Properties and Characterization of Nanoporous Materials(1)

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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 nano-meter-sized pores or channel openings, 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 ionothermal method in the synthesis of crystalline and nanoporous materials. A new series of **G1~5** inorganic-organic hybrid oxalatogallophosphite nanoporous materials with remarkable structures, has been synthesized using ionothermal method. They exhibit the same kind of the crystal structure which was primarily determined by single-crystal X-ray diffraction methods. But there exists a problem in that one of the crystallographic sites in the structure of G1-G4 could not be determined with correct P oxidation state, which may be +1 (hypophosphite) or +3 (phosphite). Therefore, we hope to make the use of X-ray Absorption Spectroscopy (XAS) to solve the problem. In this study, we need a few reference samples, NTHU5 (Figure 1) with P assured in the oxidation of +3 is one of them, for identifying the oxidation states of P in **G1~G4**. The X-ray absorption diffracton data were collected using synchrotron radiation at NSRRC 16A1 beam line.

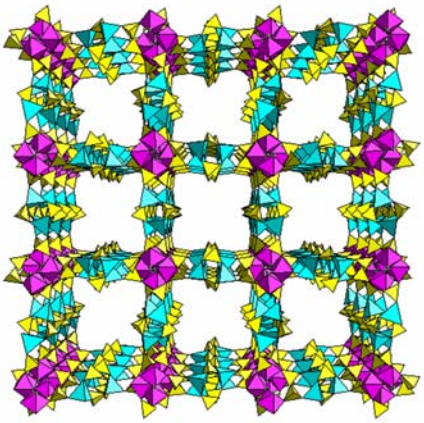

Figure 1. The metal phosphite framework of **$(C_4H_9NH_3)_2[AlFZn_2(HPO_3)_4]$** (NTHU-5). Perspective view along the *c*-axis, showing 26-ring channels encircled by helical chains (organic cations are omitted in the plot). NTHU-5 has been considered to be the first 26-ring channel structure ever reported. It is also for the first time that a microporous structure with participation of aluminum in a pore size over 20-ring is prepared. All Al^{3+} centers are difluorinated with two μ_2-F ligands forming one octahedral edge (ref. *J. AM. CHEM. SOC.* **2007**, 129, 5350).

An X-ray absorption spectrum is generally divided into 4 sections: 1) pre-edge ($E < E_0$); 2) x-ray absorption near edge structure (XANES), where the energy of the incident X-ray beam is $E = E_0 \pm 10$ eV; 3) near edge X-ray absorption fine structure (NEXAFS), in the region between 10 eV up to 50 eV above the edge; and 4) extended X-ray absorption fine structure (EXAFS), which starts approximately from 50 eV and continues up to 1000 eV above the edge. (E_O = Binding energy). We aim at the most part of E_O values and X-ray absorption near edge structure (XANES) to analyze data. We prepare three aqua solubions of H_3PO_4 、H_3PO_3 and H_3PO_2 for different oxidation states +5 、+3 and +1 respectively as our standards, **(**Figure 2).

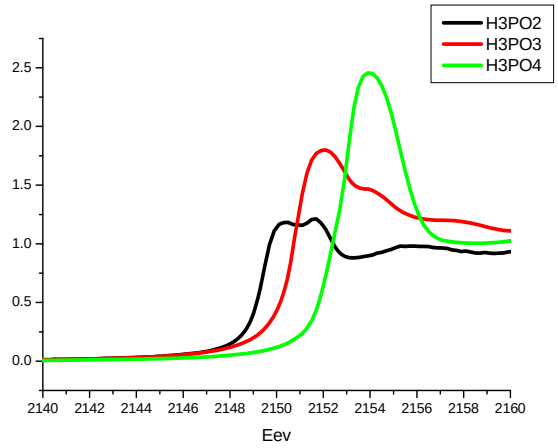

Figure 2. The H_3PO4 、H_3PO_3 and H_3PO_2 of x-ray absorption near edge spectroscopy(XANES). From spectroscopy, we can find the different oxidation states +5 、+3 and +1 of **P** have differently E_O values and waveform.

In order to establish the correct data for our systems, we choose several known compounds as references including inorganic-organic hybrid metal phosphate/phosphite to measure and analyze. According to the data shown in Table 1, we observed that the value of $\mathbf{E_O}$ for metal phosphate is near to 2153 ev and for metal phosphite 2151 ev. These results would help us to determine the oxidation states of P sites in unknowns samples. Based on these data, we can clearly draw the conclusion that all **P** sites in **G1~G4** are coming from phosphite.

	E_0		E_0
H_3PO_2	2149.5ev	H_3PO_4	2153.1ev
H_3PO_3	2150.9ev	NTHU6 in presence	2153.1ev
G2(tmdp)	2151.2ev	$(C_3H_{12}N_2)[Ga_4F_2(H_2O)(PO_4)_4]$	2153ev
G4(tmdpp)	2151.1ev	$(C_3H_{12}N_2)[Ga_4F_2(C_2O_4)(PO_4)_4]$	2152.9ev
G4-1(Cs)	2151.1ev	$(C_2H_{10}N_2)[Ga_4F_2(C_2O_4)(PO_4)_4]$	2152.8ev
G1	2151.3ev	NTHU5-Ga J. AM. CHEM. SOC. 2007, 129, 5350	2151ev
G3	2151.1ev	NTHU5-Cr	2151ev
G5	2151.1ev	$(H_2en)[Ga_3F_2(HPO_3)_4(H_2PO_3)(H_2O)]$	2151.1ev
059H	2150.9ev	$(H_2C_3N_2H_3)[Ga_4(H_2O)_3(HPO_3)_7]$	2150.9ev

Table 1. was express metal phosphate in red words; metal phosphate in black words.