Design and Synthesis of Nanopore-Modulated Heterogeneous Catalysts

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DESIGN AND SYNTHESIS OF NANOPORE-MODULATED HETEROGENEOUS CATALYSTS

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by

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Advisor: Chia-Kuang (Frank) Tsung

Abstract

In order to enhance the selectivity of metal nanoparticle heterogeneous catalysts, a method for the encapsulation of metal nanoparticles by crystalline nanoporous materials was designed and implemented through a wet-chemical, capping-agent-mediated encapsulation strategy. Two thermally and chemically stable metal organic frameworks (MOFs) with different aperture sizes were chosen as the crystalline nanoporous layers for metal nanoparticle (NP) encapsulation. Successful encapsulation and good catalytic performance depended on understanding and engineering the interface between the metal catalyst core and the nanoporous shell. After the synthesis of the NPs-MOF composite, their catalytic activity and selectivity were studied. Two kinds of capping agents (polymer and surfactant) were used to demonstrate different mechanisms for NP encapsulation. The polymer (polyvinylpyrrolidone, PVP) induced interaction between the NP surface and MOF precursors while the surfactant (cetyltrimethylammonium bromide, CTAB) controlled the alignment between the metal nanoparticles and MOFs. Furthermore, the capping-agent-directed overgrowth could be a general method of not only loading various inorganic nanoparticles into MOF single crystals but also bridging two porous materials with totally different structures.

MOF shells were further functionalized by postsynthetic linker exchange. By applying the process, a new concept was introduced for the formation of enlarged pore apertures by linker dissociation during MOF linker exchange, as demonstrated by the postsynthetic encapsulation of species much larger than the pore aperture of the MOF structure. Kinetic studies of linker exchange rely on the competition between associative and dissociative linker exchange mechanisms. It was found that guest encapsulation was enhanced under conditions that favored the dissociative pathway. Through kinetics studies, linker exchange rate was also found to vary in different solvents. The different exchange rates were then used to create hierarchical porosity in MOF structure, and a double-solvent-mediated overgrowth strategy was designed to form hollow and mesoporous MOF. The results help to provide new ideas for nanopores related heterogeneous catalysis. The discussion of active metal NP cores with a nanoporous shell, as a frontier core-shell material, may benefit further study in developing highly selective catalysts.

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Chapter 1: Introduction

Catalysts change the pathways of a chemical reaction, lowering the activation energy and accelerating the reaction rate. Among them, the heterogeneous catalysts are at the center of many industrial processes such as oil refining, chemical manufacturing, pollution treatment, and energy conversion¹. The importance of studying heterogeneous catalysis as a fundamental topic of research has quickly gained momentum in recent years as scientists investigated its significant impact on the surface electronic structure and catalytic properties of nanomaterials.

A new approach to enhance the performance of a catalyst is to fabricate the nanoparticle catalysts into a core-shell architecture. This type of core-shell nanostructure consists of inner core nanoparticles encapsulated by porous materials. Various types of metal-porous material core-shell nanostructures have been synthesized with shell materials. My research focus on metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), which are emerging as a class of very promising crystalline microporous materials. MOF have received great interest due to the use of a set of well-established principles of coordination chemistry. Other important types of porous materials, such as zeolite and mesoporous silica, however, this is beyond the scope of the thesis and they will not be discussed here.

1.1 Metal–organic Frameworks as Shell for Nanoparticle Encapsulation

The global impact of heterogeneous catalysis is estimated to be \$10 trillion per year². At the center of heterogeneous catalysis, the majority of industrial catalysts contain

active components, typically a metal, often in the nano-realm; usually smaller than 20nm dispersed on high surface area supports. The high performance of nano-structure catalysts has attracted wide efforts to develop methods for their synthesis and characterization, making this area of study an integral part of nanoscience³. Such catalysts were traditionally prepared by impregnation of cheaper high-surface-area support, commonly a porous metal oxide, with a metal salt followed by oxidation–reduction treatments⁴. Unfortunately, this approach leads to the formation of nanoparticles with wide size dispersity and shapes displaying a distribution of surface sites capable of promoting several different catalytic reactions. No molecular control on the nature of the active sites of the catalysts therefore only limited control on the selectivity of reactions can be achieved.

In recent years, metal nanoparticles (MNPs), which provide a large number of active catalytic centers, have been broadly explored in the search of selective and enhanced catalytic performances. Due to high surface energies and large surface areas, these MNPs are thermodynamically unstable, and therefore, protecting capping agents are often used to stabilize them during synthesis⁵. While the use of capping agents to decrease the surface energy and prevent particle from aggregation and deactivation, it is still a challenge to maintain pure active sites on metal surfaces. As we look to the future, heterogeneous catalysis increasingly holds the key to "green chemistry" which is promise of curbing pollution from chemical and refining processes⁶. The way to the goal is through tailoring the structure of active and selective reaction sites of MNPs catalysts.

The specific catalysts can convert reactants directly to products without generating byproducts that typically end up as harmful emissions⁷ or as wastes⁸.

The concepts of process efficiency in traditional chemical industry focus largely on chemical yield in 20th century. Nowadays the interest shift to the trend toward "green chemistry." The modern concept of process efficiency is widely accepted to require alternative and environmentally friendly catalytic processes. The alternative catalysis focus on that assigns economic value to eliminating waste at the source and avoids the use of toxic and/or hazardous substances⁹. A primary cause of waste generation is the use of stoichiometric inorganic reagents in the fine chemical manufacturing industry; for example, metals (Na, Mg, Fe, Zn) and metal hydrides (LiAlH₄, NaBH₄) are used for stoichiometric reductions, and permanganate or chromium (VI) reagents are used for oxidations. The development processes of catalytic hydrogenation and oxidation based on H₂, O₂, H₂O₂, CO and CO₂ as the green sources are good examples of highly efficient and greener processes. In addition, milder reaction conditions, e.g. low reaction temperature and pressure, of these green processes is also advantageous⁹. Fortunately, the rapid growth and improved understanding of nanoscience and nanotechnology has facilitated the precise control of NPs synthesis with variable sizes, shapes, and chemical compositions. The ability to control nano-architecture affects the activity (higher activity afford lower reaction temperature and pressure) and selectivity (higher selectivity afford higher atom efficiency) in the nanocatalyst. Combining nanotechnology with green chemistry will be a key contributor to an environmentally sustainable future.

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Figure 1.1 Core-shell architecture of nanoparticle catalyst. Metal nanoparticle core and crystalline nanoporous shell are used to demonstrate the core-shell architecture. The porous shell materials ensure reactant accessibility to the active metal surface and may increase the durability of the catalysts. The crystalline shell materials with homogeneous pore structure could potentially provide selectivity for reactants and products.

Core-shell architecture of nanoparticle catalyst could be a new approach to enhance catalytic performance as well as preventing the aggregation of the active centers (Figure 1.1). This type of core-shell nanostructure consists of inner core nanoparticles encapsulated by porous materials. The porous shell materials ensure reactant accessibility to the active metal surface and can increase the durability of the catalysts. Several possible catalytic enhancements could be tuned by the shell including introducing size selectivity toward different molecules, controlling the diffusion rate of the molecules, manipulating the orientation and configuration of the surface molecules, or enriching the reactants on the catalyst surfaces¹⁰. Among porous materials, crystalline nanoporous materials are good candidates for these approaches. Metal-organic frameworks (MOFs), in particular, have been proved to be able to regulate molecular diffusion, sorption, orientation and conformation¹¹. MOFs synthesized through metal secondary building units (SBU) and organic linking species, have become new and promising crystalline porous materials¹²⁻¹⁶ (Figure 1.2). The organic linkers are ditopic or polytopic organic ligands that can bind to metal-containing SBUs to generate crystalline framework structures with open porosity. The compositions and topologies of MOFs can be vastly varied with over 20,000 different MOFs being reported in the past decades¹⁷. Based on the geometries of the organic linkers and coordination modes of the inorganic metal ions or clusters of metal ions, MOF structures can be designed according to targeted properties¹⁸⁻²⁰. A key structural feature of MOFs is the ultrahigh porosity (up to 90% free volume) and incredibly high internal surface areas, extending beyond a Langmuir surface area of 10 000 m² g⁻¹,¹⁷ which play a crucial role in functional applications. These features endow MOFs with a wide range of functions such as, gas storage²¹, chemical separation²¹⁻²², drug delivery²³⁻²⁴, and heterogeneous catalysis^{11,25}.

Generally, porous MOFs show microporous characters (<2 nm) whereas the pore sizes could be tuned from several angstroms to several nanometers. MOF Pore size control is typically achieved by controlling the length of organic linkers. In addition, versatile framework functionalities beyond their accessible porosity can arise from the metal components (e.g. magnetism, and catalysis), organic linkers (e.g. luminescence, nonlinear optics, and chirality) or a combination of both^{21,26-30}. The tailorable chemistry of the pores and cavities has made MOFs suitable for the encapsulation of various functional species. The uniform and tunable nature of the pore sizes of MOFs provide an ideal platform for catalytic applications of functionalized guests within MOF

composites³¹⁻³². Compared with other porous materials, MOFs as a shell material offer unique advantages for catalysis³³: (i) crystalline nanopores provide a confinement effect and shape selectivity; (ii) proper organic linkers can offer interaction with nanoparticles or substrates; (iii) the great diversity and abundance of MOF structures enhances the selection of an appropriate MOF as the host matrix; (iv) milder synthetic conditions.



Figure 1.2 General components and structure of MOFs. The infinite crystalline lattices of MOFs generally involve two main components of inorganic centers (metal ions or clusters) and organic linkers. Various MOF structures could be formed including one dimensional (Chain coordination), two dimensional (Layered coordination), and three dimensional structure (3D framework)¹².

1.2 Synthetic strategies of Core-Shell NPs-MOF Composites

Two approaches to form core-shell NPs-MOF Composites have been reported: post-synthetic impregnation³⁴⁻³⁷ and encapsulation method³⁸⁻⁴³ (Figure 1.3). The traditional and widely used approach for NPs-MOF Core-shell composites is postsynthetic impregnation. This method involves MOFs serving as a template to provide confined spaces for the reduction of metal salts to form NPs from the diffusion of metal precursors into the pores, ultimately encapsulating NPs. Nevertheless, the effective control over the dispersity, size and composition of metal NPs within MOFs, as well as the morphology and size of the crystalline MOFs can still present a challenge. Moreover, the formation of metal NPs on the exterior of the MOF, along with damages⁴⁴ to the MOF nanostructures during the metal ion diffusion and NP formation process can lead to a loss in the intrinsic selectivity of MOF-based catalysts by causing the formation of defects.



Figure 1.3 Two synthetic techniques of NPs-MOF composites. The "post-synthetic impregnation" approach involves the introduction of metal precursors into the presynthesized MOF matrix and the subsequent reduction or decomposition of the precursors to yield metal particles deposited in the cavities. The second approach is the "NP encapsulation method" which involves the assembly of MOF precursors around presynthesized metal nanoparticles.

Following standards developed for the synthesis of metal-zeolite composites⁴⁵, gas-phase infiltration, solid-state grinding, and liquid-phase impregnation methods were adopted by researchers to deposit metal nanocrystals into the cavities of MOFs. Fischer and co-workers used chemical vapor deposition (CVD) to introduce gas-phase organometallics as the metal precursors⁴⁶⁻⁴⁸. In a typical synthesis, the chosen MOF is exposed to the vapor of gas-phase organometallic precursors under static vacuum. The volatile precursors diffuse into the pores of the MOFs, and then either hydrogen is introduced to reduce the organometallics or high temperature is applied to thermally decompose the precursors to form metal nanoparticles in the nanopores. Although some of the particles are of sizes larger than the pore size, most of the particle sizes are regulated by the pore confinement. Based on the same concept, Haruta group and Xu group developed a solid grinding approach to load metal particles into MOFs^{34,49}. Volatile organometallic dimethyl Au(III) acetylacetonate has been used as a metal precursor to deposit Au clusters into different MOFs including MIL-53 (Matérial Institut Lavoisier, is comprised of aluminum nitrate and 1,4-benzenedicarboxylates), MOF-5 (sometimes called IRMOF-1, is a MOF formed from Zn₄O nodes with 1,4benzodicarboxylic acid struts between the nodes), and HKUST-1 (Hong Kong University of Science and Technology, formed from copper and 1,3,5-benzenetricarboxylic acid). Surprisingly, this facile and effective method yielded nanoparticles with smaller sizes $(\sim 2.2 \text{ nm})$ than the CVD method, and these nanoparticles exhibited high catalytic activities in oxidation reactions^{34,49}.

Although the CVD and solid grinding methods have achieved great success, the precursors are limited to volatile species, and some volatile organometallic precursors are often sensitive to air and water. This can be tackled by utilizing the liquid-phase impregnation method first used by Xu and coworkers^{35-37,50}. In a typical synthesis, a porous support is immersed in the solution containing the transition metal precursors, usually in the form of chloride or nitrate salts. The metal ions infiltrate into the pores by capillary force and are subsequently reduced to yield the deposited metal nanocrystals by a reducing agent, typically hydrogen or sodium borohydride. A general drawback of this approach is metal particle formation on the external surface of the MOF crystals. To avoid this problem, Xu's group developed a double solvent method, in which a small amount of aqueous precursor solution is absorbed into the more hydrophilic pores of the employed MOFs, while an excess of organic solvent was introduced to limit the amount of precursors absorbed on the external surface of the MOF crystals, thus minimizing the outside deposition of metal (Figure 1.4)³⁶. Pt@MIL-101 was synthesized by this method and used as catalyst for hydrogen generation from ammonia borane³⁶. The morphology and composition control of the nanocrystals is another relatively challenging task in these post-synthetic impregnation approaches. Alloy metal nanoparticles can sometimes be obtained by the co-reduction of two different metal precursors, but morphology is not controlled³⁷. One of the very few preliminary methods to control these critical parameters was also developed by Xu and co-workers. The formation of shaped bimetallic metal nanocrystals embedded in MIL-101 was achieved by using two organometallic precursors and CO-directed reduction⁵¹. The preferential binding of CO on 111 facets led to the formation of Pt and Pd polyhedral. The nanocrystals showed metal segregation, with a Pd-rich core and a Pt-rich shell.



Figure 1.4 Schematic representation of impregnation of Pt nanoparticles into MIL-101 matrix by the double solvent method. The method used in this work for avoiding MNPs aggregation on external surfaces of MIL-101 framework. It is based on a hydrophilic solvent (water) and a hydrophobic solvent (hexane), the former containing the metal precursor with a volume set equal to or less than the pore volume of the adsorbent (MIL-101), which can be absorbed within the hydrophilic adsorbent pores³⁶.

Regardless of the general lack of shape and composition control, the postsynthetic impregnation strategy is an efficient way to generate ultra-small metal nanocrystals in MOFs. Some of the metal nanoparticles might be bigger than the pores but are generally restrained from growing very big due to confinement by the frameworks. This approach is facile and scalable. Nevertheless, for certain catalytic applications, composition and shape control is more important than ultra-small nanocrystal sizes. In these reactions, the MOF plays a more important role in interacting with the reactants, products, and intermediates. Therefore, different approaches need to be developed for these applications. Furthermore, the locations of metal particles within the MOF crystal are often random and unpredictable in the post-synthetic impregnation method. The loading amount of metal is also limited, because too much metal will cause the degradation of the MOF matrix.

Currently, a new method was developed to completely confine the NPs within the MOF crystal, without forming NP aggregates on the MOF exterior. The encapsulation method applies pre-formed colloidal nanoparticles which are then encapsulated³⁸⁻⁴³; the synthesis of monodispersed metal NPs prior to their incorporation into the MOF synthesis conditions. The pre-formed NPs are then introduced into the MOF precursor solution to form a MOF coating. Complete encapsulation of NPs therefore becomes possible. The encapsulation method could be a good platform for developing new heterogeneous catalyst toward novel selectivity and functionality by tuning the molecular environment "on" the active metal surface.

Compared with the post-synthetic impregnations which deposit metal precursors into MOF crystals, the encapsulation methods assemble MOFs around preformed metal nanocrystals has significant advantages. The nanoparticles are not inside the cavities, and thus the particle size will not be restricted and it will not cause damage to the MOF matrix during the formation of the nanocomposite. During the nucleation and growth of MOF crystals, the metal nanoparticles are incorporated into the MOF matrix. The size, shape, chemical composition, and active properties of the metal nanoparticles are preserved after the encapsulation. This approach provides more control in catalytic and optical applications because of the better control of shape and composition of the embedded nanoparticles. Also, control over the spatial distribution of the encapsulated nanoparticles such as the configuration of one nanoparticle in one MOF shell can be only achieved in the encapsulation approach.

