Porous organic cage stabilised palladium nanoparticles: efficient heterogeneous catalysts for carbonylation reaction of aryl halides

Yong Zhang†,[a,b] Yu Xiong†,[a] Jin Ge,[b] Rui Lin,[a] Chen Chen,[a] Qing Peng,[a] Dingsheng Wang[a] and Yadong Li[a]

[a] Department of Chemistry, Tsinghua University, Beijing 100084, China.

[b]Key Laboratory of Organo-pharmaceutical Chemistry, Gannan Normal University, Ganzhou 341000, P. R. China.

† These authors contributed equally to this work.

Contents

1. General Information

Materials

$Pd(OAc)_2$ (47.5% Pd, J&K), methanol (99 %, AR grade, Beijing Chemical Reagent Factory), ethanol (99.8%, AR grade, Beijing Chemical Reagent Factory), (R,R)-1,2-diaminocyclohexane (98%, Sigma-Aldrich), trifluoroacetic acid (99%, alfa aesar), sodium borohydride (98%, aladdin), and aryl halides were commercially available. The 1,3,5-triformylbenzene[1] and CC3-*R*[2] were prepared according to the literature procedures. Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification.

1. P. Pandey, A. P. Katsoulidis, I. Eryazici, Y. Y. Wu, M. G. Kanatzidis, S. T. Nguyen, *Chem. Mater.* 2010, **22**, 4974.

2. T. Hasell, S. Y. Chong, K. E. Jelfs, D. J. Adams and A. I. Cooper, *J. Am. Chem. Soc.*, 2012, **134**, 588.

Instrumentation

Transmission electron microscopy (TEM) images were performed on a Hitachi H-800 transmission electron microscope. The X-ray powder diffraction (XRD) were obtained on a Rigaku RU-200b with Cu Kα radiation. The X-ray photoelectron spectroscopy (XPS) was measured by a PHI Quantera SXM systemunder 3.1*10−8 Pa using Al+ radiation at room temperature. N_2 adsorption measurements were performed with a Quantachrome Autosorb-1 instrument surface area analyzer at 77K. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area. NMR spectra were recorded on a liquid NMR spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C) using $CDCl_3$ as the solvent.

2. Experimental Section

Synthesis of Pd@CC3-*R*-MeOH

CC3-*R* (20 mg) and Pd(OAc)$_2$ (22.5 mg) were stirred vigorously in MeOH (50 mL) for 6 h at room temperature. The resulting solution was then stirred at 80 ^oC for 1 h. After completion of the reaction, solvent was removed under vacuum, and the obtained solid was washed several times with ethanol-acetone mixture via centrifugation, followed by drying under vacuum (45^{o}C) overnight to obtain Pd@CC3-*R*-MeOH as a black solid.

Synthesis of Pd@CC3-*R*-NaBH$_4$-1

CC3-*R* (80 mg) was dissolved in 15 mL of dichloromethane and methanol mixture (volume ratio = 2:1) and subsequently added Pd(OAc)$_2$ (90 mg). The resulted mixture were stirred vigorously for 30 min to form a homogeneous solution at room temperature. Then, NaBH$_4$ (100 mg) was added to the above solution. The solution immediately changed color from yellow to dark, indicating the formation of Pd NPs. After 5 min, the mixture was evaporated to remove dichoromethane and methanol. Subsequently, the mixture was diluted with 20 mL CHCl$_3$ and 10 mL H$_2$O. The organic phase was concentrated in vacuo, and the residue was washed several times with ethanol-acetone mixture via centrifugation, followed by drying under vacuum (45^{o}C) overnight to obtain Pd@CC3-*R*-NaBH$_4$-1as a black solid.

Synthesis of Pd@CC3-*R*-NaBH$_4$-2

The synthesis method is the same as Pd@CC3-*R*-NaBH$_4$-1, the time of the reduce step is 12 h.

Alkoxycarbonylation reactions of aryl iodides.

