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A Family of Metal-Organic Frameworks Exhibiting Size-Selective Catalysis with Encapsulated Noble-Metal Nanoparticles

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Noble-metal nanoparticles (NPs),^[1] especially platinum (Pt) and palladium (Pd), supported on high-surface-area carriers have been attracting increasing research attention as important heterogeneous catalysts. On one hand, the high surface area of the carrier can increase the availability of the active sites and facilitate the contact between reactants and catalysts. On the other, nanoscopic catalysts with uniform size, stability, and unique properties compared to their larger counterparts^[2] are constantly appealing in a broad range of scientific studies, including materials science,^[3] computational chemistry,^[4] and catalysis.^[5] Unfortunately, aggregation and/or fusion of noblemetal NPs is commonly observed during catalytic reactions using existing carriers, such as silica,^[6] zeolites,^[7] and carbon,^[8] owing to the high surface energies of free noble-metal NPs. Thus, in order to preserve the unique properties of NPs in a wide range of applications, it is necessary to search for new types of carriers that overcome the NP aggregation challenge and, ideally, simultaneously impart new functionalities to the catalyst.

Metal-organic frameworks (MOFs), synthesized by means of assembly of metal ions and organic ligands in an appropriate solvent, have recently emerged as promising new porous

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crystalline materials because of their large internal surface areas, uniform but tunable cavities, and tailorable chemistry.^[9] As a result, MOFs have been widely used in gas storage,^[10] separation,^[11] chemical sensing,^[12] and heterogeneous catalysis^[13] in the past decade. In addition, as unique host matrices, MOFs can offer a platform for loading functional species, resulting in MOF-based composites with novel chemical and physical properties.^[12,13d,e] Consequently, recent research interest has gradually shifted from the preparation of new MOF structures to the incorporation of functional materials into the MOF matrices for potential applications.^[13c] Currently, NP/MOF composites are commonly prepared by reduction of a metal precursor within a MOF template,^[14] or by encapsulating presynthesized NPs in MOFs.^[15] Unfortunately, in the former case, such a preparation strategy possesses intrinsic limitations, namely, NP aggregation, poor control over NP size, and restricted species composition. Moreover, the precursor can actually diffuse out through the pores of MOFs to form NPs on the external surface, rendering the size and shape selectivity of MOF-based catalysts hard to realize. Great efforts have been made to overcome the above-mentioned drawbacks. In the latter encapsulation strategy, pre-synthesized nanoparticles are usually stabilized with certain surfactants, capping agents, or even ions and usually the hydrodynamic radius of the NPs is much larger than the cavity size of the MOF. The nanoparticles do not occupy the MOF cavities, but instead are surrounded by the MOF lattice. Recently, we developed an encapsulation strategy that achieved incorporation of various NPs modified by polyvinylpyrrolidone (PVP) within zeolitic imidazolate framework material (ZIF-8) under ambient conditions.^[16] Other members of the MOF family with carboxylic-acid-based ligands, by contrast, show promise for future applications owing to their greater chemical variety, better thermal or chemical stability, and larger aperture and pore size. To the best of our knowledge, a general and versatile strategy for incorporation of NPs in MOFs with carboxylic acid-based ligands has not yet been well developed, in spite of the need and the significance of applications of NP/MOF hybrid materials.

In the work reported here, we have developed the encapsulation of noble-metal NPs in MOFs with carboxylic-acid-based ligands, which is the largest branch of the MOF family. The obtained NP/MOF composites were employed as novel catalysts in heterogeneous catalysis. Interestingly, in addition to the fact that NPs can be successfully incorporated inside various MOFs with carboxylic-acid-group ligands, such as UiO-66, NH₃-UiO-66, and NH₃-MIL-53, the NP/MOF composites exhibited



Scheme 1. The catalytic reactions of Pt/UiO-66 composites.

excellent shape-selectivity in olefin hydrogenation, aqueous reaction in reduction of 4-nitrophenol, and higher molecular diffusion rate in CO oxidation (**Scheme 1**).

Noble-metal NPs with uniform size were successfully encapsulated in MOFs with carboxylic-acid-group ligands. UiO-66, a class of zirconium-based MOFs^[17] with molecular formula $Zr_6O_4(OH)_4$, was chosen as an example in this work to study the encapsulation of Pt NPs because of its high surface area and unprecedented stability. Pt NPs with uniform sizes were synthesized by reported methods^[18] and modified with PVP. In

