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Ionic liquid microphase enhances the catalytic activity of Pd nanoparticles supported by metal-organic framework

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Here we demonstrate the utilization of ionic liquid (IL) microphase for enhancing the catalytic activities of the metal nanoparticles supported on MOF. The IL microphase offers excellent environment for stabilizing metal nanoparticles. A new heterogeneous catalyst Pd/IL/MOF is developed, which combines the advantages of highly dispersed small Pd nanoparticles, IL microphase and porous MOF. The as-synthesized Pd/IL/MOF catalysts have shown high catalytic activity and reusability for selective hydrogenation under mild condition.

In recent years, metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), have become one kind of the most researched porous materials.¹⁻⁵ MOFs have found wide applications in different fields, including catalysis,⁶ gas storage and separation,⁷⁻⁸ sensing,⁹ drug delivery,¹⁰ etc. Among these applications, depositing metal nanoparticles onto MOFs as heterogeneous catalysts is an emerging field because of the large surface area, tunable topologies and designable surface properties of MOFs.¹¹⁻¹² However, the aggregation of metal nanoparticles supported on MOF is often observed and hardly prevented, which greatly reduces their catalytic activities. To limit the aggregation of metal nanoparticles, the functionalized MOFs or surfactants are requisite for stabilizing metal nanoparticles.¹³⁻¹⁴

Ionic liquids (ILs), as tunable and environmentally friendly solvents, have attracted tremendous attention owing to their very low vapor pressures, high chemical and thermal stability, wide electrochemical windows, and excellent solvency for both organic and inorganic compounds.¹⁵ Now ILs have been used to replace volatile organic solvents for different processes such as material synthesis,¹⁶ chemical reactions,¹⁷⁻¹⁸ gas adsorptions¹⁹ and energy production²⁰. Despite many advantages, ILs have some shortcomings such as high viscosity, difficulties in product purification, recycling, and so on, which hinder their chemical industry applications. Immobilizing ILs onto solid supports could

solve the recycle problem and make it convenient to be applied in industrial processes.²¹

Here we propose for the first time the utilization of IL microphase for enhancing the catalytic activities of the metal nanoparticles supported on MOF. The IL microphase offers excellent environment for stabilizing metal nanoparticles and thus highly dispersed small metal nanoparticles are expected to be immobilized on MOF. By this strategy, a new heterogeneous catalyst Pd/IL/MOF is developed, which combines the advantages of the three components, i.e. small Pd nanoparticles, IL microphase, and porous MOF. The as-synthesized Pd/IL/MOF catalysts have shown high activities in catalyzing the selective hydrogenation of acetylene hydrocarbon under mild condition.

For a typical synthesis of Pd/IL/MOF catalyst, the precursors of Cu₃(BTC)₂ MOF and Pd precursor were loaded into the IL 1,1,3,3-tetramethylguanidinium trifluoroacetate (TMGT). After stirring for a certain time, the MOF was gained and a desired amount of reducing agent was added into the reaction system to produce Pd/IL/MOF catalyst (denoted as **Catalyst-1**, detailed synthesis procedures are shown in ESI†). FT-IR spectra reveal that the carboxylate groups of 1,3,5-tricarboxybenzene (H₃BTC) are coordinated to Cu (II) ions (Fig. S1†). The powder XRD pattern of **Catalyst-1** is shown in Fig. S2. The XRD peak positions and relative intensities of the as-synthesized sample are in accordance with those of the reported Cu₃(BTC)₂,²² revealing the successful synthesis of Cu₃(BTC)₂ MOF. No obvious diffractions of Pd were observed in the XRD pattern, suggesting the formation of ultra-small Pd nanoparticles²³ or/and the low content of Pd in the catalyst.²⁴ The weight percentage of Pd in **Catalyst-1** was measured to be 1.27 wt% by inductively coupled plasma atomic emission spectroscopy (ICP-AES). According to the TGA analysis (Fig. S3†), the IL content in **Catalyst-1** is 13.2 wt%.