Aryl iodide (1 mmol), Pd@CC3-*R*-MeOH dispersed in ethanol (2 mL), and NEt$_3$ (3.0 equiv) were added to an oven-dried Schlenk tube under N$_2$ atmosphere, and the system was evacuated and refilled with CO (balloon) for three times. The reaction was assumed to start when the reactor was introduced into the oil bath at 80 ^{o}C with vigorously stirred. Aliquots were taken at specific time for determination of component concentrations by ISQ GC-MS with a ECD detector (Thermo Trace GC Ultra) using a capillary column (TR-5MS, from Thermo Scientific, length 30 m, i.d. 0.25 mm, film 0.25 μm). After completion of reaction, the Pd nanoparticles were precipitated by acetone, separated via centrifugation. The liquid phase was concentrated under reduced pressure. The product was purified by silica gel column chromatography.

Reusability of Pd@CC3-*R*-MeOH catalyst.

After the alkoxycarbonylation of iodobenzene, Pd@CC3-*R*-MeOH catalysts were precipitated by acetone and separated via centrifugation. The resultant powder was washed several times with ethanol-acetone mixture via centrifugation, followed by drying under vacuum. The obtained Pd@CC3-R-MeOH catalysts were used directly for the next catalytic cycle.

3. Supplementary Figures

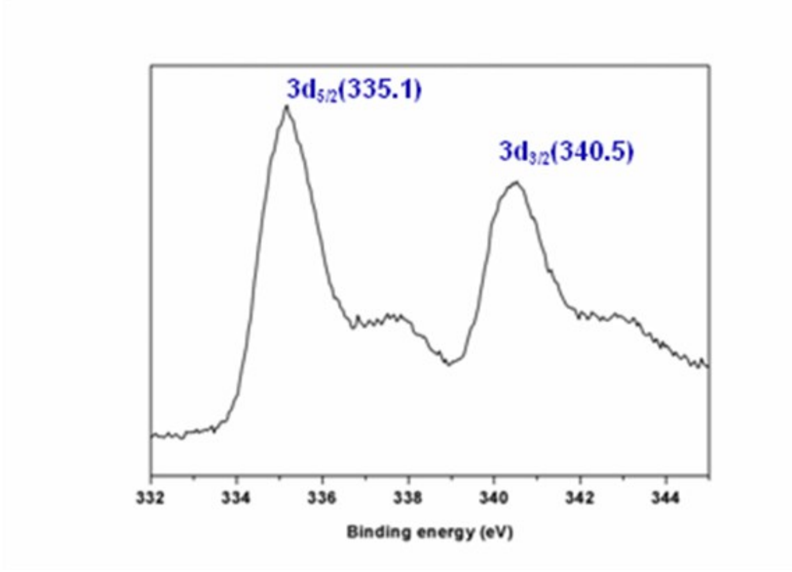


Fig. S1. XPS spectra of Pd@CC3-*R*-MeOH

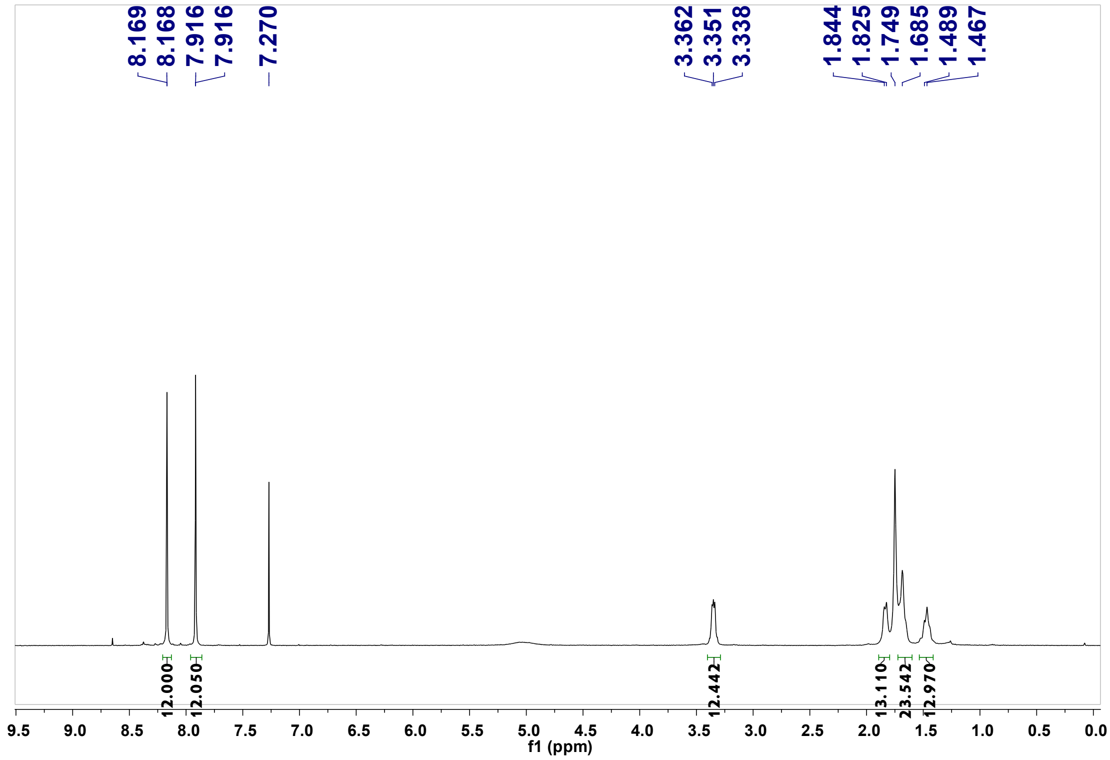
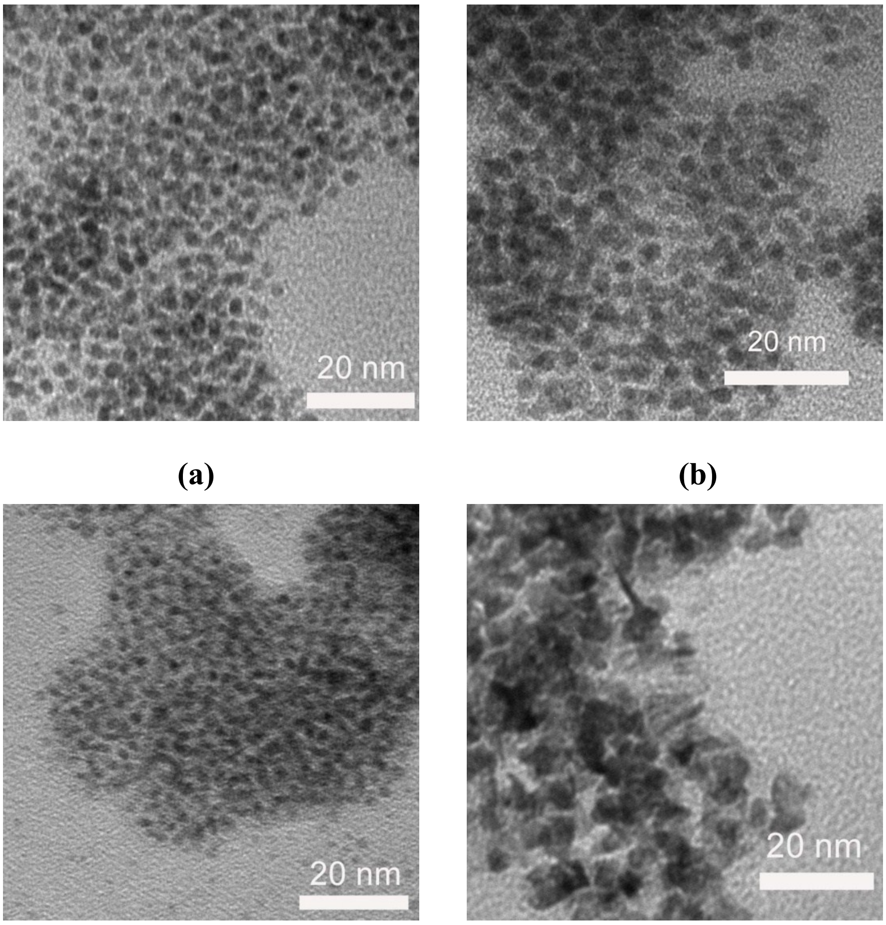


Fig. S2. ^{1}H NMR of Pd@CC3-*R*-MeOH in $CDCl_3$.