a typical experiment, 5 mL solution of ZrCl₄ (8.75 mM) and 5 mL solution of terephthalic acid (benzene-1,4-dicarboxylic acid, BDC) (8.01 mM) were mixed in a glass vial. Subsequently, 1.2 mL acetic acid and 0.2 mL Pt NP solution were added to afford a homogeneous mixture, and the reaction was kept at 120 °C for 24 h without stirring . Products were collected by centrifugation and then washed with dimethylformamide (DMF) and methanol. Importantly, during the encapsulation strategy, PVP favors the continuously forming fresh surfaces of the growing MOF spheres. Thus, NPs can successfully adhere to the growing MOF crystal without altering the crystal structure. Moreover, the encapsulation process was further investigated by means of time-dependent transmission electron microscopy (TEM) analysis. Figure S1a (Supporting Information) shows a TEM image of the products obtained after a reaction time of 30 min, which were hybrid spheres with an average diameter of 50 nm. The hybrid spheres were composed of coordination polymer and encapsulated Pt nanoparticles. The hybrid spheres gradually grew larger (150 nm at a reaction time of 1 h, Figure S1b), and exhibited a structure with a NP-rich core and NP-free shell owing to the depletion of the free nanoparticles during the reaction. The hybrid spheres evolved into octahedron crystals (320 nm) after 3 h (Figure S1c). After 24 h, the perfect octahedron crystal structure of Pt/UIO-66 can be obtained (Figure S1d). In addition, the encapsulation strategy is suitable for various solvents, including water, DMF, methanol, and benzyl alcohol, and is applicable to a broad range of classes of MOFs (Figure 1).

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Figure 2a shows the TEM image of the obtained Pt/UiO-66 composites, exhibiting intact crystal morphology. Notably, no Pt NP aggregation was observed inside the UiO-66 frameworks. The crystal structure, thermostability, and porosity of Pt/UiO-66 composites were further characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), and nitrogen-sorption measurements, respectively. Compared to the XRD spectrum

of intrinsic UiO-66, no significant loss of crystallinity can be detected in the XRD pattern (Figure 2b) after loading with Pt NPs. The absence of Pt peaks could presumably be attributed to the low NP concentration as well as the encapsulation by UiO-66. TGA spectra demonstrate the effect of Pt NP loading on the thermal stability of UiO-66 (Figure 2c). The decomposition temperature of Pt/UiO-66 was 499 °C, which is only marginally lower than that of intrinsic UiO-66 crystals (505 °C), possibly due to the movement and decomposition of PVP chains (PVP glass transition temperature, 175 °C; decomposition



Figure 1. TEM images of different kinds of Pt/MOFs. a) Pt/NH₃-UiO-66. b) Pt/MIL-53 (120 °C). c) Pt/MIL-53 (180 °C). d) Pd/UIO-66.



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Figure 2. Structure properties of Pt/UiO-66. a) TEM image of Pt/UiO-66. b) Powder XRD patterns of UiO-66 and Pt/UiO-66. c) TGA spectra of UiO-66 and Pt/UiO-66. d) The nitrogen adsorption-desorption isotherm at 77 K of UiO-66 and Pt/UiO-66.

temperature, 435 °C). The steep increase in N₂ uptake at low relative pressure in the nitrogen-sorption spectra indicates a microporous structure of UiO-66 and Pt/UiO-66. The lower surface area of Pt/UiO-66 (1340 m² g⁻¹) composites compared with intrinsic UiO-66 (1492 m² g⁻¹) is mainly due to the contributions of nonporous Pt NPs, and the existence of PVP in the composites (Figure 2d).

Liquid-phase hydrogenation of hex-1-ene, cyclooctene, transstilbene, cis-stilbene, triphenyl ethylene, and tetraphenyl ethylene were carried out to study the molecular-size selectivity of Pt/UiO-66 composites. The difference of catalytic activity is mainly due to the difference in the size of the reactant. As the molecular size of these reactants gradually increased, the conversion rate of reactants decreased correspondingly (Figure 3a). For hexene, Pt/UiO-66 composites showed high activity with 100% conversion after 24 h reaction, indicating that there was no significant diffusion limitation caused by the UiO-66 frame. Hex-1-ene molecules (2.5 Å) are small enough to diffuse through the pore aperture of the UiO-66 frame (6 Å).^[19] For other reactants, Pt/UiO-66 showed different catalytic activity after 24 h reaction (cyclooctene (5.5 Å), 65.99% conversion; trans-stilbene (5.6 Å), 35%; triphenyl ethylene (5.8 Å), 8%), mainly owing to the retarded diffusion of reactant in the MOF matrix. In contrast, Pt/UiO-66 composites showed no propensity to catalyze the hydrogenation of the sterically more demanding tetraphenyl ethylene (6.7 Å), which is consistent with the pore size for UiO-66 (6 Å) and also suggests the absence of Pt NPs on the outer surface of the composite. In the control experiment, pure UiO-66 crystals showed no

catalytic activity toward olefins while pure Pt NPs supported on carbon nanotubes displayed indiscriminating catalytic capability towards olefin hydrogenation (hex-1-ene 100%, cyclooctene 100%, cis-stilbene 100%, trans-stilbene 100%, triphenyl ethylene 89%, and tetraphenyl ethylene 18%). Note that, in this case, triphenyl ethylene and tetraphenyl ethylene showed lower catalytic activity, probably owing to steric hindrance of the molecules, making it difficult for the C=C bond to contact the Pt NP surface. The high reusability of Pt/UiO-66 composites for hydrogenation of hex-1-ene is demonstrated from the observation of similar conversion efficiencies for three consecutive recycle runs (Figure S3b, Supporting Information). The porous structures of UiO-66 are preserved after catalytic reaction and no significant degradation was detected by XRD measurement (Figure S3c), though a minor number of small pores could be observed in the middle of UiO-66 after catalytic reaction (Figure S3d). In addition, cis-cyclooctene was taken as an example to study the catalytic activity of Pt/UiO-66 composites that were treated at different temperatures (room temperature, 120 °C, and 340 °C) under nitrogen gas (Figure S3a). The catalytic activity of Pt/UiO-66 treated at 120 °C was similar to that treated at room temperature, while Pt/UiO-66 treated at 340 °C showed the highest catalytic activity. The discrepancy is likely due to the decomposition of PVP molecules surrounding the NPs at elevated temperature, making it easier for reactants to touch the Pt catalytic centers.