The strategy is straightforward, however, in this approach, the controllable overgrowth of MOFs on nanoparticles rather than self-nucleation is challenging, due to the large interfacial energy barrier between the two materials. Many synthetic parameters need to be considered and optimized, including the interactions between the MOF and nanoparticle surfaces, the capping agents on the surface of metal nanoparticles, the interface between the MOF and nanoparticle surface, and the compatibility of the nanoparticles and the MOF synthesis conditions. Within the synthetic parameters, providing a proper interaction between the MOF and nanoparticle surface is the critical parameter of this approach because MOFs tend to self-nucleate and form individual particles rather than overgrow on the metal particles. An additional challenge is that the structure control of MOF shell is not optimized. NPs may be surrounded by a polycrystalline MOF shell during encapsulation. The polycrystalline MOF shell may have defects or cracks which can cause loss of selectivity for heterogeneous catalysis.

1.3 Capping Agent Mediated Nanoparticle Encapsulation

NPs-MOF composites formed by encapsulation require certain interactions to compensate for interfacial energy differences between MOF precursors and the metal

surface of NPs. Organic capping agents like surfactants and polymers on the surface of NPs were found to be the bridge for the necessary interaction. The organic capping agents act as a protective barrier maintaining the separation of the NPs and initiating and attracting MOF growth on their surface. In 2011, Professor Akamatsu's group first developed the encapsulation method by loading Au nanoparticles prepared by 11mercaptoundecanoic acid (MUA) into MOF $[Cu_3(btc)_2]_n^{39}$ (formed from copper ions and 1,3,5-benzenetricarboxylic acid). They found the encapsulation mechanism starts from the copper ions binding on MUA. The high concentration of copper ions then triggers the self-assembly of MOF framework around NPs. In 2011, PVP coated NPs were used as an encapsulation agent in the formation of ZIF-8 (Zeolitic Imidazolate Framework, a MOF made by zinc ions coordinated by four imidazolate rings) crystals containing metal NPs⁴². PVP and MUA may provide certain interactions between NPs and the surfaces of the growing MOF crystal. Due to the successful encapsulation of NPs-MOF composites, interfacial control might be feasible by using the correct capping agents. The understanding and engineering of the interface between the metal catalyst core and the nanoporous material shell will be critical to the catalytic performance⁵². The structure of the interface may change the sorption behaviors of reactant molecules to the catalyst surface which significantly affects the yield and selectivity of the desired products.



Figure 1.5 Illustration of a MOF anchor onto a self-assembled monolayers (SAM). The major interaction is the coordination of the exposed functional groups of the SAM to the metal centers of the MOF⁵³.

An understanding of interfacial surface chemistry in MOF synthesis is the first step toward interfacial control. For the coordinative attachment of MOFs, the same or similar binding groups as within the respective materials should be on the surface. Several methods exist for the functionalization of surfaces, such as the hydroxylation of metal oxide surfaces. A more flexible and efficient method is the use of self-assembled monolayers (SAM), which are ordered molecular assemblies spontaneously formed by the chemisorption of suitably functionalized molecules onto the surface of substrates⁵⁴⁻⁵⁵. If the respective molecules carry coordinating groups at the other end, the respective monolayers can act as seed layers for MOF growth (Figure 1.5)⁵³. Huo and co-workers studied the oriented growth of ZIF-8 on a patterned SAM on Au (111) surface⁵⁶. The Au (111) substrate was covered by a SAM of 1-octadecanethiol (ODT), and the rest of the 14

area was passivated by 16-mercaptohexadecanoic acid (MHA). It was found that ZIF-8 preferentially grew on the low-energy ODT-patterned area rather than the high-energy MHA region. The crystal orientation was affected by the odd-even effect for SAMs. The oriented growth of ZIF-8 only occurred on the alkane thiol-functionalized Au surface with C_{12} , C_{16} , and C_{18} carbon chain lengths. The oriented growth of the ZIF-8 crystals was found to result from the fast crystallization of the nuclei triggered by the specific SAM surfaces. The studies of liquid-solid interface, MOF nucleation, and MOF growth provide knowledge of the formation mechanism at molecular level. The knowledge can be used to guide the future development of MOF composite materials.

Recently, our group reported a new proof-of-concept colloidal synthetic method for core-shell composites with controlled alignment between metal NPs and MOFs⁴³ (Figure 1.6). The surfactant cetyltrimethylammonium bromide (CTAB) was chosen to control the interface and facilitate the overgrowth of ZIF-8 on well-defined Pd and Au nanocrystals. The lattice constants of the precious metal core and the ZIF-8 shell differ by almost an order of magnitude. The metal nanocrystals were individually encased in single crystalline ZIF-8 to generate the core-shell structure in a one-to-one fashion. An alignment between the (100) planes of the metal and the (110) planes of ZIF-8 was observed, demonstrating the first example of lattice alignment between a metal nanoparticle core and a MOF shell. This surfactant-directed overgrowth could be a general method to fabricate various inorganic nanoparticles in MOF core-shell structures with controlled alignments.



Figure 1.6 SEM, scheme and TEM images of controlled alignment between Pd NPs and ZIF-8. SEM image of Pd nanocubes individually incased in single crystalline ZIF-8 particles. The scheme shows the alignment between the Pd core {100} and ZIF-8 shell {110}. TEM image of Pd-ZIF-8 shows the accordance with the illustration⁴³.

1.4 Functionalization of NPs-MOF Composites



Figure 1.7 General scheme for the postsynthetic modification (PSM) of MOFs. PSM is the chemical modification of a framework after it has been synthesized⁵⁷.

NPs-MOF Composites could be further functionalized by modifying MOF shell after MOF formation. Postsynthetic modification (PSM) (Figure 1.7) and linker/node exchange (Figure 1.8) have become powerful tools to engineer MOFs⁵⁷⁻⁵⁸. PSM is

defined as the chemical modification of a framework after it has been synthesized while linker/node exchange is a framework transformation in which the linkers or nodes of a parent framework are exchanged with a desired linker or metal node. Such postsynthetic processes could be used to form a basis to extend the applications of NPs-MOF core-shell composites. The extended applications rely on tailored chemical functionality and structure in the pores.



Figure 1.8 General scheme for the linker and node exchange of MOF. Linker/node exchange is a framework transformation in which the linkers or nodes of a parent framework are exchanged with a desired linker or metal node⁵⁸.

PSM strategies for MOFs were developed from mesoporous silica, which have long been functionalized after synthesis⁵⁹. The process exploits the abundant silanol groups present on the mesoporous silica surface. MOFs offer even more versatility for postsynthetic transformations due to their functionalizable organic linkers and more diverse coordination chemistry⁶⁰. The most common chemical handle for covalent PSM of MOFs is amines, particularly 2-aminoterephthalate for MOF-5 and UiO-66 (University of Oslo, formed from Zirconium and 1,4-benzodicarboxylic acid). For example, Rosseinsky and coworkers executed the first dual covalent and coordinate covalent modification using IRMOF-3 by converting the free amine groups into Schiff base ligands with salicylaldehyde. The resulting chelator was metallated with VO(acac)₃ and the material was examined as a heterogeneous oxidation catalyst (Figure 1.9)⁶¹. Coordinative PSM uses the unoccupied sites found in many MOFs such as HKUST-1 and MIL-101 (Matérial Institut Lavoisier, is comprised of trimeric chromium (III) and 1,4-benzenedicarboxylates) to datively bind functional molecules. Postsynthetic linker exchange has been demonstrated in a variety of MOFs and can be a route to frameworks that cannot be synthesized *de novo*⁶².



porous framework functionalisation and catalyst binding

Figure 1.9 A specific example of PSM on IRMOF-3 by converting the free amine groups into Schiff base ligands with salicylaldehyde and sequentially metallated with VO(acac)₃. The material was examined as a heterogeneous oxidation catalyst⁶¹.

While PSM is often effective for circumventing problems associated with direct MOF preparation^{57,60}, replacement of linkers is another viable strategy. It has variously been termed "stepwise synthesis⁶³", "bridging linker replacement⁶³", "post-synthetic exchange⁶⁴", isomorphous ligand replacement⁶⁵, and stepwise ligand exchange⁶³.

Solvent-assisted linker exchange (SALE)⁵⁸ as it highlights the importance of the solvent during linker exchange. Conceptually SALE occurs at the solid-solution interface; a parent MOF is placed in a solution containing a second linker and a daughter MOF retaining the parent MOF topology is obtained. The pore environment can also be readily controlled and modified via SALE. Karagiaridi et al. demonstrated that pore functionality could be readily controlled in zeolitic imidazolate frameworks (ZIFs)⁶⁶. The 2-ethylimidazole (eim) linkers in Cd(eim)2 (CdIF-4), a ZIF possessing RHO topology and Cd²⁺ nodes, could be exchanged for nitroimidazole (nim) and 2-methylimidazole (mim) linkers to form Cd(nim)2 (CdIF-9), and Cd(mim)2 (SALEM-1) respectively. The SALE reactions that occur between CdIF-4, CdIF-9 and SALEM-1 are summarized in Figure 1.10. The importance of the study demonstrates that some of the most robust MOF structures known are indeed amenable to SALE.



Figure 1.10 A specific example of pore environment modification through SALE in ZIFs. The study demonstrates that SALE could modify functionality of MOF pore even on some of the most robust MOF structures.

PSM and SALE have the potential to enhance the performance of metal-MOF structures for catalysis by adding functionality that could (1) dock substrates by molecular recognition⁶⁷, (2) act as acid/base catalytic sites, or (3) bind transition metals for tandem catalysis with the metal core. Since many functional groups of interest for these purposes bind transition metals, they may be considered a nuisance during metal nanocrystal encapsulation, during which they could interfere with proper placement in the MOF crystals and/or be metalated and hence not available for further chemistry. Linker exchange allows MOF synthesis and linker functionalization to be decoupled and therefore is an attractive route for adding functionality to the linkers of NPs-MOF composites.

In addition, solvent effects observed in coordination chemistry suggest that the solvents could have a strong directing effect on the pathways of formation or decomposition of MOFs. Varying the solvent could alter the formation energy of MOFs, stabilize intermediates and transition states, and even provide new pathways from its direct participation in elementary reactions. The solvent has been observed to affect many properties of MOFs, such as their stability, crystal sizes and shapes, as well as the rates of crystal growth and post-synthetic ligand and ion exchange.^{64,68-71} The solvent effect could

also be utilized as a part of the synthetic toolbox for adding more functionalities to NPs-MOF composites.

My research goal is to demonstrate the concept of new NPs-MOF catalysts by (1) studying the selectivity and activity of NPs-MOF core-shell architecture (2) study the formation mechanism of NPs-MOF composite (3) further improve and create more useful core-shell architecture by applying the formation mechanism we learned. This study could potentially benefit the design of heterogeneous catalyst in the future by providing more precise control over the NPs, nanoporous materials, and interface between them.

Chapter 2: Core-shell NPs-MOF composites

The proof of concept of my research is to study selectivity and activity of NPs-MOF core-shell architecture. In order to fulfill it, my strategy is to choose two thermally and chemically stable MOFs which have different aperture sizes. Then I should figure out the method for NP Encapsulation. Finally, I can test selectivity and activity over the new NPs-MOF catalysts I synthesized.

2.1 The criteria of MOFs for catalysis

Core-shell NPs-MOF composites formed by encapsulation could potentially have benefits for catalytic performance especially for size selectivity due to the inherent selective sieving of the MOF cages. Three areas of control are available to increase selectivity performed on the surface of NPs (Figure 2.1). First, the pore and aperture size could be controlled by changing the linkers imparting stricter molecular size constraints. Second, the chemical properties of the MOF pore could be controlled by functionalizing the linkers. Third, the properties of the metal surface could be controlled by changing the shape and composition of the metal core. Here, we choose the first type of control to demonstrate the concept of reactant selectivity provided by the MOF for catalytic purposes. The idea is to test the size selectivity of reactants by controlling the pore size and structure of MOF shell allowing only those of the correct size to pass through. The option of the correct MOF with the appropriate pore size and stability will be necessary.



= Pore size and structure control = Chemical property control = Metal surface control

Figure 2.1 Illustration of interface of core-shell NP-MOF composites. Three types of controls for catalytic selectivity could be performed on the surface of NPs. Green dashed triangle illustrates the control of pore size and structure of MOF shell. Red dashed circle illustrates the control of chemical property of MOF shell. Blue dashed line illustrates the control on metal surface.

Zeolitic imidazolate frameworks (ZIFs) and Zr-based MOFs (UiOs, University of Oslo) are two chemically stable subclasses of MOF materials. ZIF-8, a subclass of ZIFs, is one of the few commercially available MOFs due to its great potential in gas separation⁷²⁻⁷³ and gas storage⁷⁴⁻⁷⁵. The high thermal and chemical stability of ZIFs comes from their zeolite-like structures. Imidazolate bonds of ZIFs formed by metal

centers (Zn(II) or Co(II)) and linkers (imidazole derivatives). The bond angle of metallinker-metal is close to 145°, which is similar to that of the Si-O-Si angle in many common zeolites⁷⁶. On the other hand, highly oxophilic metals, such as group four elements with high oxidation state have been presented as a route to form stable MOFs. Zirconium, one of good examples of common transition metal atoms on earth, is highly resistant to corrosion and has a high affinity for hard oxygen donor ligands⁷⁷. UiO-66, a Zr(IV)-based MOF, is therefore one of the most stable MOF thus far⁷⁸.

Monodisperse ZIF-8 and UiO-66 crystals with sub-micron sizes have both been reported. ZIF-8 consists of extended three-dimensional structures, characterized by their sodalite zeolite-like structure, constructed from tetrahedral zinc ions bridged by imidazolate linkers. The pore structure of ZIF-8 features large cavities (11.6 Å) and small apertures (3.4 Å)⁷⁶. UiO-66 is constructed by $Zr_6O_4(OH)_4$ secondary building unit (SBU) and 1,4-benzenedicarboxylate (BDC) as the organic linkers⁷⁸. The structure of UiO-66 shows that it is composed of octahedral and tetrahedral cages in a 1:2 ratio. The cavities of octahedral cage is 11Å and tetrahedral cage is 8 Å found from structural modeling⁷⁸. 5 Å triangular windows connecting the cages was determined by N₂ adsorption⁷⁹. A variety of ZIF and UiO family materials with different pore structures and linker functional groups have been found. The variety of pore sizes and high stability of ZIFs and UiOs family make them ideal for our purpose.

2.2 Material and Methods

Chemicals and Materials:

Zirconium(IV) chloride (ZrCl₄, Aldrich, 99.5%), terephthalic acid (Aldrich, 98%), 2aminoterephthalic acid (Aldrich, 99%), acetic acid (Sigma-Aldrich, 99.7%), zinc nitrate hexahydrate (Zn(NO₃)₂•6H₂O, Sigma-Aldrich, 99%), 2-methylimidazole (Sigma-Aldrich, 99%), polyvinylpyrrolidone (PVP, Mw~40,000, Sigma-Aldrich), N,N-Dimethylformamide (Sigma-Aldrich, 99.8%), ammonium tetrachloroplatinate (II) ((NH₄)₂PtCl₄, Sigma-Aldrich, 99%), cyclohexene (Sigma-Aldrich, 99%), ciscyclooctene (Sigma-Aldrich, 95%), tetramethylammonium bromide (N⁺(CH₃)₄Br⁻, Sigma-Aldrich, 99%), ethylene glycol (Sigma-Aldrich, >99%) were purchased from the indicated sources and used without further purification. Hydrogen (Airgas, 99.999%), ethylene (Airgas, 99.995%) and helium (Airgas, 99.999%) were used for heterogeneous gas phase catalysis.

Characterization:

Transmission electron microscope (TEM) images were obtained on JEOL JEM2010F operated at 200 kV.

Synthesis of PVP Capped 5 nm Pt Nanocrystals:

The synthesis was carried out following the previous report with modifications⁸⁰. A total of 0.025 mmol of Pt ions $(NH_4)_2PtCl_4$, 0.75 mmol of tetramethylammonium bromide, and 0.5 mmol of polyvinylpyrrolidone (in terms of the repeating unit; Mw 40000) were dissolved into 5 mL of ethylene glycol in a 25 mL round-bottom flask at room

temperature. The mixed solution was stirring and heated to 200°C in an oil bath for 20 minutes.

