.5
P_1	12.7	29.4	93.7	27.6

The thermal dehydration of $VOHPO_4$ hydrates into $(VO)_2P_2O_7$ proceeds in two ways. One is dehydration by cleaving hydrogen bonds between (001) planes, and the other is by condensation of HPO_4^{2-} groups. Therefore, $VO(HPO_4)•1.5H_2O$ with weak hydrogen bonds in the layer space of the (001) plane is more subject to the cleavage of the layer space of the (001) plane, compared with $VO(HPO_4)•0.5H_2O$ having strong hydrogen bonds which are necessary to retain the layered structure. Accordingly, $VO(HPO_4)•1.5H_2O$ gives $(VO)_2P_2O_7$ with higher specific surface area after the thermal dehydration. Also its apparent catalytic activity is increased.

References

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