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In situ Synthesis of Sub-nanometer Metal Particles on Hierarchically Porous Metal-Organic Frameworks via Interfacial Control for Highly Efficient Catalysis

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In this work, we developed a strategy to in situ synthesize sub-nanometer metal particles/hierarchically mesoporous metal-organic frameworks (MOFs) composites in emulsion. In this route, water droplets in the emulsion acted as both solvent of metal precursors and template for hierarchical mesopores of MOFs, and the surfactant was emulsifier and reductant for generating metal particles. Au/Zn-MOF (MOF formed by Zn^{2+} and methylimidazole), Ru/Zn-MOF, Pd/Zn-MOF, and Au/Cu-MOF (MOF formed by Cu^{2+} and methylimidazole) were prepared using this method, in which ultrafine metal particles (e.g. 0.8 nn) were immobilized uniformly on hierarchically mesoporous MOFs. Au/Zn-MOF and Au/Cu-MOF showed outstanding catalytic performances for selective aerobic oxidation of cyclohexene to 2-cyclohexen-1-one in the absence of initiator, and Ru/Zn-MOF was very active and selective for hydrogenation of diphenyl sulfoxide to diphenyl sulfide. In addition, the catalysts were also very stable in the reactions.

Introduction

Metal-organic frameworks (MOFs) represent an emerging class of crystalline materials with diverse and uniform porosity, which are very promising for applications in heterogeneous catalysis.[1-3] Hierarchically porous supports are particularly desired in many catalytic processes because they integrate the advantages of pores with different sizes in diffusion and adsorption of the species in reaction systems.[4-7]

Emulsions are made of liquids, which can dissolve both polar and non-polar substances. The dispersed droplets in emulsions are both highly deformable and easily removable after the accomplishment of templating. Emulsions offer advantages for preparing a wide variety of materials with controlled particle size, morphologies and composition at mild condition.[8-11] Utilization of emulsions as heterogeneous media is a way to obtain porous materials with hierarchical porosity and various structures.

Sub-nanometer metal particles have unique electronic structures, surface geometric effects, and intrinsic chemical properties.[12-14] For instance, it has been reported that Au particles smaller than 2 nm were effectively for catalyzing oxidation reactions and exhibited size-sensitive catalytic properties.[15,16] Controlling the size of metal particles is very difficult because aggregation readily occurs due to high cohesive energy and low melting points.[17,18] Immobilization of sub-nanometer metal particels uniformly on hierarchically porous MOFs is very interesting in different fields, but still remains a major technical challenge.

In this work, we found that the bio-based surfactant sorbitol-alkylamine (SAAS-C_{12}, Scheme S1)[19] could form stable W/O emulsion. A method to synthesize sub-nanometer metal particles/hierarchically mesoporous MOFs composites was proposed using water droplets in the emulsion as template of the hierarchical pore and solvent of precursors, and the surfactant acted as both emulsifier and reductant in situ. Au/Zn-MOF (MOF formed by Zn^{2+} and methylimidazole), Ru/Zn-MOF, Pd/Zn-MOF, and Au/Cu-MOF were prepared using this method, in which the ultrafine metal particles (e.g. 0.8 nm) were immobilized uniformly on hierarchically mesoporous MOFs. The catalysts demonstrated outstanding catalytic performances because they integrated the advantages of ultrafine metal particle catalysts and the hierarchically porous supports.

Results and discussion

The formation of emulsion was confirmed by fluorescence microscopic analysis with water soluble dye (Rhodamine B), and the size distribution of water droplets in emulsion was determined using dynamic light scattering (DLS). The sizes of water droplets ranged from about 5 nm to 60 nm. The results

