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Gold Nanoparticles Embedded into Imidazolium-Functionalized Porous Aromatic Frameworks as Heterogenous Nanoreactors for Nitroaromatics Hydrogenation

Yuting Yang,[a] Yadong Shi,[b] Yuzhuo Zhang,[c] Xiaofei Jing*[b] and Yunling Liu,*[a]

[a] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China.
[b] Key Laboratory of Polyoxometalate and Reticular Material Chemistry of Ministry of Education, Northeast Normal University, Changchun 130024, P. R. China.
[c] State Key Laboratory of Chemical Resource Engineering, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China.
*Corresponding author E-mail: yunling@jlu.edu.cn (Y.L. Liu); jingxf100@nenu.edu.cn (X.F. Jing)

1. Characterization

Fourier transforms infrared spectra (FTIR) was tested on a Nicolet IS50 FTIR spectrometer, and the pellets were prepared by adding KBr. ^{13}C CP/MAS solid-state NMR spectra of iPAFs and Au-iPAFs were measured on a Bruker Avance III model 400 MHz NMR spectrometer at a MAS rate of 5 kHz. X-ray photoelectron spectroscopy (XPS) was performed by an Escalab-MK II photoelectronic Spectrometer with Al Kα (1200 eV). Power X-ray diffraction was carried out by a Rigaku SmartLab X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 50 kV and 200 mA. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were measured by field emission scanning electron microscopy (FE-SEM, SU-8010, Hitachi) and a JEOL JEM-2100PLUS TEM at an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) was measured by a METTLER-TOLEDO TGA/DSC 3+ analyzer at a heating rate of 10 °C min^{-1} in air atmosphere. N_2 adsorption isotherms at 77 K were obtained by a Quantachrome Autosorb-iQ2 analyzer with N_2 as probe molecule. The Au contents of Au-iPAFs were detected using Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) on a LEEMAN Labs Prodigy. UV-vis spectra were recorded on a Cary 50 Conc UV-visible spectrophotometer and the wavelength was tested from 200 to 600 nm. Gas Chromatography Mass Spectrometry (GC-MS) analysis was employed for determining the catalytic reaction products using a Thermo Scientific Trace 1310-ISQ 7000 system.

2. Experimental section

2.1 Chemicals and materials

All chemicals were purchased from commercial suppliers without further purification. 1,3,5-Tris(4-ethynylphenyl)benzene (Tepb), 1,4-dibromo-2,5-bis(bromomethyl)benzene (Dbbb), 1,4-dibromo-2,3,5,6-tetramethylbenzene (Dttb), 1-methylimidazole, n-bromosuccinimide (NBS), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) and copper(I) iodide (CuI) were purchased from Innochem. Tetrachloroauric acid ($HAuCl_4$), sodium borohydride ($NaBH_4$), nitroaromatics and amino aromatics compounds were obtained from Acros Orangic. Other solvents were obtained from local commercial suppliers.

2.2 Synthesis of 1,4-dibromo-2,5-bis(3-methylimidazolyethyl)benzene (Dbmb)

Dbbb (1 mmol) was added into a 100 mL two-neck flask with a condenser pipe and magnetic stirring. 1-Methylimidazole (3 mmol) and anhydrous acetonitrile (50 mL) were injected into the reaction system under N_2 atmosphere. Then, the mixture was reacted for 12 h at 120 °C. After cooling to room temperature, the solid product was filtered and washed using acetonitrile, then off-white power (yields for 69%) was collected and dried under vacuum at 80 °C for 24 h. ^1H NMR (500 MHz, d6-DMSO, 298 K, TMS): δ 9.25 (s, H), 7.79 (s, H), 7.77 (s, H), 7.78 (s, H), 5.78 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, d6-DMSO, 298 K, TMS) δ 36.42, 51.61, 123.03, 123.44, 124.53, 135.53, 136.72, 137.75.

2.3 Synthesis of 1,4-dibromo-2,3,5,6-tetrakis(3-methylimidazolyethyl)benzene (Dtmb)

2.3.1 Synthesis of 1,4-dibromo-2,3,5,6-tetrakis(bromomethyl)benzene. The 100 mL round-bottom flask with Dttb (2 mmol), NBS (14.4 mmol) and 30 mL of chloroform was heated to 78 °C, and white precipitates was observed after refluxing and stirring for 5 h. After cooling to room temperature, the product was collected by filtration and washed three times by cold dichloromethane. The pure compound (yields for 75%) was obtained after dried for 24 h at 60 °C.

