Supporting Information

Fe_3O_4@SiO_2@Pd-Au: A Highly Efficient and Magnetically Separable Catalyst for Liquid-Phase Hydrodechlorination of 4-Chlorophenol

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Experiment Section:

Synthesis of silica

The silica was synthesized by the hydrolysis of TEOS. In a typical procedure, 0.020 mol/L dodecylamine (DDA) was composed in a mixed solution of ethanol (0.16 L) and distilled water (0.1 L). Then 0.3 L 0.20 mol/L TEOS was added dropwise to the above solution at 25 ^{o}C. After continuous stirring for 4 h, the product was collected by centrifugation, and repeatedly washed with water and ethanol for four times, then dried in a vacuum oven at 80 ^{o}C for 4 h, finally calcined at 400 °C for 4 h in a muffle furnace to remove the templates, respectively.

Synthesis of amine modified silica

The surface functionalization of the silica with amine groups was carried out by adding 300 μL (3-aminopropyl) triethoxysilane (APTS) to 30 mL of dry toluene containing 200 mg of silica nanoparticles. The resulting mixture was stirred for 2 h and then centrifuged and washed with toluene and acetone for 3 times. The solid was finally treated at 100 ºC for 20 h.

Synthesis of Pd, Au and Pd-Au catalysts

The first step is the loading of Pd^{2+} and Au^{3+} onto the functionalized supports. In

a typical preparation: 100 mg of functionalized silica were added to 40 mL of palladium acetate or $Au(en)_3Cl_3$ (en: ethylene diamine) aqueous solution (0.5 mmol/L) under inert atmosphere. The suspension was stirred for two hours at room temperature. The solid was collected by magnetic separation, washed with ethanol and acetone, and dried in vacuum. The metal loaded solid was suspended in cyclohexene, and reduced by 0.1 M KBH_4 solution at 25 ^oC. The metal loading of Pd and Au was controlled at 1.0 wt. %.

UV-visible spectra of samples

Diffuse reflectance UV-vis spectra were recorded using a Harrick Scientific diffuse reflectance attachment (DRP) with a reaction chamber (DRA-2CR) and a Varian Cary 500 spectrophotometer. Samples were placed in the chamber and heated them at 2 ^oC/min to 110 ^oC for 1 h. Spectra were recorded at room temperature. MgO was used as the reference spectrum.

Results

Here, we included the UV-vis spectra (Figure S1) of silica supported Pd-Au nanoparticles using our synthesis strategy (Scheme 1) to clarify the successful formation of alloy at our current synthesis conditions. The UV-Vis spectra show surface plasma absorption around 520 nm for the Au nanoparticles (Figure S1). In order to confirm the bimetallic nature of the particles, a physical mixture is prepared from the already prepared individual components and its absorbance is compared to that of the bimetallic Pd-Au nanoparticles of the same composition (Figure S1 b and c). The absorbance band characteristic of gold that appears at 520 nm is absent in the

case of the bimetallic Pd-Au (Figure S1c) while it is present in the case of the physical mixture (Figure S1b). The absence is ascribed to that the presence of Pd in the bimetallic nanoparticles suppresses the surface plasma energies of Au, which is consistent with the reported results [1, 2], and suggests the formation of Pd-Au alloy nanoparticles.

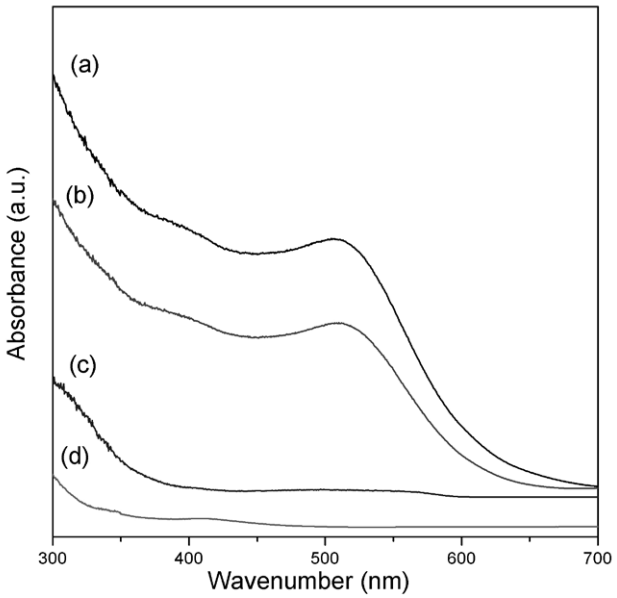

Figure S1. UV-Vis absorbance spectra of samples: (a) SiO_2@Au, (b) physical mixture of SiO_2@Au and SiO_2@Pd with a molar ratio of Pd/Au=64/36, (c) SiO_2@Pd_{64}-Au_{36}, and (d) SiO_2@Pd.

Reference:

1. M. L. Wu, D. H. Chen, T. C. Huang, *Langmuir* 2001, **17**, 3877-3883

2. H. Kobayashi, M. Yamauchi, R. Ikeda, H. Kitagawa, *Chem. Commun*, 2009, **32** 4806-4808.