

A highly stable and active Pd catalyst on monolithic cordierite with graphene coating assistant by PDDA

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Supporting information

1. Experimental

1.1. Catalyst preparation

Commercial cordierite honeycomb ($2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 2\text{MgO}$) with size $\Phi 47 \times 11.5$ mm and 400 holes/inch² was treated in 10% nitric acid at 130 °C for 2 h followed by washing with water and keeping dry in oven. Then the aqueous solution of GO nanosheets (0.08 mg/mL, 50mL) obtained by Hummers method was mixed with PDDA aqueous solution with a concentration (1.30×10^{-4} g/L, 3mL) by ultrasound for 20 min. Then a cordierite honeycomb was immersed into the mixture by ultrasound for 20 min followed by wash with water. The resulting sample is denoted as (GO+PDDA)/Cor. Subsequently, the (GO+PDDA)/Cor was immersed in a 0.01M H_2PdCl_4 solution by ultrasound for 20 min, and then dried at 60 °C for 6 h. Finally, the sample was calcined in air at 350 °C for 2 h followed by reduction in potassium borohydride (KBH_4) solution. The resulting catalyst is denoted as Pd/(Gr+PDDA)/Cor. As comparison, Pd/PDDA/Cor catalyst was prepared by modifying cordierite with a PDDA aqueous solution with a concentration 0.261 g/L for 20 min, and then loading Pd as previous steps. Pd/Gr/Cor catalyst was prepared by modifying cordierite with GO with a concentration 0.8 mg/mL for 20 min, and then loading Pd as previous steps.

1.2. Characterization

The surface groups of cordierite before and after introducing PDDA and graphene were determined by Fourier Transform Infrared spectroscopy (FT-IR) measurement on a Nicolet6700 infrared spectrometer (America). The actual Pd loadings on monolithic catalysts were determined by inductive graft plasma atomic emission spectrograph (ICP-AES) on Perkin Elmer Optima5300 (America). The morphology and size of palladium particles on monolithic catalysts were recorded by transmission electron microscopy (TEM) on a JEOL JEM-2100 (Japan) operated at 200 kV. The Zeta potentials of samples were investigated by Malvern ZEN3600 Zetasizer (UK). X-ray photoelectron spectroscopy (XPS) analysis was conducted on an ESCALAB 250Xi photoelectron spectrometer (Thermo Fisher Scientific) by using monochromatic Al K α X-ray beam as the excitation source and all binding energies were calibrated by the C 1 s peak of the surface adventitious carbon at 284.6 eV. CO chemisorption experiment were performed using a micromeritic AUTOCHEM II 2920 (America). UV-vis spectra were performed on a Shimadzu UV-2450 spectrophotometer (Kyoto, Japan).

1.3. Reaction experiments

Catalytic performance of the monolithic catalysts was tested on hydrogenation of styrene to ethylbenzene. The catalytic reaction was carried out in a glass batch reactor with a magnetic stirrer at 25 °C. The monolithic catalysts was suspended in 100 mL ethanol and pretreated in H_2 flow (30 mL/min) at 25 °C for 1 h. Then styrene (2 mL) together with n-decane (0.1 mL), which was used as the internal standard, was added. The reaction was allowed at 25 °C at atmospheric pressure in H_2 flow under stirring. The reaction was monitored by gas chromatographic (SHIMAZU 2010, column RTX-5 with inner diameter 0.25 mm, film depth 0.25 μm and length 30 m) analysis of the effluents withdrawn from the reactor at every 10 min. The absence of external diffusion limitations has been verified by performing under different stirring rates.

Styrene hydrogenation intrinsic kinetics coincides with zero order reaction law. The rate of the conversion of styrene keeps constant in the entire reaction process, namely, $-r_{ST} = \frac{dn_{ST}}{dt} = k$. And the activity of catalyst is defined as the conversion rate per mass Pd, denoted as A.

2. Characterizations

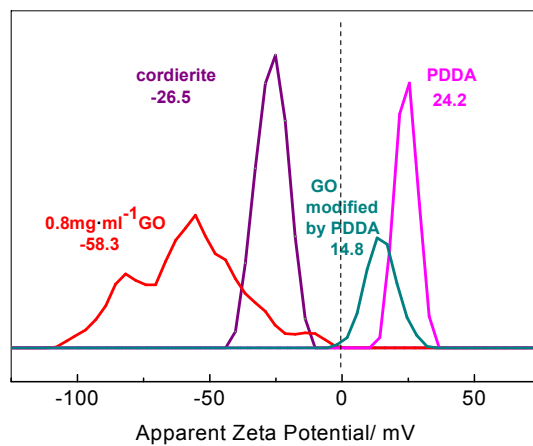


Fig. S1. Zeta potentials of GO, Cordierite, PDDA and GO modified by PDDA.

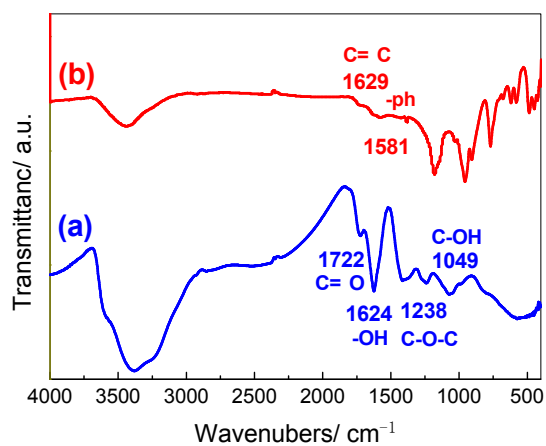


Fig.S2. FT-IR spectra of (GO+PDDA)/Cor (a) and (Gr+PDDA)/ Cor (b).