Synthesis of ZIF-8:

5 mL 30 mM 2-methylimidazole and 5 mL 30 mM $Zn(NO_3)_2 \cdot 6H_2O$ and kept undisturbed at room temperature for 24 hours. The isolated samples were washed three times in methanol and dried in a vacuum oven at 100 °C overnight.

Synthesis of PVP coated 5nm Pt NPs-ZIF-8 composite:

100 L of 1 mg/mL of the methanol solution of PVP capped Pt particles was mixed with 5 mL 30 mM 2-methylimidazole and 5 mL 30 mM $Zn(NO_3)_2 \cdot 6H_2O$ and kept undisturbed at room temperature for 24 hours. The isolated samples were washed three times in methanol and dried in a vacuum oven at 100 °C overnight.

Synthesis of UiO-66:

In a typical synthesis reaction for UiO-66, 18.6 mg (0.08 mmol) ZrCl₄ and 13.3 mg (0.08 mmol) terephthalic acid were dissolved in 8.622 mL DMF, then 1.378 mL acetic acid was added into the solution to make the final volume to 10 mL. The solution was transferred into a 20mL scintillation vial and heated for 24 hours in a 120 °C oil bath. After cooling down, the formed UiO-66 was collected by centrifugation. The isolated samples were washed three times in methanol and dried in a vacuum oven at 100 °C overnight.

Synthesis of PVP coated 5nm Pt NPs-UiO-66 composite:

Following a similar procedure as the synthesis of UiO-66, another 1 mL of 0.25 mg/mL of the DMF solution of PVP capped Pt particles was added the UiO-66 synthetic solution to make the final volume to 10 mL. The solution was transferred into a 20mL scintillation vial and heated for 24 hours in a 120 °C oil bath. The isolated samples were washed three times in methanol and dried in a vacuum oven at 100 °C overnight.

Catalysts Preparation:

All nanostructures were homogeneously diluted with mesoporous silica (MCF-17) by mixing them together as a solution in ethanol, with stirring and then drying the mixture in the vacuum oven overnight for heterogeneous catalysis. To prepare the samples of Pt nanocrystals deposited directly on the surface of MOFs (ZIF-8 and UiO-66), the desired amount of solution containing Pt nanocrystals was mixed with MOFs in methanol with stirring. After the mixture gradually settled down, the precipitate was collected by centrifugation. The mixture was dried in the vacuum oven overnight.

Catalytic study:

0.5 wt% Pt NPs/MOF samples were diluted with low surface area quartz and loaded into glass reactors for size selective alkene hydrogenations. Temperature was controlled by a furnace (Carbolite) and PID controller (Diqi-Sense) with a type-K thermocouple. Gas flows, including helium, hydrogen gas and ethylene were regulated using calibrated mass flow controllers. The desired partial pressure of cyclohexene and *cis*-cyclooctene were achieved by bubbling helium through the liquid and assuming saturation⁸¹. For all
reactions, gas composition was analyzed with a mass spectroscope (MKS special V2000P). The turnover frequency of ethylene hydrogenation is normalized by using the percentage of surface atoms following the palladium cluster diameter⁸².

2.3 PVP Mediated Nanoparticle Encapsulation

The encapsulation strategy was applied for core-shell NPs-MOF composite formation (Figure 2.2a, b). The encapsulation strategy allows for the nanoparticles to be incorporated fully within MOF crystals. This strategy involves using pre-formed colloidal nanoparticles (5nm Pt particles) encapsulated within MOF crystals (ZIF-6 or UiO-66). The method for Pt-ZIF-8 encapsulation is modified from previous works⁴². Pt NPs with uniform sizes were synthesized with polyvinylpyrrolidone (PVP) as a capping agent. PVP is an amphiphilic, non-ionic polymer used extensively, as a capping agent to stabilize various nanoparticles in polar solvents⁸³⁻⁸⁴ (such as water, methanol, ethylene glycol and N,N-dimethylformamide) and to assist in controlling the size and shape of certain nanoparticles during their syntheses⁸⁴⁻⁸⁵.



Figure 2.2 TEM images (a-b) and pore structures (c-d) of different kinds of NPs-MOF composites. (a) and (c), Pt-ZIF-8 composites show that 5nm Pt NPs fully encapsulation in ZIF-8 single crystal with 3.4 Å shell aperture sizes. (b) and (d), Pt-UiO-66 composites show that 5nm Pt NPs also fully encapsulation in UiO-66 single crystal with 5 Å shell aperture sizes.

PVP provides specific interaction between NPs and the surfaces of the growing MOF crystals. Pyrrolidone groups of PVP on NPs could provide weak coordination interactions with metal atoms of MOF nodes. Apolar groups of PVP may also contribute hydrophobic interactions to organic linkers. Thus, NPs can adhere to the growing MOF crystal without altering the crystal structure. By applying a similar strategy, core-shell Pt-UiO-66 composites are successfully synthesized (Figure 2.2b). The successful encapsulation of Pt-UiO-66 composites shows that the encapsulation strategy can not

only extend to various MOF sub-families with very different metal centers and linkers but also distinct synthetic conditions (solvent and temperature). The results were confirmed by similar observations reported currently⁸⁶. TEM images of Pt-ZIF-8 (Figure 2.2a) and Pt-UiO-66 (Figure 2.2b) exhibit intact crystal morphology in both NPs-MOF composites.. In addition, all Pt NPs are completely encapsulated and no Pt NP aggregates are observed inside both MOF crystals. The encapsulation fails if capping agents are not used (Figure 2.3). The result confirms PVP provides specific interaction for NP encapsulation.



Figure 2.3 TEM images of failing encapsulation of Pt NPs into UiO-66 single crystal. UiO-66 crystals grow without assembling around Pt NPs.

2.4 Activity and Selectivity of NPs-MOF Composites

NPs-MOF composites with different aperture sizes could be used to demonstrate the molecular-size-selective property of ZIF-8 (3.4 Å) (Figure 2.2c) UiO-66 (5 Å) (Figure 2.2d) shells. The gas-phase hydrogenation of ethylene, cyclohexene and cyclooctene were carried out to study the molecular-size-selective catalytic behavior of the NPs-MOF composites. The composite catalysts consisting of Pt nanocrystals directly deposited on the ZIF-8 crystal surfaces (Pt on ZIF-8), Pt nanocrystals directly deposited on the UiO-66 crystal surfaces (Pt on UiO-66), Pt nanocrystals coated by a ZIF-8 shell (Pt-ZIF-8) and Pt nanocrystals coated by a UiO-66 shell (Pt-UiO-66) were prepared for comparison. Table 2.1 shows the activities of the reactions. For ethylene hydrogenation, all of the catalysts show high activity. It indicates that ethylene and hydrogen can move freely through the pores of both MOFs and is able to access the surface of NPs. The slightly lower activity for Pt-ZIF-8 shows there might be some diffusional influence caused by the ZIF-8 shells. On the other hand, there is no diffusional influence caused by the UiO-66 shells due to the relatively larger aperture size of UiO-66 than that of ZIF-8. For cyclooctene hydrogenation, both of the core-shell catalysts show no detectable activity. In comparison, the Pt on ZIF-8 and Pt on UiO-66 catalyst show higher activity. This result clearly exhibits the molecular-size-selective property of the ZIF-8 and UiO-66 shells. Ethylene molecules are small (2.5 Å) enough to diffuse through the pore apertures of the ZIF-8 shells (3.4 Å) and UiO-66 shells (5 Å) without serious hindrance; however, the size of the cyclooctene molecules (5.5 Å) is much larger than the size of the pore aperture and cannot diffuse through the ZIF-8 shell. This result clearly suggests that the ZIF-8 and UiO-66 shells are devoid of cracks or fractures. Cyclohexene hydrogenation can be used to further confirm the molecular-size-selective property of the MOF shells. The size of cyclohexene molecules (4.2 Å) is between the pore apertures of the ZIF-8 shells (3.4 Å) and UiO-66 shells (5 Å). For cyclohexene hydrogenation, only Pt-ZIF-8 shows no detectable activity but all of the other catalysts show comparably good activity. This result demonstrates that pore apertures of the UiO-66 shells (5 Å) can allow cyclohexene molecules (4.2 Å) to diffuse through but the pore apertures of the ZIF-8 shells (3.4 Å) cannot. This series of hydrogenation reactions clearly illustrate molecular size selectivity by using various aperture sizes of MOF shells.

Table 2.1 Catalytic behavior of different Pt NPs-MOF nanostructures. Size-selective alkene hydrogenation of core-shell Pt-ZIF-8, Pt on ZIF-8, core-shell Pt-UiO-66, and Pt on UiO-66. All alkene hydrogenations are running at 50 °C.

Hydrogenation Activity (mmol g ⁻¹ s ⁻¹)			
	Ethylene	Cyclohexene	Cyclooctene
Pt-ZIF-8	7.68	_	_
Pt on ZIF-8	11.8	1.01	5.23×10 ⁻³
Pt-UiO-66	11.0	0.74	-
Pt on UiO-66	11.7	1.13	5.01×10 ⁻³

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2.5 Thermal Stability of NPs-MOF Composites

The high thermal stability of ZIF-8 $(470 \text{ °C})^{76}$ and UiO-66 $(540 \text{ °C})^{78}$ has been reported by using thermogravimetric analysis (TGA) and powder X-ray diffraction (PXRD). The thermal stability of the NP-MOF catalysts, however, will be hard to be determined by using TGA or PXRD. The decomposition temperature provided from TGA or PXRD may not necessarily be equal to the deactivation temperature. Deactivation temperature of catalyst can be detected by measuring catalyst deactivation after heat treatment in catalysis condition. Here, we used ethylene hydrogenation activity to show the deactivation temperature of the Pt-ZIF-8 and Pt-UiO-66 core-shell catalysts. Ethylene hydrogenation is structure insensitive reaction so the activity of the reaction could reflect active sites of Pt NPs. It was shown in previous results the ethylene molecules are small enough to diffuse through the pore apertures of both MOF shells. The NPs-MOF catalyst was prepared for ethylene hydrogenation at 40 °C. The ethylene hydrogenation activity was actively measured after heat treatments at different temperature points in pure helium for 30 minutes. The heat treatment temperature is consistently increased until the ethylene hydrogenation activity dramatically decreases. The deactivation temperature of Pt-ZIF-8 is up to 150 °C (Figure 2.4c). TEM images of Pt-ZIF-8 after 150 °C (Figure 2.4a) and after 200 °C (Figure 2.4b) treatments clearly point out the deactivation is from the crash of catalyst morphology. The isolated Pt NPs outside the remains of ZIF-8 shell imply the activity loss is not from NPs sintering (Figure 2.4b). The activity loss may result from the destruct pore structure of ZIF-8 which makes surfaces of NPs inaccessible to guest molecules. Following the same procedure, the deactivation temperature of Pt-UiO-66 is up to 230 °C (Figure 2.4d). These temperatures are lower than the decomposition temperature of the pure MOF crystals as measured by TGA (470 °C and 540 °C) which may be due to the interface of metal NPs in the frameworks destroyed.



Figure 2.4 Thermal stability of Pt-ZIF8 was performed with heat treatment in He for 30 minutes then monitored catalytic activity by ethylene hydrogenation at 40 °C. TEM

images of Pt-ZIF8 composites (a) after 150 °C and (b) after 200 °C heat treatment. The morphology change after 200 °C heat treatment implies the thermal stability of Pt-ZIF8 is up to 200 °C. The deactivation temperatures of (c) Pt-ZIF-8 and (d) Pt-UiO-66 from 40 °C ethylene hydrogenation activities are consistence with the observation of TEM images.

In summary, we have successfully utilized PVP to mediate nanoparticle encapsulation in ZIF-8 and UiO-66. Size selective alkene hydrogenations were carried out in NPs-MOF Composites. The data demonstrated molecular size selectivity by using various aperture sizes of MOF shells. Heat treatment over the NPs-MOF composites showed that deactivation temperatures of NPs-MOF composites are lower than decomposition temperatures of pure MOF shells. The results imply deactivation temperature of NPs-MOF composites is necessary scale for thermal stability of NPs-MOF composites.

Chapter 3 Surfactant oriented lattice alignment

The understanding and engineering of the interface between the metal catalyst core and the nanoporous shell is critical to the catalytic performance⁵². The structure of the interface changes the sorption behaviors of reactant molecules to the catalyst surface which significantly affects the yield and selectivity of the product molecules. However, interfacial control of NPs-MOF core-shell composites is challenging due to the large interfacial energies of crystal lattice mismatches between the different materials. Recently, our group reported a colloidal synthetic method for core-shell composites with controlled alignment between metal nanoparticles and MOFs⁴³. This surfactant-directed overgrowth could be a general method for the fabrication of not only various inorganic nanoparticles within MOF structures with controlled alignments but also the alignment of two porous materials with totally different structures.

3.1 Formation mechanism of controlled alignment

Portions of the following section have been reproduced in part with permission from Pan, H.; Zhuang, J.; Chou, L. -Y.; Lee, H. K.; Ling, X. Y.; Chuang, Y. -C.; Tsung, C. K., "Surfactant-Directed Atomic to Mesoscale Alignment: Metal Nanocrystals Encased Individually in Single-Crystalline Porous Nanostructures," Journal of the American Chemical Society 2014, 136,10561-10564., Copyright 2014 American Chemical Society.

Our lab demonstrates first example of nanocrystals encased individually in MOF with specific lattice alignment between the metal core and porous shell⁴³. The self-assembled CTAB layer and the time of metal NP introducing are critical. The proposed

mechanism is illustrated in Scheme 3.1. 50 nm Pd or Au nanocubes are synthesized first and then delivered to the ZIF-8 synthesis solution ~10 s after the ZIF-8 precursors are mixed. Small ZIF-8 nuclei are first formed and enclosed by low surface energy {110} facets in the solution. Then the ZIF-8 nuclei attach via the bridging CTAB layer to a single metal NP and generate a ZIF-8 {110} to metal {100} interface. The rest of the ZIF-8 shell grows exclusively on this orientated crystal nucleus to capture the metal nanocrystal, instead of through a layer-by-layer conformal overgrowth mechanism. Ostwald ripening process would be involved if more than one ZIF-8 nucleus grows on metal surface of NP. This process finally leads the one-in-one single-crystalline structure. Due to the small energy difference between {110} and {100} of ZIF-8, a small portion of {100} to {100} alignment is also formed. The key step of this mechanism, ZIF-8 nucleus selective attachment to the metal {100} facet, is reasonable in the metal cube case because of the dominant {100} facets of the metal cubes.



Scheme 3.1 Formation of nanocrystals encased individually and aligned in singlecrystalline porous materials. (A) Introduction of well-defined nanocrystals after the nucleation of ZIF-8. (B) Single-crystalline ZIF-8 nucleus attachment to the metal surface with selective orientation. (C) ZIF-8 crystal growth on the nucleus. (D) Single nanocrystal captured in single crystalline ZIF-8 with lattice alignment.

In order to test the mechanism we proposed, 50 nm Au octahedra are used for the same encapsulation procedure. The {100} metal planes still align with the ZIF-8 {110} planes although the octahedra are mainly enclosed by eight {111} surfaces. The octahedral geometry allows for a few, small {100}-terminated surfaces. These {100}-terminated surfaces are exclusively located at the vertices and arise from truncation due to the increase in under-coordinated (higher surface energy) atoms at the apex⁸⁷. The {100} metal facets may still serve as the attachment site for the ZIF-8 nucleus, despite their limited abundance. The highly selective attachment can be explained by the result of extensive studies in SAM system⁵⁶. Huo et al. has shown that the ZIF-8 nucleus on the SAM is sensitive to the metal surface because the orientation of nuclei is determined by the distance between the self-assembled molecules and the distance of the molecules is determined by the surface metal lattices. In our case, CTAB self-assembled layers on the metal {100} facets might have a more ideal structure compared to other facets for the nucleus attachment.

3.2 Controlled lattice alignment of two different MOFs

The following work was done in collaboration with my previous lab members Jia Zhuang. Half of sample preparation and most of the diffraction analysis was done by Jia Zhuang, while my own contributions were in the materials synthesis, and catalysis, and portions of this section have been reproduced in part with permission from Zhuang, J.; Chou, L. -Y.; Sneed, B. T.; Cao, Y.; Hu, P.; Feng, L.; Tsung, C. K., "Surfactant-Mediated Conformal Overgrowth of Core-Shell Metal-Organic Framework Materials with Mismatched Topologies," Small 2015, 11, No. 41, 5551–5555. Copyright 2015 Wiley.

