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In- situ preparation of palladium nanoparticles loaded ferrocene based metal-organic framework and its application in oxidation of benzyl alcohol

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ABSTRACT

Noble metals nanoparticles exhibit outstanding catalytic ability in various reactions and it is of great significance to provide suitable supports for them. A ferrocene based metel-organic framework, named FMOF was synthesized using $ZrCl_4$ and 1,1'-ferrocene-dicarboxylic acid (FDC) through a tradition solvothermal method. The as-prepared FMOF featured nanosheet morphology with a thickness of *ca*.10 nm and lateral size of *ca*. 500 nm. Since the Fe²⁺ in the FDC ligands could act as a reducing agent, this FMOF was employed for the *in-situ* reduction of Pd²⁺ and the Pd nanoparticles (NPs) with a diameter of *ca*. 3.5 nm were successfully obtained and loaded on the surface of FMOF. Though this facile approach Pd/FMOF with Pd loading amount of 3.39 wt% was obtained and no obvious change of the crystal structure was found after the reduction process for FMOF. It was found that the Pd/FMOF performed good catalytic activity in the oxidation of benzyl alcohol with conversion of 89.3%, and the catalytic activity maintained well after 3 cycles.

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1. Introduction

Noble metal nanoparticles (NPs) like Au. Pt and Pd have been recognized as remarkable catalysts in modern chemistry industry. With outstanding catalysis activity and special selectivity, their performance in a wide range of reactions has attracted innumerable interests [1-4]. However, it still faces the challenge that inevitable aggregation of NPs may happen during the reaction causing decrease in catalytic ability [5,6]. A stable support for loading of NPs would help to circumvent this drawback. Metalorganic framework (MOF) has been regarded as an attractive class of porous materials in the past decades. Due to their highly regular structures, well-defined pores, large surface areas and facial modification on ligands or nodes, their applications on gas separation, catalysis, energy storage and chemical/bio-sensors have been extensively studied [7-11]. Given the property that the pore size of MOF could be tuned easily by changing the ligands, employing MOF as catalyst supports especially for NPs, has gained increasing interests. The channels and cavity inside MOF would be favorable for dispersion of NPs and suppress the aggregation of nanoparticles [12]. Moreover, MOF exhibit excellent stability under various chemical conditions so they are recognized as an ideal support for catalysts [13,14]. A series of MOFs have been synthesized and loaded with noble metal NPs. A double-solvents method was token by Sun et al. to obtain NH₂-UiO-66 containing Pd²⁺ inside the pore cavities [15]. Then the Pd^{2+} were reduced to Pd nanoparticles by visible light and the as-prepared Pd@NH₂-UiO-66 showed satisfactory catalytic ability in Suzuki reaction. Chen and coworkers first encapsulated Pd²⁺ into 2,2'-bipyridine-5,5'-dicarboxylic acid then this hybrid ligand was employed to form UiO-67 [16]. In this way Pd species were introduced into MOF successfully and their outstanding performance in Heck reaction was demonstrated. However, to overcome the diffusion resistance between NPs and MOF, the pristine metal ions were usually first encapsulated into MOF followed with a reduction procedure to convert the metal ions to nanoparticles. This is a so-called ship-in-a-bottle method [17]. This two-step manipulation is tedious and introduction of reducing agent such as NaBH₄ or other organic agent may complicate the system [6,18]. On the other hand, the doublesolvents method is also laborious and time consuming to make





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sure the metal NPs could be immobilized into the cavities or channels in MOF.