The SEM images show that **Catalyst-1** displays a porous structure, formed by stacked MOF nanoparticles in size of several dozen nanometers (Figs. 1a and 1b). The surface of the MOF was coated with small particles, as evidenced by TEM images (Figs. 1c and 1d). From the high-resolution TEM (HRTEM) images, the lattice fringe of Pd (2 0 0) can be clearly seen and the size of Pd nanoparticles is about 2 nm (Figs. 1e and 1f). Electron energy loss spectroscopy reveals that Pd and N (resulting from IL) are uniformly dispersed on

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the surface of MOF (Fig. 1g). Energy-dispersive X-ray (EDX) further confirms the presence of Pd in the prepared **Catalyst-1** (Fig. S4†). **Catalyst-1** has a BET surface area of 708 m²/g, as determined by N₂ adsorption-desorption method. The surface area of **Catalyst-1** is lower than that of pure Cu₃(BTC)₂ (1026.7 m²/g), resulting from the incorporation of IL and Pd into Cu₃(BTC)₂.

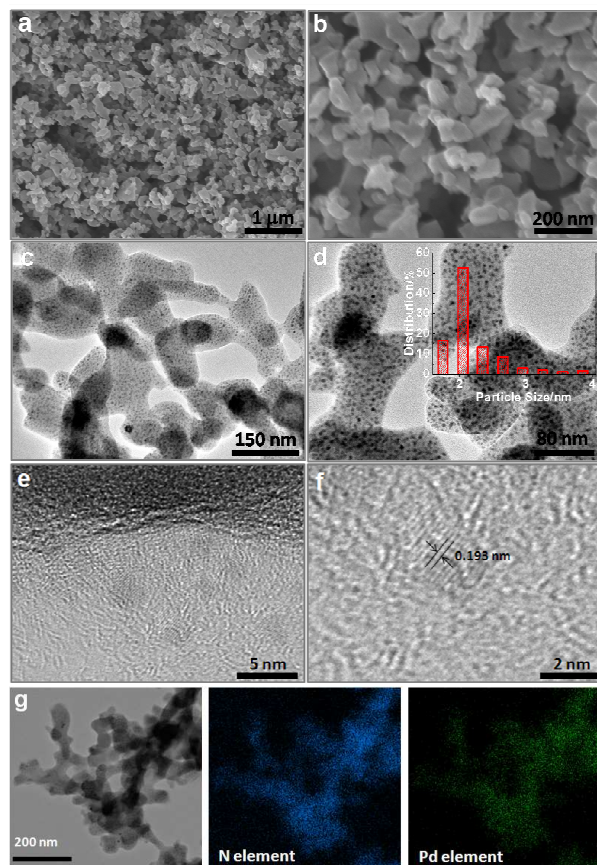


Fig. 1 (a and b) SEM; (c and d) TEM; (e and f) HRTEM images and (g) element mapping images of Pd/IL/MOF (**Catalyst-1**).

The catalytic performance of **Catalyst-1** for the selective hydrogenation of phenylacetylene was tested. Selective hydrogenation of alkynes to alkenes, without further reduction to less valuable alkanes, is of great importance in the polymer and fine chemical industries.²⁵ The phenylacetylene was almost completely converted (>99 %) in 40 min with high selectivity (>99 %) toward styrene (Table 1, Entry 3). A hot extraction experiment confirmed that the catalysis was exclusively heterogeneous (Fig. S5†). For comparison, the IL-free Pd/MOF (**Catalyst-2**) was synthesized in ethanol/water system and its catalytic activity for the selective hydrogenation of alkynes was detected under the same experimental conditions. **Catalyst-2** shows much slower reaction rate, i.e. a 83.1% conversion was obtained even as the reaction time was prolonged to 12 hours (Table 1, Entries 4-5). The main reason may be that the Pd nanoparticles obtained in the absence of IL are aggregated (Fig. S6†). Further, the catalytic performance of **Catalyst-1** was compared with those of commercial Pd/C catalyst and the reported Pd catalysts²⁶ (Table 1, Entries 6-10). Apparently,

