

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

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1. Experimental

Materials. 1,1,3,3-Tetramethylguanidine (TMG) was produced by Alfa Aesar. Trifluoroacetate was provided by Beijing Chemical Reagent Company. Copper(II) acetate monohydrate ($\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$) (A. R. Grade) was purchased from Alfa Aesar. Poly(oxyethylene)iso-octylphenyl ether (TX-100) with a purity of 99%, was purchased from Sigma. H_3BTC (99%), phenylacetylene (98%), 1,3,5-trimethylbenzene (98%), L-Ascorbic acid (99%), 1-ethynyl-4-fluorobenzene (99%), 4-ethynyltoluene (98%), 3-ethynyltoluene (98%), and 1-octyne (99%) were provided by J&K scientific Co., Ltd. 4-Methoxyphenylacetylene (99%) and Pd/C (5%wt, dry) were obtained from Alfa Aesar. K_2PdCl_4 was produced by Acros. DMF (A. R. grade) and ethanol were produced by Beijing Chemical Reagent Company. 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIm]OTf), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF₄), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm]PF₆), 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIm]PF₆) and 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIm]PF₆) with >98% purity were provided by Lanzhou Greenchem ILS, LICP, CAS. All chemicals were used as received without any further purification. Water used in all experiments was deionized.

Characterization. The morphologies of the catalyst were characterized by high-resolution transmission electron microscopy (HRTEM) (JEOL-2100F) and HITACHI S-4800 SEM equipped with EDX. The product was characterized by XRD (Model D/MAX2500, Rigaku) with Cu K α radiation at a scanning rate of 5° min⁻¹. FT-IR spectra were determined using a Bruker Tensor 27 spectrometer, and the samples were prepared by the KBr pellet method. The TGA measurements were carried out using pyris 1 TGA under air atmosphere. The porosity properties were gained from nitrogen adsorption-desorption isotherms using a Micromeritics ASAP 2020M system. The loading content of Pd was determined by ICP-AES (VISTA-MPX). XPS measurement was performed on the VG Scientific ESCALab220i-XL spectrometer using Al K α radiation.

Synthesis of TMGT: In a typical experiment, 100 mL ethanol and 23 g TMG (0.2 mol) were loaded into a 250 mL flask in a water bath of 15 °C. Then 0.2 mol trifluoroacetate in 35 mL ethanol was charged into the flask under stirring. The reaction lasted for 2 hours. The reaction mixture was evaporated under reduced pressure. Then the IL was dried under vacuum at 100 °C for 48 hours, and product was obtained.

Synthesis of Catalyst-1: In a typical experiment, H₃BTC (0.1 g) and Cu(OAc)₂·H₂O (0.1 g) were added into TMGT (5 g), which was loaded in a round bottom flask. Then 0.2 mL triethylamine and 2 mL K₂PdCl₄ solution (0.005 mol/L V_{C₂H₅OH}: H₂O=1:1) were added into the flask. The mixture was stirred at room temperature for 23 hours, then L-Ascorbic acid (0.05 g) was added. After stirring for further 5 hours, the product was washed with ethanol for many times and collected by filtration. The final product was obtained after being dried at 40 °C under vacuum for 24 hours.

Synthesis of Catalyst-2: H₃BTC (0.1 g), Cu(OAc)₂·H₂O (0.1 g), C₂H₅OH (5 mL) and H₂O (3 mL) were loaded into a round bottom flask. Then 0.3 mL acetic acid and 2 mL K₂PdCl₄ solution (0.005 mol/L V_{C₂H₅OH}: H₂O=1:1) were added into the flask. The mixture was stirred at room temperature for 23 hours, then L-Ascorbic acid (0.05 g) was added. After stirring for further 5 hours, the product was washed with ethanol for

many times and collected by filtration. The final product was obtained after being dried at 40 °C under vacuum for 24 hours.

