Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supporting Information for

The *In-situ* Shape-controlled Synthesis and Structure-activity Relationship of Pd Nanocrystal Catalysts Supported on Layered Double Hydroxide

Qiang Zhang,[a] Jing Xu,[a] Dongpeng Yan,[a] Shuangde Li,[a] Jun Lu*[a], Xingzhong Cao,[b] and Baoyi Wang[b]

[a] *State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, P. Box 98 Beisanhuan East Road 15, Beijing, 100029, P. R. China*

[b] *Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, P. R. China*

* Corresponding author. E-mail: lujun@mail.buct.edu.cn

Fax: +86-10-64425385; Tel: +86-10-64412131

1. Characterization of materials:

Fourier transform infrared (FT-IR) spectra was recorded in the range 4000 to 400 cm^{-1} with 2 cm^{-1} resolution on a Bruker Vector-22 Fourier transform spectrometer using the KBr pellet technique (1 mg of sample in 100 mg of KBr). UV-vis/Diffuse Reflectance spectra for samples was recorded on a UV-vis spectrophotometer (UV-3100, Shimadzu, Japan). $BaSO_4$ was used as a reflectance standard in a UV-vis diffuse reflectance experiment. The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS) measurement, which was performed using a Perkin-Elmer PHI-5702 X-ray photoelectron spectrometer. X-ray source was a Mg standard anode (1253.6 eV) at 12 kV and 300 W.

2. FT-IR spectra

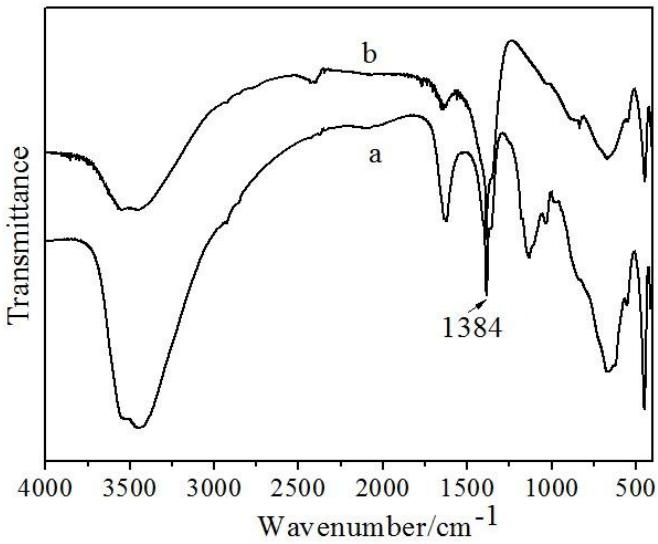


Figure S1. FI-IR spectra of (a) NO_3^--LDH and (b) $PdCl_4^{2-}$-LDH.

Figure S1 shows the FT-IR spectrums of NO_3^--LDH and $PdCl_4^{2-}$-LDH samples in the region 400–4000 cm^{-1}. A strong and broad absorption band centered at ~ 3448 cm^{-1} in the two samples can be identified as the hydroxyl stretching band, arising from metal hydroxyl groups, hydrogen-bonded interlayer water molecules[1]. The absorption band owing to the hydroxyl deformation mode of water,

δ(H_2O), is recorded at around 1600 cm^{-1}. Bands observed in the range 500 – 800 cm^{-1} are mainly due to M–O, M–O–M, and O–M–O lattice vibrations. The absorption band attributed to the v_3 (asymmetric stretching) mode of NO_3^- can also be observed at ~ 1384 cm^{-1} in $PdCl_4^{2-}$-LDH, suggesting that NO_3^- is not fully exchanged. The characteristic absorption peak of CO_3^{2-} does not exist in the FI-IR spectra, which can explain that the size reduction of $d_{(003)}$ for $PdCl_4^{2-}$-LDH sample is due to the intercalation of the $PdCl_4^{2-}$ rather than CO_3^{2-}, suggesting that $PdCl_4^{2-}$ and NO_3^- are co-existed in the LDH interlayer.