2.3.2 Synthesis of 1,4-dibromo-2,3,5,6-tetrakis(3-methylimidazolylethyl)benzene (Dtmb). 1 mmol 1,4-dibromo-2,3,5,6-tetrakis(bromomethyl)benzene was added into a two-neck flask and the system was degassed and then filled with of N_2. 5 mmol 1-methylimidazole and 50 mL of anhydrous acetonitrile were injected into the system, which was stirred at 120 °C for 12 h and cooled down. The precipitate was filtered and purified by washing with acetonitrile, and then dried under vacuum at 80 °C for 24 h (yields for 63%). ^1H NMR (500 MHz, d6-DMSO, 298 K, TMS): δ 9.25 (s, H), 7.79 (s, H), 7.77 (s, H), 5.78 (s, H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, d6-DMSO, 298 K, TMS): δ 36.26, 52.03, 123.27, 124.05, 133.85, 137.12, 137.72.

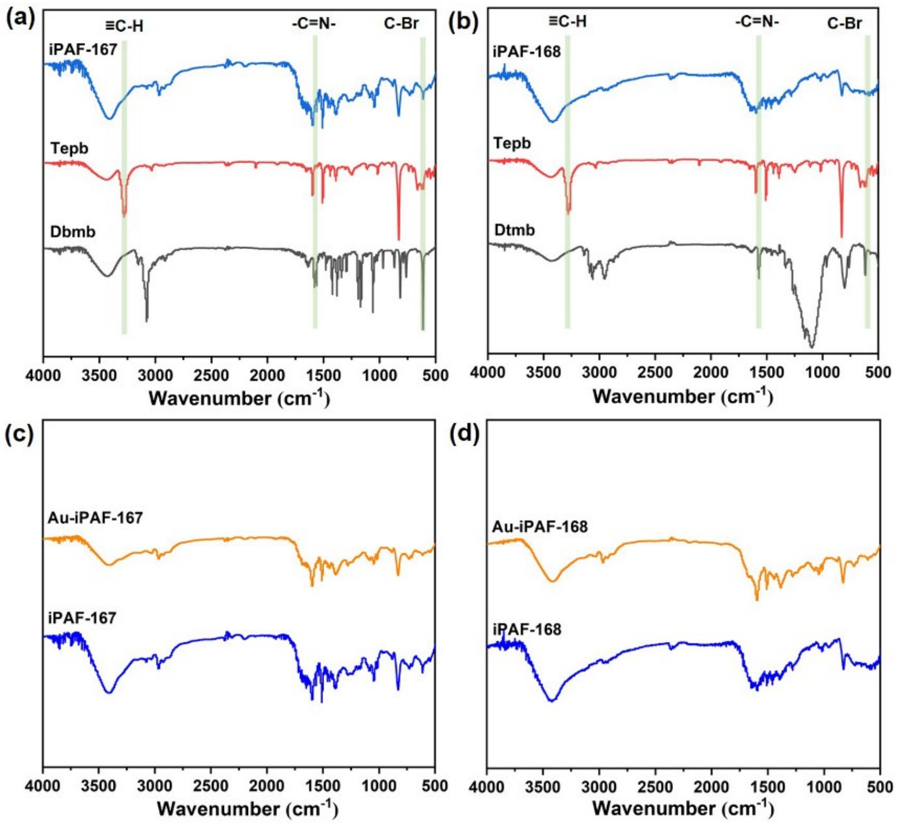

Fig. S1 FTIR spectra of iPAF-167 (a), iPAF-168 (b) and their corresponding monomers. FTIR spectra of Au-iPAF-167 (c) and Au-iPAF-168 (d) before and after AuNPs immobilization.