Hydrogenation of acetylene hydrocarbon: The hydrogenation of acetylene hydrocarbon was carried out in a 5 mL flask at room temperature. The flask was charged with catalyst (Pd : 0.59 μ mol), acetylene hydrocarbon (100 μ L), acetonitrile (2 mL) and 1,3,5-trimethylbenzene (126 μ L) as the internal standard. H₂ was introduced into the flask from an H₂ balloon under atmospheric pressure. After reaction for a certain time, the catalyst was separated and the product was analyzed by gas chromatograph (Agilent 6820).

Synthesis of Catalyst-3, Catalyst-4, Catalyst-5, Catalyst-6 and Catalyst-7. The Pd/IL/MOF catalysts synthesized by using [BMIm]BF₄, [BMIm]OTf, [BMIm]PF₆, [HMIm]PF₆ and [OMIm]PF₆ are denoted as **Catalyst-3, Catalyst-4, Catalyst-5, Catalyst-6** and **Catalyst-7**, respectively. As for the synthesis of Catalyst-3, H₃BTC (0.1 g) and Cu(OAc)₂·H₂O (0.1 g) were added into [BMIm]BF₄ (5 g), which was loaded in a round bottom flask. Then 0.2 mL triethylamine and 2 mL K₂PdCl₄ solution (0.005 mol/L V_{C₂H₅OH}: H₂O=1:1) were added into the flask. After the mixture was stirred at room temperature for 23 hours, the product was washed with ethanol for many times. Then it was collected by filtration. The final product was obtained after being dried at 40 °C under vacuum for 24 hours. As for the synthesis of Catalyst-4, Catalyst-5, Catalyst-6, Catalyst-7, the procedure was the same as the synthesis of Catalyst-3 only using different ionic liquids named [BMIm]OTf, [BMIm]PF₆, [HMIm]PF₆, [OMIm]PF₆, respectively.

2. Results

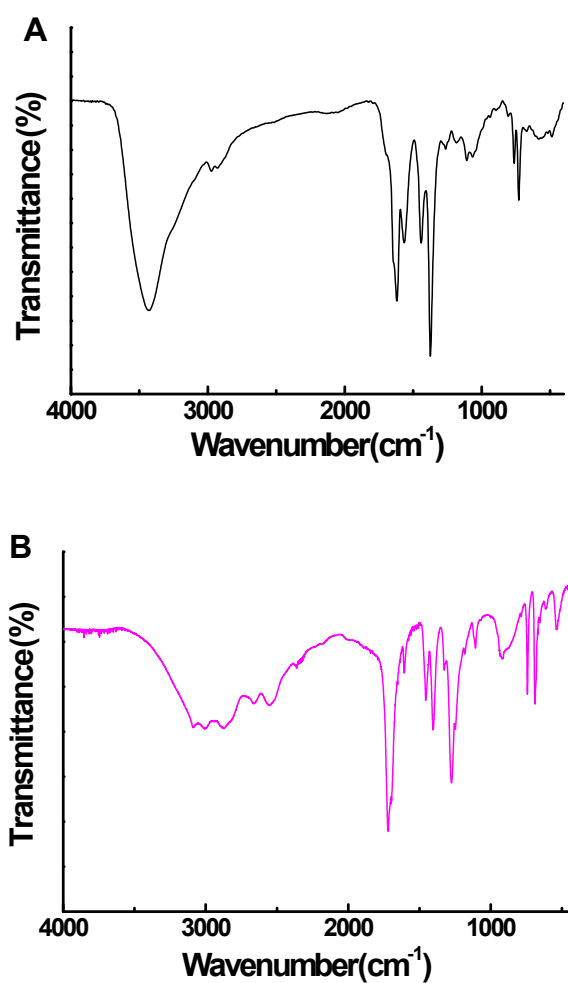


Fig. S1 FT-IR spectra of the **Catalyst-1** (A) and H₃BTC (B). The FT-IR spectra of **Catalyst-1** is similar to that of HKUST-1,¹ displaying the characteristic asymmetric (1630cm⁻¹, 1562cm⁻¹) and symmetric vibration (1443 cm⁻¹, 1373 cm⁻¹) of carboxylate anions in deprotonated H₃BTC. In comparison with the IR spectrum of H₃BTC (B), the wavenumber difference of asymmetric and symmetric vibration of carboxylate anions is narrowed. This indicates that carboxylate groups of BTC are coordinated to Cu (II) ions.