(a) (b)

(c) (d)

Fig. S3. TEM images of (a) Pd@CC3-*R*-MeOH, (b) Pd@CC3-*R*-MeOH catalysts after the 5th cycle of catalytic reaction, (c) Pd@CC3-*R*-$NaBH_4$-1, and (d) Pd@CC3-*R*-$NaBH_4$-2.

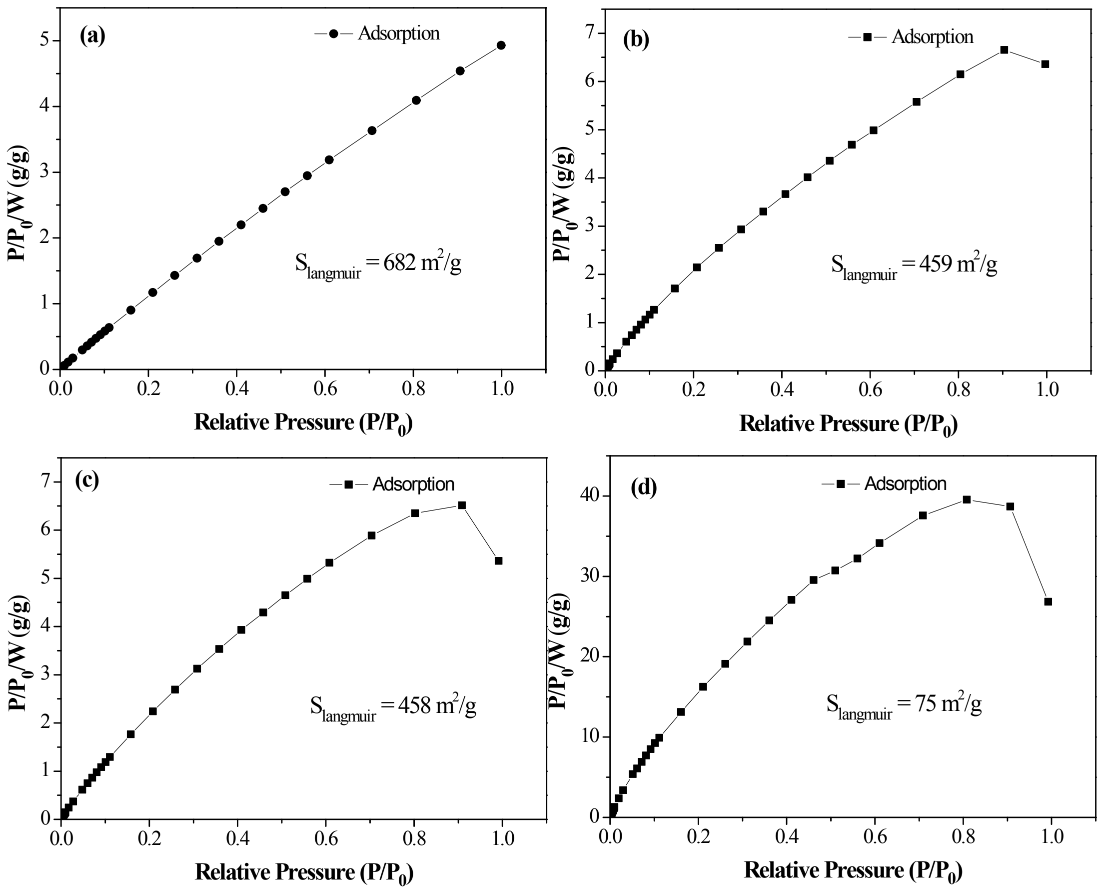


Fig. S4. Languir model of CC3-*R* (a), Pd@CC3-*R*-MeOH (b), Pd@ CC3-*R*-$NaBH_4$-1 (c) and Pd@ CC3-*R*-$NaBH_4$-2 (d).

