

Supporting Information

Experimental section:

Reagents: All reagents were purchased from Aladdin Reagent Company and Alfa-Aesar Company without further purification. The catalysts Rh/C (5.0wt% Rh contained), Pd/C (5.0 wt% Pd contained) and Pt/C (5.0 wt % Pd contained) were purchased from Aladdin Reagent Company, and the specific surface areas (BET) were about 1300 m²/g for all the 3 catalysts (the Rh/C, Pd/C and Pt/C) as provided by Aladdin Reagent Company.

Analytical Methods:

Gas chromatography analysis were performed on a Hewlett Packard 5890 instrument with a FID detector and Hewlett Packard 24 m x 0.2 mm i.d. HP-5 capillary column. TEM (Transmission electron microscopy) images were obtained on a transmission electron microscope (Tecnai 12) with an accelerating voltage of 120 kV.

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 400 MHz instrument with chemical shifts reported in ppm relative to the residual deuterated solvent or the internal standard tetramethylsilane.

Element analysis was carried out on the Elementar Vario EL III instrument.

The specific surface areas and the average pore sizes of the materials were measured on a Belsorp II physical adsorption apparatus by BET and BJH methods.

The preparation of the PICP material was the same as reported recently ^[1], and the detailed procedure was presented as following.

Preparation of the ionic monomer for PICP:

1,1,3,3-Tetramethylguanidinium (TMG, 0.625 ml, 5.0 mmol) was added into a 25 mL pressure tube under argon, then 4-Vinylbenzyl chloride (1.41 ml, 10.0 mmol) was dropped slowly into the tube with stirring. The mixture was heated to 80 °C for 1 h, and then the mixture turned into a white solid. Dichloromethane (10 ml) was added to the tube to dissolve the solid under argon when the mixture cooled to room temperature, and the sealed tube was kept at 80 °C for 24 h with stirring. When the mixture cooled to room temperature, Na₂CO₃ (0.53 g, 5.0 mmol) was added under argon, and the sealed tube was kept at 80 °C for another 24 h. After the reaction mixture was cooled, the solid was filtered. The filtrate was concentrated with rotary evaporator to give an oil, and then the oil was washed with diethyl ether (3×10 mL) to give the ionic monomer as a white solid (1.8 g, 93% yield). ¹H-NMR (CDCl₃, 300 MHz): δ 7.39–7.36 (d, 4H, *J*=7.92 Hz), 7.17–7.14 (d, 4H, *J*=8.04 Hz), 6.69–6.59 (q, 2H, *J*=10.95 Hz), 5.75–5.69 (d, 2H, *J*=17.61 Hz), 5.26–5.22 (d, 2H, *J*=12.63 Hz), 4.29–4.25 (d, 2H, *J*=13.71 Hz), 3.96–3.92 (d, 2H, *J*=13.41 Hz), 3.14–2.94 (m, 12H). ¹³C-NMR (CDCl₃, 300 MHz): δ 162.7, 138.0, 135.7, 133.4, 129.0, 126.8, 114.9, 53.1, 40.9 and 40.2. Calc. for C₂₃H₃₀ClN₃: C, 71.95%; H, 7.88%; N, 10.94%; Cl, 9.23%. Found: C, 68.65%; H, 8.98%; N, 10.27%; Cl, 12.1%.

Preparation of the PICP:

The ionic monomer (1 g), AIBN (azobisisobutyronitrile, 40 mg), divinylbenzene (1.25 g) and anhydrous ethanol (20 ml) was added into a 100 mL Schenck tube under argon and sealed. After stirring at 70 °C for 4 h, the mixture was heated to 80 °C for another 24 h without stirring. When the mixture was cooled to room temperature, a white solid was collected by filtration and washed with ethanol (3×10 mL) and water (3×10 mL). And then the PICP (1.64 g, 72% yield) was obtained by washing with water, and dried at 100 °C under vacuum for 24h. The composition of the PICP was examined by elemental analysis, and the result indicated that the content of the ionic monomer was 30.0 wt% (13.0 mol %). Element analysis: C 78.48%, H 7.52%, N 3.15%.

The specific surface area of the PICP was up to 528 m²/g after vacuum pretreatment at 250 °C based on the nitrogen adsorption-desorption analysis. In order to detect the surface and thermal stability of the PICP material, the PICP was characterized by SEM and TG (Fig S1, S2). The PICP was found with irregular pores of macropores, mesopores and micropores, and the total pore volume of 0.96 mL/g was detected by BJH analysis (Fig S3).