As the nodes in MOF are usually limited to metals or metal oxide clusters, it is more meaningful to employ multifunctional ligands to give MOF special properties. For instance, Xu and coworkers utilized 2.5-dihydroxyterephthalic acid (H₄DOBDC) as ligands to synthesize NTU-9-NS MOF [19]. Due to the specific DOBDC moiety, the NTU-9-NS MOF could be used to detect the Fe³⁺ in water though the luminescence quench effect between Fe^{3+} and DOBDC. Huang and coworkers took advantage of metalloporphyrinic ligands - TCPP (M) [TCPP = tetrakis(4-carboxyphenyl) porphyrin, M = Fe, Co] to act as a peroxidase mimic in the oxidation of TMB [20]. Here we used 1,1 '-ferrocene-dicarboxylicacid (FDC) as ligand with ZrCl₄ to synthesize novel ferrocene based MOF nanosheets (FMOF). It has been proved that the Fe²⁺ in FDC molecular exhibited certain degree of reducibility [21]. For the standard electrode potential of Pd^{2+}/Pd (0.951 V) was higher than that of Fe^{3+}/Fe^{2+} (0.771 V), we hypothesized that the FDC ligands in MOF could reduce the Pd²⁺ into Pd NPs and well dispersed NPs on the MOF support without additional reduce process. In this study, FMOF was successfully synthesized through a traditional solvothermal reaction using acetic acid (AA) as modulator. Pd loaded MOF was prepared by simply mixing K₂PdCl₄ and FMOF suspension at room temperature under stirring. Successful introduce of Pd NPs was confirmed by HRTEM and ICP. The catalytic ability was investigated by employing this as-prepared Pd loaded MOF in the selective oxidation of benzyl alcohol into benzaldehyde. An exceptional conversion of 89.3% were achieved and reusability test also demonstrated the catalytic activity as well as stability of this Pd loaded MOF maintained well after 3 cycles.

2. Materials and methods

2.1. Materials

All chemicals were commercial available and used without further purification. Zirconium chloride (Aladdin, 99.9%), 1,1 '-ferrocene-dicarboxylic acid (Energy, 98%), acetic acid (SCR, 99.5%), potassium tetrachloropalladate (Aladdin, 98%), benzyl alcohol (SCR, 99%), benzaldehyde (Aladdin, 99%) absolute ethanol (SCR, 99.7%) and N,N-Dimethylformamide (SCR, 99.5%).

2.2. Synthesis of FMOF

FMOF nanosheets were synthesized though a traditional bottom-up solvothermal method as described in our previous work [22]. In a typical synthesis process, 0.6 mmol of $ZrCl_4$ (139.6 mg) and 0.6 mmol of FDC (164.4 mg) were dispersed in 20 mL DMF with 30 mmol (1.7 mL) acetic acid as the modulator. Then the mixed solution was ultrasonicated for 30 min and transferred into a sealed Teflon vessel and heated under 120 °C for 12 h. After cooling to room temperature, the as-obtained FMOF suspension was centrifuged and washed with 40 mL of DMF three times, followed being freeze-dried for 5 days.

Pd-FMOF was prepared through a "bottle-around-ship" method. The preparation process of Pd-FMOF was all the same as the preparation of FMOF except that 30 mg of K_2 PdCl₄ was added into the mixed solution containing ZrCl₄, FDC and acetic acid before heat.

2.3. Synthesis of Pd loaded FMOF

In a typical process, 15 mg of as-prepared FMOF were ultrasonicated at room temperature and dispersed in 500 mL water then a certain amount K_2PdCl_4 (21/43/65 mg) was added into the suspension. After stirring at 30 °C for 2 h and washed with 40 mL of deionized water three times, Pd/FMOF with different loading amount of Pd NPs could be obtained. Finally the Pd/FMOF was freeze-dried for 5 days.

2.4. Characterization

The morphology, thermal stability, crystallinity and thickness of FMOF was determined by scanning electron microscope (SEM; Zeiss, Utral 55), X-ray diffraction (XRD; PANalytical B.V. X-pert Powder; anode material: Cu), X-ray photoelectron spectroscopy (XPS; Thermo Fisher, Escalab 250Xi), thermogravimetric analysis (TGA; TA instrument, TA-Q500) and atomic force microscope (AFM; VEECO, MultiMode), respectively. A specific surface area measuring instrument (Micromeritics, 3 Flex) was used to calculate the BET surface areas and pore size distribution. High resolution transmission electron microscope (HRTEM; JEOL, JEM 2100F) was taken to observe the dispersion and size distribution of Pd nanoparticles on Pd/FMOF. Loading amount of Pd NPs was calculated by inductively coupled plasma (ICP; Thermal, iCAP6300).

2.5. Catalytic performance

The as-prepared Pd/FMOF were washed with m-xylene twice and dispersed in 10 mL m-xylene, then 1 mL of Pd/FMOF suspension (5 mg/mL) was token out as weight sample and dried under vacuum for 12 h. The weight abovementioned sample was calculated so the concentration of Pd/FMOF suspension could be determined. In the catalytic reaction, Pd/FMOF suspension containing certain amount of Pd/FMOF was dispersed in 3 mL of m-xylene and the reaction was token at 130 °C with 0.2 mmol benzyl alcohol. A continuous flux of air was bubbled into the vial using an air pump to provide oxygen. After the reaction, 1 mL suspension was token out as samples and filtered with 0.22 μ m filter. Concentration of components in the samples was determined by gas chromatography (GC; SGE, Agilent 6890) analysis.

