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Engineering channels of metal–organic frameworks to enhance catalytic selectivity

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This report describes a facile strategy to enhance the catalytic selectivity by tuning the pore sizes of metal–organic frameworks (MOFs) in nanoparticles (NPs)/MOF composite catalysts. A general post-synthetic modification method was used to adjust the pore sizes of MOFs by using anhydrides with different chain lengths to react with amino groups in the ligands. The modified NPs/MOF catalysts exhibited enhanced size selectivity performance in the hydrogenation of olefins, which revealed the flexibility of MOFs as supporting materials for heterogeneous catalysis.

As a relatively new type of crystalline porous solids, metal–organic frameworks (MOFs) have drawn great attention in recent decades.^{1,2} They are hybrid organic–inorganic supermolecular materials, the extended networks of which are formed by connecting metal ions or clusters with bi- or multi-nodal organic linkers.^{3,4} Compared to zeolites, MOFs can be achieved through numerous combinations of metal nodes and organic linkers. Up to now, more than 20 000 different MOFs have been designed and reported worldwide.⁵ Featuring light weight, high specific surface area and outstanding flexibility, MOFs are considered as good candidates in applications of gas storage,^{6,7} separation,⁸ sensing,^{9,10} drug delivery,¹¹ photocatalysis,¹² as well as chemical catalysis.^{3,13–18} In the last few years, the encapsulation of metal nanoparticles (NPs), such as Au,¹⁹ Pd,^{20–22} Pt^{23,24} and Ru,²⁵ into MOFs has been frequently reported.^{26,27} The unique porous nature of MOFs influences the activity and selectivity of the nanoparticle

catalysts while still maintains the transport activity of reactant and product.^{28–30} However, these reported NPs/MOF composites achieved their catalytic selectivity by simply using MOFs with suitable intrinsic pore sizes. Based on this traditional idea, various MOFs need to be applied to different chemical reactions. Since the channel environment of MOFs can be conveniently engineered through modification of organic ligands,³¹ it is worthwhile to develop a general approach to adjust the pore size of NPs/MOF composites, in order to fulfil the requirement of different catalysis reactions.

The current strategy for engineering the channel environment of NPs/MOF composites is the encapsulation of NPs into different kinds of MOFs. MOFs can either serve as templates for the growth of NPs within their channels,^{20,32–35} or directly grow around the pre-synthesized NPs.^{14,24,28,36–38} A large variety of NPs/MOF catalysts were fabricated based on these strategies. However, the pore sizes of these catalysts were fixed once the target MOFs were selected; therefore, one need to carefully choose a specific kind of MOFs to match the size of reactants and products in a catalytic reaction. Moreover, the stability of a MOF is highly dependent on its metal–ligand interaction. Some MOFs with suitable pore sizes may collapse upon exposure to chemicals or thermal treatment,^{11,39} limiting their applications in chemical catalysis. Hence, NPs/MOF composites with suitable size as mentioned above cannot be practically used in the reaction. To the best of our knowledge, there are currently few reports about engineering the pore size of NPs/MOF catalysts for enhancing catalytic selectivity.

Herein, we have reported an example to demonstrate the possibility of tuning pore sizes of NPs/MOF composites based on the requirement of catalytic reaction by post-synthetic modification (PSM). Amino groups in the ligands were modified with alkyl chains of different lengths and thus the pore sizes can be adjusted. Both the intrinsic and modified NPs/MOF composites were employed respectively as heterogeneous catalysts for olefin hydrogenation (Scheme 1), and the modified ones exhibited enhanced size selectivity.

A zirconium-based MOF, *i.e.* UiO-66-NH₂, was selected as the supporting material in this study due to its thermal and

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Scheme 1 The catalytic reaction of modified Pt/Uio-66-AMn composites.

chemical stability,⁴⁰ while amino groups on ligands can be easily modified by PSM *via* the reaction between amino groups and anhydrides. PVP-stabilized Pt NPs with size of 3 nm were synthesized first.⁴¹ Pt/Uio-66-NH₂ composite was then obtained through solvothermal synthesis in the presence of Pt NPs. Transmission electron microscopic (TEM) images of intrinsic Pt/Uio-66-NH₂ (Fig. 1a and Fig. S1, ESI†) showed a regular octahedron crystal (200 nm) with smooth surface. Pt NPs were successfully encapsulated at the center of octahedron crystals, proving the effectiveness of the encapsulation strategy. For the PSM of Pt/Uio-66-NH₂, three anhydrides were used, *i.e.*, acetic anhydride, butyric anhydride and hexanoic anhydride, and the resulting composites were denoted as Pt/Uio-66-AM1, Pt/Uio-66-AM3 and Pt/Uio-66-AM5 respectively, where the numbers stood for attached carbon chain length. After PSM in chloroform solution, no obvious changes in morphology were observed from Pt/Uio-66-AM1, Pt/Uio-66-AM3 and Pt/Uio-66-AM5, confirming their stability under the PSM conditions (Fig. 1b and c).