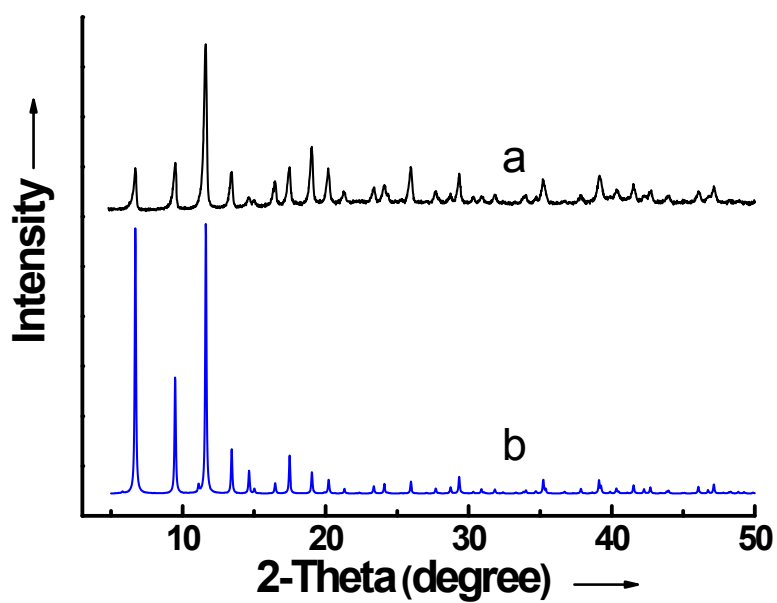


Fig. S2 XRD patterns of Catalyst-1 (a) and the the reported $\text{Cu}_3(\text{BTC})_2$.

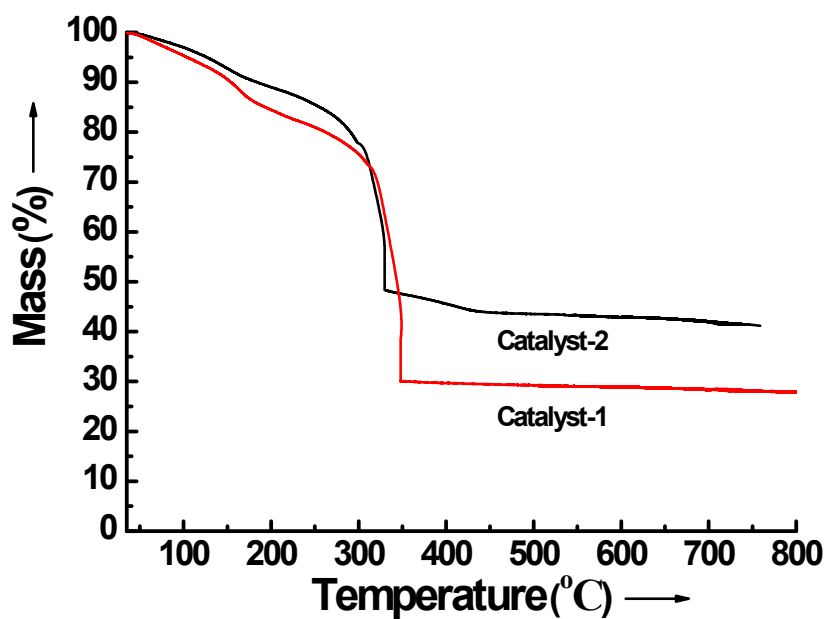


Fig. S3 Thermogravimetric curves of Catalyst-1 and Catalyst-2.

