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Pd(0)@UiO-68-AP: chelating-directed bifunctional heterogeneous catalyst for stepwise organic transformations

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A bifunctional heterogeneous catalyst Pd(0)@UiO-68-AP based on a chelating-directed post-synthetic approach is reported. It exhibits a typical heterogeneous catalytic nature and can promote benzyl alcohol oxidiation-Knoevenagel condensation in a stepwise way.

Heterogeneous catalysis, owing to the features of cost savings and eco-friendliness, has received more and more attention during the last decade. Composite type of catalytic materials is one of the most important solid catalysts for heterogeneous catalysis.¹ For creating composite catalysts, various inorganic materials, such as $CeO_2^2 SiO_2^{,3} ZrO_2^{,4}$ and porous carbon,⁵ and organic materials, such as polystyrene,⁶ amphiphilic resin⁷ and copolymers,⁸ have been utilized as supports to immobilize active catalytic metal species, especially the active catalytic Pd nanoparticles (Pd NPs).⁹ In contrast, the use of inorganicorganic hybrid materials as a supporting matrix to load active catalytic entities have not yet attracted much attention.¹⁰

Among various heterogeneous catalyst carriers, metalorganic frameworks (MOFs) can be considered a new type of supports for the fabrication of heterogeneous composite catalysts.¹¹ It is well known that the catalytically active species, such as active metal nanoparticles, could be incorporated into MOF matrix by solid grinding,¹² vapour deposition,¹³ solution infiltration¹⁴ and microwave-assisted diffusion.¹⁵ Recently, Lin¹⁶ and Cohen's¹⁷ groups reported that the catalytic metal centers can be introduced into MOFs by a chelation-assisted approach. For example, direct assembly of the metalloligands with bpy-metal or ppy-metal moieties, or encapsulation of metal center at reservation open chelating sites on the framework rungs by post-synthetic method. It is anticipated that the bidentate chelating coordinating sites should tightly bind and stabilize active metal precursors; thus, generating a stable, but highly unsaturated nano metal particles after

reduction. In addition, such chelating-directed approach would allow the active metal presurors to be readily implanted at the chelating positions to result in a well-proportioned metal species binding, consequently, a uniformly distributed metal@MOF matrix.

More importantly, such MOFs-based composite catalyst frication would allow for fine-tuning of solid materials with multifunctional catalytic behaviors by combination of the different types of active species. So such kind of heterogeneous composite catalysts might be used to perform several steps in a reaction sequence. Although great efforts have been made in this field, general and facile method that can easily introduce the active catalytic species into MOF matrix are still imperative.

In this contribution, a new composite solid catalyst of Pd(0)@UiO-68-AP which is prepared by chelating-directed post-synthetic approach is reported. By combining the aerobic oxidation activity of the encapsulated Pd NPs and Knoevenagel condensation activity of the Zr-Lewis acid sites and generated secondary amino moiety on UiO-MOF, the obtained Pd(0)@UiO-68-AP exhibits a bifunctional catalytic behaviour and can promote benzyl alcohol oxidation-Knoevenagel condensation in a stepwise way.



Scheme 1. Synthesis of UiO-68-NH₂, Pd(II)@UiO-68-IP (1) and Pd(0)@UiO-68-AP (2).

 $UiO-68\text{-}NH_2$ was prepared as yellowish crystalline solids according to the reported method (ESI).^{18} Pd(II)@UiO-68-IP (1)

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was obtained by the amine-aldehyde condensation and postsynthetic metalation. As shown in Scheme 1, UiO-68-NH₂ was treated with excess of pyridine-2-carboxaldehyde in EtOH at 70°C for 10 h to afford UiO-68-IP with 2-iminopyridine (IP) chelating coordination sites (Yield, 80% based on elemental analysis, ESI). After separating the solids by centrifugation and washed with fresh EtOH, the precipitate was mixed with Pd(NO₃)₂ by ultrasound in CH₃CN, and the mixture was heated at 70°C for additional 1 h to generate 1 as yellow brown crystalline solids. Pd(0)@UiO-68-AP (2) was synthesized by the reduction of $\mathbf{1}$ with NaBH₄ in aqueous solution along with a distinct colour change (from yellow-brown to dark brown) (Scheme 1). The imino group was also reduced to the corresponding secondary amino group along with the Pd(II) reduction because of the large excess of NaBH₄, which is unambiguously demonstrated by the MS analysis (Fig. S1).

IR spectrum of UiO-68-NH $_2$ shows that the weak double peaks at 3336 and 3297 cm⁻¹ are attributed to the symmetrical and asymmetrical vibration adsorption of amino group. In addition, the peaks at 1599 and 831 cm⁻¹ corresponding to primary amino out-of- and in-plane bending vibrations are also observed.¹⁹ These characteristic amino peaks are basically disappeared after the Schiff base condensation. Meanwhile, a new sharp peak associated with N=C stretching vibration at 1604 cm⁻¹ appeared in 1, indicating the formation of iminopyridyl moiety (Fig. S1). After reductive reaction, a new weak single peak at 3380 cm⁻¹, together with 1595 cm⁻¹, clearly indicates the formation of the secondary amino group (Fig. S1). For further confirmation of this post-synthetic metalation, the metalation of the esterified 2-iminopyridyl group attached organic linker was examined before the synthesis of MOF. The reaction proceeded very smoothly under the same reaction

conditions and the expected metalation product was well confirmed using MS spectrum (Fig. S2).