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are discussed in detail in the supporting information (Fig. S1 and the corresponding discussion). Taking the synthesis of Au/Zn-MOF as the example, the proposed method to prepare metal particles/MOF composites is illustrated in Scheme 1, and the details are given in the method section. In the preparation, Zn^{2+} and Au^{3+} were dissolved in water droplets, and the ligand methylimidazole was in oil phase. Zn-MOF was firstly formed at water/oil interfaces surrounding the water droplets which acted as templates for the mesopores. Then Au^{3+} ions were reduced in situ after heat treatment by the secondary amine and hydroxy groups in the surfactant, which acted both as emulsifier and reductant.[20,21] Therefore, the Au^{3+} ions were reduced by the surfactant in situ after heating from 25 °C to 35 °C, and the yielded Au particles were immobilized on the wall of the porous MOFs. Au/Zn-MOF composites were obtained after removing the solvents. It can be known that the characteristics of the pores of the composites is closely related with the size of droplets (Fig. S1). In addtion, hierarchically porous MOFs without metal particels could also be prepared in the absence of Au^{3+} (Fig. S2).
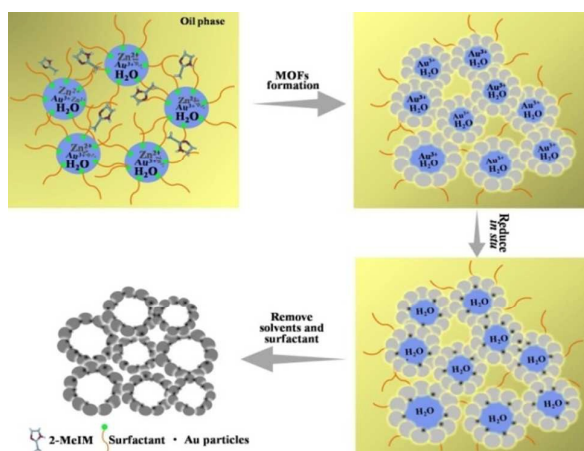
Scheme 1 Schematic illustration of the method for in situ preparation of Au/Zn-MOF in emulsion.

The transmission electron microscopy (TEM) images of Au/Zn-MOF are shown in Fig. 1A. The HRTEM and high-angle annular dark-field HAADF images with a high magnification showed that sub-nanometer Au particles (0.8 nm) were decorated uniformly on the hierarchically porous Zn-MOF (Fig. 1B and 1C). The corresponding energy dispersive X-ray spectroscopy (STEM-EDX) elemental mapping analysis (Fig. 1C) also revealed that Au particles were evenly immobilized on the supports. Powder X-ray diffraction (PXRD) pattern of the obtained Zn-MOF was the same as that reported,[22] and patterns of Zn-MOF and Au/Zn-MOF were nearly the same (Fig. 1D). In the XRD pattern of Au/Zn-MOF, the diffraction peaks for Au particles were very weak due to their small size. The porosity of Au/Zn-MOF was characterized by N_2 adsorption/desorption measurement. The BET surface area, total pore volume, and average pore diameter were provided in Table S1. The size distribution of the mesopores of Au/Zn-MOF was similar to that of water droplets in the emulsion (Fig.

1E, Fig. S1), indicating the template function of water droplets. The X-ray photoelectron spectroscopy (XPS) analysis of Au (Fig. 1F) emerged two pairs of spin-orbit doublets, indicating the existence of Au^0 at 84.8 and 88.5 eV and Au^+ at 86.4 and 91.3 eV. The positive shift in binding energy of Au $4f_{7/2}$ confirmed the electronic effect of small particle size.[23] Furthermore, a shift to higher binding energy of Au $4f_{5/2}$ was consistent with the negative shift of Zn^{2+} spectrum with respect to the origin Zn-MOF (Fig. S3). Thus, the interaction between Au particles and Zn^{2+} existed in the composites,[24,25] which also indicated the immobilization of Au on the support. In this route, the water droplets in emulsion acted both as solvent of the metal precursors (Zn^{2+} and Au^{3+}) and template for the mesopores of Zn-MOF. The surfactant behaved as emulsifier and reducing agent of Au^{3+}, Zn-MOF was firstly formed from Zn^{2+} and the ligand around water droplets in the emulsion, leaving Au^{3+} ions in water droplets and being isolated by the mesopores of Zn-MOF. Due to the wide size distribution of water droplets in the emulsion, hierarchically mesoporous Zn-MOF was formed. After Au^{3+} ions were reduced in situ, the Au particles were immobilized uniformly on Zn-MOF. For comparison, the experiment was conducted by adding $HAuCl_4$ solution after the formation of Zn-MOF. Clearly, the agglomeration of Au particles occurred as shown in Fig. S4, further showing the advantage of the in situ method proposed in this work. In addition, the size of Au particles could be tuned by the concentration of Au precursor using the procedures, and Au/Zn-MOF composites with average Au particle sizes of 0.8 nm, 1.0 nm, 1.5 nm, 2.0 nm were obtained (Fig. 1, Fig. S5).
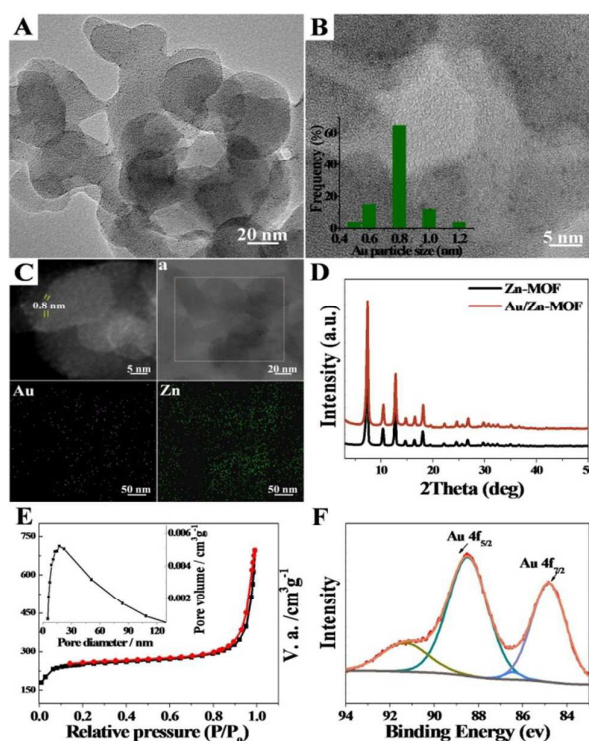