3. UV-vis/diffuse reflectance spectroscopy

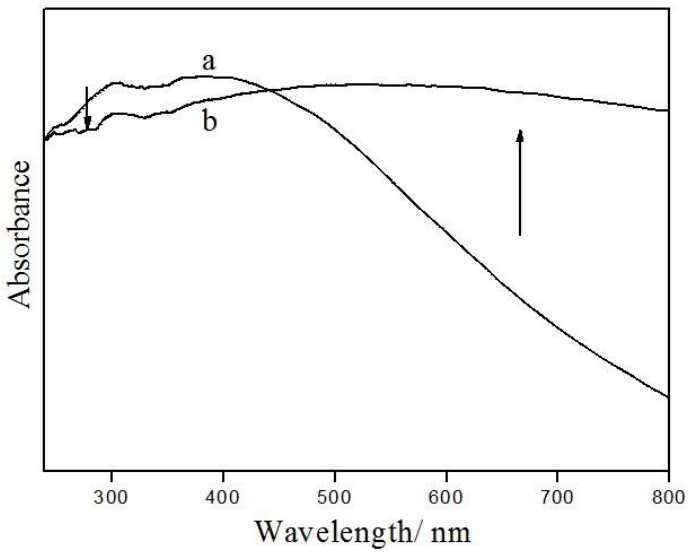


Figure S2. UV-vis/diffuse reflectance spectra of (a) $PdCl_4^{2-}$-LDH and (b) Pd-CUs/LDH.

The appearance of LDH-supported Pd NCs was determined by UV-vis/diffuse reflectance spectra. The peak at 280 nm attributed to $PdCl_4^{2-}$ disappears after the reduction reaction, and the absorption in the visible region increases,[2] indicating that the Pd NCs are formed.

4. The lattice parameters of samples

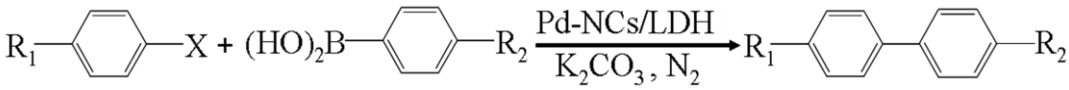
Table S1. The lattice parameters of NO_3^--LDH, $PdCl_4^{2-}$-LDH and Pd-CUs/LDH.

LDH	NO_3^--LDH	$PdCl_4^{2-}$-LDH	Pd-CUs/LDH

d_{003}/nm	0.841	0.792	0.762
d_{006}/nm	0.432	0.403	0.379
d_{009}/nm	0.255	0.256	–
d_{110}/nm	0.152	0.152	0.152
a/nm	0.304	0.304	0.304
c/nm	2.523	2.376	2.286

5. Suzuki cross-coupling reactions catalyzed by Pd-NCs/LDH catalysts

Table S2. The Suzuki cross-coupling reactions catalyzed by different Pd-NCs/LDH catalysts.



Entry	X	R_1	R_2	Time/h	Conv/%	Yield/%[d]
1	I	H	Me	4	95[a] 92[b] 85[c]	90[a] 88[b] 81[c]
2	I	NO_2	H	4	99[a] 97[b] 84[c]	98[a] 95[b] 78[c]
3	I	NO_2	OMe	4	97[a] 92[b] 89[c]	95[a] 89[b] 87[c]
4	I	OMe	H	4	90[a] 83[b] 78[c]	84[a] 76[b] 69[c]
5	Br	H	Me	10	92[a] 87[b] 80[c]	90[a] 82[b] 75[c]
6	Br	NO_2	H	10	97[a] 93[b] 82[c]	92[a] 85[b] 72[c]
7	Br	OMe	H	10	83[a] 75[b] 62[c]	80[a] 71[b] 56[c]
8	Cl	NO_2	H	24	82[a] 71[b] 64[c]	76[a] 67[b] 56[c]
9	Cl	Me	H	24	73[a] 62[b] 54[c]	63[a] 56[b] 45[c]

Reaction conditions: Aryl halide (1.0 mmol); arylboronic acid (1.2 mmol); K_2CO_3 (2.4 mmol);

Pd-NCs/LDH (80 mg, 2 mol%); ethanol : water = 4 : 1(10ml); 75°C; N_2 atmosphere and 24 h.
[a]The Suzuki reactions of aryl halide with arylboronic acid catalyzed by Pd-CUs/LDH catalysts.
[b]The Suzuki reactions of aryl halide with arylboronic acid catalyzed by Pd-TROCs/LDH catalysts.
[c]The Suzuki reactions of aryl halide with arylboronic acid catalyzed by Pd-TRPLs/LDH catalysts.
[d]GC yield.