X-ray powder diffraction (XRPD) indicated that the crystallinity of UiO-68-NH₂ was maintained in both **1** and **2** after the post-synthetic metalation reactions (Fig. 1), which supports that UiO-68-NH₂ was chemically stable during the palladium loading and following reducing process. To get a further insight into the structure of **2**, high resolution transmission electron microscopy (HRTEM) was used to investigate the dispersion and size distribution of the Pd NPs in **2**. HRTEM analysis revealed that the Pd NPs were crystalline and highly dispersed with an average particle size of ≤ 2 nm (Fig. 1). The lattice fringes with interplanar spacing of 0.24 nm, corresponding to 1/3 (4 2 2) fringes of face-centered cubic (fcc) Pd.²⁰



Fig. 2 Top: SEM and elemental maps of Zr and Pd images of 2. Bottom: EDS pattern of 2.

Scanning electron microscope (SEM) shows that the octahedral shape of UiO-68-NH₂ crystals was maintained after post-synthetic modification (Fig. 2). Inductively coupled plasma (ICP) measurement of the Zr : Pd ratio of digested metalated MOF is 1:0.68 (5.1 wt % Pd loading). The energydispersive X-ray spectrum (EDS) measurement (Fig. 2) shows that the uploaded zero-valent palladium homogeneously distributes in 2. It is known that the active catalytic metal precursors loading based on traditional impregnation method is variable, and it can be significantly affected by the soaking time, temperature and many other subtle factors.²¹ This would lead to an unrepeatable catalyst preparation process, consequentially, an inaccurate the catalyst evaluation. Chelation-assisted Pd loading herein might be an alternative approach to overcome the drawback caused by the traditional impregnation. On the other hand, the generated Pd NPs could be stabilized by the introduced multitudinous nitrogen donors in the framework. The Pd-loading on UiO-68-NH₂ crystals by traditional impregnation was also tested under the same conditions. The ICP measurement indicates that the Zr : Pd ratio is only 1: 0.08. The existence of Pd(0) in 2 was further confirmed by the X-ray photoelectron spectroscopy (XPS) (Fig. S3). It is similar to UiO-68-NH₂, thermogravimetric analysis (TGA) indicated that the initial weight loss of 1 and 2 occurred at ca. 125°C, but with a more smoothly weight loss processes (Fig. S4).

Selective catalytic oxidation of benzyl alcohols to corresponding benzaldehydes is one of the most important issue in modern synthetic chemistry and chemical industry.²² Hitherto a great deal of research effort has been devoted to finding novel and efficient catalysts for this type reactions. **2** herein showed excellent activity in aerobic oxidation of benzylic alcohol to benzaldehyde.



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 Table 1. Oxidation of benzyl alcohol in different solvent systems at different temperature in air



entry	T (°C)	cat./solv.	t (h)	conv. ^b (%)	select. ^b (%)
1	80	UiO-68-NH ₂ /xylene	32	~2.6	>99
1	60	2/xylene	32	~2.3	>99
2	80	2/xylene	24	>99	>99
3	100	2/xylene	20	>99	>99
4	120	2/xylene	12	>99	>99
5	80	2/toluene	24	>99	>99
6	80	2 /CH₃CN	30	>99	>99

 $^{\rm a}$ Reaction conditions: air, benzyl alcohol (1.0 mmol), catalyst (1 mol % Pd), solvent (2 mL). $^{\rm b}$ based on GC analysis.

Using 2 (1 mol% in Pd), nearly quantitative yield of benzaldehyde was achieved in 12-30 h at 80-120°C (Table 1, entries 2-4) in different solvent systems. By comparison, UiO-68-NH₂ gave very low conversion under the same reaction conditions (Table 1, entry 1). As shown in Table 1, it seems that all the solvents used such as xylene, toluene and CH₃CN are suitable for this oxidation reaction, but took different reaction time. Based on an overall consideration of various factors, toluene and 80°C were chosen as the reaction medium and temperature (ESI). In order to confirm the heterogeneous nature of 2, a hot filtration experiment was performed, removing the catalyst by filtration after 7.5 h of the reaction (Fig. 3). Time-dependent gas chromatography (GS) indicated no additional conversion to benzaldehyde was observed (up to 30 h) after filtration. In addition, 2 exhibits excellent recyclability without a detectable decrease in yields (>99 %) over five catalytic cycles (Fig. 3). After each run, 2 can be easily recovered by centrifugation and directly reused in the next run under the same reaction conditions. The crystallinity of the MOF was maintained after each cycle, as confirmed by XRPD pattern (Fig. S5).

