

Structures and Properties of Nanoporous Metal Phosphate/Phosphate (2)

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In the last decade, the synthesis of nanoporous materials with extended network topologies has advanced extensively owing to the increasing demand for functional materials. Until now, two major categories of nanoporous structures have been under intense investigation: one with whole inorganic framework, and another with organic – inorganic hybrid frameworks. Aryl carboxylates, such as benzene-1,2,4,5-tetracarboxylate (btec), which are effective organic building units of MOFs, had not been found to adapt to MPOs. Herein we report the first btec-mediated metal phosphate compound, $(\text{Hbpy})[\text{Zn}_2\text{PO}_4(\text{btec})(\text{Hbpy})_2]$ (bpy=4,4'-bipyridine), designated **NTHU-8**. This compound exhibits an unusual network topology (Fig. 1), and has porosity and hydrogen gas adsorption that is superior to previously reported OMPOs.

A kind of the crystal structures was determined by single-crystal X-ray diffraction and thermogravimetric analysis (TGA) observed their thermal stabilities. In order to confirm the relations between structure forms and temperature. We hope using in-situ powder X-ray diffraction to detect how the structure is changed with the temperature immediately. The in-situ powder X-ray diffraction patterns were collected using synchrotron radiation at NSRRC 01C2 beam line.

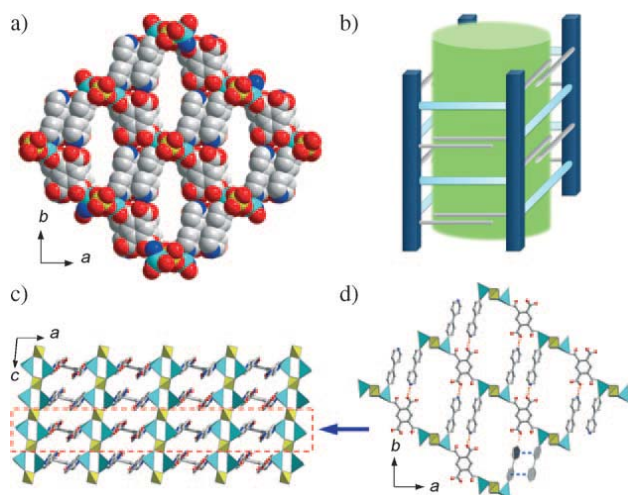


Fig. 1: The structure of **NTHU-8** Hydrogen atoms are omitted for clarity. a) Space-filling model showing oval-shaped channel windows (Zn cyan, P yellow, O red, N blue, C gray); b) representative drawing showing the one-dimensional inorganic columns ($[\text{Zn}_2\text{PO}_4]$ in navy blue) with two organic ligands (btec in cyan and Hbpy in gray); c) view perpendicular to the channel direction; d) section of a two-dimensional hydrogen-bonded sheet (region marked in red in (c)), showing face-to-face π - π pairs formed by Hbpy ligands (blue dashes).

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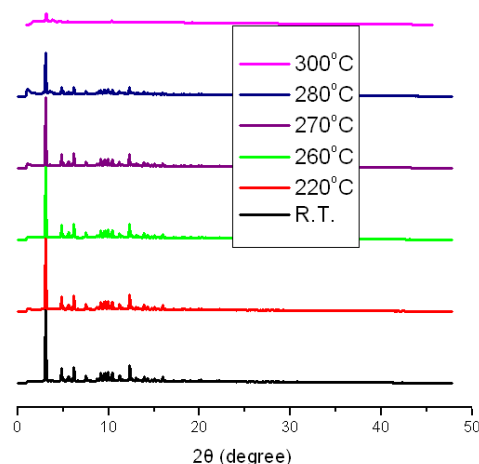


Fig. 2: The in-situ PXRD patterns

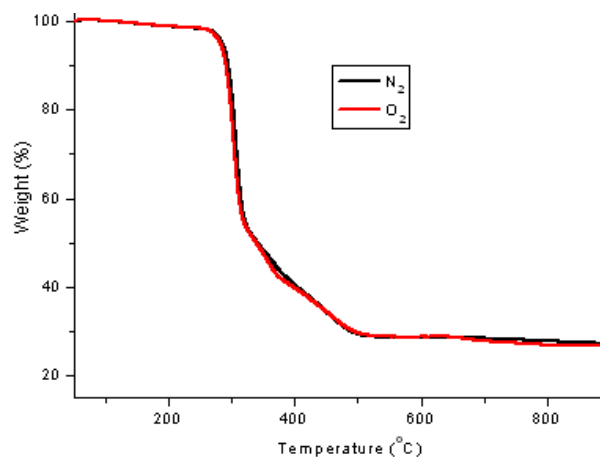


Fig. 3: The TGA data of **NTHU-8**

We did in-situ PXRD experiment to adopt the method of gradual heating and keep isothermal at room temperature, 220°C, 260°C, 270°C, 280°C and 300°C for three minutes (Fig. 2). In this period, we collected data simultaneously. Due to heating method of in-situ PXRD experiment as well as thermogravimetric analysis, we can combine two kinds of different data to understand whether the framework remains or not. From TGA data (Fig. 3), we can observe thermal stabilities of **NTHU-8** sustaining up to 270°C and measure in-situ PXRD as the auxiliary method to confirm our observation. We can find that thermal treatment of **NTHU-8** up to 300°C has destroyed structure, because peaks of PXRD pattern in 300°C has already become relatively weak. With in-situ PXRD patterns and TGA data verifying each other, they noticeably explain thermal stabilities of the structures. However some detail on the experiment needs to be noticed, for example the correction of temperature the factor is very important in research of properties and characterization of nanoporous materials.