To expand upon the functionality of MOF materials, several other materials have been incorporated into MOF crystals to create hybrid MOF materials^{31,88-89}. Incorporating one type of MOF into another MOF to form core–shell microcrystals, denoted as MOF-MOF, is an effective way to create multifunctional hybrid MOF materials⁹⁰⁻⁹². The core– shell MOF-MOF materials combine the functionalities of each individual MOF. For example, a MOF core with high gas storage capability, was recently enveloped by an MOF shell with molecular sieving behavior in order to fabricate size-selective gas storage materials⁹¹. It has been demonstrated that MOF-MOF structures offer new characteristics as a result of the MOF–MOF interface. For instance, secondary building unit scrambling and missing linker defects are more prevalent at the MOF-MOF interface and are of interest for catalysis applications⁸⁹.

Having a uniform and fracture-free shell of MOF-MOF structures is critical for these applications. Pioneering work has been conducted on the conformal overgrowth of fracture-free shells. In most of these works, the two integrated MOFs have similar crystal topologies; for example, the two MOFs are of the same crystal structure but with differing functional groups on the linkers (e.g., terephthalic acid vs. 2-aminoterephthalic acid)^{90,92}, or the two MOFs are composed of different metal nodes with the same linker ligands⁹³⁻⁹⁴. Although it could greatly expand the functionality of MOF-MOF materials, currently, no work has been reported on the conformal overgrowth of two MOFs with

entirely different nodes, linkers, and topologies. The challenges lie mainly with the topological mismatch of the two MOFs leading to high interfacial energy. Our group has demonstrated that the use of cationic capping agents, e.g., Cetyltrimethylammonium bromide (CTAB) could promote a conformal and orientated overgrowth of MOF on metal particles, despite little structural similarity. Here, we extend this idea by using CTAB to direct and bridge two MOF interfaces with different crystal structures and chemical properties.

3.3 Material and Methods

Chemicals and Materials:

Cetyltrimethylammonium bromide (CTAB, Calbiochem, 98%), zirconium(IV) chloride (ZrCl₄, Aldrich, 99.5%), terephthalic acid (Aldrich, 98%), 2-aminoterephthalic acid (Aldrich, 99%), acetic acid (Sigma-Aldrich, 99.7%), zinc nitrate hexahydrate (Zn(NO₃)₂•6H₂O, Sigma-Aldrich, 99%), 2-methylimidazole (Sigma-Aldrich, 99%), tetradecyl trimethyl ammonium bromide (TTAB, Sigma, 99%), cetyltrimethylammonium chroride (CTAC, TCI, 95%), sodium dodecyl sulfate (SDS, Sigma-Aldrich, 99%), polyvinylpyrrolidone (PVP, Mw~40,000, Sigma-Aldrich), palladium(II) 2.4pentanedionate (Pd(acac)₂, Alfa Aesar, Pd 34.7%), ethylene (Airgas, 99.995%), cyclohexene (Sigma-Aldrich, 99%), sodium hydroxide (NaOH, Sigma-Aldrich, 98%), tetraethyl orthosilicate (TEOS, Sigma-Aldrich, 98%) were used without further purification. Ultrapure deionized water (d. i. H₂O, 18.2 M) was used for all solution preparations. Hydrogen (Airgas, 99.999%) and helium (Airgas, 99.999%) were used for heterogeneous catalysis.

Characterization:

Transmission electron microscopy (TEM), including high-resolution transmission electron microscopy (HRTEM) was performed on a JEOL JEM2010F electron microscope operated at 200 kV. Samples for TEM were prepared by diluting 50 µL sample solution to 500 µL and placing 2.0 µL droplets onto carbon-coated copper grids, then allowed to dry under a heat lamp. Normal scanning electron microscopy (SEM) was performed on a JEOL JSM6340F scanning electron microscope. Samples were prepared for SEM by diluting 50 µL sample solution to 500 µL and placing a 1.0 µL droplet onto silicon wafer and drying under a heat lamp. The samples were then placed on silver glue atop double-sided copper tape on sample holder. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D2 diffractometer. Samples for XRD were prepared by drying the sample solution in an oven and scraping the sample powder onto a sample holder. BET measurement was performed on a Micromeritics ASAP 2020 Physisorption Analyzer.

Synthesis of UiO-66:

18.6 mg (0.08 mmol) $ZrCl_4$ and 13.3 mg (0.08 mmol) terephthalic acid were dissolved in 8.622 mL DMF, then 1.378 mL acetic acid was added into the solution as the modulator to make the final volume to 10 mL. The solution was transferred into a vial, Teflon sealed, and heated for 24 hours in a 120 °C oven. After cooling down, the formed UiO-66 was collected. The sample was washed by methanol, and stored in 10 mL methanol. Aqueous synthesis of UiO-66-ZIF-8 and Pd-UiO-NH₂-ZIF-8:

200 μ L UiO-66 was first collected and re-dispersed in 1 mL water. 150 μ L 0.01 M CTAB aqueous solution was added to the UiO-66 solution. 1 mL 1.32 M 2-methylimidazole aqueous solution was mixed with 150 μ L 0.01 M CTAB solution in a separate vial and put in sonicator and sonicated for 5 minutes. With sonication, 1 mL 24 mM Zn(NO₃)₂ • 6H₂O aqueous solution was injected into the mixture, subsequently all UiO-66 solution was also injected into the mixture. The whole solution was sonicated for another 5 minutes. The solution was then stirred for 3 hours at 500 rpm. The formed core-shell particles were collected, washed once by methanol, and finally re-dispersed in methanol. For the sonication time study, the only change was the sonication time, all the other synthetic variables were kept the same. For synthesis with other surfactants, CTAB was replaced by the chosen surfactant with the same concentration (0.01 M aqueous solution).

The synthesis of Pd-UiO-NH₂-ZIF-8 was similar to the synthesis of UiO-66-ZIF-8. Pd-UiO-NH₂ was synthesized first and the synthesis was similar to UiO-66, the only change was the use of 2-aminoterephthalic acid, instead of terephthalic acid, and the introduction of 2.44 mg Pd(acac)₂ in the synthetic solution. As-synthesized Pd-UiO-NH₂-ZIF-8 was separated from synthetic solution and re-dispersed in 1 mL water. With stirring, this Pd-UiO-NH₂-ZIF-8 suspension solution, together with 1 mL 24 mM Zn(NO₃)₂ • 6H₂O aqueous solution, was injected into a vial which had 1 mL 1.32 M 2-methylimidazole aqueous solution and 150 μ L 0.01 M CTAB solution. The reaction was stirred for 1 hour, collected, washed by methanol, and re-dispersed in methanol.

PVP-methanol synthesis of UiO-66-ZIF-8 and Pd-UiO-NH₂-ZIF-8:

10 mL UiO-66 was mixed with 2 mL 0.5M PVP methanol solution at room temperature for 10 hours. The PVP coated UiO-66 was collected by centrifugation, washed twice with methanol, and stored in 10 mL methanol. 100 μ L PVP coated UiO-66 was mixed with 5 mL 30 mM 2-methylimidazole and 5 mL 30 mM Zn(NO₃)₂ • 6H₂O and kept undisturbed at room temperature for 24 hours. The PVP-methanol UiO-66-ZIF-8 was collected by centrifugation, and washed twice with methanol.

The synthesis of Pd-UiO-NH₂-ZIF-8 was similar to the synthesis of UiO-66-ZIF-8. Pd-UiO-NH₂ synthesis was mentioned above. 25 μ L PVP coated Pd-UiO-NH₂ was mixed with 5 mL 60 mM 2-methylimidazole and 5 mL 60 mM Zn(NO₃)₂ • 6H₂O and kept undisturbed at room temperature for 24 hours. The sample was collected by centrifugation, and washed twice with methanol.

Catalytic study:

0.5 wt% sample was diluted with low surface area quartz and loaded into glass reactors. Temperature was controlled by a furnace (Carbolite) and PID controller (Diqi-Sense) with a type-K thermocouple. Gas flows, including helium, hydrogen gas and ethylene were regulated using calibrated mass flow controllers. The desired partial pressure of cyclohexene was achieved by bubbling helium through the liquid and assuming saturation⁸¹. For all reactions, gas composition was analyzed with a mass spectroscope (MKS special V2000P).

3.4 Fracture-free shell of MOF-MOF structures

In this work, uniform and fracture-free MOF-MOF particles are synthesized. The overgrowth of uniform ZIF-8 shells on monodisperse UiO-66 microcrystal cores to form UiO-66-ZIF-8 composite particles with the assistance of CTAB (Figure 3.1) were synthesized. ZIF-8 and UiO-66 were chosen to demonstrate the concept because of their high thermal and chemical stability as well as their completely different chemical compositions and topologies. In addition, we have already shown both MOFs can be used to encapsulate metal NPs and provide size selectivity for gas phase catalysis. To demonstrate the benefit of combining two distinct MOFs, a Pd-UiO-66-NH₂-ZIF-8 catalyst was furtherly synthesized. We take advantage of UiO-66-NH₂ as a MOF core with affinity to metals for Pd nanoparticle encapsulation. ZIF-8 known as excellent molecular sieving behaviors was overgrown as MOF shell. Size-selective heterogeneous catalysis over this Pd-UiO-66-NH₂-ZIF-8 was demonstrated. We believe this method can be extended to other MOF systems to form a series of core-shell MOF-MOF with mismatched topologies.



Figure 3.1 SEM image (a) and TEM images (b-d) of UiO-66-ZIF-8. Highly monodisperse UiO-66-ZIF-8 octahedral particles keep the shape of the pre-formed UiO-66 cores with uniform and fracture-free ZIF-8 shells overgrowth.

In a typical synthesis of UiO-66-ZIF-8 core-shell particles, UiO-66 microcrystals are synthesized first. The UiO-66 microcrystals, ZIF-8 precursors, and CTAB are then mixed together in water. Our previous study has shown that controlled nucleation is important for the surfactant-mediated overgrowth; therefore, in order to promote the formation of uniform and small ZIF-8 nuclei, 5 minutes of sonication is performed⁹⁵⁻⁹⁶. The mixed solution is then stirred for 3 hours before the products are collected via

centrifugation. Scanning electron microscopy (SEM) images show the highly monodisperse UiO-66-ZIF-8 octahedral particles (Figure 3.1a), which is consistent with the shape of the pre-formed UiO-66 cores. No particle aggregation was observed and all the particles are found to be around 500 nm in size. Under transmission electron microscopy (TEM), the clear core-shell structure was observed. The UiO-66 core appears darker compared to the brighter ZIF-8 shell due to the higher Z-contrast of zirconia clusters. (Figure 3.1b, c). Very few small pure ZIF-8 cubes were observed, suggesting most of the UiO-66 octahedra serve as templating substrates for the ZIF-8 overgrowth⁹⁷. Higher magnification TEM images show a smooth interface between the two MOFs (Figure 3.1d).

3.5 Characterization of Fracture-free UiO-66-ZIF-8

The ZIF-8 shell is uniform, smooth, fracture-free, and approximately 40 nm in thickness, which indicates a conformal overgrowth. The thickness of the ZIF-8 shells could be controlled by the amount of precursor to affect the overgrowth. Powder X-ray diffraction (PXRD) was performed on the dry core–shell particles and patterns of both ZIF-8 shell and UiO-66 core closely match the simulated patterns (Figure 3.2a). Each XRD peak can be assigned to either ZIF-8 or UiO-66, while some are a result of peak overlap. Well-defined peaks indicate the crystallinities of both UiO-66 core and ZIF-8 shell. N₂ adsorption data were collected at 77 K. The BET isotherm shows the porosity of the material, as a type I sorption isotherm. The steep initial region ($P/P_o < 0.15$) was expected based on the presence of micropores in the structure⁹⁸ (Figure 3.2b). The BET

surface area of the core–shell particles was calculated to be 1240 m² g⁻¹, which is between the surface area of ZIF-8⁹⁷ and UiO-6⁹⁹.



Figure 3.2 (a) PXRD of fractured UiO-66-ZIF-8 (black), conformal UiO-66-ZIF-8 (orange), simulated ZIF-8 (red), and simulated UiO-66 (blue), black arrows indicate narrowed ZIF-8 peaks in conformal ZIF-8 coating; (b) BET isotherm plot of UiO-66-ZIF-8, inset: steep increase at low pressure region.

Surfactants have known effects on the surface of MOF crystals^{97,100-101}. Optimizing the surfactant to MOF precursor ratio is critical for the conformal overgrowth. In the absence of CTAB, individual microcrystals of ZIF-8 formed, leaving UiO-66 octahedra uncoated (Figure 3.3 a-c). On the other hand, if the CTAB amount goes beyond the optimal amount (150 μ L 0.01 M CTAB), it inhibits ZIF-8 growth and no complete coating can be observed (Figure 3.3 d-f). When the appropriate amount of CTAB is introduced during the overgrowth, the CTAB layers mediate the conformal nucleation and overgrowth of ZIF-8 on the UiO-66 surface (Figure 3.1).



Figure 3.3 TEM images of UiO-66-ZIF-8 with addition of a) 0 μ L; b) 40 μ L; c) 75 μ L; d) 200 μ L; e) 300 μ L; f) 500 μ L 0.01 M CTAB in UiO-66 solution and synthetic solution, respectively. Without appropriate amount of CTAB (150 μ L 0.01 M) introduced

during the overgrowth, the CTAB cannot mediate the conformal overgrowth of ZIF-8 on the UiO-66 surface imply the importance of optimal CTAB layers.

The ability to control the overgrowth is highly related to the type of the surfactant used. We attempted UiO-66-ZIF-8 synthesis with other micelle forming surfactants, such as tetradecyltrimethylammonium bromide (TTAB), cetyltrimethylammonium chroride (CTAC), and sodium dodecyl sulfate (SDS), as well as a neutral polymer stabilizer PVP (polyvinylpyrrolidone). Each representing common surfactants which have been widely employed in nanoparticle synthesis¹⁰². Ionic surfactants (i.e. CTAC, TTAB, and SDS) give polycrystalline and fractured ZIF-8 shell. The fractured ZIF-8 layers are composed of small random-shaped ZIF-8 nanocrystals with boundaries between crystallites and have an average thickness of 60 nm (Figure 3.4). When compared the PXRD patterns of conformal and fractured ZIF-8 shell, the peak widths of fractured ZIF-8 shells are much broader than those of the conformal shells (Figure 3.2a, indicated by arrows), which suggests smaller crystal domains of the fractured ZIF-8 shells¹⁰³. We hypothesize that these non-CTAB surfactants indeed promote the interaction of ZIF-8 and UiO-66, but they lack the precise control of ZIF-8 nucleation and subsequent overgrowth. CTAB reportedly affects the ZIF-8 growth by adsorption to nuclei; this type of assembly via tail and head group effects is analogous to those of metal nanoparticle synthesis¹⁰⁴⁻¹⁰⁵. Moreover, the PVP system shows no overgrowth (Figure 3.5a). This is believed to be because PVP does not have the proper interaction with the two MOFs in water solvent. We also performed the same PVP-mediated overgrowth in methanol solvent since PVP have been shown affinity to both MOFs^{42,86}. PVP shows a more favorable interaction between the two MOFs in methanol. However, without controlled overgrowth, multiple UiO-66 crystals were encapsulated in a larger ZIF-8 microcrystal (Figure 3.5b).



Figure 3.4 TEM images of UiO-66-ZIF-8 when a) CTAC; b) TTAB; c) SDS was used as surfactant. Scale bar is 200 nm in each image. The non-CTAB surfactants lack the precise control of ZIF-8 nucleation and subsequent overgrowth



Figure 3.5 TEM images of UiO-66-ZIF-8 when a) PVP was used as surfactant, and b) PVP was used as surfactant and methanol used as solvent. Scale bar is 200 nm in each image. PVP shows no proper interaction with the two MOFs in water solvent but a favorable interaction between the two MOFs in methanol without controlled overgrowth.

3.6 Formation mechanism of Fracture-free UiO-66-ZIF-8

Our previous study has shown that the formation of small MOF nuclei is important to have a conformal MOF overgrowth on metal surfaces⁴³. Thus, the sonication step is critical because it promotes the formation of small and uniform ZIF-8 nuclei⁹⁵⁻⁹⁶. We found that 5 minutes of sonication makes the solution become opaque at a quicker rate (Figure 3.6) and leads to a conformal ZIF-8 shell. If sonication is not applied during the synthesis, a fractured ZIF-8 shell is observed (Figure 3.7b). In addition to this information, the sonication time is also critical. If the interval of sonication is extended beyond 15 minutes, an incomplete shell is observed (Figure 3.7c). If the sonication is prolonged for 1 hour, a yolk-shell nanostructure is formed. The ZIF-8 layer encases the UiO-66 core in it, with a void space between the two components (Figure 3.7d). The formation of the void space may be a result of etching of ZIF-8 at the interface under longer sonication times.