The Pt/UiO-66 composites were also tested for catalytic reduction of 4-nitrophenol by $NaBH_4$ in water. It is well known that the reaction does not proceed without a catalyst but

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Figure 3. Catalytic properties of Pt/UiO-66 composites. a) Size-selective hydrogenation of olefins catalyzed by Pt/UiO-66 composite (2% content of 2.9 nm Pt NPs). b) UV-vis spectra showing gradual reduction of 4-nitrophenol over Pt/UiO-66. c,d) CO oxidation catalysis by Pt/UiO-66. Conversion versus temperature (c) and at 180 °C versus time (d).

proceeds rapidly in the presence of a metallic surface.^[20] The reduction mixture was monitored by UV-vis absorption spectroscopy after the addition of Pt/UiO-66 composites (Figure 3b). The absorption peak of 4-nitrophenol aqueous solution was located at 317 nm while this characteristic peak red-shifted to 400 nm after NaBH₄ had been added. When pure Pt NPs were used as the catalyst, the absorbance of the reaction mixture at 400 nm gradually decreased as the reaction proceeded, along with a concomitant increase of the 300 nm peak corresponding to 4-aminophenol. However, interestingly, the characteristic peak of 4-aminophenol did not appear when Pt/UiO-66 composites were used as the catalyst (Figure S4a, Supporting Information), presumably as a result of the formation of intermediate products in the limited pore space of UiO-66. The complete reduction of 4-nitrophenal with Pt/UiO-66 required more time than with pure Pt NPs because of the reduced molecular diffusion rate caused by the uniform pores and limited cavity size. In the control experiment, UiO-66 exhibited no catalytic activity with respect to the reduction of 4-nitrophenol. The reusability of Pt/UiO-66 composites as a catalyst for the reduction of 4-nitrophenol was demonstrated again by the observation of similar conversion efficiencies for three consecutive recycle runs. The crystal structure of UiO-66 was preserved after catalytic reaction with some degree of degradation detected by XRD measurement (Figure S4b). A small number of pores existed in the middle of UiO-66 after catalytic reaction, as observed in the TEM image (Figure S4d), presumably owing to the production of a large quantity of H₂ resulting from the decomposition of NaBH₄.

To assess the catalytic functionality of the Pt/UiO-66 composite for gas-phase reactions, we carried out the CO oxidation reaction at room temperature and at higher temperatures. As shown in Figure 3c, the Pt/UiO-66 composite began to catalyze the oxidation of CO at 90 $^\circ\mathrm{C}$ and a conversion rate of near 100% is achieved at 180 °C. The activity of Pt/UiO-66 composites was higher than that of the Pt/ZIF-8 composites as a catalyst for CO oxidation, probably due to the large aperture size of UiO-66 (6 Å) compared to ZIF-8 (3.4 Å), thus enhancing the diffusion rate. Notably, Pt/UiO-66 composites retained good catalytic activity for as long as 30 h at 180 °C (Figure 3d). Nevertheless, UiO-66 exhibited no catalytic activity with respect to the CO oxidation reaction over the whole temperature range. After the catalytic reaction, the crystallinity of the Pt/UiO-66 host matrix remain unchanged, although a few MOF particles had a mild degree of collapse at the corner, which can all be confirmed by the TEM image and XRD spectra before and after CO oxidation (Figure S5, Supporting Information). More importantly, no Pt NP aggregation was observed after CO oxidation, as confirmed by TEM measurement. Thus, the accessibility of embedded Pt NPs modified with PVP in UiO-66 for catalysis has been examined for the first time for CO oxidation; high activity was exhibited.

In conclusion, an efficient NP encapsulation strategy for MOFs has been successfully extended to various kinds of MOFs with carboxylic-acid-group ligands. Nobel metal NPs of uniform size were encapsulated completely inside the MOF matrix without sticking to the outer surface. The obtained Pt/UiO-66 composites exhibited excellent shape-selective



catalytic properties in olefin hydrogenation, aqueous reaction in 4-nitrophenol reduction, and enhanced molecular diffusion in CO oxidation. Importantly, the MOF matrix demonstrated convincing advantages as a catalytic carrier, not only preventing the aggregation of NPs but also imparting new functionalities to the catalyst composite. Furthermore, the results shed light on new ways to develop high-performance heterogeneous catalysts by using functionalized cavities of MOFs as hosts for different metal NPs.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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