

Supplementary Material (ESI) for Chemical Communications

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Supplementary Information

Pd-on-Si catalysts prepared via galvanic displacement for selective hydrogenation of para-chloronitrobenzene

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1 Experimental

1.1 Catalyst preparation

Pd-Si catalyst was prepared by galvanic reaction method which could be expressed by the following equation.



A desired amount of H_2PdCl_4 (PdCl_2 , 99.9 %, J&K) in HCl (AR, Beijing Chemical Reagent Company) aqueous solution (100 mM) and 2 g Si powder (99.9 %, 325 meshes, Hebei Hengxinda Silicon Co., Ltd.) were added to 50 mL aqueous solution of HF (5 %, AR, Beijing Chemical Reagent Company) with vigorous stirring for 2 h. The resulting solid was then thoroughly washed with deionized water until electric conductivity of filtrate (centrifugal liquid) is below 10 μS , and dried in 100 °C under vacuum. The loading of xPd-Si was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES), where x represents the Pd loading in weight percentage (wt%).

1.2 Characterization

BET measurements were carried out with Kr adsorption at -196 °C on a Micromeritics Tristar II 3020 instrument after the samples were degassed at 100 °C for 2 h.

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-ray diffractometer using $\text{Cu K}\alpha$ ($\lambda = 0.15406$ nm) radiation source at 40 kV and 40 mA. All the spectra were recorded at 20° ~ 90° with a scan rate of 6° min^{-1} , the weaker peaks being scanned for longer time (1° min^{-1}) to ensure adequate signal/noise ratios. The average crystallite sizes were calculated according to the well-known Scherrer equation, $D = 0.90\lambda/\beta\cos\theta$, where θ is the diffraction angle and β the full width at the half-maximum (FWHM).

X-ray photoelectron spectroscopy (XPS) spectra were recorded by an SKL-12 spectrometer equipped with Mg K α radiation. The residual pressure in the analytical chamber was maintained below 10^{-8} Torr during data acquisition. The binding energies of Pd 3d were corrected for surface charging by referencing them to the energy of C 1s peak of contaminant carbon at 284.8 eV.

1.3 Hydrogenation reaction of *p*-CNB

The conditions of hydrogenation of para-chloronitrobenzene (*p*-CNB) was reported as previous.^{1,2} 5 mL toluene (AR, Sinopharm Chemical Reagent Co., Ltd.), certain amount of *p*-CNB (99 %, J&K) and xPd-Si catalyst (10 ~ 100 mg) were added to a 25 mL steel autoclave. The reactor was purged with hydrogen six times and then pressurized to the desired pressure of 1 MPa. Zero reaction time was taken as soon as the autoclave was heated to the reaction temperature (e.g., 100 °C), and the magnetic stirring (900 rpm) was not switched on until that very moment. The selected stirring speed (900 rpm) enabled the reaction to proceed under kinetic control, independent of speed of stirring, which was checked by varying stirring speeds in the range of 300-1100 rpm. An ice-water bath was used to cool the autoclave at the end of each reaction. The reacted liquid was separated from catalyst powders by filtration and then analyzed by a HP-7890A gas chromatograph (GC) equipped with a Shimadzu HiCap CBP20 capillary column and a flame ionization detector, using diphenylamine (99 %, Acros) as an internal standard. Special attention has been paid to distinguish products of the reaction with GC-MS analysis, any products amounted to 0.05% in the reaction liquid could be unambiguously detected. The carbon balance of the reaction on xPd-Si catalyst was always within 100 ± 5 %.