Figure 3.6 Images of ZIF-8 water-phase synthesis with (left) and without (right) sonication at (a) 0 min (right after Zn^{2+} and mim mixing); (b) 5 min; (c) 10 min; (d) 15 min. Turbidity of solution appears faster under sonication treatment, which indicates that ZIF-8 nucleation is faster under sonication.



Figure 3.7 TEM images of ZIF-8 overgrowth on UiO-66 when sonicated for (a) 5 minutes; (b) 0 minute; (c) 30 minutes; (d) 1 hour. Scale bar is 200 nm in each image. The results imply ZIF-8 nuclei formation under sonication. Only proper amount of ZIF-8 nuclei can grow into conformal shells on UiO-66.

Based on our observations, we propose a possible mechanism for the formation of the MOF-MOF particles. In the first step, Zn²⁺ ions and 2-methyl imidazole are mixed together and form the initial ZIF-8 nuclei¹⁰⁶; if sonication is applied during the nuclei formation, small and uniform nuclei form. Subsequently, the formed ZIF-8 nuclei attach to the surface of UiO-66 crystals with a specific orientation via CTAB micelle layers⁴³. The small, uniform, and oriented nuclei then grow into conformal shells; in contrast, larger nuclei formed under no sonication, grow into a fractured shell. On the other hand, if the sonication is applied for too long, the attachment of ZIF-8 nuclei on the UiO-66 surface is affected and this results in some uncovered UiO-66 surface.

3.7 Advantage of combining two distinct MOFs

To demonstrate the advantage of combining two distinct MOFs and the importance of conformal overgrowth, proof-of-concept core–shell catalysts, Pd-UiO-NH₂-ZIF-8, were synthesized, where each different component is employed for a distinct purpose. The great affinity to metal nanoparticles and larger aperture size of UiO-66-NH₂ (Figure 3.8a) make it an excellent core material for loading Pd nanoparticles without interfering with diffusion¹⁰⁷⁻¹⁰⁸. The outstanding molecular sieving behavior of ZIF-8 makes it ideal for realizing size-selective catalysis¹².



Figure 3.8 TEM images of (a) UiO-66-NH₂; (b) Pd-UiO-NH₂; (c) conformal Pd-UiO-NH₂-ZIF-8; (d) fractured Pd-UiO-NH₂-ZIF-8. (e) Size-selective hydrogenation of conformal Pd-UiO-NH₂-ZIF-8, PVP-methanol Pd-UiO-NH₂-ZIF-8, fractured Pd-UiO-

NH₂-ZIF-8, and Pd-UiO-NH₂ (from left to right); back columns for ethylene hydrogenation running at 20 °C, front columns for cyclohexene hydrogenation running at 70 °C. Catalytic behavior of cyclohexene hydrogenations show that fractured Pd-UiO-NH₂-ZIF-8 with the presence of boundaries between adjacent ZIF-8 crystallites could allow cyclohexene diffusion through the ZIF-8 shell.

Pd-loaded UiO-66-NH₂, was synthesized first, denoted as Pd-UiO-NH₂ (Figure 3.8b). Sub-10 nm Pd nanoparticles were embedded in UiO-66-NH₂ and dispersed uniformly. We then performed overgrowth twice to obtain conformal and fractured ZIF-8 shells with an average thickness of around 150 nm on Pd-UiO-NH₂ (Figure 3.8c, and d). Pd nanoparticles were still observed under TEM after ZIF-8 overgrowth. Alkene hydrogenations were carried out in a gas phase flow microreactor to exam catalytic activity of Pd nanoparticles and the impact of the ZIF-8 layer integrity on catalytic performance. Four samples, Pd-UiO-NH₂ (before ZIF-8 overgrowth), Pd-UiO-NH₂-ZIF-8 (conformal shell), Pd-UiO-NH₂-ZIF-8 (fractured shell), and Pd-UiO-NH₂-ZIF-8 (synthesized in methanol with the presence of PVP) were compared. 0.14 mg of Pd was used in all samples confirmed by ICP-AES analysis. All samples show similar activities for ethylene hydrogenation due to the relatively small kinetic diameter of ethylene molecule (2.5 Å) (Figure 3.8e) which is smaller than both the ZIF-8 and UiO-66 aperture sizes, so it can easily diffuse through, and reach the Pd catalysts. When cyclohexene hydrogenation was performed, high catalytic activity was only observed for the sample of Pd-UiO-NH₂, while Pd-UiO-NH₂-ZIF-8 (conformal shell) and Pd-UiO-NH₂-ZIF-8 (methanol-PVP) have almost no activities because the kinetic diameter of cyclohexene

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(4.2 Å) is larger than ZIF-8 aperture size so it cannot penetrate the conformal crystalline ZIF-8 shell or large ZIF-8 microcrystals. However, for the Pd-UiO-NH2-ZIF-8 (fractured shell) sample, a notable cyclohexene hydrogenation activity was observed. It is likely due to the presence of boundaries between adjacent ZIF-8 crystallites. The cyclohexene molecules have a possible diffusion pathway through the ZIF-8 shell. This clearly demonstrates the importance of the crystallinity and conformity of the shell. Catalysts showed no significant changes of selectivity and activity for prolonged (17 hour) reactions. Catalysts were collected after reaction for TEM study. No significant structural changes were observed, showing the high stability of our material (Figure 3.9). Our Pd-UiO-NH₂-ZIF-8 is the first MOF-MOF example and shows great applications in heterogeneous catalysis. Each component has a distinct role, which proves the concept of our design. It is worth mentioning that although UiO-66-NH₂-ZIF-8 (conformal shell) and Pd-UiO-NH₂-ZIF-8 (methanol-PVP) samples show similar selectivity here, the conformal shell will benefit more the applications due to the better controlled shell.



Figure 3.9 TEM images of Pd-UiO-NH₂-ZIF-8 (conformal shell) (a) before and (b) after catalytic reaction. No significant morphology changes were observed, showing the high stability of our Pd-UiO-NH₂-ZIF-8.

In summary, we successfully created a core-shell MOF material with mismatched topologies, i.e., UiO-66-ZIF-8, via a surfactant-mediated overgrowth method. The importance of sonication and surfactant is discussed in the generation of the conformal and fracture-free shell. The selective catalysis result highlights the importance of conformity, crystallinity, and integrity of the shell component. Our method could be used to guide the future synthesis of novel MOF-MOF materials with MOFs of mismatched topologies and chemical properties for a number of potential applications.

Chapter 4 SALE Functionalization

Postsynthetic processes, PSM and linker exchange, have been reported as powerful tools to engineer MOFs⁵⁷⁻⁵⁸. The process could be used to extend the applications of NPs-MOF composites. The extended applications rely on tailored chemical functionality and structure in the pores. We intended to functionalize our NPs-MOF core-shell composites by exchanging functional linkers. However, we found linker exchange process required specific condition to be able to succeed. The high exchanging rate might not be easy to reach as well. We decided to study linker exchange process before using it since it was more complicated than we thought. Here we used kinetic experiments to study the mechanism and the loading of dye to prove our mechanism.

4.1 Linker Exchange for Functionalization

The following work was done in collaboration with Joseph Morabito. Most of the kinetic study was done by Joseph Morabito, while my own contributions were in the materials synthesis, sample preparation and diffraction analysis, and portions of this section have been reproduced in part with permission from Morabito, J. V.; Chou, L. -Y.; Li, Z.; Manna, C. M.; Petroff, C. A.; Kyada, R.; Palomba, J, M.; Byers, J. A.; Tsung, C. K., "Molecular Encapsulation beyond the Aperture Size Limit through Dissociative Linker Exchange in Metal-Organic Framework Crystals," Journal of the American Chemical Society 2014, 136, 12540-12543. Copyright 2014 American Chemical Society.

It has been reported that the bridging organic linkers in MOF crystals can be exchanged with compatible but chemically distinct ligands without disrupting the

underlying MOF crystal structure and morphology. This phenomenon was first reported by Choe for pillared porphyrin paddlewheel frameworks⁶³ and has been optimized by several groups^{64,66}. The ligand exchange process has become extremely popular for the diversification of MOFs and is most commonly called solvent-assisted linker exchange $(SALE)^{66}$ or postsynthetic exchange $(PSE)^{64}$. SALE is a versatile technique for the synthesis and modification of MOF materials. After the synthesis of the NP-MOF catalysts via encapsulation method, SALE could be performed to exchange the linkers in order to change the pore structure and linker functional groups. By doing so, the structural and chemical environment of the active cavities at the interface will be finetuned without damaging the overall NP-MOF structures. The chemical properties and pore structure of both ZIFs and UiOs can be tuned^{62,109}. A selective SALE on ZIFs has been demonstrated recently, which will provide even more tunable interface¹¹⁰. Besides, many MOFs that are not accessible by de novo synthesis have been synthesized indirectly via SALE⁵⁸. Therefore, SALE would be a very useful tool for NP-MOF catalyst development. It is worth a systematical study in order to have a fundamental understanding of SALE.

Herein we introduce a new concept for the formation of enlarged pore apertures by linker dissociation during MOF linker exchange, as demonstrated by the postsynthetic encapsulation of species much larger than the pore aperture of ZIF-8 (Scheme 4.1). In this approach, we take advantage of ligand exchange reactions to "open" part of the framework of the pre-synthesized MOFs. Expanded apertures created by the ligand exchange process allow large guest molecules to diffuse into the MOF pore. After guest incorporation, the large aperture is closed by association of the ligand which traps the guest molecule in the MOF pore. This new approach to guest incorporation is expected to be general because framework linker exchange has been carried out under various conditions and exists in a large number of MOFs with diverse secondary building units.^{64,66,111-118} An additional practical advantage of kinetic studies of linker exchange proceeds the understanding the mechanism of linker exchange process to functionalize the NPs-MOF core-shell composites for catalytic purpose.



Scheme 4.1 Postsynthetic guest encapsulation through liker exchange. Large guest molecule (Rhodamine 6G, 11.3-13.7 Å) could be loaded to small pore aperture (ZIF-8, 3.4 Å) by linker dissociation during MOF linker exchange process.

4.2 Material and Methods

General considerations:

Unless otherwise stated, all the reactions were carried out in the air without taking any precaution to protect reactions from oxygen or moisture. Zinc nitrate hexahydrate (Aldrich, 99%), 2-methylimidazole (Aldrich, 99%), imidazole (Alfa Aesar, 99%), Basolite Z1200 (ZIF-8, Aldrich, produced by BASF), *n*-butanol (Alfa Aesar, \geq 99.4%), acetonitrile (Aldrich, 99.8%), Rhodamine 6G (Acros, dye content ~95%), sodium hydroxide (VWR), polyvinylpyrrolidone (PVP, Mw~29,000, Aldrich), deuterium oxide (Aldrich, 99.9 atom % D), and sulfuric acid-d₂ solution (96-98 wt. % in D₂O, 99.5 atom % D) were purchased from the indicated sources and used without further purification.

Characterization:

Transmission electron microscope (TEM) images were obtained on JEOL JEM2010F operated at 200 kV. The powder x-ray diffraction patterns (PXRD) were collected on a Bruker AXS diffractometer with Cu K α radiation (λ = 1.5418 Å). ¹H NMR spectra obtained for the kinetic experiments were recorded on a Varian (Agilent) (600 MHz) spectrometer. The line listing for the NMR spectra are reported as chemical shift in ppm. The nitrogen gas adsorption-desorption was carried out on Micromeritics ASAP 2020

provided by the University of Massachusetts Boston. Visible light absorption spectra were measured on a Thermo Scientific NanoDrop 2000c.

Kinetic study



Figure 4.1 The illustration of linker exchange of ZIF-8 with exogenous imidazole (Him). After linker exchange process, original $Zn(mim)_2$ (ZIF-8) becomes $Zn(mim)_{2-x}(im)_x$ (SALEM-2).

The kinetics of exchange of $Zn(mim)_2$ (ZIF-8) with exogenous imidazole (Him) to yield $Zn(mim)_{2-x}(im)_x$ (SALEM-2) were followed using a modified procedure based on literature precedence⁶². (Figure 4.1) Due to the heterogeneous nature of the exchange reaction, accurate sampling could not be guaranteed, and thus, for the kinetics experiment, each point shown in Figure 4.2 is the result of independent measurements carried out at different reaction times. Generally, each reaction was repeated three times, the average of which is used for the kinetic fits.



Figure 4.2 Representative ¹H-NMR spectra of acid-digested $Zn(mim)_{2-x}(im)_x$ over the course of the exchange reaction time for the series with im/mim = 30. Peak A and B stand for two different types of H atoms from imidazole while peak C and E stand for two different types of H atoms from 2-methyl imidazole.

Dried ZIF-8 (5.0 mg, 0.022 mmol Zn(mim)₂) was placed in a 3 mL glass serum vial. Solids were suspended by sonication in an appropriate volume of *n*-butanol (tabulated below) before the reaction was initiated with exogenous linker. A 588 mM solution of imidazole in *n*-butanol was added in an appropriate volume (Table 4.1), and vials were immediately sealed with PTFE-lined aluminum crimp caps, shaken manually for 5 s, and placed into the aluminum heating blocks of a Labmate synthesizer thermostated at 70 °C.
The reactions were incubated at 70 °C with 450 rpm shaking for a predetermined amount of time.

Table 4.1 The linker exchange conditions with different mole ratios of exogenous imidazole (Him) and $Zn(mim)_2$ (ZIF-8) for kinetic study.

im/mim (mol/mol)	5	10	20	30
Vol. <i>n</i> -butanol (mL)	2.625	2.250	1.500	0.750
Vol. 588 mM Him (mL)	0.375	0.750	1.500	2.250

The spin-lattice relaxation times (T₁) of each proton in solution were determined by the inversion recovery method and are detailed in the table 4.2 In light of the measured relaxation times^{, 1}H-NMR spectra were acquired using an acquisition time (at) of 18 s and an interpulse delay (d1) of 54 s, in order to make (at + d1) ~ 5 × the longest T₁. A pulse angle of 90 ° was used and 16 transients were taken per acquisition.

Table 4.2 The spin-lattice relaxation times (T_1) determined for each proton in the aciddigested solutions of the $Zn(mim)_{2-x}(im)_x$ products, which were used to choose the acquisition parameters given in the kinetics section. The longest T1 in the solutions is 13.74 s.

proton (in red)	HN N	HN N H H	HN N H	H ₂ O	$\begin{array}{c} CH_3\\ H_3C \longrightarrow \overset{I \oplus}{\underset{CH_3}{\overset{O}{\overset{O}}} CH_3\\ CH_3\end{array}$	HN N
δ (ppm)	7.85	6.66	6.45	4.94	2.35	1.79
T ₁ (s)	13.74 ± 0.28	12.06 ± 0.21	9.72 ± 0.26	3.01 ± 0.11	5.65 ± 0.12	4.44 ± 0.32

At the end of the allocated time, the vials were removed and immediately immersed in a water bath held at 0 °C. Suspended solids were transferred quickly into 3 mL of methanol chilled at 0 °C in a 15 mL centrifuge tube and centrifuged at 3300 rpm for 5 min. The solid precipitate was triturated by decanting the supernatant, and the product was resuspended in fresh methanol (6 mL). The centrifugation and trituration was repeated 3 times with 6 mL of methanol each time. The isolated solids were transferred to preweighed glass vials and the residual solvent was removed in a vacuum oven at 100 °C overnight. Dried samples were weighed and then digested in a solution of 0.900 mL deuterium oxide and 0.100 mL 98% d_2 -sulfuric acid in D₂O along with tetramethylammonium bromide (0.7 mg) that was used as an internal standard for analysis by ¹H-NMR spectroscopy.

Dye loading via linker exchange:

Variable amounts (9.3 mg/0.02 mmol, 29.2 mg/0.06 mmol, 73.9 mg/0.15 mmol, and 292.4 mg/0.61 mmol) of Rhodamine 6G (R6G) were placed in a 20 mL glass scintillation vial. 2-methylimidazole (Hmim) (181 mg, 2.2 mmol) and activated ZIF-8 crystals (75 mg, 0.33 mmol Zn(mim)₂) were added to the vial with the guest molecules. Next, *n*-butanol or acetonitrile (15 mL) was added to the vial, and the solids were suspended by sonication for 10 minutes. The vial was capped and placed in an isothermal oven at 100 °C for 7 days. The guest-loaded ZIF-8 was collected by centrifugation at 5000 rpm for 10 minutes. The solid precipitate was triturated by decanting the methanol supernatant then re-suspended into fresh methanol (10 mL). The centrifugation and trituration steps were

repeated at least 5 times until the supernatant was completely transparent. The residual solvent was removed from the isolated solids in a vacuum oven at 100 °C overnight. The mass recovery of the product was 92%.