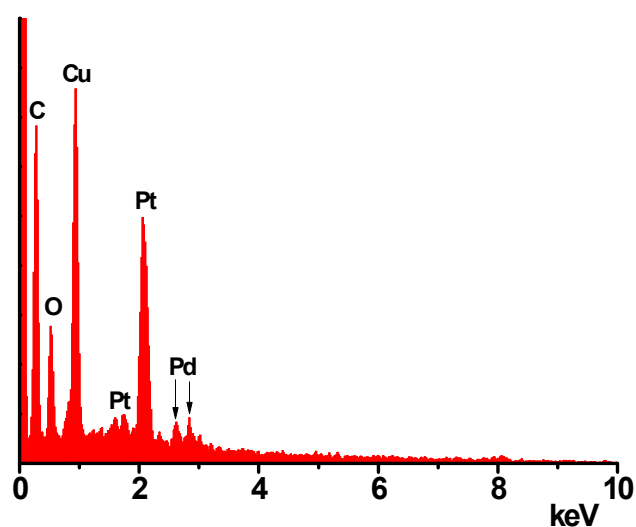


Fig. S4 Energy dispersive X-ray (EDX) spectrum of **Catalyst-1**. It demonstrates the presence of copper, oxygen, carbon and Palladium in the prepared **Catalyst-1**. The Pt results from sample spraying for better conductivity, in order to gain better SEM images.

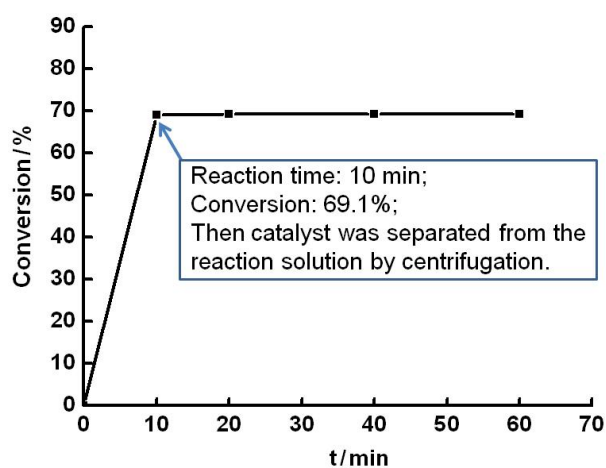


Fig. S5 Hot extraction experiments of Catalyst-1.

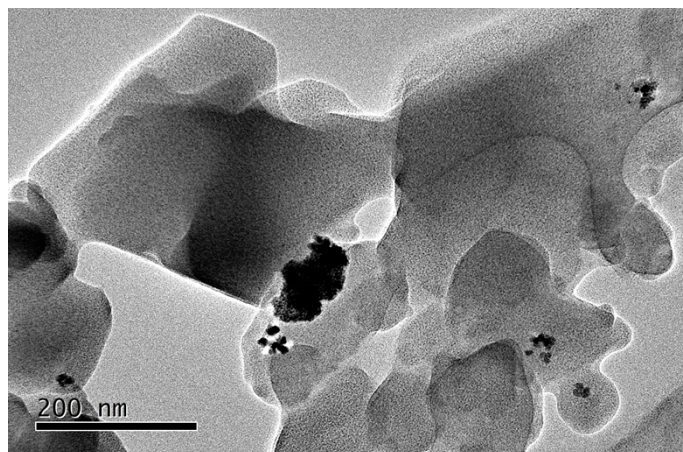


Fig. S6 TEM image of **Catalyst-2**.

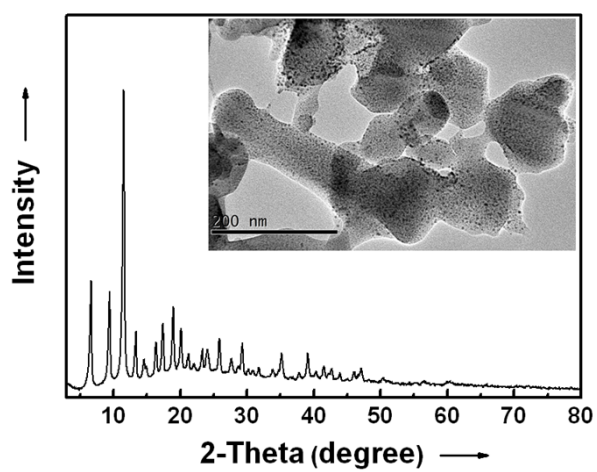


Fig. S7 XRD and TEM image of catalyst-1 after running for five runs for hydrogenation.

