Metal-Organic Frameworks: Their Microwave Synthesis and Applications as Adsorbents for Preconcentration

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University of Illinois at Urbana-Champaign, 2007
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Metal-Organic Frameworks (MOFs) have been a focus of intense activity in recent years because of their many unique features, such as extremely high porosities and tailorable molecule cavities. In this thesis work, I have explored different aspects of MOF concerning their syntheses and applications.

In the first part of this work, a detailed investigation has been carried out to explore the potential of using MOFs as adsorbent for trapping and preconcentration on a portable micro gas detector. Previously people have tried nanotubes, Tenax and different active carbons as adsorbents for this purpose, but neither their adsorption capacities and selectivities could meet the requirements for the micro device. In this study, IRMOF1, a well-known MOF materials, was tested as an adsorbent for preconcentration for the first time using dimethly methylphosphonate (DMMP) as a test case. DMMP is a stimulant of nerve agent. We find that DMMP is selectively adsorbed on IRMOF1 and is easily released upon heating to 250 °C. Concentration gains of more than 5000 were observed for DMMP with a 4-s sampling time. Sorption capacities are 0.95 g of DMMP/g of IRMOF1. By comparison, dodecane shows a preconcentration gain of ~5 under similar

conditions. These results demonstrate that MOFs can be quite useful in selective preconcentrators.

In the second part, we have developed a new method for rapid synthesis of MOFs, which we named “microwave-assisted solvothermal synthesis”(MASS). So far most of the reported MOF syntheses were either solvothermal or hydrothermal syntheses, which take from half a day to few weeks. Other effective syntheses such as evaporation and diffusion methods may take even longer time. Here we show that MASS method allows many well known MOF crystals to be synthesized in under a minute. The properties of the crystals made by MASS method are of the same quality as those produced by the standard solvothermal method, but the synthesis is much more rapid and resulting MOF products are no longer dependent on the initial nucleus and wall conditions. The homogeneous effects of microwave could create a uniform seeding condition, therefore the size and shape of the crystals can be well controlled by simply change a few reaction conditions.

MASS method provides us a simple and fast approach to quickly build a library of other new MOFs. In the third part, we demonstrate the syntheses of 14 new MOF materials based on the MASS method. Each has been tested by TGA to explore its sorption behavior with 4 different vapors. The crystals of some new MOFs can also been grown under a similar condition using solvothermal method. The structures for 3 of our new MOFs are given based on the single X-ray analysis, and their sorption features are explained based on the structure information.