Leaching experiment:

(Table 4.4) The dried R6G-ZIF-8 (15 mg) and 2-methylimidazole (36.2 mg, 0.44 mmol) were placed in a 5 mL scintillation vial. n-butanol (3 mL) was added to the vial and the solids were suspended by sonication for 10 minutes. The vial was capped and placed in an isothermal oven at 100 °C for 7 days. The product was collected by centrifugation at 5000 rpm for 10 minutes. The residual solvent was removed from the isolated solids in a vacuum oven at 100 °C overnight. The guest leaching experiment in methanol was carried out at the same condition in n-butanol except 20 °C for 1 month.

Photophysical measurement:

(Table 4.5) To measure the fluorescence lifetimes (τ) of the dye loaded ZIF-8 samples, we used picosecond time-resolved fluorescence spectroscopy performed on a home-built system centered around a Coherent Libra HE Ti: Sapphire Amplifier System¹¹⁹. Samples were pumped with 450 nm monochromatic light and recorded by a streak camera at 550 nm with a long-pass filter cutting off wavelengths below 480 nm to eliminate the strong scattering peak caused by the solid particles. The amount of solid was held constant at 15 mg, which was dispersed into 3 mL of methanol. In the fluorescence intensity measurement, we used the ratio of the fluorescence emission intensity to the UV-Vis absorbance (I/A) to establish normalized intensity. Steady state emission spectra were

recorded using an Agilent Cary Eclipse spectrophotometer with a Xe flash lamp. Acquisition parameters were held constant for all samples, which necessitated diluting the free R6G in methanol solution used for UV-Vis by a factor of 26 for the fluorescence measurement, due to its vastly higher I/A values.

PPh₃ loading via linker exchange:

Variable amounts of PPh₃ (866 mg/3.3 mmol and 649 mg/2.5 mmol) were placed in a 20 mL scintillation vial. 2-methylimidazole (181 mg, 2.2 mmol) and activated ZIF-8 crystals (75 mg, 0.33 mmol Zn(mim)₂) were added to the vial with the guest molecules. Next, n-butanol (15 mL) that had been sparged with Ar gas for 30 min to remove dissolved O₂ was added to the vial. The vial was capped and the solids were suspended by sonication for 10 minutes. The vial was placed in an isothermal oven at 100 °C for 7 days. The guest-loaded ZIF-8 was collected by centrifugation at 5000 rpm for 10 minutes. The solid precipitate was triturated by decanting the methanol supernatant then re-suspended into fresh methanol (10 mL). The centrifugation and trituration steps were repeated at least 5 times. The residual solvent was removed from the isolated solids in a vacuum oven at 100 °C overnight. The mass recovery of the product was 92%.

The effect of exogenous linker concentration:

(Figure 4.5b) R6G (73.9 mg, 0.15 mmol) and activated ZIF-8 crystals (75 mg, 0.33 mmol Zn(mim)₂) were placed in a 20 mL scintillation vial. Variable amounts (0 mg, 60.3 mg/0.73 mmol, 120.6 mg/1.47 mmol, 181.0 mg/2.21 mmol, and 482.4 mg/5.88 mmol) of 2-methylimidazole were added to the vial with the guest and ZIF-8 mixture. Next, n-

butanol (15 mL) was added to the vial, and the solids were suspended by sonication for 10 minutes. The vial was capped and placed in an isothermal oven at 100 °C for 7 days. The guest-loaded ZIF-8 was collected by centrifugation at 5000 rpm for 10 minutes. The solid precipitate was triturated by decanting the methanol supernatant then re-suspended into fresh methanol (10 mL). The centrifugation and trituration steps were repeated at least 5 times until the supernatant was completely transparent. The residual solvent was removed from the isolated solids in a vacuum oven at 100 °C overnight.

Synthesis of micron-sized ZIF-8:

A 25 mM solution of $Zn(NO_3)_2 \cdot 6H_2O$ in methanol (0.125 mmol, 5 mL) was combined with a 25 mM solution of 2-methylimidazole (0.125 mmol, 5 mL) in a 20 mL scintillation vial. The reaction was carried out at room temperature for 24 hours without stirring. The product was collected by centrifugation at 5000 rpm for 10 minutes. The solid precipitate was triturated by decanting the methanol supernatant then re-suspended with fresh methanol (10 mL). The centrifuging and trituration steps were repeated 3 times. The residual solvent was removed from the isolated solids in a vacuum oven at 100 °C overnight. The yield of ZIF-8 was 8.4%.

Synthesis of nano-sized ZIF-8:

The synthesis of nano-sized ZIF-8 is based on a previous procedure with some modifications¹²⁰. $Zn(NO_3)_2 \cdot 6H_2O$ (150 mg, 0.504 mmol) and 2-methylimidazole (330 mg, 4.02 mmol) were weighed and transferred to a 30 mL glass jar and 20 mL scintillation vial, respectively. The solids were dissolved in methanol (7.15 mL each).

The glass jar was then equipped with a magnetic stir bar, and placed on a stir plate. Next, under vigorous stirring, the 2-methylimidazole solution was poured into the jar and the mixture was stirred at room temperature for 6 hours. The product was collected by centrifugation at 7000 rpm for 10 minutes. The solid precipitate was triturated by decanting the methanol supernatant then re-suspended with fresh methanol (10 mL). The centrifuging and trituration steps were repeated 3 times. The residual solvent was removed from the isolated solids in a vacuum oven at 100 °C overnight. The yield of ZIF-8 was 83%.

Visible light absorption spectroscopy:

Dried R6G-ZIF-8 (10 mg) was digested in a 1 wt% hydrochloric acid/methanol solution (2 mL). After stirring for 1 minute, the resulting solution was transferred to a glass cuvette to measure the visible light absorption spectrum at 530 nm on a Thermo Scientific NanoDrop 2000c. The amount of R6G loading was determined by calibration curve between absorbance of light at 530 nm and R6G concentration ($\epsilon = 0.0934 \,\mu M^{-1} cm^{-1}$ at 530 nm).

PVP washing:

Dried R6G-ZIF-8 (15 mg) was suspended in a 14 wt. % PVP/methanol solution (10 mL) by sonication for 10 minutes. The solid precipitate was collected by trituration after centrifugation at 5000 rpm for 10 minutes. The isolated solid was then re-suspended with fresh 14 wt. % PVP/methanol (10 mL), and the centrifugation and trituration steps were repeated at least 5 times until R6G content was constant as determined by UV-Vis

absorption spectroscopy. The PVP-washed product was then re-suspended with 10 mL methanol to remove any excess PVP, and the final product was collected by centrifugation at 5000 rpm for 10 minutes and decanting of the supernatant. The solid was then dried overnight in vacuum oven at 100 °C to remove any residual solvent. The mass recovery was 66%.

Molecular size calculations:

The molecular size of R6G was estimated by using the Spartan 10 software package to minimize structures using the Hartree-Fock method with the basis set 3-21G. The greatest interatomic distances for each molecule are given as the effective molecular sizes in Figure 4.5a.

4.3 Kinetic Study of Linker Exchange

The ability of linkers to be exchanged between metal centers is ubiquitous in coordination chemistry, where the two limiting pathways for ligand substitution reactions are associative or dissociative mechanisms. In a MOF, the metal centers are typically coordinatively saturated; a property that we reasoned would make a dissociative mechanism more likely. To test the hypothesis that linker substitution is dissociative, we examined the kinetics of the linker exchange reaction under pseudo-first-order conditions by varying the initial concentration of exogenous im linker.

The quantity of imidazole and 2-methylimidazole in solution were determined using the formulae:

$$A_{P} = \text{area determined by integration of peak (P), as defined in Figure 4.2}$$
$$\left(A_{A} \times \frac{[\text{TMA}^{+}]}{A_{D}} \times \frac{12 \text{ protons}}{1 \text{ protons}}\right) + \left(A_{B} \times \frac{[\text{TMA}^{+}]}{A_{D}} \times \frac{12 \text{ protons}}{2 \text{ protons}}\right) = 2[im]$$
$$\left(A_{C} \times \frac{[\text{TMA}^{+}]}{A_{D}} \times \frac{12 \text{ protons}}{2 \text{ protons}}\right) + \left(A_{E} \times \frac{[\text{TMA}^{+}]}{A_{D}} \times \frac{12 \text{ protons}}{3 \text{ protons}}\right) = 2[mim]$$
$$\frac{[mim]}{[im] + [mim]} = \text{conversion}$$

From the ¹H-NMR data, a plot of conversion versus time could be made at each concentration, using the average deviation to estimate error (Figure 4.3). To obtain the observed rate constants (k_{obs}), linear regression analysis of the data collected at time points from 10 minutes to 60 minutes was carried out, with the slope *m* being k_{obs} . Values of k_{obs} and the accompanying R² values for the linear fits are outlined in the table 4.3.

Table 4.3 The observed rate constants (k_{obs}) determined by the method of initial rates (k_{obs} = slope m) from the conversion vs. time plots in Figure 4.3, with the coefficients of determination (R^2) for each linear fit.

im/mim (mol/mol)	[im] (M)	$k_{\rm obs}~({\rm s}^{-1})$	\mathbf{R}^2
5	0.0735	$7.2 (\pm 1.3) \times 10^{-6}$	0.98622
10	0.147	$8.1 (\pm 1.2) \times 10^{-6}$	0.98121
20	0.249	$14.0 (\pm 1.3) \times 10^{-6}$	0.99413
30	0.441	$21.0 (\pm 1.8) \times 10^{-6}$	0.99036



Figure 4.3 Plot of conversion vs. time of the $Zn(mim)_2$ to $Zn(mim)_{2-x}(im)_x$ exchange reaction at varying concentrations of imidazole with conversion expressed as the disappearance of 2-methylimidazole from the framework. The molar fraction of the total imidazolate linker content of the solid. Least squares linear regressions are shown.

Observed rate constants (kobs) for the linker exchange reaction were obtained using the method of initial rates (<10% conversion). By plotting kobs versus [im], we observed a linear correlation with a nonzero slope and intercept (Figure 4.4). These data suggest that there is a competition between associative and dissociative linker substitution reactions, with the slope of this line (m = $38.6 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$) being the second-order rate constant for associative exchange and the intercept (b = $3.37 \times 10^{-6} \text{ s}^{-1}$) being the first-order rate constant for dissociative exchange. Under the empirically determined conditions employed for linker exchange ([im] = 147 mM), the apparent rate constant for associative linker exchange.



Figure 4.4 Observed rate constants (k_{obs}) for exchange of ZIF-8 with imidazole are measured at different concentrations of imidazole. The dissociative linker substitution reactions with the slope of this line (m = $38.6 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$) is the second-order rate constant for associative exchange. The intercept (b = $3.37 \times 10^{-6} \text{ s}^{-1}$) is the first-order rate constant for dissociative exchange.

4.4 Dissociative Linker Exchange for dye encapsulation

If dissociative linker substitution occurs in MOFs, we hypothesized the existence of short-lived linker vacancies that would momentarily expand the pore aperture size to allow the passage of larger guests into the framework. Subsequent reincorporation of the dissociated linker reassembles the MOF with an aperture size that is smaller than the incorporated guest. As a proof of principle, we used the commercially available zeolitic imidazolate framework ZIF-8 as a model MOF. We also identified two criteria that would be most appropriate for a suitable guest molecule. First, to maximize guest retention, the guest molecule should be larger than the MOF aperture size. For encapsulation in ZIF-8, this requirement makes the ideal guest size between 3.4 and 11.6 Å, the aperture and pore sizes of ZIF-8, respectively. Second, in order to better quantify the loading, we initially targeted guest molecules that could be easily detectable by UV-vis spectroscopy. Rhodamine 6G (R6G) was selected as an ideal candidate that meets both criteria outlined above: it is a fluorescent dye (λ max = 530 nm) with a molecular diameter of 11.3-13.7 Å (Figure 4.5a). The amounts of encapsulated R6G were determined by UV-vis spectroscopy after acid digestion of the ZIF-8 crystals.



Figure 4.5 (a) Rhodamine 6G model of molecular size and (b) encapsulation through ZIF-8 linker exchange relative to the concentration of 2-mim exogenous linker. More exogenous linkers result in less R6G loading.

To test whether linker exchange can facilitate guest incorporation, R6G was incubated with ZIF-8 in the presence of 2-methylimidazole (2-mim) as an exogenous linker in butanol at 100 °C for 7 days (Figure 4.5b). After the reaction, the material, henceforth denoted as R6G-ZIF-8, took on a cloudy light-pink hue. The structure of the guest encapsulation products was characterized by transmission electron microscopy (TEM) and powder X-ray diffraction (PXRD). Both techniques showed no apparent differences after guest encapsulation, suggesting that the guest loading method was not destructive (Figures 4.6 and 4.7). Importantly, under the conditions that worked best to maximize guest incorporation ([im] = 0), the associative exchange mechanism was

completely shut down. Indeed, the lower guest incorporation seen at higher linker concentrations may be due to a competing associative exchange process that precludes the formation of an "open" state for guest incorporation.



Figure 4.6 Transmission electron microscope (TEM) images and particle size distributions (PSDs) of ZIF-8 crystals (a) as synthesized (micron-sized), (b) as synthesized (nano-sized), (c) PSD of as synthesized (nano-sized), d) after R6G loading (micron-sized), (e) after R6G loading (nano-sized), and (f) PSD of after R6G loading (nano-sized). The loading was carried out with 10.3 mM R6G at 100 °C for 7 days in n-butanol.



Figure 4.7 Powder X-ray diffraction patterns of R6G-ZIF-8 (red) and pure ZIF-8 (blue). The results show that ZIF-8 crystal structure is not affected by R6G loading and linker exchange process.

To confirm that the R6G was indeed incorporated into ZIF-8 instead of attached to its surface; a method to remove the surface-bound R6G in all samples prior to UV-vis analysis was sought. The affinity of R6G for ZIF-8 likely arises from its ester and amine functional groups, which can interact with the hydrophilic external surfaces of ZIF-8. We discovered that briefly exposing ZIF-8 to R6G at room temperature led to coloration of the MOF even though linker exchange had not occurred to an appreciable extent (Figure 4.8).



Figure 4.8 ZIF-8 surface interaction experiments. Loading of R6G for 7 days and 30 minutes. All other R6G loading parameters were the same (10.3 mM R6G, n-butanol, 25 °C).

To remove surface bound R6G from ZIF-8, the samples were washed with methanolic solutions of polyvinylpyrrolidone (PVP), a polar polymer with polyketone functional groups that interact strongly with MOF crystals through the polyvalency effect.¹²¹ Because of its large size, PVP cannot penetrate the interior of ZIF-8. Therefore, any R6G that remains associated with ZIF-8 after PVP washing is likely trapped in the pores of ZIF-8 rather than on its surface. As expected, repeated washings of R6G-ZIF-8 with PVP led to liberation of some R6G, but after several PVP washings, the pink color of R6G-ZIF-8 remained unchanged (Figure. 4.9). UV-vis analysis of the PVP-washed R6G-ZIF-8 allowed the encapsulation efficiency of R6G in R6G-ZIF-8 to be quantitatively determined. A similar PVP washing procedure carried out under conditions where linker exchange does not occur led to full removal of R6G from the ZIF-8 crystals (Figure 4.9).



Figure 4.9 PVP washing experiments. (a) Digital photograph of R6G-ZIF-8 precipitates and supernatants after centrifugation: (left) as synthesized R6G-ZIF-8 after 5 times methanol washing and (right) methanol-washed R6G-ZIF-8 re-suspended in 14 wt. % PVP/methanol solution. Surface bound R6G was washed by PVP solution. In b) and c), R6G content tracking by absorbance after PVP washing cycles. The R6G loading was carried out with 1.29 mM R6G in n-butanol at (b) 100 °C for 7 days, and (c) 25 °C for 10 min.

After R6G was removed from the surface, the effects of temperature, solvent, and initial concentration of R6G on R6G encapsulation in ZIF-8 were studied (Figure 4.5b and 4.10). This study indicated that the guest loading was temperature- and solvent dependent. Higher encapsulation was observed at higher temperatures as a result of an increased linker exchange rate. Likewise, the guest loading in acetonitrile was lower because linker exchange is slower in acetonitrile than in n-butanol (Figure 4.11). As expected for diffusion-controlled guest incorporation, the R6G loading was found to be directly proportional to the initial concentration of R6G (Figure 4.10). As expected for guests that are kinetically trapped, re-subjection of R6G-ZIF-8 to the linker exchange reaction conditions led to diffusion of the dye into solution (Table 4.4). Importantly, leaching can be prevented by subjecting R6G-ZIF-8 to conditions where linker exchange is slow (Table 4.4).



