resulting in high selectivity for guest inclusion or multi-step adsorption behaviors.[2-4] Dynamic effects can arise either locally from flexible ligands and/or flexibility of the coordination geometry of the metal ions, or from the global cooperative movement of the framework on a periodic scale. The mechanism of the dynamics of flexible PCPs was investigated by a coincident adsorption/X-ray powder diffraction measurement system.

In addition, we will report a new photo-responsive PCP composed of azide modules as dormant precursors. The pore surface of PCP can be activated by UV irradiation and the resulting reactive species were regularly arranged in the framework, which was observed not only by spectroscopic measurements but also crystallographic analysis using synchrotron X-ray diffraction data. The highly reactive species can react or interact with gust molecules. According to the result of adsorption measurement under photoirradiation, we found that the adsorption activity for oxygen was significantly improved by photoirradiation.[5]

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Keywords: coordination, microporous, adsorption

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Negative thermal expansion in porous framework materials

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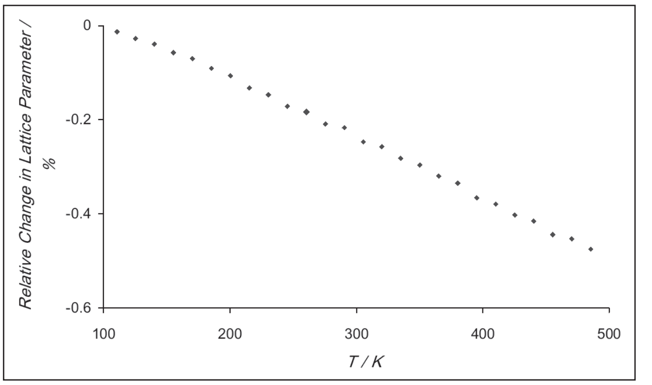
The recent interest in metal-organic frameworks (MOFs) has stemmed from their wide range of potential applications, from gas storage devices to drug delivery systems [1]. Here we focus on a selection of MOFs that display the unusual property of negative thermal expansion (NTE; i.e., contraction upon warming). NTE materials have potential applications in composite materials that show zero thermal expansion over wide temperature ranges, thus being suitable for high precision instruments that are affected by thermal expansion. Through establishing mechanisms for NTE and investigating how systematic structure changes affect the size of the NTE, materials may be tailored to meet specific needs.

In this study members of the IRMOF series of compounds were investigated. These materials share a common tetranuclear metal cluster, Zn_4O(carboxylate)$_6$, bridged by varying dicarboxylate ligands. Synchrotron powder X-ray diffraction (S-PXRD) reveals the materials show linear thermal expansion from 500 – 100K, with all except one investigated here exhibiting NTE. Through comparison of the coefficients of thermal expansion (CTEs) the impact on the NTE of the variations in structure has been observed. The use of single crystal X-ray diffraction (SCXRD) to compare bond lengths at varying temperatures has also provided valuable insight into the mechanisms responsible for NTE in these multi-hinged structures.



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Tuning of the structural flexibility and chemical properties of the MIL53-Al and MIL47-V

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The Porous Coordination Polymers (PCPs) or Metal-Organic Frameworks (MOFs) are a unique class of hybrid solid-state materials with bright future due to their permanent porosity and high thermal stability. The use of these materials ranges from gas storage, separation and catalysis, to a number of diverse potential applications, including optoelectronics, sensors, smart membranes etc. To incorporate the new functions into the 1-D channel PCPs we performed detailed study of the broad series of inclusion compounds into $[Al(OH)(bdc)]_n$ (MIL53-Al) and $[V(O)(bdc)]_n$ (MIL47-V) [1], [2], [3]. $[Al(OH)(bdc)]_n$ shows a well-pronounced breathing effect on the contrary to $[V(O)(bdc)]_n$ which demonstrates neither breathing effect but has well documented catalytical and electrochemical activities. Nevertheless, both phases have the same framework topology, which makes possible to prepare mixed Al/V frameworks in a broad concentration range.

Here, we present our results obtained in the course of preparation and investigation of the mixed metal $[\{Al(OH)\}_x/\{V(O)\}_{1-x}(bdc)]_n$ and $[\{Al(OH)\}_x/\{V(O)\}_{1-x}(ndc)]_n$ ($0<x<1$, bdc = benzeneterephthalate, ndc = naphtaleneterephthalate) phases which show new structural and chemical features. Crystal structures, flexibility and inclusion phenomenon were investigated in details using PXRD, spectroscopic and electrochemical techniques. Structural characteristics (cell parameters and volume) show linear dependence on the composition in the whole range. On the other hand, structural flexibility and stability show behavior characteristic for $[V(O)(bdc)]_n$. Inclusion compounds Cobaltocene@$[\{Al(OH)\}_x/\{V(O)\}_{1-x}(bdc)]_n$ and benzene@$[\{Al(OH)\}_x/\{V(O)\}_{1-x}(bdc)]_n$ were synthesized to characterize chemical properties and flexibility of the mixed-metal phases. Crystal structures of the inclusion compounds were also solved using PXRD technique. Guests molecules are localized in the middle of the 1-D channel and their positions show flexibility of the framework induced by the framework reduction and charge transfer between cobaltocene and vanadium centers of the backbone. The phases obtained proposed as electrochemically, magnetic and catalytically active porous materials with CO_2 vs. N_2 selectivity.

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