2 Results

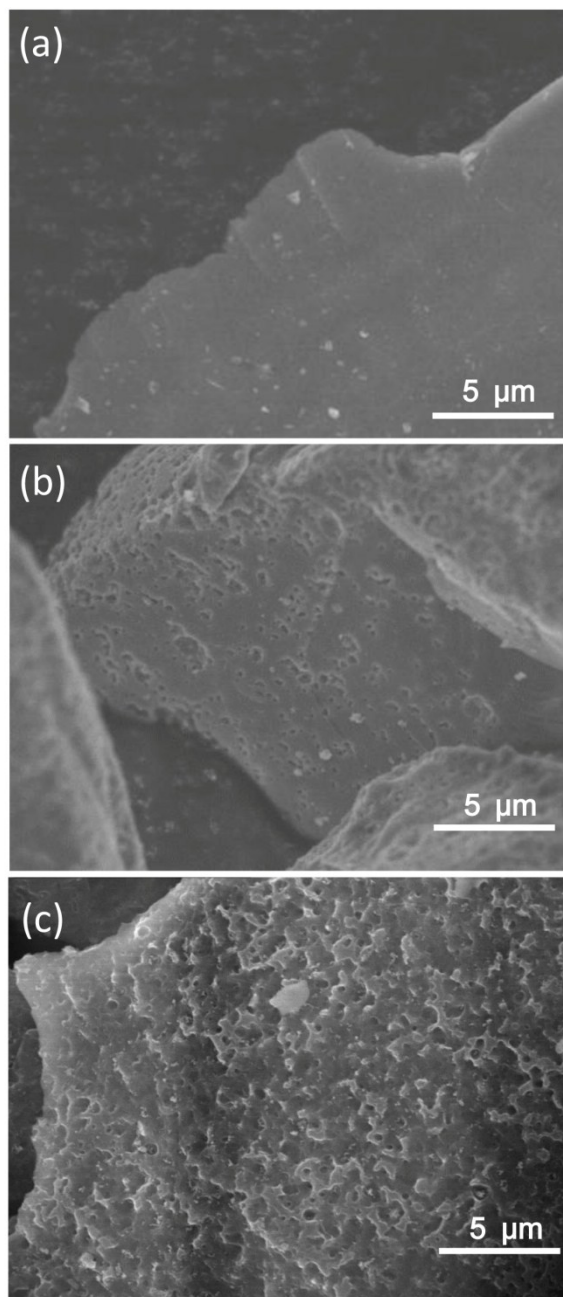


Fig. S1 Representative SEM images of Si powder (a); 0.12-Pd-Si (b) and 1.05-Pd-Si (c).

Pd was deposited on Si galvanic replacement, the depth and number of the pores increased with Pd loading.

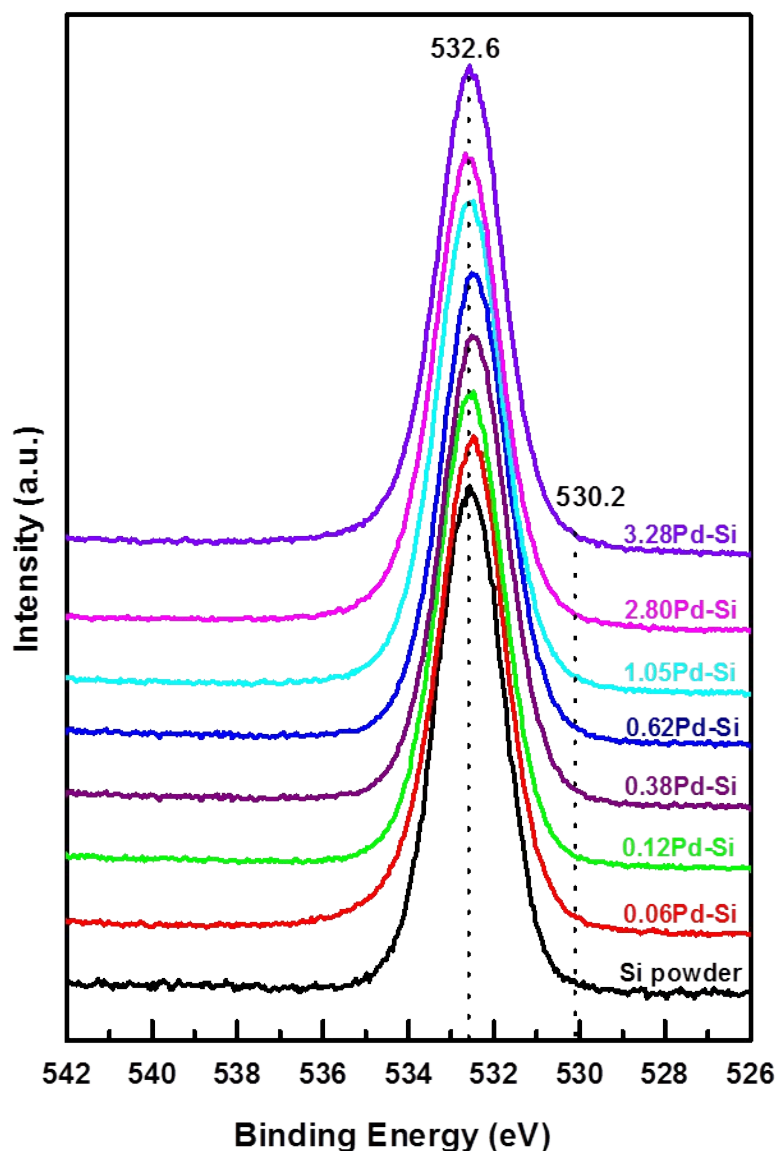


Fig. S2 XPS spectra of Pd 3p-O1s regions

xPd-Si catalysts exhibit an intense O 1s peak at 532.6 eV corresponding to native Si oxides (SiO_x)³. PdO surface should have a strong O 1s peak appeared at 530.2 eV.⁴ Evidently, there is insufficient intensity at 530.2 eV to identify PdO as a quantifiable component.

References:

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