Fig.1 Structural characterizations of Au/Zn-MOF. (A) Representative TEM image of Au/Zn-MOF; (B) High-resolution TEM (HRTEM) image

and down-inset is the particle size distribution of Au particles; (C) Representative HAADF-STEM image and STEM-EDX elemental mapping of Au/Zn-MOF, the selected area is framed in (a); (D) XRD patterns of the obtained Au/Zn-MOF (b) and Zn-MOF (a); (E) N_2 adsorption/desorption isotherms and the mesopore size distribution (inset); (F) XPS spectra of Au 4f; Au loading was 0.8 wt% determined by ICP-AES.

Ru/Zn-MOF and Pd/Zn-MOF were also prepared by this method using $RuCl_3$ and $Pd(NO_3)_2$ as metal precursors, respectively. The characterizations showed that Ru or Pd particles of 0.8 nm could also be supported on hierarchically porous Zn-MOF uniformly (Fig. 2). These composites were characterized by TEM, XPS, XRD, N_2 adsorption/desorption methods, and the corresponding results were provided in Fig. S6 and Fig. S7. The BET surface area, total pore volume, and average pore diameters of the composites were listed in Table S1.
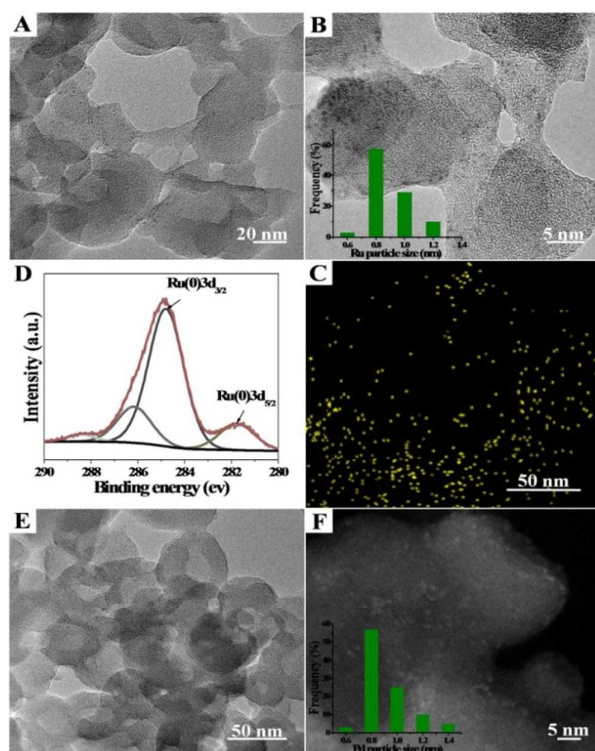

Fig.2 Characterizations of Ru/Zn-MOF and Pd/Zn-MOF composites. (A) Representative TEM image of Ru/Zn-MOF; (B) HRTEM images and down-inset is the particle size distribution of Ru particles; (C) STEM-EDX elemental mapping of Ru/Zn-MOF, Ru elements; the selected area is framed in (A); (D) XPS spectra of Ru 3d; (E, F) Representative TEM image and HAADF-STEM image of Pd/Zn-MOF. Ru loading in Ru/ZIF-8 was 0.6 wt% and Pd loading in Pd/Zn-MOF was 2.3 wt% determined by ICP-AES.