3. Results

3.1. Characterization

UiO-66 was a famous kind of MOF which was composed of ZrCl₄ and 1,4-dicarboxybenzene (BDC). The Zr₆O₄ cluster in metal center could coordinate with 12 ligands so notable stability could be accomplished on account of the high degree of crystal network [23,24]. In this study we chose ZrCl₄ as metal nodes and a dicarboxylic acid, FDC as the ligands, expecting a stable framework structure. To our surprise, the as-obtained FMOF exhibited a nanosheets-structure (Fig. 1a-b) but not a traditional octahedron like UiO-66 (Fig. S1). The lateral size of this FMOF was ca. 500 nm and the thickness was ca. 10 nm according to the AFM image (Fig. 1c-d). Moreover, the characterized peaks in the PXRD pattern of FMOF at 6.27°, 8.87°, 14.00°, 19.98°, 22.63°, 28.25° and 34.29°, which could be assigned to the $(0\ 0\ 1)$, $(-1\ 0\ 1)$, $(0\ 0\ 2)$, $(0\ 3\ 1)$, $(3\ 2)$ 1), (2 4 1) and (4 2 1) lattice planes manifesting the highly crystalline degree of this FMOF (Fig. 2a). Besides, the lattice distance of FMOF was calculated to be 1.41 nm from simulated crystal structure of FMOF, so the nanosheets were proposed to feature a seven-layers stacking. Considering that the structure of FDC is composed of iron ion and two parallel cyclopentadienes, while the former mentioned BDC in which most atoms are in the same plane, a plausible explanation for the formation of FMOF nanosheets is that the steric hindrance effect of FDC would suppress the growth on certain direction during the crystallization stage (Fig. S2). Previous researches have reported the synthesis of 2D MOF nanosheets by



Fig. 1. (a, b) SEM images of FMOF in different magnification; (c) AFM image and (d) height profile of FMOF.



Fig. 2. (a) XRD patterns of simulated FMOF, experimental FMOF and Pd/FMOF; (b) TG curve of Pd/FMOF under N2 atmosphere.

using obstacle ligands or surfactant like PVP [25–27], and in this study the abnormal FDC was recognized as a malformed ligand so that the MOF would cline to grow on a plane because of the steric obstacle. On the other hand, the acetic was proposed to play a curtail role in the formation of FMOF nanosheets. As was observed in the SEM images of FMOF prepared with various modulator (Fig. S3), e.g. no modulator hydrochloric acid or formic acid, the FMOF prepared without any modulator was found to be irregular aggregations with few productions after the reaction. Meanwhile the hydrochloric acid seemed to be of no assistance for the formation of FMOF russ found to be broadly staking films morphology with a similar XRD pattern as FMOF-acetic acid

(Fig. S4), suggesting they had the same crystal unit. Thus the monoacid was also considered as a key modulator in the formation of FMOF nanosheets, which was assumed to coordinated with the Zr nodes in the early crystallization stage and favored the growth of FMOF by ligand exchange with FDC. Fig. 2b showed the TG curve of FMOF, in which a weight loss of about 10% before 400 °C was corresponded to the escape of solvent molecules inside FMOF as well as the coordinated acetic acid. A quickly loss of 10% happened between 450 °C and 520 °C was due to the collapse of FDC result in decomposition of MOF structure, and finally a slight loss at 650 °C was attributed to the disruption of Zr clusters. Fig. 3a exhibited the N₂ adsorption/desorption isotherms of FMOF, which featured a typical type IV mode, and the hysteresis loop implied the existence



Fig. 3. (a) N₂ adsorption/desorption isotherms of FMOF; (b) Pore width distribution of FMOF.