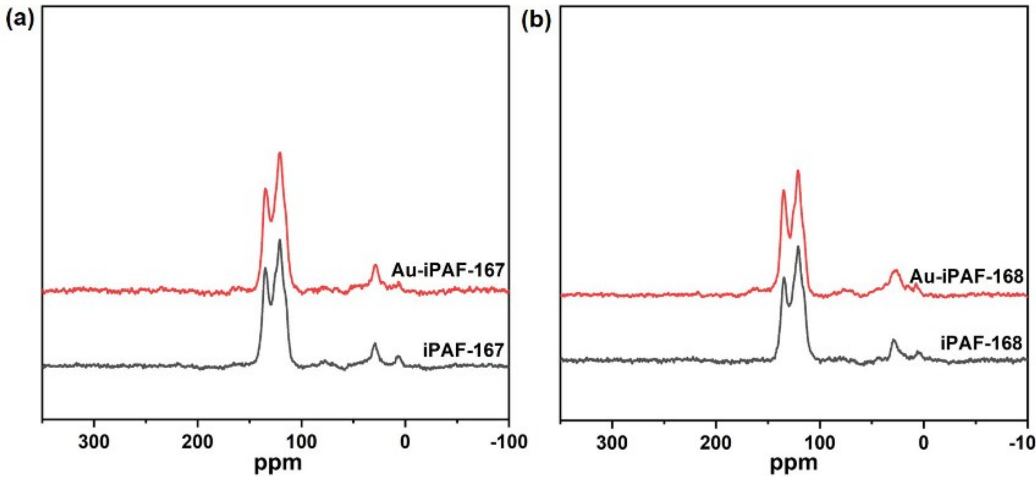

Fig. S2 (a) ^{13}C MAS/NMR spectra of iPAF-167 and Au-iPAF-167. (b) ^{13}C MAS/NMR spectra of iPAF-168 and Au-iPAF-168.

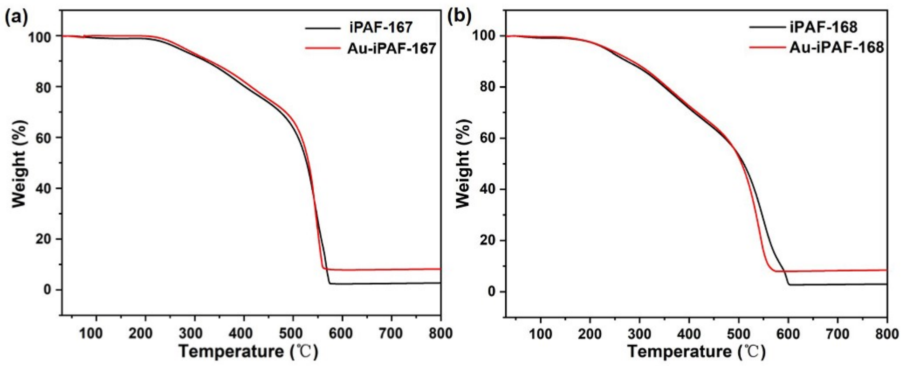

Fig. S3 TGA curves of iPAF-167/Au-iPAF-167 (a) and iPAF-168/Au-iPAF-168 (b).

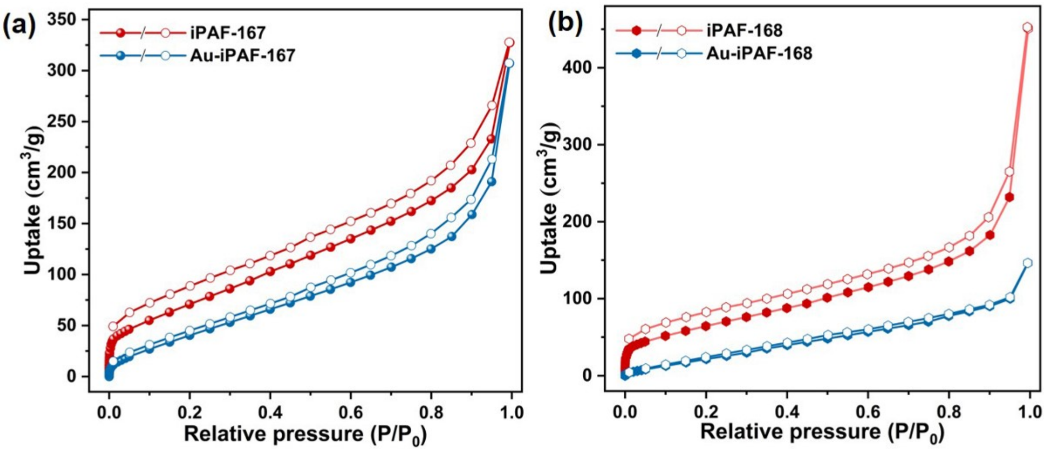

Fig. S4 N_2 adsorption-desorption isotherms at 77 K of iPAF-167/Au-iPAF-167 (a) and iPAF-168/Au-iPAF-168 (b).