Figure 4.10 R6G encapsulation through ZIF-8 linker exchange. (A) R6G loading vs [R6G] at 100 °C (red) and 25 °C (blue) in n-butanol and at 100 °C in acetonitrile (green).

The inset image shows ZIF-8 after R6G loading at various [R6G] during linker exchange at 100 °C in n-butanol.



Figure 4.11 The dependence between the imidazole linker exchange rate and R6G loading amount in different solvents. (a) PXRD patterns of the R6G-ZIF-8 samples after the exchange process in various solvents at 100 °C for 7 days. The samples were prepared and MeOH/PVP washed as described in the experimental section for n-butanol. (b-c) The dependence of the R6G loading (wt. %) on the imidazole exchange rate for (b) without exogenous linker and (c) with 147 mM exogenous 2-methylimidazole during the dye encapsulation process. *The imidazole exchange rate was approximated by measuring the fraction of linkers exchanged to imidazole from 2-methylimidazole after 18 hours at 100 °C in the various solvents.

Sample	Preparation	Loading
Original R6G@ZIF-8	10.29 mM R6G, 2.2 mmol 2-methylimidazol, BuOH at 100 °C for 7days	0.370 mol (%)
Under linker-exchange condition	2.2 mmol 2-methylimidazol, BuOH at 100 $^{\circ}\mathrm{C}$ for 7days	0.027 mol (%)
Under non-linger-exchange condition	2.2 mmol 2-methylimidazol, MeOH at 20 $^{\circ}\mathrm{C}$ for 1 month	0.340 mol (%)

Table 4.4 Leaching experiments.

4.5 Confirmation of guest encapsulation via linker exchange

To further confirm that the R6G was encapsulated in ZIF-8 during linker exchange, photophysical measurements were made (Table 4.5). Comparison of the normalized fluorescence intensities of R6G-ZIF-8 (prepared by linker exchange in n-butanol with R6G), surface-bound R6G (prepared by brief exposure of ZIF-8 to R6G), and free R6G in solution provided some insight. A dramatic decrease in fluorescence intensity was observed for R6G-ZIF-8 and surface-bound R6G compared with free R6G in solution. Moreover, the normalized intensity for surface-bound R6G (0.096) was more than double that of R6G-ZIF-8 (0.042). The lower intensity observed for R6G-ZIF-8 compared with surface-bound R6G is likely due to dye encapsulation in R6G-ZIF-8, which is expected to alter light absorption and/or emission as a result of differing interactions between the guest molecule and the framework. Regardless of the specific rationale, the difference in fluorescence intensity observed for R6G-ZIF-8 compared with surface-bound R6G provides further support that R6G is encapsulated in ZIF-8 during linker exchange instead of bound to the external ZIF-8 surface.

Table 4.5 Fluorescence lifetime and fluorescence intensity measurement. R6G-ZIF-8 samples prepared with 147 mM 2-methylimidazole exogenous linker (+ Hmim) and 82

without any exogenous linker (no exog.) in n-butanol. Both R6G@ZIF-8 samples were PVP washed to remove surface bound dye as described in the manuscript. The "surface only control" was prepared by exposing ZIF-8 particles to R6G in a methanolic solution for 10 min, followed by extensive (5x) washing with methanol. In previous control experiments we found that PVP washing of a sample prepared this way led to complete removal of the dye (see Figure 4.9), demonstrating that dye loading is solely on the surface. The fluorescence intensities were normalized by the amount of the R6G loading measured by absorption after the ZIF-8 particles were digested by acid. The R6G standard consisted of R6G dissolved in methanol with a UV-vis absorbance of 0.3.

Sample	WT. % R6G	τ(ns)	I /A (a.u.)	I / A normalized
R6G	-	2.84 ± 0.14	18800 ± 100	1.0
Surface only control	0.023	3.63 ± 0.10	1800 ± 40	0.096
R6G@ZIF-8 + Hmim	0.024	3.50 ± 0.03	790 ± 6	0.042
R6G@ZIF-8 no exog.	0.064	3.79 ± 0.02	195 ± 3	0.010

To gain a better understanding of the guest encapsulation process, the effect of the exogenous 2-mim linker concentration on the guest loading was explored next. Somewhat surprisingly, the R6G loading was inversely proportional to the concentration of exogenous linker (Figure 4.5b). In fact, the highest loading of R6G was observed when the reaction was carried out without any exogenous 2-mim linker. Although unexpected, this result could be rationalized by a dissociative linker substitution mechanism where dissociation of 2-mim from ZIF-8 led to the formation of a linker-deficient "open" state (Scheme 4.1). At low concentrations of free im, the "open" state is not as readily arrested by free linker, which allows more time for the guest to diffuse into the pores of the MOF.

Consequently, higher guest loadings are observed at lower concentrations of exchanging linker.

To further examine the mechanism of guest encapsulation, the relationship between the im linker exchange rate and the R6G loading was evaluated in different solvents (Figure 4.11). PXRD suggested that the guest loading method was not destructive in these solvents (Figure 4.11a). As expected, higher R6G loading was observed in solvents where the linker exchange rate is higher. Moreover, every solvent that promoted facile linker exchange also demonstrated higher guest encapsulation in the absence of exogenous 2-mim compared with reactions carried out in the presence of 2mim.

4.6 Linker Exchange for PPh₃ encapsulation



Figure 4.12 Molecular sizes of triphenylphosphine model

Finally, to probe the generality of the methodology, encapsulation of a ligand suitable for incorporating transition metal complexes in ZIF-8 was targeted. Because it is ubiquitous in organometallic catalysis and has the appropriate molecular size (Figure

4.12), triphenylphosphine (PPh₃) (molecular diameter = 9.56 Å) was chosen as the initial guest ligand. The same method used for dye encapsulation was adopted to encapsulate PPh₃ in ZIF-8 (henceforth denoted as PPh₃-ZIF-8) using initial [PPh₃] = 165 and 220 mM. Elemental analysis of the product obtained with initial [PPh₃] = 220 mM indicated a PPh₃ loading of 2 wt % (Figure 4.13).



Figure 4.13 A representative energy dispersive X-ray spectrum of PPh₃-ZIF-8 loaded with initial [PPh₃] of 220 mM. Inset shows the TEM image of the area used for analysis, with the focused particle indicated by an arrow. The 10 % pore loading of PPh₃ was estimated by multiplying the P/Zn atomic ratio of 0.016 by 6 (the number of unique Zn atoms per sodalite cage of ZIF-8).

To demonstrate that the PPh₃ was mainly encapsulated within the pores of ZIF-8 and not on its surface, N₂ adsorption data were collected at 77 K on PPh₃-ZIF-8 at both loadings and commercial ZIF-8, with a high resolution of points in the micropore adsorption region (Figure 4.14). Saturation of the micropore volume with N₂ occurred for the reference ZIF-8 material at 485 cm³/g, and the BET surface area was calculated to be 1554 m²/g using a P/P₀ range of 5 \times 10⁻⁴ to 5 \times 10⁻³ (before gating) or 1885 m²/g with a range of 5×10^{-4} to 10^{-2} (after gating). These surface areas are in agreement with ZIF-8 values from the literature⁷⁶. For the PPh₃-ZIF-8 samples, micropore saturation occurred at 459 cm³/g for the sample exchanged with 165 mM PPh₃ and at 405 cm³/g for that with 220 mM PPh₃; these values are 5% and 16% lower than for ZIF-8. This decrease in the micropore adsorption capacity was in excess of the decrease anticipated from the weight gain upon loading (only 2%) and is consistent with guests occupying some pores of the MOF. From these data, we estimated that ~ 1 in every 10 pores in ZIF-8 was occupied by a PPh₃ ligand. Such loadings are possible only by the linker exchange process that facilitates incorporation of the large ligand guest.



Figure 4.14 (A) N_2 absorption (\circ) and desorption (\bullet) isotherms of ZIF-8 (red), 165 mM PPh₃-ZIF-8 (blue), and 220 mM PPh₃-ZIF-8 (green). (B) Plot vs $log_{10}(P/P_0)$ to show the detailed N_2 sorption at low pressure.

In summary, we have developed a method for postsynthetic encapsulation of large guests (R6G and PPh₃) with molecular diameters that exceed the framework aperture size in ZIF-8 nanocrystals beyond what could be explained by framework flexibility. The approach capitalizes on the existence of linker exchange reactions, which were shown by our kinetic studies to proceed by a competition between associative and dissociative

exchange mechanisms. Maximum guest encapsulation was observed under conditions where the dissociative mechanism predominates because the dissociation of at least one aperture-defining 2-mim linker facilitates the formation of a short-lived "open" state in the pore with an expanded pore aperture size. In contrast to other encapsulation strategies, this approach does not require any specific electrostatic interaction between the guest and the MOF host, which may significantly expand the scope of molecular guests and MOF hosts suitable for forming host–guest composites.

In addition to the impact of these findings on the ability to incorporate large guests in MOFs, important insight into the mechanism for linker exchange processes in MOFs has been garnered. Such processes have already been exploited for the synthesis of novel MOF architectures⁶³, useful catalyst species¹²², and sophisticated nanocomposite materials¹¹⁷. Future investigations will look at the application of these findings to the new encapsulation methodology for the development of catalysts that take advantage of the size-selective capabilities of MOFs as well as the use of the mechanism for new MOF morphology synthesis, hollow MOF formation for example.

Chapter 5: Single Crystalline Hollow MOF Formation

We have learned, through kinetics studies, that linker exchange rate can vary in different solvents. The different exchanging rate could be used to create hierarchical porosity in MOF structure. With this in mind, we developed a doublesolvent mediated overgrowth strategy to form hollow and mesoporous MOF.

5.1 Double-solvent mediated overgrowth of ZIF-8

Portions of the following section have been reproduced in part with permission from Chou, L. -Y.; Hu, P.; Zhuang, J.; Morabito, J. V.; Ng K. -C.; Kao Y. -C.; Wang, S. -C.; Shieh, F. -K.; Kuo, C. -H.; Tsung, C. -K., "Formation of hollow and mesoporous structures in single-crystalline microcrystals of metal–organic frameworks via doublesolvent mediated overgrowth," Nanoscale, 2015, 7, 19408-19412., Copyright 2015 The Royal Society of Chemistry.

Creating MOF crystals with hierarchical porosity, such as hollow cavities or mesopores, has gained attention recently due to their greater storage capacity and diffusion promotion.¹²³⁻¹³⁰ One synthesis method, the use of surfactant ligands to create mesopores and macropores in MOF crystals, has been reported.¹³¹ Though this method has a simple one-step synthesis and high degree of crystallinity, the selection of surfactant ligands can be quite MOF-specific. Overgrowth of MOFs on sacrificial templates, and subsequent template removal, is a more straightforward and general method to generate hierarchical porosity in MOF crystals.¹³²⁻¹³⁴ The template selection and removal conditions must be carefully

designed to avoid defect formation and preserve crystallinity, critical concerns for applications that require molecular selectivity¹³⁵. These works demonstrate a rational combination of template and removal, highlighting the advantages of hierarchical porosity the need for more general methods to create hierarchical porosity in single-crystalline MOF microcrystals.



Scheme 5.1 Double-solvent mediated overgrowth of ZIF-8. MOF microcrystals with the first solvent (H_2O) trapped in their pores are used as cores to seed the overgrowth of a MOF shell in the second solvent (methanol).

Solvent effects observed generally in coordination chemistry suggest that the solvent could have a strong directing effect on the pathways of formation or decomposition of MOFs. Varying the solvent could alter the formation energy of MOFs, stabilize intermediates and transition states, and even provide new pathways from its direct participation in elementary reactions. The solvent has been observed to affect many properties of MOFs, such as their stability, crystal sizes and shapes, as well as the rates of crystal growth and post-synthetic ligand and ion exchange.^{64,68-71} We believe that the solvent effect could be utilized as a part of the synthetic toolbox.

Toward this design principle, we developed a double-solvent mediated overgrowth strategy. In this method, uniform MOF microcrystals with the first solvent trapped in their pores are used as cores to seed the overgrowth of a MOF shell in the second solvent (Scheme 5.1). During the overgrowth, the solvent molecules trapped in the MOF crystal cores sluggishly exchange with the solvent molecules in the overgrowth solution due to the slow diffusion rate in the microporous materials.¹³⁶⁻¹³⁷ This lethargy creates a local double-solvent environment of internal core solvent and external overgrowth solvent. We found that, with the appropriate combination of solvents, the core MOF could serve as a sacrificial template to form uniform MOF microcrystals with hollow or mesoporous structures (Figure 5.1). Because the template core and overgrowth shell are exactly the same MOF and the core is single-crystalline, single-crystalline overgrowth is promoted.¹³²



Figure 5.1 TEM images of (a-b) hollow ZIF-8, (c-f) mesoporous ZIF-8, and (g-h) solid ZIF-8. Narrow size dispersed single crystal MOF shells are created by the

double solvent method. Same area of hollow and mesoporous region can be seen from the synthesis.

5.2 Materials and Methods

General considerations:

Unless otherwise stated, all reactions were carried out in air without taking any precaution to protect against oxygen and moisture. Cetyltrimethylammonium bromide (CTAB, Calbiochem, 98%), hydrogen tetrachloroaurate trihydrate (HAuCl₄ · 3H₂O, Sigma-Aldrich, ~50% Au basis), sodium citrate tribasic dehydrate (Sigma-Aldrich, >99%), zinc nitrate hexahydrate (Zn(NO₃)₂ · 6H₂O, Sigma-Aldrich, 99%), cobalt(II) nitrate hexahydrate (Co(NO₃)₂ · 6H₂O, Sigma-Aldrich, 99.999%), 2-methylimidazole (Sigma-Aldrich, 99%), and ultrapure deionized water (d.i. H₂O, 18.2 M) were used for aqueous solution preparations.

Characterization:

Transmission electron microscope (TEM) images were obtained on a JEOL JEM2010F operated at 200 kV. Scanning transmission electron microscope (STEM) and energydispersive X-ray spectroscopy (EDS) mapping experiments were performed on an FEI Probe Cs corrected Titan operating at 200 kV. Scanning electron microscope (SEM) images were obtained on a JEOL JSM6340F. The powder x-ray diffraction patterns (PXRD) were collected on a Bruker AXS diffractometer with Cu K α radiation (λ = 1.5418 Å). The nitrogen gas adsorption-desorption was carried out on Micromeritics ASAP 2020. Synthesis of 200 nm ZIF-8 and ZIF-67 nanocubes:

The synthesis was carried out following the previous procedure in our lab with some modifications⁴³. 1.75 mL of aqueous solution of 0.55 mM CTAB and 790 mM of 2methylimidazole mixture was stirred at 500 rpm for 5 minutes. Then 0.25 mL of 97.5 mM Zn(NO₃)₂ • $6H_2O$ aqueous solution was injected. The whole solution was stirred for another 5 minutes at 500 rpm. The reaction solution was then left undisturbed at room temperature for 3 hours. The formed ZIF-8 nanocubes were spun down at 5000 rpm for 10 minutes. To form the ZIF-67, the same reaction parameters were followed, but 97.5 mM Co(NO₃)₂ • $6H_2O$ aqueous solution replaced Zn(NO₃)₂ • $6H_2O$. For the synthesis of 150 nm ZIF-8 nanocubes, similar reaction parameters were followed, but 0.83 mM CTAB was used instead of 0.55 mM CTAB.

Synthesis of 150 nm ZIF-8 nano-crystals in methanol:

The synthesis was carried out following the previous procedure in our lab with some modifications²⁴. 7.15 mL of a methanol solution of 562 mM 2-methyl imidazole was stirred at 500 rpm. Then, 7.15 mL of a methanol solution of 70.5 mM $Zn(NO_3)_2 \cdot 6H_2O$ was injected. The whole solution was stirred for another 12 hours at 500 rpm. The formed ZIF-8 nano-crystals were spun down at 5000 rpm for 10 minutes.