The size of metal particles is a crucial factor for the catalytic performance in heterogeneous catalysis.[26] It has been shown that Au nanoparticles of small size could selectively catalyze

oxidation of alkenes, which is a very important reaction.[27,28] However, performing the oxidation of alkenes without addition of initiator both selectively and efficiently remains a challenge.[29] We studied the catalytic performances of the Au/Zn-MOF composites with different Au particles sizes for aerobic oxidation of cyclohexene to 2-cyclohexen-1-one in the absence of initiator, and the results are given in Table 1.The catalyst with Au size of 0.8 nm had outstanding activity and selectivity. Au/Zn-MOF catalysts with larger Au particles showed lower activity and selectivity. The stability of the catalyst with Au size of 0.8 nm was studied, and the activity and selectivity did not change after reused four times (Fig. S8a). The TEM and XRD characterizations indicated that the morphology and structure of the catalyst did not change obviously after four cycles (Fig. S8b and S8c), further indicating the excellent stability of the catalyst.

Table 1. Conversion and selectivity of cyclohexene oxidation over Au/Zn-MOF catalysts with different Au particle sizes.[a]

Entry	Au size (nm)	C (%)	Selectivity (%)		
			![ketone]	![alcohol]	![epoxide]
Au/Zn-MOF[b]	0.8	82	98	—	—
Au/Zn-MOF[c]	1.0	79	95	< 2	—
Au/Zn-MOF[d]	1.5	64	81	11	< 3
Au/Zn-MOF[e]	2.0	34	66	21	—
Au/Cu-MOF[f]	0.8	77	97	—	< 1
Zn-MOF	—	7.4	23	19	14

[a] Reaction conditions: 30 mg catalyst, 0.5 mmol cyclohexene, 2 ml dioxane, 100 °C, 1 MPa O_2, 8 h; [b] Au loading 0.8 wt%; [c] Au loading 1.1 wt%; [d] Au loading 1.3 wt%; [e] Au loading 2.0%; [f] Au loading 0.6 wt%; Metal loadings were determined by ICP-AES; The conversion and selectivity were determined by gas chromatography, and conversion was defined based on the initial cyclohexene present. C = Conversion.

To further confirm that ultrafine Au particle was crucial for the high activity and selectivity, Au particles with size of 0.8 nm on the Cu-MOF were also prepared by this route, and the characterizations are provided in Fig. S9. The activity and selectivity of the reaction over Au/Cu-MOF were also very high as shown in Table 1.

In order to study the catalytic nature of Au particles, reaction profiles with time over Au/Zn-MOF with Au particles

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of 0.8 nm and 1.5 nm were investigated, and the results are given in Fig. 3. It can be observed that the conversion and selectively of the reaction over the catalyst with smaller Au particles (0.8 nm) were higher at all reaction time. The mechanism of reaction has been well studied.[30,31] In the reaction, cyclohexene was oxidized to form hydroperoxide, which can be further transformed into 2-cyclohexen-1-one immediately, or react with substrate to form cyclohexen-1-ol and epoxide. It can be deduced from the results in Fig. 3 that both reaction rates from cyclohexene to intermediate hydroperoxide and further to 2-cyclohexen-1-one over the smaller Au particles were higher, yielding higher conversion and selectivity.
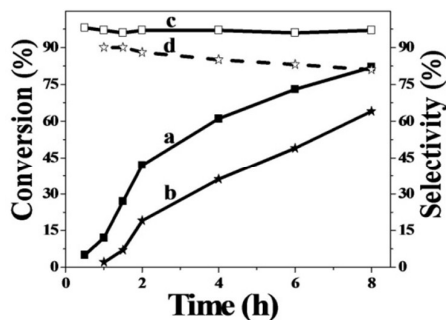

Fig.3 Dependence of cyclohexene conversion and 2-cyclohexene-1-one selectivity on reaction time over Au/Zn-MOF catalysts at the reaction conditions of Table 1. (a, c) Conversion and selectivity with 0.8 nm Au particle; (b, d) Conversion and selectivity with 1.5 nm Au particle.