of micropores and mesopores. The BET surface area of FMOF was calculated to be 296.69 m²/g which was quite lower than that of UiO-66 (more than $1000 \text{ m}^2/\text{g}$). This may be explained that the lack of inner pores especially in ultrathin-film MOF nanosheets result in significant decline of both pore volume and surface area. Besides, as was shown in Fig. 3b, the average pore size of FMOF was ca. 0.7 nm, demonstrating the existence of micropores in FMOF. For the loading of Pd NPs, Zoetebier's study has elucidated that the ferrocene moiety in hydrogel could be employed for the *in-situ* formation of Pd NPs [28]. In this study, the role of FDC in the reduction of Pd²⁺ was also demonstrated. No Pd NPs could be found in the clear solution of K₂PdCl₄ with ZrCl₄, while Pd NPs with obvious lattices could be detected in the HRTEM image of K₂PdCl₄ and FDC mixture (Fig. S5), excluding the possibility that other species in the reaction system would act as reduce agent. However, when K₂PdCl₄ was added with ligands and metal nodes before the formation of FMOF, the FMOF failed to constructed regular crystal structure meanwhile the reduced Pd particles seemed to aggregate seriously with large size (Fig. S6). The Pd^{2+} ions in the solution were supposed to exhibited strong affinity to FDC ligands that hindered the coordination between FDC and Zr^{4+} . Meanwhile as were surrounded by adequate reducing agent, Pd particles would be formed rapidly thus resulted in aggregated Pd clusters. It should be pointed out that though the Fe^{2+} in FDC ligands had been oxidized to Fe^{3+} for the formation of Pd⁽⁰⁾, no obvious changes of FDC could be detected as the XPS patterns of Fe 2p before and after the *in-situ* reduction were almost the same (Fig. 4a and b). Besides, Fig. 4c showed the XPS patterns of Pd-3d in Pd/FMOF, in which the bonding energy peaks at 341.68 eV and 336.18 eV confirmed the existence of $Pd^{(0)}$ [29]. And the full XPS patterns of FMOF before and after loading of Pd showed no obvious changes (Fig. 4d). As was observed in HRTEM images, Pd ions were successfully reduced into Pd NPs and dispersed uniformly on the surface of FMOF (Fig. 5). The average dimension of Pd NPs was about 3.5 nm from statistics, which would be of great preponderance in practical catalytic application. It is also worth noting that by take different addition amounts of K₂PdCl₄, Pd/FMOF with Pd NPs of 0.64 wt%, 1.62 wt% and 3.39 wt% could be obtained as were calculated from the ICP test. Pd/FMOF with Pd NPs of 3.39% was chosen as the optimum catalyst in the oxidation of benzyl alcohol. Compared with the XRD pattern of blank FMOF (Fig. 2a), the peaks in the pattern of Pd/FMOF were highly similar with those in FMOF, confirming that the crystal structure

maintained well after the loading of Pd NPs. It should also be pointed out that no peaks corresponded to metal Pd could be observed in the pattern of Pd/FMOF, which could be explained that the loading amount of Pd was not that insufficient to be detected. And this result also implied the as-prepared FOM was quite stable in water during the loading process.

3.2. Catalytic ability in the oxidation of benzyl alcohol

The oxidation of benzyl alcohol into benzaldehyde was thought as an important reaction in modern chemistry industry. As abovementioned, the well dispersed Pd NPs on the support of FMOF would be of great benefit for the reaction to achieved high catalytic activity. In the oxidation of benzyl alcohol, it could be found that the reaction temperature played an important in this reaction. Limited the low boil point of toluene (ca. 111 °C), conversion in the case that toluene was used as solvent, the conversion was lower than 50% after 10 h' reaction (Table 1, entry 1). Other high-boil point solvents all exhibited better catalytic ability in the oxidation of benzyl alcohol and m-xylene was chosen as the optimum solvent (Table 1, entry 2 and 3). Taking m-xylene as solvents and reaction temperature of 130 °C, conversion of 88.6% and 89.3% could be realized after 9 h and 12 h (Table 1, entry 4 and 5). As for the selectivity, it could also be confirmed there was no other byproduct or the over-oxidized benzoic acid generated during the reaction. Other trace signals in the GC patterns were supposed to be impurity from the solvent or substrate (Fig. S7), implying an extremely high selectivity of this Pd/FMOF in the oxidation of benzyl alcohol. Furthermore, control experiment was carried out and almost no benzaldehyde could be detected when blank FMOF was employed under the same conditions (Table 1, entry-6).