Catalyst-1 shows outstanding activity and excellent selectivity among the tested catalysts and the reported catalysts under the same reaction conditions. It has been widely reported that the N containing compounds can be used as surface modifiers to improve the selectivity of the catalyst for alkyne hydrogenation to alkene.²⁷⁻³⁰ Herein the ligand effect of N element in the IL integrated in the catalyst is believed to be responsible for the high selectivity.³¹⁻³²

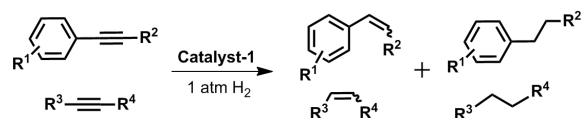
Table 1 Hydrogenation of phenylacetylene with different catalysts.

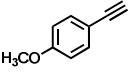
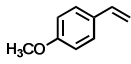








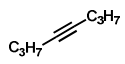

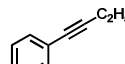

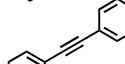

Entry	Catalyst	Time	Conversion	Selectivity	TOF ^[c]
1 ^[a]	Catalyst-1	10 min	69.1%	>99%	6322 h ⁻¹
2 ^[a]	Catalyst-1	20 min	80.8%	>99%	3696 h ⁻¹
3 ^[a]	Catalyst-1	40 min	>99%	>99%	2287 h ⁻¹
4 ^[a]	Catalyst-2	5 h	39.9%	>99%	114 h ⁻¹
5 ^[a]	Catalyst-2	12 h	83.1%	>99%	99 h ⁻¹
6 ^[a]	Pd/C (5wt%)	40 min	57.4%	93.8%	333 h ⁻¹
7 ^[b]	Pd@mpg-C ₃ N ₄	85 min	>99%	94%	779 h ⁻¹
8 ^[b]	Pd@Al ₂ O ₃	45 min	>99%	90%	1471 h ⁻¹
9 ^[b]	Pd@MgO	105 min	>99%	91%	630 h ⁻¹
10 ^[b]	Pd@CeO ₂	150 min	95%	91%	419 h ⁻¹

[a] reaction condition for Entries 1-6: catalyst (5 mg, Pd loading: 1.27 wt% for entries 1-3, 1.35 wt% for entries 4-5 and 5 wt% for entry 6), phenylacetylene (0.91 mmol) in 2.0 mL acetonitrile using the 1,3,5-trimethylbenzene as the internal standard, atmospheric H₂ balloon, 30 °C. [b] 5.85 mmol, 10 mg catalyst (5.64 wt% Pd), 50 mL solvent, atmospheric H₂ balloon, 30 °C.²⁶ [c] Turnover number (TON)=mol of product per mole of Pd; TOF=TON h⁻¹.

The catalytic activities of **Catalyst-1** were tested for the selective hydrogenation of other alkynes. The reaction conditions are the same with those for the hydrogenation of phenylacetylene. The phenylacetylenes with electron-donating and electron-withdrawing groups are all selectively hydrogenated to the corresponding terminal alkenes with high activity (Table 2, Entries 1-4). **Catalyst-1** also shows high activity and good selectivity for the hydrogenation of aliphatic alkynes that 4-octyne and 1-octyne could be converted completely in 45 and 50 minutes with >96% selectivity (Table 2, Entries 5 and 6). The reaction rates of hydrogenation of diphenylacetylene and 1-phenyl-1-butyne (Table 2, Entries 7 and 8) are slower than those of the above, which could be ascribed to the steric effect.