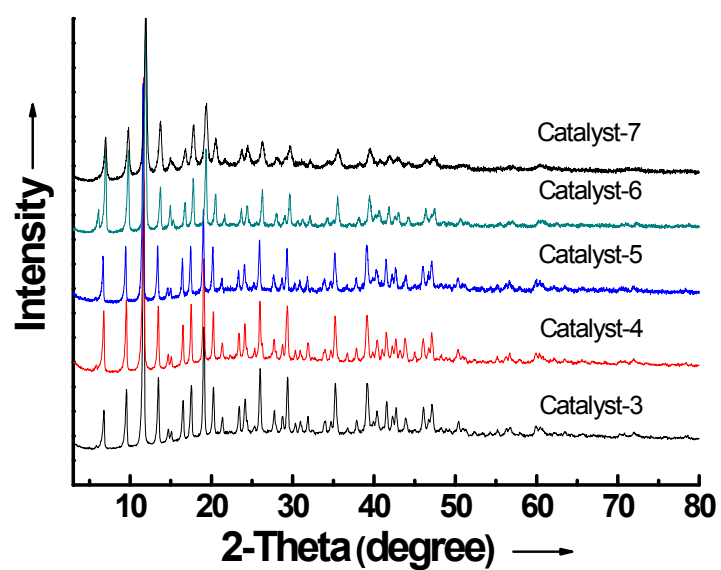


Fig. S8 XRD patterns of Catalyst-3, Catalyst-4, Catalyst-5 Catalyst-6 and Catalyst-7.

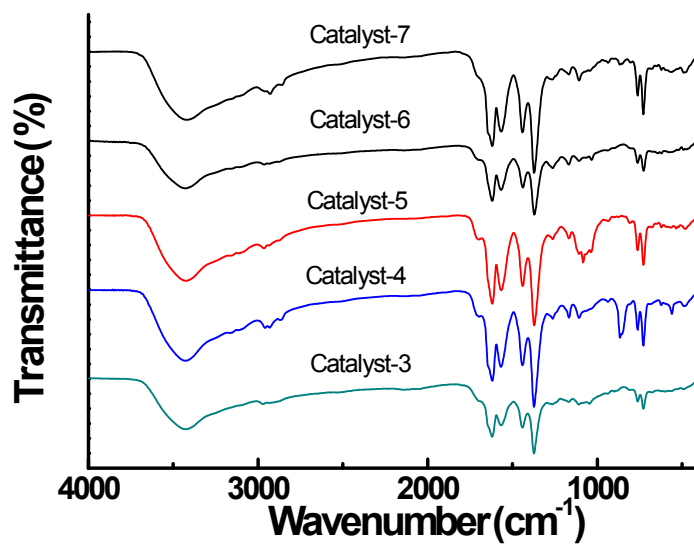


Fig. S9 FTIR spectra of Catalyst-3, Catalyst-4, Catalyst-5, Catalyst-6 and Catalyst-7.