Fig. 1
Pt/Uio-66-AMn

In addition, X-ray diffraction (XRD) patterns of Pt/Uio-66-AM1, Pt/Uio-66-AM3 and Pt/Uio-66-AM5 showed similar patterns as intrinsic Pt/Uio-66-NH₂, indicating that the UiO-66-NH₂ in the composite still maintained its crystal structure after PSM (Fig. 2a). The XRD peaks of Pt NPs could not be identified probably due to their small size and low concentration. To further confirm the successful modification of Pt/Uio-66-NH₂ composites, FT-IR spectra of all the samples were collected and compared (Fig. 2b). As is generally known, the reaction between UiO-66-NH₂ and the anhydrides would result in the formation of amides, and several changes can be observed from the FT-IR spectra. Firstly, the bands at 1673 cm⁻¹ of the modified samples corresponded to C=O stretching after the formation of amides.^{42,43} In addition, for modified samples UiO-66-AM3 and -AM5, several bands ranging from 2850 to 2990 cm⁻¹ were witnessed, which were assigned to the sp³ C-H stretching of aliphatic compounds due to the introduced -CH₂- groups during the modification process. These two bands did not appear in UiO-66-NH₂, indicating the successful PSM reaction.

Due to the presence of the alkyl groups after PSM, the surface area and pore size of the composites were supposed to be decreased gradually. To confirm this, the nitrogen adsorption/desorption isotherms (Fig. 3a) at 77 K were plotted, and the isotherm plots of Pt/Uio-66-NH₂ and three modified composites exhibited similar shapes. Steep increase in nitrogen uptake was observed in a very low relative pressure region, indicating physical adsorption in micropores. When micropores were filled, low slope region in middle of isotherms showed multilayer adsorption. Calculated results of Brunauer–Emmett–Teller (BET) surface area were listed and compared in Table S1 (ESI†). BET surface area of intrinsic UiO-66 is 1492 m² g⁻¹. When Pt NPs were loaded, this composite experienced lower surface area (1340 m² g⁻¹) due to the presence of Pt.²⁴ In this case, it is certain that Pt/Uio-66-NH₂ has even lower surface area (1222 m² g⁻¹) owing to additional amino groups. With the chain length of anhydride increased, the surface area of modified MOFs decreased gradually and Pt/Uio-66-AM5 with the longest functional groups displayed the lowest surface area among our four samples. Pore size distribution of the samples was illustrated in Fig. 3b. With the alkyl chain length increased, pore width was reduced from approximately 5.5 Å to 5.2 Å.

Selective hydrogenation of olefins is one of the most important chemical process in industry, which contributes to the production of numerous fine chemicals. With the modification

Fig. 2 (a) Powder XRD pattern and (b) FT-IR spectra of Pt/Uio-66-NH₂ and three modified composites.

Fig. 3 (a) Nitrogen adsorption-desorption isotherms at 77 K and (b) pore size distribution of Pt/Uio-66-NH₂ and three modified composites.

of pore sizes, the NP/MOF composites are expected to possess improved catalytic selectivity to fulfil the requirement of different catalysis reactions. The catalytic selectivity of these four samples were tested in liquid-phase hydrogenation of triphenylethylene, *trans*-stilbene and cyclooctene. As listed in Table S2 (ESI[†]), all four composites showed barely no catalytic activity for hydrogenation of triphenylethylene, indicating that the size of triphenylethylene molecules exceeds the pore apertures of Uio-66-NH₂ and the modified samples, namely, CQC double bonds could not contact with Pt NPs encapsulated inside MOFs.

Being smaller in size than triphenylethylene (10.71 Å × 8.76 Å × 6.48 Å), *trans*-stilbene (11.65 Å × 5.06 Å) can be diffused into our MOF composites and then be hydrogenated (Fig. S3, ESI[†]). When comparing conversion data of these four samples, a clear trend was found: with lengths of the attached functional groups increased, conversions of *trans*-stilbene were reduced from 49% to 4% due to retarded diffusions of *trans*-stilbene into micropores. Besides, hydrogenation of cyclooctene (5.29 Å × 5.21 Å × 3.55 Å) showed a similar trend, but higher conversion as a result of its smaller molecular structure size. Conversions of cyclooctene and *trans*-stilbene were plotted in Fig. 4. The ratio between cyclooctene conversion and *trans*-stilbene conversion could be considered as selectivity towards cyclooctene. A clear trend of improved selectivity was witnessed with alkyl chain lengths increased until Pt/Uio-66-AM3 exhibited the highest selectivity. Pt/Uio-66-AM5 showed very low catalytic performance due to a restricted diffusion of reactants caused by long alkyl chain on ligands, suggesting it is not an

ideal catalyst for hydrogenations of cyclooctene and *trans*-stilbene in this study. After hydrogenation experiments, the NPs/MOF composites were collected and characterized by TEM images, FT-IR and ¹H-NMR. These results showed no obvious changes in both morphology and crystallinity (Fig. S2, S4 and S5, ESI[†]), which proved the stability and reliability of the catalysts.

In conclusion, pore sizes of NPs/MOF composites was modified by utilizing chemical variety of MOFs. Modified NPs/MOF composites showed enhanced size selectivity in olefin (triphenylethylene, *trans*-stilbene, cyclooctene) hydrogenation corresponding to the increased alkyl chain lengths, until Pt/Uio-66-AM5 blocked most of the reactants outside. This study revealed the advantages of MOFs as supporting materials for heterogeneous catalysis: by utilizing their incredible chemical variety, environments of pores and channels can be conveniently tailored to meet the requirements of different chemical reactions.

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Conflicts of interest

There are no conflicts to declare.

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Fig. 4 Size-selective hydrogenation catalytic performance of Pt/Uio-66-NH₂ and three modified composites.

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