Table 2 Hydrogenation of alkynes with **Catalyst-1**.^[a]



Entry	Substrate	Time	Product	Conversion	Selectivity
1		45 min		>99%	97%
2		40 min		>99%	>99%
3		50 min		>99%	>99%
4		40 min		>99%	>99%
5		45 min		>99%	96%
6		50 min		>99%	99%
7		90 min		>99%	>99%
8		180 min		>99%	>99%

[a] reaction condition: **Catalyst-1** (5 mg, Pd loading: 1.27 wt%), Substrate (100 μ L for Entries 1-7, 0.91 mmol for Entry 8) in 2.0 mL acetonitrile using the 1,3,5-trimethylbenzene as the internal standard, atmospheric H_2 balloon, 30 $^{\circ}C$.

The reusability of **Catalyst-1** for the hydrogenation of phenylacetylene was investigated. After the reaction, **Catalyst-1** was recovered by simple centrifugation and washing. There is no any loss of activity and selectivity after the catalyst was reused for 4 cycles (Fig. 2). In the fifth run, a little loss of activity was observed, which could be attributed to the unavoidable catalyst loss during the washing process. The TEM image of the catalyst after used for five runs shows no particle aggregation and no major difference was observed for the XRD patterns of the fresh and recovered catalyst (Fig. S7[†]). ICP-AES analysis showed Pd loading of the recovered catalyst was 1.23 wt%, which was very close to the original value (1.27 wt%). This result implied the Pd leaching during the cycle process was negligible.

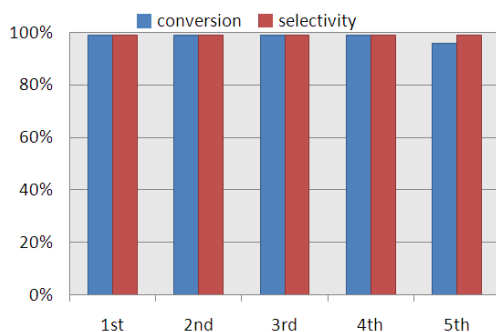


Fig. 2 Reusability of **Catalyst-1** for hydrogenation of phenylacetylene.

Different ILs including 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF₄), 1-butyl-3-methylimidazolium

trifluoromethanesulfonate ([BMIm]OTf), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm]PF₆), 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIm]PF₆) and 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIm]PF₆) were used to synthesize Pd/IL/MOF catalysts, the experimental conditions being the same with those for synthesizing **Catalyst-1**. See XRD patterns, FT-IR spectra and TGA analysis of the catalysts in Figs. S8[†], S9[†] and S10[†]. All these Pd/IL/MOF catalysts show high activity and selectivity in catalyzing the hydrogenation of phenylacetylene to styrene (Table S1). It indicates that the IL microphase is versatile in enhancing the activity of Pd nanoparticles supported on MOF.

To understand the IL-promoted catalytic activity of Pd nanoparticles supported on MOF, the interactions between IL, Pd and MOF were investigated by XPS spectra (Fig. S11[†]). As shown in Fig. 3A, the binding energies of Pd 3d_{5/2} in **Catalyst-1** (335.5 eV) shift down slightly compared with that of **Catalyst-2** (335.7 eV). It indicates that there is interaction between IL and Pd nanoparticles, possibly through the nitrogen in IL.³³⁻³⁴ Moreover, Pd 3d XPS spectra of **Catalyst-1** show Pd²⁺ characteristic peaks, which is absent in **Catalyst-2**, implying that IL TMGT participated in the bonding of Pd.³⁵ As seen from Fig. 3B, the Cu 2p_{3/2} binding energy of **Catalyst-1** (934.5 eV) is lower than that of **Catalyst-2** (934.8 eV). It is indicative of the interactions between IL and Cu-MOF, which might be derived from N...Cu interaction between N of TMGT and Cu²⁺ of Cu-MOF.³⁶⁻³⁷ The XPS results prove that IL interacts with both Pd nanoparticles and MOF support, through which the small Pd nanoparticles can be well stabilized on MOF support.