Synthesis of solid, hollow and mesoporous ZIF-8:

As-synthesized ZIF-8 cubes were collected by centrifugation and re-suspended in 1 mL methanol. 0.20 mL of ZIF-8 cubes were mixed with 2.5 mL of 30 mM 2-

methylimidazole methanol solution. 2.5 mL of 30 mM $Zn(NO_3)_2 \cdot 6H_2O$ methanol solution were then added. The reaction solution was left undisturbed at room temperature for 1 hour (hollow ZIF-8) or 6 hours (mesoporous ZIF-8). The formed ZIF-8 nanoparticles were spun down at 5000 rpm for 10 minutes. To form solid ZIF-8, the same reaction parameters were followed, but the ZIF-8 cubes used in preparing seeds solution were dried in a vacuum oven.

Synthesis of ZIF-67-ZIF-8:

Following a procedure similar to the synthesis of hollow ZIF-8, as-synthesized ZIF-67 cubes were suspended in 1 mL of methanol prior to the overgrowth step. The reaction solution was left undisturbed at room temperature for 1 hour (hollow ZIF-67-ZIF-8) or 6 hours (mesoporous ZIF-67-ZIF-8). The formed ZIF-67-ZIF-8 nanoparticles were spun down at 5000 rpm for 10 minutes.

Synthesis of Au octahedra:

The synthesis was carried out following our previous procedure with some modifications⁴³. 550 mg of CTAB was dissolved in 97 mL of d.i. H₂O, followed by the addition of 2.50 mL 0.01 M HAuCl₄ and 0.50 mL 0.1 M trisodium citrate. The mixture solution was transferred into a 200 mL pressure vessel and heated at 110 °C for 24 hours. The formed Au octahedra were spun down at 6000 rpm for 20 minutes and redispersed in d. i. H₂O.

Synthesis of Au-ZIF-8 nanocubes:

The synthesis was carried out following the previous procedure in our lab with some modifications⁴³. Following a similar procedure to the synthesis of ZIF-8 nanocubes, 10 seconds after the addition of $Zn(NO_3)_2 \cdot 6H_2O$, 500 µL of a Au octahedra solution was injected into the mixture, while the Au octahedra solution concentration had already been adjusted to 9.6 µmol metal in a 1 mL solution. The whole solution was stirred for another 5 minutes at 500 rpm. The reaction solution was then left undisturbed at room temperature for 3 hours. The formed Au-ZIF-8 nanocubes were spun down at 5000 rpm for 10 minutes.

Synthesis of mesoporous and solid Au-ZIF-8:

Synthesis of mesoporous Au-ZIF-8 followed a procedure similar to the synthesis of mesoporous ZIF-8: as-synthesized Au-ZIF-8 cubes were suspended in 1 mL of methanol prior to the overgrowth step. The reaction solution was then left undisturbed at room temperature for 6 hours. The formed mesoporous Au-ZIF-8 nanoparticles were spun down at 5000 rpm for 10 minutes. To form solid Au-ZIF-8, the same reaction parameters were followed, but with vacuum-oven-dried Au-ZIF-8 cubes used to prepare the seed solution.

5.3 Hollow, Mesoporous, and Solid MOF Formation

Our first indication that solvent effects could be useful for generating MOF crystals with hierarchical porosity came during attempts to carry out overgrowth of ZIF-8 microcrystals under a water-methanol double-solvent condition. ZIF-8 forms

in both water and methanol, but the formation conditions are very different. Stable ZIF-8 microcrystals form in water only with a large excess of linker molecules relative to the methanol condition.¹³⁸⁻¹³⁹ For the aqueous synthesis and overgrowth condition, we used a growth solution with the precursors 2-methylimidazole (2-mim) and Zn(NO₃)₂ in a ratio of 55:1 (2-mim/Zn); for the methanol condition the ratio is 1:1. Cetyltrimethylammonium bromide (CTAB) is used in the aqueous condition in order to control the size and shape of ZIF-8.¹⁴⁰ The crystal shape of ZIF-8 synthesized or overgrown is cubic in water and truncated rhombic dodecahedral or rhombic dodecahedral in methanol. This CTAB-induced shape difference has been reported before and provides a great tool to track the overgrowth in different solvents.¹⁴¹



Figure 5.2 SEM images of characteristic water-synthesized MOF cores. (a) 150 nm ZIF-8 nanocubes, and (b) 200 nm ZIF-67 nanocubes. Size can be tuned between 100 nm and 500 nm. Both water-synthesized MOFs show narrow size dispersed single crystal.

We synthesized uniform cubic size-tunable ZIF-8 microcrystal cores (Figure 5.2a) under aqueous condition and then collected the solid products via centrifugation without removal of the water molecules adsorbed in the ZIF-8 pores. These ZIF-8 microcrystal cores (200 nm) and trapped water molecules were then transferred to the methanol solution of $Zn(NO_3)_2$ and 2-mim to carry out the overgrowth. After 1 hour, instead of the anticipated larger solid ZIF-8 microcrystals, we observed large microcrystals (450 nm) with hollow central cavities (Figures 5.1a, b). The imprint left by the cubic ZIF-8 cores could be clearly seen. The sharp truncated rhombic dodecahedral shape was observed in all the samples, indicating that the hollow ZIF-8 microcrystals were single-crystalline. Powder X-ray diffraction (PXRD) patterns demonstrate that ZIF-8 is the only crystalline phase (Figure 5.3) and N₂ adsorption-desorption isotherms collected at 77 K are type I, indicating the microporosity of the hollow ZIF-8 (Figure 5.4). The BET surface area of the hollow ZIF-8 was calculated to be 1276 m²/g.



Figure 5.3 Powder X-Ray diffraction patterns of hollow ZIF-8 and mesoporous ZIF-8. The results show that crystal structure of the ZIF-8 crystals synthesized by double solvent method is exactly the same to conventional ZIF-8 synthesis method.


Figure 5.4 Nitrogen adsorption (\circ) and desorption (\bullet) isotherms of hollow (blue) and mesoporous (red) ZIF-8. Mesoporous ZIF-8 shows higher surface area than hollow ZIF-8.

To verify whether the hollow structure was generated due to the watermethanol double-solvent environment, three control experiments were carried out. First, we carried out the overgrowth under aqueous condition instead of methanol on the same ZIF-8 cores with water trapped in the pores. In this case, both internal and external solvent environments were water. Solid larger ZIF-8 crystals with cubic shape formed under this water-water overgrowth condition and no hollow structure was observed under TEM (Figure 5.5a, b). Second, we removed water from the ZIF-8 cores (150 nm) by heating at 150 °C under vacuum and then filled the pores with methanol before the overgrowth under methanol condition. This methanol-methanol overgrowth also led to solid ZIF-8 crystals, here with rhombic dodecahedral crystallinity (Figures 5.1g, h). Finally, we carried out the overgrowth under aqueous conditions on the ZIF-8 cores with methanol trapped in the pores. Again, solid, larger ZIF-8 crystals formed under this methanol-water condition (Figure 5.5c, d). These three control experiments clearly indicate that only the double-solvent conditions of internal water and external methanol lead to the formation of the hollow structure. Notably, these control experiments confirm that the cavities do not come from the surfactant micelles due to CTAB surfactant.¹⁴²



Figure 5.5 (a) SEM and (b) TEM images of overgrown ZIF-8 nanocubes in water from water-synthesized ZIF-8 cores. (c-d) TEM images of overgrown ZIF-8

nanocubes in water from methanol-synthesized ZIF-8 cores. As-synthesized ZIF-8 cores can be seen in both cases. Larger ZIF-8 crystals confirm the overgrowth. 150 nm of ZIF-8 nanocubes would be formed under the overgrowth condition if no additional ZIF-8 cores.

We propose that, during the formation of shell ZIF-8 under the watermethanol double-solvent overgrowth, the pH of the internal water environment drops due to the deprotonation of the 2-mim in the external methanol environment.¹⁴³ ZIF-8 is not stable at this condition in water, so it dissociates and forms a hollow cavity.²⁴ It is worth mentioning that the water-water or methanolwater condition generates the solid product because of the large excess of linker molecules during the aqueous overgrowth. Without the excess of linkers, the ZIF-8 cores are etched away in water. When an excess of linkers (2-mim:Zn = 55:1) was used under the water-methanol condition, however, we observed the formation of free ZIF-8 nanocrystals rather than overgrowth, and it is clear that no hollow structure formed (Figure 5.6). These results show that an excess of linkers is needed to stabilize ZIF-8 cores with the presence of water.



Figure 5.6 TEM images of (a-b) overgrown ZIF-8 nanocubes in methanol with the precursors 2-methylimidazole (2-mim) and $Zn(NO3)_2$ in a ratio of 55:1 (2-mim:Zn) from water-synthesized ZIF-8 cores. About 20 nm of ZIF-8 nanocrystals were formed under the overgrowth condition because of the excess of 2-mim.

5.4 Investigation of the Cavity Formation Mechanism

To monitor the cavity formation, we used ZIF-67 microcrystals as the cores to carry out the same overgrowth and energy-dispersive X-ray (EDX) spectroscopy associated with TEM to trace the metal ions. ZIF-8 and ZIF-67 can be synthesized under similar aqueous and methanol conditions. They are of the same crystal topology but have different metal ion nodes. ZIF-8 contains Zn ions as the metal nodes, but ZIF-67 contains Co ions.^{75,144} Uniform ZIF-67 microcrystals were synthesized under aqueous conditions (Figure 5.2b), and subjected to the same overgrowth of ZIF-8 under methanol condition. Under this water-methanol double-solvent condition, similar hollow microcrystals were obtained after 1 hour of overgrowth (Figure 5.7a). EDX mapping and line-scan showed that the hollow 103

microcrystals were mainly composed of Zn ions (ZIF-8). ZIF-67 cores were dissociated and the Co ions were located at the inner surface of the central cavity (Figure 5.7b, c). We also observed higher contrast at the interface of the hollow central cavity under TEM. This could indicate that dissociated species of ZIF-67 were trapped and deposited on the inner surface of the hollow core when the sample was dried. The observation suggested that the linker molecules decomposed from ZIF-67 were also trapped in the hollow cavities. A control experiment of overgrowth of ZIF-8 on ZIF-67 cores under water-water condition was performed. As expected, a solid ZIF-67-ZIF-8 core-shell microcrystal structure was obtained. (Figure 5.8).



Figure 5.7 STEM/EDX line scan and elemental mapping of Co-ZIF-8 overgrowth in methanol. (a-c) 1 hour of overgrowth and (d-f) 6 hours of overgrowth. Green color represents Co and red color represents Zn. Scale bar is 100 nm in each image.



Figure 5.8 (a-b) TEM images of ZIF-67-ZIF-8 overgrowth in water. (c) STEM/EDS line scan and (d) elemental mapping of ZIF-67-ZIF-8 overgrowth in water. Green color represents Co and red color represents Zn

After 1 hour of reaction in the water-methanol condition, the Co ions and linkers trapped in the hollow central cavities could be removed by thorough washing to yield hollow ZIF-8. If instead we kept the product under the methanol 106

condition for 6 hours, a mesoporous ZIF-67 core formed (Figure 5.7d). Elemental mapping and line-scan showed a Co-rich core, which indicates that ZIF-67 reforms (Figure 5.7e, f). Compared to water, methanol promotes the reforming of ZIF-67 under low linker concentrations,¹³⁸ which may help explain why the core reforms after solvent equilibration. We observed the evolution of the products through a time-dependent TEM study (Figure 5.9). Completely hollow ZIF-8 formed after 1 hour of overgrowth. ZIF-67 started to reform after 3 hours and a clear mesoporous core-shell structure was observed after 6 hours. Solid cores are never observed in these prolonged reactions, which could be due to some of the trapped linkers and metal ions diffusing out to solution during the overgrowth or serving as nutrients for the growing ZIF-8 shell. The same process occurred on pure ZIF-8. Hollow (Figure 5.1a, b) and mesoporous (Figure 5.1c, d) ZIF-8 were formed. The observation of core metal ion deposition on the inner surface of hollow ZIF-8 may also explain the lower surface area (1276 m^2/g) of hollow ZIF-8 as compared to pure ZIF-8. After the reformation of mesoporous core ZIF-8, the BET surface area of the mesoporous ZIF-8 increased to 1441 m^2/g (Figure 5.4).



Figure 5.9 Time study of hollow MOF overgrowth in methanol. TEM images of (a and d) 1 hour of overgrowth, (b and e) 3 hours of overgrowth and (c and f) 6 hours of overgrowth.

5.5 Nanoparticle Encapsulation through Double-solvent method

The detailed mechanism of this double-solvent-mediated method is under investigation; however, it is already clear that it is an efficient way to generate ZIF-8 with hierarchical porosity. To demonstrate the versatility of this method, we have tuned the size of mesoporous ZIF-8 and formed structures with metal nanoparticles embedded in mesoporous ZIF-8. Mesoporous ZIF-8 microcrystals with sizes of 250 nm (Figure 5.1e, f) and 450 nm (Figure 5.1c, d) were synthesized by using different cores with sizes of 150 nm and 200 nm, respectively. Microcrystals of ZIF-8 with a single Au nanoparticle embedded per crystal were synthesized by the method previously reported by our group,¹⁴⁰ and then either water-methanol or methanol-methanol overgrowth of ZIF-8 was carried out. The formation of mesoporous Au-ZIF-8 (Figure 5.10a, b) or solid Au-ZIF-8 (Figure 5.10c, d) was directed by using either double-solvent or single-solvent conditions. We believe that by varying the guests (e.g. metal oxide, quantum dot, small molecule), the structures will have great applications in electrochemistry,¹⁴⁵ luminescence,¹⁴⁶ delivery,¹⁴⁷ and catalysis.⁵⁰



Figure 5.10 TEM images of (a-b) mesoporous Au-ZIF-8, and (c-d) solid Au-ZIF-8. Both NP-MOF composites show narrow size dispersed single crystal shell.

In summary, we have developed a double-solvent mediated overgrowth method to form cavities in single-crystalline MOF microcrystals. ZIF-8 cores with water adsorbed in the pores are used as templates to carry out overgrowth of ZIF-8 shells in methanol. Due to the different solvent effects, hollow and mesoporous structures are created. We believe that this solvent-mediated overgrowth method will have great applications in forming other MOFs with hierarchical porosity.

Chapter 6: Conclusions

Over the past few decades, significant progress has been made in the combination of metal nanocatalysts and nanoporous materials. From the stiff, solid zeolite to the flexible, modifiable MOF, scientists have developed advanced materials that can be integrated with metal catalysts for a variety of applications. Various synthetic strategies for incorporating metal nanoparticles within nanoporous materials (e.g., MOFs) have also been developed, with several demonstrated applications of the composite materials in heterogeneous catalysis. The NPs-MOF composite is becoming one of the most promising materials for heterogeneous catalysis in terms of the selectivity that the MOF shell may provide. We have successfully utilized a capping agent (PVP) to mediate nanoparticle encapsulation in two thermally stable MOFs (ZIF-8 and UiO-66) with different aperture sizes. Size-selective alkene hydrogenations were then carried out in the NPs-MOF composites. The results demonstrated molecular size selectivity through various aperture sizes of MOF shells. Heat treatment over the NPs-MOF composites showed that deactivation temperatures could be a quick and general method to determine thermal stability of NPs-MOF composites. Due to the successful encapsulation of NPs by MOFs, interfacial control was deemed feasible through the choice of the correct capping agent. We found that a surfactant (CTAB) could orient lattice alignment between NPs and MOF structure. We extended the alignment mechanism to two porous materials with mismatched topologies (UiO-66 and ZIF-8). The importance of sonication and surfactant is discussed in the generation of the conformal and fracture-free shell. The selective catalysis result highlights the importance of the conformity, crystallinity, and integrity of the shell component. Our method could be used to guide the future synthesis of novel

MOF-MOF materials with MOFs of mismatched topologies and chemical properties for a number of potential applications. These findings could be used to develop catalysts that take advantage of the size-selective capabilities of MOFs. We then turned to study linker exchange, intending to functionalize our NPs-MOF composites. Through the dissociated linker exchange mechanism, we developed a new concept for the formation of enlarged pore apertures by linker dissociation during MOF linker exchange, as demonstrated by the postsynthetic encapsulation of species much larger than the pore aperture of ZIF-8. This finding could be applied to the new encapsulation methodology for the development of catalysts that take advantage of the size-selective capabilities of MOFs. By applying knowledge of the linker exchange process, we finally developed a double-solventmediated overgrowth method to form single-crystalline, hollow MOF microcrystals. Due to the different solvent effects, hollow and mesoporous structures were created. We believe that this solvent-mediated overgrowth method will have applications in forming other MOFs with hierarchical porosity. Different types of catalytic reaction applications were shown here to demonstrate the potential of NPs-MOF composite materials. The promising properties of this class for heterogeneous catalysis will be further promoted by mechanistic studies of their action and development of applications.

Appendix

A.1 References

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