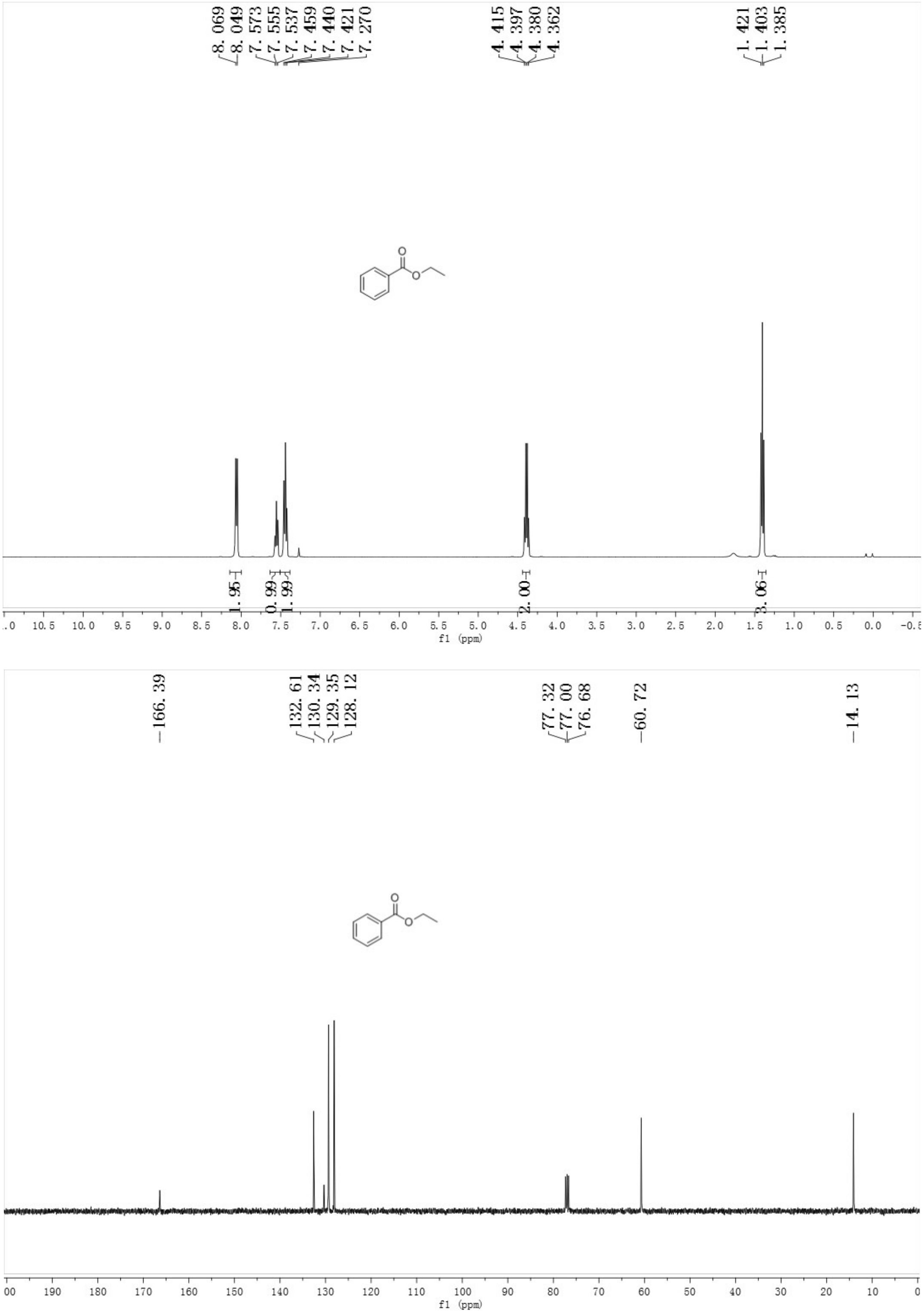


Fig. S5. ^{1}H NMR and 13C NMR of the isolated product (ethyl benzoate as an example).