In-situ reduction by Fe^{2+} in FDC gives the chance that Pd ions could only be reduced by FDC so the generated Pd NPs would be cline to attach with the ligands and dispersed uniformly. In addition, the Fe^{2+} could be recognized as a weak reducing agent compared to H₂ or NaBH₄, the reduction process would be quite mild so that the formation of large Pd NPs could be avoided. The thin-film FMOF serving as the support would help avoid the aggregation of Pd NPs during the reaction, meanwhile the Pd NPs on the surface are more accessible to the substrate. However, one inevitable dilemma was that the loading amount was unable to be so satisfactory, as revealed above a maximum loading amount was



Fig. 4. XPS pattern of (a) Fe 2p of FMOF, (b) Fe 2p of Pd/FMOF, (c) Pd 3d of Pd/FMOF, (d) Full patterns of FMOF and Pd/FMOF.



Fig. 5. HRTEM images of Pd/FMOF with different loading amount: (a) FMOF, (b) Pd/FMOF-0.64 wt%, (c) Pd/FMOF-1.62 wt% and (d) Pd/FMOF-3.39 wt%.

only 3.39 wt%.

3.3. Reusability and stability

The reusability of catalyst is a critical property for the practical application of the Pd/FMOF. To investigate the stability and catalytic

active of Pd/FMOF in long-period operation, after each cycle of reaction, the catalyst was collected by centrifuge and washed with mxylene twice before next cycle. The conversion of benzyl alcohol after cycles was showed in Fig. 6, and it was indicated that the conversion exhibited slight decrease of about 10% after 3 cycles with reaction time of 9 h, while prolonged the reaction time to 12 h Table 1

Table 1
Conversion of benzyl alcohol under various conditions.

Entry	Solvent	m-MOF/mg	Temperature/°C	Time/h	Conversion/%
1	Toluene	10	110	10	46.9
2	Xylene	10	130	12	61.6
3	m-Xylene	10	130	3	52.5
4	m-Xylene	10	130	9	88.6
5	m-Xylene	10	130	12	89.3
6 ^a	m-Xvlene	0	130	12	<1

^a Using 10 mg blank Zr-FDC MOF as catalyst.



Fig. 6. Reusability test of Pd/FMOF in different reaction time.

in each cycle, a sharp conversion decrease of about 30% happened in the third cycle. The decrease in catalytic ability may be ascribed to the aggregation of MOF and loss of Pd NPs after several cycles, as was revealed from the supernatant collected from the suspension with light yellow color. Also, according to the SEM and HRTEM images (Fig. 7a and c), severe aggregation of the FMOF was observed and almost no regular MOF nanosheets could be found. As was showed in the HRTEM image, though the Pd NPs could be found on the MOF, the average size of Pd NPs increased from 3.5 nm to 6.2 nm (Fig. 7b and d).

4. Conclusion

In summary, a novel ferrocene based MOF has been successfully synthesized using ZrCl₄ and 1,1 '-ferrocene-dicarboxylic acid as metal node and ligand. The as-obtained FMOF featured nano-sheet morphology with thickness of ca. 10 nm, which was corresponded with a seven-layer nanosheets structure from theory calculation. Taking advantage of Fe²⁺ in FDC ligands, Pd²⁺ had been successfully reduced to Pd NPs on the surface of FMOF with diameter of ca. 3.5 nm. Besides, by adjusting the addition amount of K₂PdCl₄, various loading amount of Pd/FMOF could be obtained and the Pd/ FMOF with a maximum Pd content of 3.39 wt% was used as heterogeneous catalyst in the oxidation of benzyl alcohol. Conversion of 89.3% could be achieved and no other by-product was found according to GC analysis which implying the exceptional selectivity of this Pd/FMOF towards benzyl alcohol. Reusability test indicated that the catalytic active of Pd/FMOF maintained well after three cycles when the reaction time was 9 h in a single cycle. However, as prolonging reaction time to 12 h, a sharp decrease in conversion of 30% happened in the 3rd cycle. This could be explained that such long period of operation might cause harsh aggregation of Pd NPs as well as the decompose of FMOF that observed in HRTEM and SEM images, thus declined the catalytic active of this composite. In a word, a straightforward in-situ reduction of Pd NPs was explored by natural reducing moiety of FDC in FMOF without introduce of additional agent. Despite the aggregation of Pd NPs and MOF nanosheets after several reaction cycles that resulted in loss of catalytic active, this study may give the idea of utilizing functional ligands to form MOF and realize specific applications.

Conflicts of interest

We declare we have no conflict of interests in this paper.



Fig. 7. SEM and HRTEM images of Pd/FMOF used after 3 cycles with reaction time of (a,b) 9 h and (c,d) 12 h.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2019.126895.

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