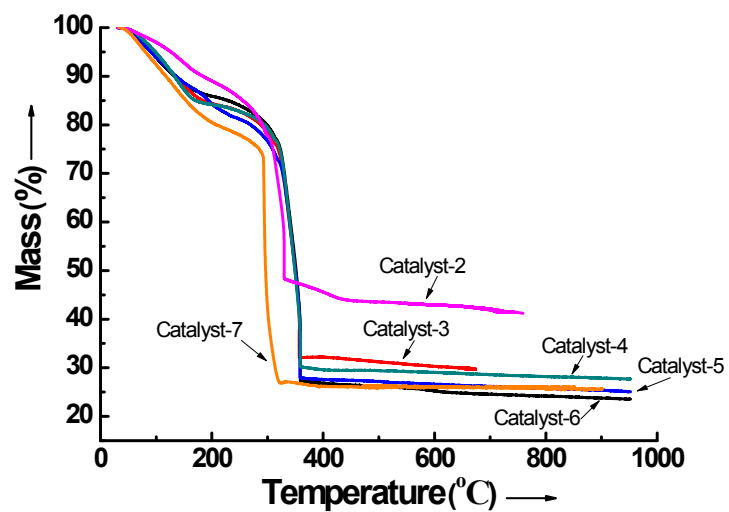
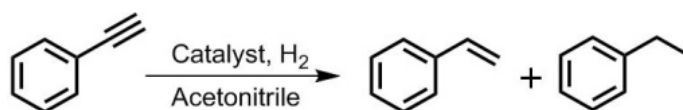


Fig. S10 Thermogravimetric curves of **Catalyst-2**, **Catalyst-3**, **Catalyst-4**, **Catalyst-5**, **Catalyst-6** and **Catalyst-7**. The IL contents in **Catalyst-3**, **Catalyst-4**, **Catalyst-5**, **Catalyst-6** and **Catalyst-7** are 12.6 wt%, 12.8 wt%, 15.9 wt%, 17.2 wt% and 15.9 wt%, respectively.

Table S1 Hydrogenation of phenylacetylene with different catalysts. ^[a]

Entry	Catalyst	Time	Conversion	Selectivity
1	Catalyst-3	40 min	46%	>99%
2	Catalyst-3	70 min	>99%	98%
3	Catalyst-4	40 min	51.1%	>99%
4	Catalyst-4	65 min	>99%	>99%
5	Catalyst-5	40 min	57.9%	>99%
6	Catalyst-5	55 min	>99%	98%
7	Catalyst-6	40 min	58.4%	>99%
8	Catalyst-6	65 min	>99%	>99%
9	Catalyst-7	40 min	40.1%	>99%
10	Catalyst-7	70 min	62.8%	>99%
11	Catalyst-7	110 min	>99%	97%

[a] reaction condition: catalyst (Pd : 0.59 μ mol), 1a (100 μ L, 0.91 mmol) in 2.0 mL acetonitrile using the 1,3,5-trimethylbenzene as the internal standard, atmospheric H₂ balloon, 30 °C.

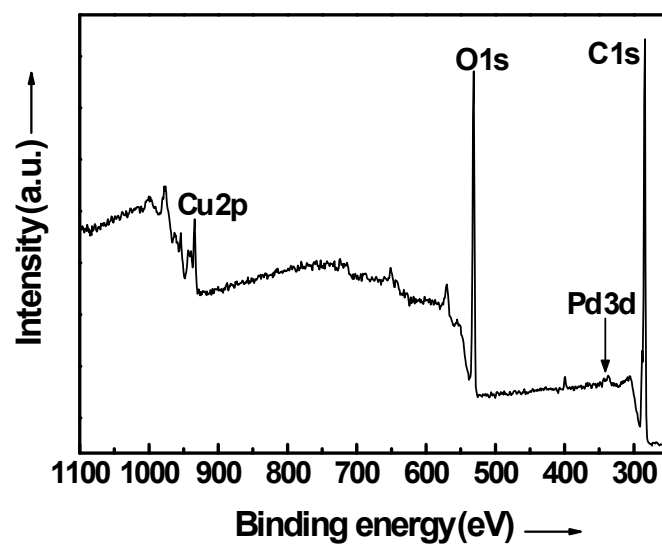


Fig. S11 XPS spectra of Catalyst-1.

Reference

- 1 L. -B. Sun, J. -R. Li, J. Park and H. -C. Zhou, *J. Am. Chem. Soc.* 2012, **134**, 126.