Structures and Properties of Nanoporous Metal Phosphate/Phosphate (3)

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The synthesis of open-framework nanoporous materials has been extensively studied. It is a highly challenging task to design an inorganic structure with a desired pore size, since metal-oxygen building units can exist in various geometric polyhedra and display an assorted connectivity. To search for more exotic structures, we have taken the lead in using hydrothermal method in the synthesis of crystalline and nanomaterials. A new compound of **B74** (Fig. 1) inorganic-organic hybrid vanadium(III) phosphite nanoporous materials with remarkable structures have been synthesized from hydrothermal method. A kind of the crystal structures was determined by single-crystal X-ray diffraction. Three of the V sites in the crystal data we would like to confirm whether oxidation state is +3, +4 or +5. So we hope using X-ray Absorption Spectroscopy (XAS) to identify oxidation states of V. The X-ray absorption diffracton data were collected using synchrotron radiation at NSRRC 16A1 beam line.

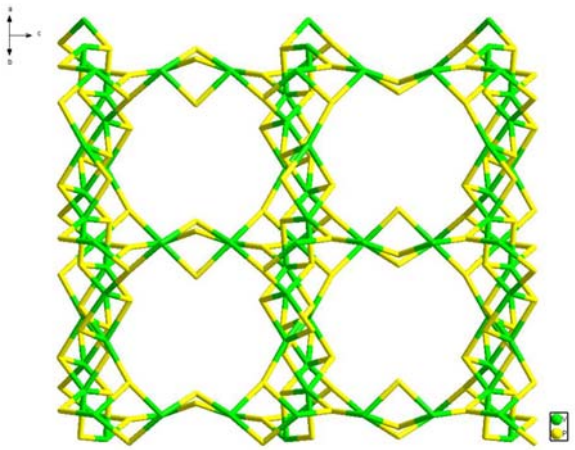

Fig. 1: A new vanadium(III) phosphite constructs the 3D open framework along [110] without templates possessed extra-large 16-ring channels. The hybrid structure has an internal diameter (the measured distance between the closest oxygen atoms across the apeture) of over 1 nm. (V, green; P, yellow, respectively.)

An X-ray absorption spectrum is generally divided into 4 sections. We aim at the most part of E_O (Binding energy) values and X-ray absorption near edge structure (XANES) to analyze data. Because we want to research the relation between oxidation states and $E_{O,}$ we prepared three kinds of powder (V metal, $VOSO_4$ and V_2O_5) that show different oxidation states 0, +4 and +5, respectively, as our standards. **(**Fig. 2).

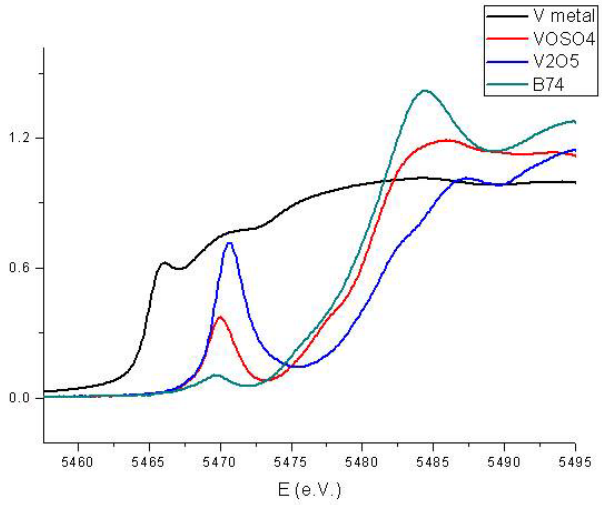

Fig. 2: The V metal, B74, $VOSO_4$ and V_2O_5 of X-ray absorption near edge spectroscopy (XANES). From spectroscopy, we can observe the different oxidation states 0, +3, +4 and +5 of **V** that have different E_O values.

In order to establish data base of our laboratory, we use some compounds as samples including inorganic-organic hybrid metal phosphate/phosphite to measure and analyze them. According to the data base, Table 1, we can methodically generalize a conclusion. It is that $\mathbf{E_O}$ of V(III) is near to 5478 eV, V(IV) is near to 5479 eV, and V(V) is near to 5481eV. The result reveals that other compounds with V(III) metal center all show a E_0 value near to 5478 eV. This is a good agreement with B74.

	E_0 (eV)		E_0 (eV)
V metal	5465.2	NTHU-6-V	5478.4
$VOSO_4$	5479.2	VZn-1	5478.3
V_2O_5	5480.8	VZn-13	5478.3
B74	5478.5	B93	5478.5

Table 1: It shows that different oxidation states of vanadium affect the E_0 value in about 1 eV difference.