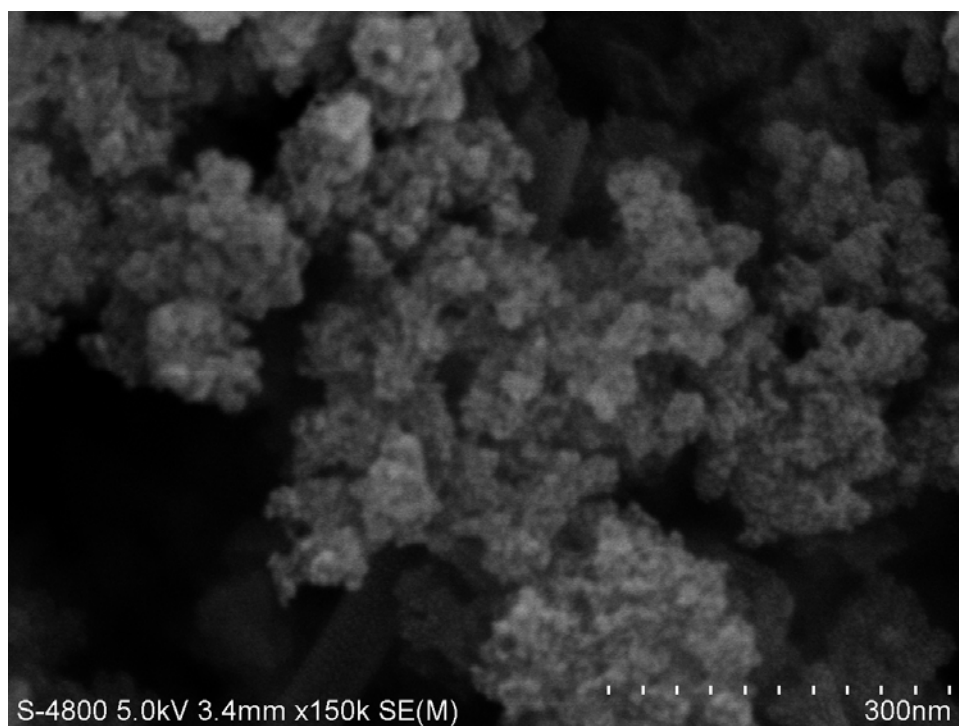


Figure S1. SEM image of the PICP.

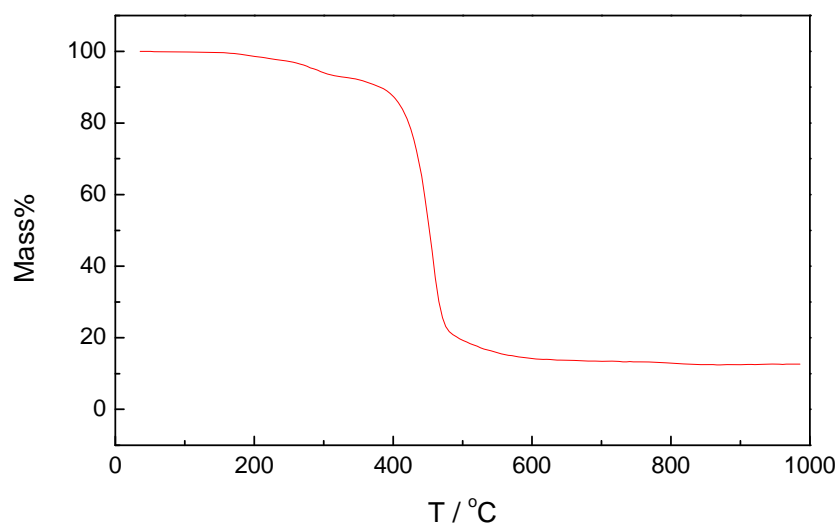


Figure S2. TG analysis of the PICP.

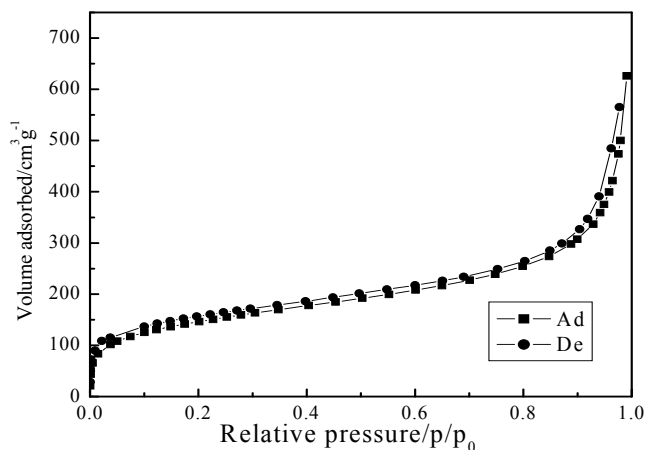


Figure S3. Nitrogen adsorption-desorption isotherms of PICP.