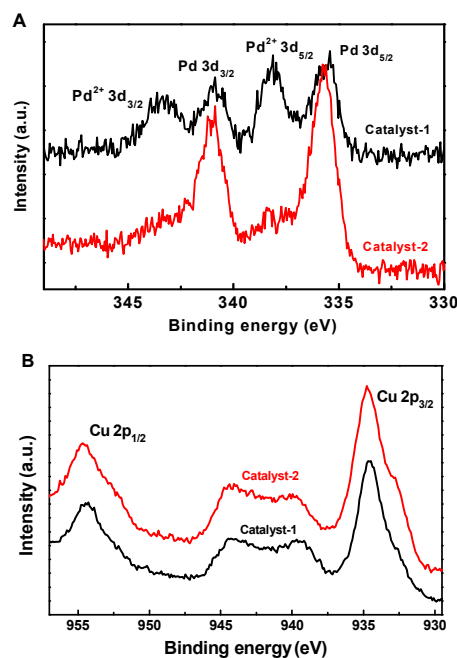
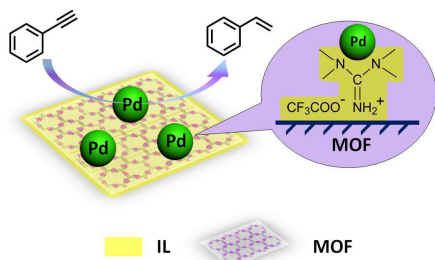


Fig. 3 Pd 3d (A) and Cu 2p (B) XPS spectra of **Catalyst-1** and **Catalyst-2**.

Based on the above results, the structure of the as-synthesized Pd/IL/MOF catalyst and its catalytic activity for the selective hydrogenation of phenylacetylene is illustrated in Scheme 1. The IL could anchor on the MOF surface through the interaction between

N of the IL and the unsaturated Cu^{2+} sites of the MOF. Simultaneously, the IL immobilized on the MOF support interacts with Pd nanoparticles. Therefore, the IL microphase supplies an excellent environment for preventing the aggregation or growth of Pd nanoparticles and small Pd nanoparticles (about 2 nm) could be finely dispersed on MOF. The small Pd nanoparticles stabilized by IL and the porous MOF structure co-contribute to the high catalytic activity of Pd/IL/MOF in phenylacetylene hydrogenation. On one hand, the small size of Pd nanoparticles is favorable to increase the density of catalytic active sites,³⁸⁻³⁹ thus accelerate the reaction efficiently. On the other hand, the porous structure of MOF can facilitate the diffusion of substrates and products because of large surface area, and thus accelerate the reaction rate.¹²



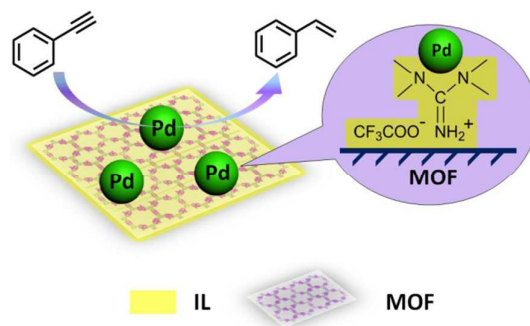
Scheme 1 Structure of Pd/IL/MOF catalyst and its catalytic activity for the selective hydrogenation of phenylacetylene.

In summary, we designed a Pd/IL/MOF catalyst by taking advantage of the IL microphase. IL could stabilize the Pd nanoparticles and highly dispersed small metal nanoparticles are immobilized on MOF. The Pd/IL/MOF catalyst shows excellent catalytic activity and high selectivity for the hydrogenation of terminal alkynes. The synthetic route for the Pd/IL/MOF catalysts is simple and can be applied to the synthesis of different kinds of MOF-supported metal nanoparticles. We anticipate that other high efficient heterogeneous catalysts stabilized by IL microphase can be designed for various catalytic reactions.

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Here Pd/ionic liquid/metal-organic framework catalyst is developed, which shows high activities in catalyzing the selective hydrogenation of alkynes under mild condition.