Oxidation and reduction of sulfur-based compounds have been studied widely.[32] However, designing of highly efficient catalysts is still desirable. It was reported that heterogeneous Ru nanoparticle catalyst could accelerate the hydrogenation of sulfoxides to sulfides.[33] Herein, we studied the catalytic performance of the obtained Ru/Zn-MOF with particle size of 0.8 nm, and the results are presented in Table 2. The activity of Ru/Zn-MOF was much higher than commercial Ru/C catalyst with Ru size of 2.5 nm (characterization in Fig. S10) and the reported Ru/TiO$_2$ catalyst with Ru particle of 1.6 nm.[33] Moreover, the reusability of the Ru/Zn-MOF with Ru particle size of 0.8 nm was checked, which showed no change of the activity after recycling 5 times (Fig. S11a). The morphology and XRD pattern of the used catalyst were not changed (Fig. S11 b and c), showing excellent stability of the catalyst.

Table 2. Catalytic performances of Ru/Zn-MOF for the hydrogenation of diphenyl sulfoxide. [a]

Entry	Ru size (nm)	T (°C)	C[b]	Y[c]	TOF[d] (h^{-1})
1[e]	0.8	95	>99	98	207.6
2[f]	2.5	95	21	19	2.4
3[g]	1.6	100	>99	>99	20.8

[a] Reaction conditions: catalyst (40 mg), diphenyl sulfoxide (0.5 mmol), 1,4-dioxane (2 ml), 5 atm H$_2$, 1 h; [b, c] Determined by GC using isopropanol as internal standard; [d] TOF denotes moles of sulfide per mole of Ru per hour; The Ru loading was 0.6 wt% as determined by ICP-AES; [e] Ru/Zn-MOF catalysts synthesized by the route proposed herein; [f] Commercial Ru/C catalyst with 5 wt% Ru loading; [g] Ref 17; C= Conversion %; Y= Yield %.

Conclusions

In conclusion, Au/Zn-MOF, Au/Cu-MOF, Ru/Zn-MOF, and Pd/Zn-MOF with sub-nanometer metal particles were in situ synthesized in emulsion using surfactant SAAS-C$_{12}$ as emulsifier and reductant. In this route, metal precursors of MOFs (*e.g.* Zn^{2+}) and metal particles (*e.g.* Au^{3+}) were dissolved in water droplets, and the ligand existed in oil phase. MOFs were firstly formed around water droplets to produce hierarchically mesoporous structure. Then, the metal precursors isolated in the mesopores were reduced in situ by the surfactant, leaving metal particles immobilized uniformly on the hierarchical porosity of MOFs. In addition, the size of metal particles could be easily controlled by the content of metal precursors. The Au/MOFs with sub-nanometer Au particles (0.8 nm) had much higher activity and selectivty for aerobic oxidation of cyclohexene to 2-cyclohexen-1-one than those with larger Au particles, and the Ru/Zn-MOF with Ru particles of 0.8 nm was much more effective than those with larger Ru particels catalyst for hydrogenation of diphenyl sulfoxide to diphenyl sulfide. We believe that this simple one-step method can also be used to synthesize some other supported metal catalysts, in which sub-nanometer metal particles are decorated uniformly on hierarchically mesoporous MOFs.

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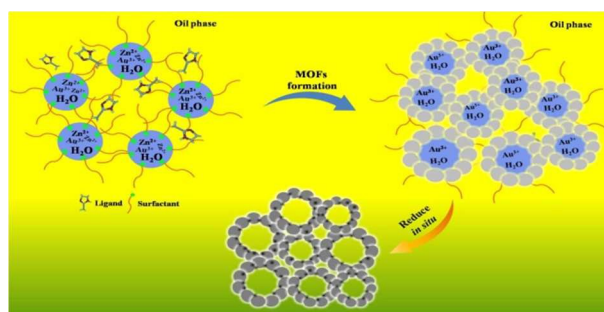
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