Preparation of the Rh/PICP:

The PICP (200 mg) was added into a solution of $\text{Rh}(\text{AcO})_2$ ($\text{Rh}(\text{AcO})_2$, 8.8 mg, 0.039 mmol in 10 mL H_2O) in a round bottom flask. After the resulting slurry was stirred for 3 h, a solution of NaBH_4 (contain 14.7 mg/0.39 mmol NaBH_4) was added to this suspension with stirring within 2 min. After stirring for another 2 hours, the solid was filtered off, washed thoroughly with water, and then dried under vacuum to afford Rh/PICP catalyst (106 mg). The content of Rh (2.01 wt %) was detected by ICP-OES (inductively coupled plasma optical emission spectroscopy) analysis. The ICP-OES analysis was performed with Perkin Elmer OPTIMA 2000DV.

The specific surface area of the Rh/PICP was about $358 \text{ m}^2/\text{g}$ after vacuum pretreatment at 250°C based on the nitrogen adsorption-desorption analysis. The total pore volume of 0.67 mL/g was detected by BJH analysis (Fig S4).

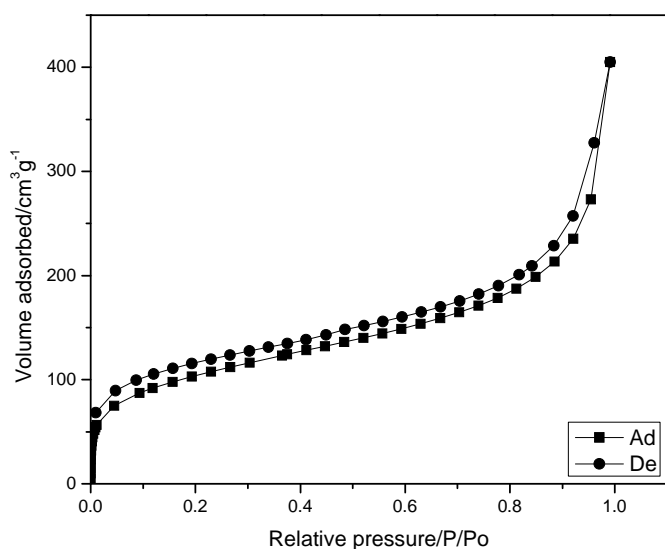


Figure S4. Nitrogen adsorption-desorption isotherms of Rh/PICP.

Reusability of the Rh/PICP:

When the reaction completed and the reaction mixture was cooled, the catalyst was collected by filtration. The catalyst was washed by ethyl ether (3×2 mL) and dried under vacuum at the 25 °C for 12 h. The recycled catalysts were used again for the next reaction cycle of hydrogenation of nitrobenzene.

Typical procedure for the hydrogenation of nitroarenes:

A nitroarene (1.0 mmol), hydrazine monohydrate (4.0 mmol) and ethanol (2.0 mL) were added to a schlenk tube which contained Rh/PICP (Rh: 0.1-1.0 mol %) catalyst and a stir bar under argon. The reaction mixture was stirred for 1 hour at 60 °C. After the reaction was cooled, 100 µL C₁₆H₃₄ was added to the reaction mixture. The Rh/PICP catalyst was filtrated off and washed with diethyl ether (3×2.0 mL). The products (in the filtrate mixture) were analyzed by GC. All prepared anilines are commercially available and identified by comparison (GC/MS) with authentic samples (purchased from Aladdin Reagent, Alfa-Aesar and Sigma-Aldrich Company).

The hydrogenation of mixture of nitrobenzene and styrene

Nitrobenzene (51 µL, 0.5 mmol), styrene (57 µL, 0.5 mmol), hydrazine monohydrate (2.0 mmol) and ethanol (1.0 mL) were added to a schlenk tube which contained Rh/PICP (Rh: 1 mol%, 25.5 mg) catalyst and a stir bar under argon. The reaction mixture was stirred at 80 °C. After a specific time, the reaction mixture was analyzed by GC to determine the contents of the mixture.

References

1. T. Hu, X. Chen, J. Wang, J. Huang, *ChemCatChem* 2011, **3**, 661-665; b) K. Xu, Y. Zhang, X. Chen, L. Huang, R. Zhang, J. Huang, *Adv. Synth. Catal.* 2011, **353**, 1260-1264.