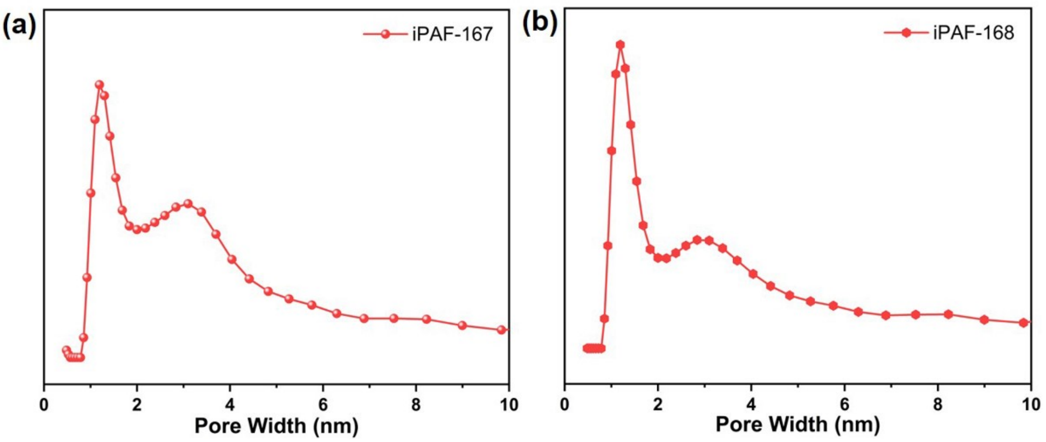

Fig. S5 Pore size distribution of iPAF-167 (a) and iPAF-168 (b).

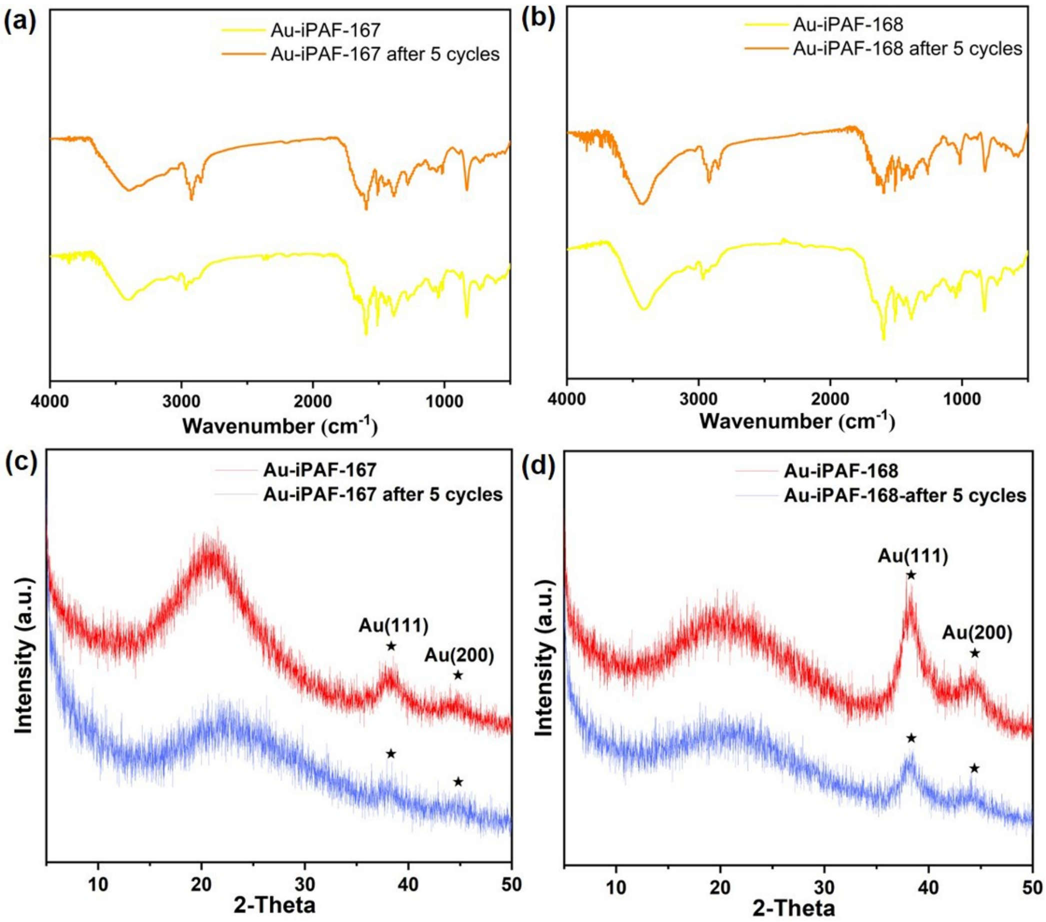

Fig. S6 FTIR spectra of fresh Au-iPAF-167 (a), Au-iPAF-168 (b) and corresponding recycled Au-iPAFs catalysts. PXRD patterns of fresh Au-iPAF-167 (c), Au-iPAF-168 (d) and corresponding recycled Au-iPAFs catalysts.