 $\label{eq:table_cond} \mbox{Table 2. Catalytic data for the Knoevenagel condensation of malononitrile with benzaldehyde in different solvent systems^a$

CHO + CN + C								
entry	cat.	solvent	T (°C)	conversion ^b (%)	selectivity ^b (%)			
1	2	MeOH	r.t.	>99	>99			
2	2	CH ₂ Cl ₂	r.t.	0	0			
3	2	CH ₃ CN	r.t.	0	0			
4	2	toluene	r.t.	0	0			
5	2	DMF	r.t.	88.5	>99			
6	2	toluene	50	25.4	>99			
7	UiO-68-NH ₂	MeOH	r.t.	>99	>99			

^aReaction conditions: benzaldehyde (1mmol), malononitrile (1.2 mmol), catalyst (1 % with respect to the amount of benzaldehyde). ^a based on GC analysis.

On the other hand, the $[Zr_6O_4(OH)_4(CO_2)_{12}]$ cluster nodes in **2** possesses the coordination-unsaturated Zr atoms, together with the generated amino moieties, they should both serves as active catalytic sites to promote Knoevenagel reaction, which is an important C-C coupling reaction and widely used in the synthesis of fine chemicals.²³ In a typical reaction, a MeOH solution of benzaldehyde and malononitrile (1 : 1.2, molar ratio) in the presence of **2** (1 mol %) in MeOH was stirred at room temperature, the GC analysis (ESI) indicated that the condensation reaction was finished in 7 h to afford 2-benzylidenemalononitrile as the expected product with the excellent conversion (> 99%) and selectivity (> 99%) (Table 2, entry 1).



2 catalysed Knoevenagel reaction herein is very sensitive to the solvent systems. As shown in Table 2, MeOH is the best solvent medium for this reaction (entry 1). The conversions in weak polar solvent are very low or even no expected condensing product was detected (entries 2-6). It is noteworthy to point out that UiO-68-NH₂ exhibits the same catalytic activity as that of 2 for Knoevenagel condensation (entry 7 and ESI), indicating the effective catalytic site for this reaction is Zr-cluster cores and amino groups instead of the encapsulated Pd NPs. Again, 2 can be reused. As indicated in Fig. 4, after five consecutive catalytic runs, the conversion is still above 99 %, indicating no degradation in catalytic activity of 2 during the reusable process. Moreover, 2 was demonstrated to be highly crystalline from XRPD patterns even after five catalytic runs (Fig. S6). Besides, the heterogeneity of 2 was also confirmed the hot filtration test. The reaction solution was removed quickly from the solid catalyst and transferred to another reaction vessel under the same conditions at 2 h. No further increase in the conversion of condensing product was observed during following 7 h in the absence of 2 (Fig. 4).

Based on above observation, **2** could be a bifunctional catalyst²⁴ to promote benzyl alcohol oxidation and the following Knoevenagel condensation in due succession.

When a toluene solution (2 mL) of benzyl alcohol (1.0 mmol) in the presence of **2** (1 mol%) was heated at 80°C for 30 h, a MeOH solution (2 mL) of malononitrile (1.2 mmol) was added to above system after cooling down to the room temperature. The mixture was stirred for additional 8 h at room temperature to afford 2-benzylidenemalononitrile with excellent conversion (>99%) and selectivity (>99%) (Table 3, entry 1, ESI). ICP measurement showed that the Zr : Pd ratio is 1 : 0.67 after the oxidation-condensation reactions, indicating

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no Pd leaching during the reaction process. Again, the comparison of XRPD patterns before and after reaction supported that **2** is stable, as further confirmed by its SEM image after catalysis.

Table 3. Benzyl alcohol oxidation-Knoevenagel condensation catalysed by 2.^a



^aReaction conditions: catalyst (1 mol %), benzyl alcohol and substituted benzyl alcohols (1.0 mmol), toluene (2 mL), 80°C, 30 h, in air; malononitrile (1.2 mmol), 8 h. r.t. ^b based on GC analysis (ESI).



Fig. 5 Left: simulated (UiO-68-NH₂) and measured XRPD patterns of 2 before and after catalysis. Right: SEM image of 2 after catalysis. The morphology of the microcrystals of 2 is well remained after two step reaction.

The scope of the bifunctional catalytic system was investigated by performing the oxidation-condensation reaction of other various substituted benzyl alcohols. Table 3 summarized the results of these reactions. Compared to benzyl alcohol, we found that benzyl alcohols with either electron-donating or electron-withdrawing groups gave lower overall conversions, which is resulted from the lower conversion rates of the first oxidation step. The oxidation conversions for CH₃-, CH₃O-, F- and NO₂-substituted substrates are 66, 60, 65, 29 % (ESI), respectively. However, the following condensation step for the obtained aromatic aldehydes is a nearly quantitative catalytic process.

In summary, a new Pd NPs loaded Pd(0)@UiO-68-AP was prepared based on a chelating-directed post-synthetic approach. The obtained Pd NPs embedded Pd(0)@UiO-68-AP can be a highly active bifunctional heterogeneous catalyst to successively facilitate benzyl alcohol oxidation- condensation reaction under relative mild conditions. The results herein might provide an alternative way to access to versatile family of the multifunctional catalysts of this type for a broad scope of organic transformations in practical application. Further work on exploring new catalytic reactions based on such NPs@MOF catalytic systems is currently underway.

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