6. Mercury poisoning test

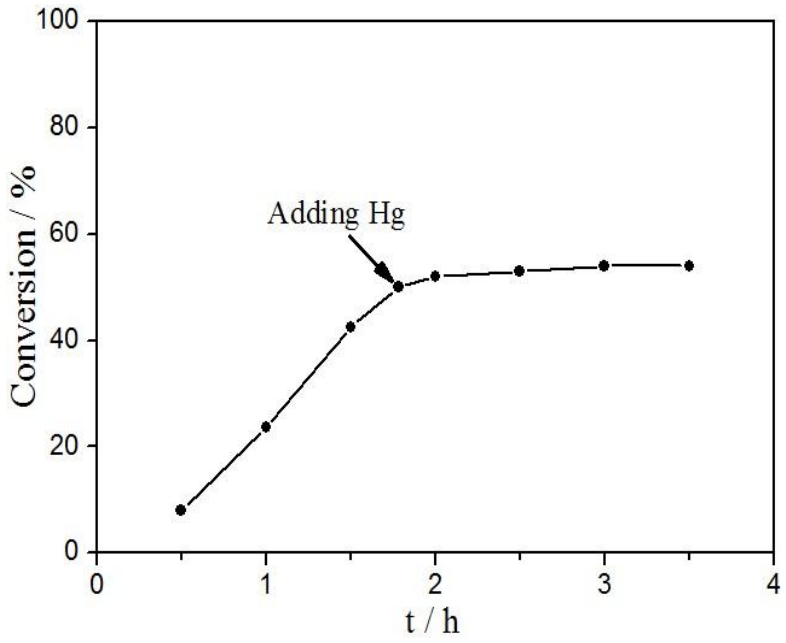


Figure S3. The mercury poisoning test of the Pd-CUs/LDH catalysts in Suzuki reaction of phenylboronic acid and iodobenzene.

7. TEM image of the spent Pd-CUs/LDH catalyst

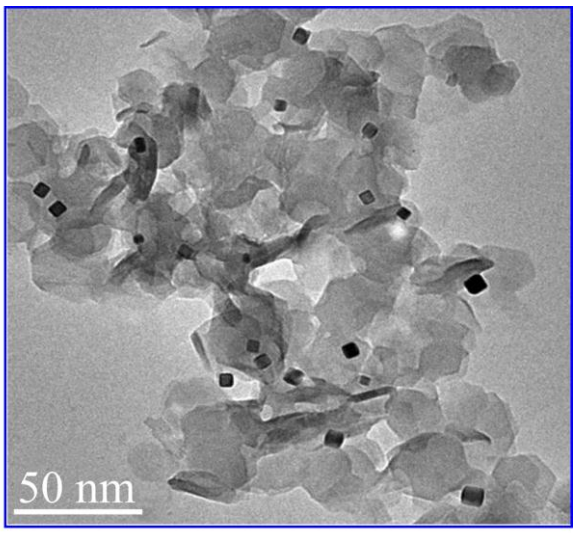


Figure S4. The TEM image of Pd-CUs/LDH catalyst after four catalytic cycles confirms that the

morphology of Pd nanocubes can be well maintained.

8. X-ray Photoelectron Spectroscopy (XPS) analysis

The solution containing the as-prepared Pd-CUs/LDH catalysts (80 mg), bromobenzene (1 mmol), K_2CO_3 (2.4 mmol, 332 mg) and 10 mL of ethanol/water (4 : 1 volume ratio) solvent was added into a 100-mL, three-neck flask and stirred at 75 °C for 10 h under nitrogen atmosphere. The recovered catalysts were designated as sample 1; the preparation of sample 2 was similar to that for sample 1, except that phenylboronic acid (1.2 mmol) was also added into the mixed solution. The pristine Pd-CUs/LDH catalysts, sample 1 and 2 were characterized by XPS.

The XPS spectra of Pd-CUs/LDH catalysts shows the binding energy (BE) peaks of Pd^0 $3d_{5/2}$ and $3d_{3/2}$ at 335.1 and 340.4 eV, respectively (Figure S4A). Furthermore, the Pd^{2+} peaks (BE = 336.7 and 341.6 eV) can be observed. Considering the $3d_{5/2}$ peak of Pd^{2+} in the K_2PdCl_4 is located at 337.9 eV, the possibility of the $PdCl_4^{2-}$ absorbed on LDH sheet is excluded; here the Pd^{2+} peaks can be assigned to PdO at the surface of Pd NCs due to its exposure to an oxygen-containing environment.[3] For sample 1 and 2, besides of the BE peaks of Pd $3d_{5/2}$ and $3d_{3/2}$ for Pd^0 and PdO, the XPS of Pd $3d_{5/2}$ and $3d_{3/2}$ shows new peaks at 336.4, 342.1 and 336.5, 342.0 eV respectively (Figure S5B, C), which can be attributed to the formation of organopalladium intermediate such as Ph-Pd-Br and/or Ph-Pd-$B(OH)_3^-$ during the catalytic reactions.[1,4] The BE peaks of I $3d_{5/2}$ and $3d_{3/2}$ at 618.4 and 631.2 eV respectively can also be observed (Figure S5D, inset), which can be attributed to the existence of I^- ions on the surface of Pd NCs by chemical absorption. Here we acknowledge that the halide ions adsorbed on the surface of Pd NCs may have a potential influence on the catalysts. Due to the limitation of experimental conditions, however, we ignore the influence of chemically adsorbed halide ions on the Pd-NCs/LDH catalysts, and primarily focus on the role of

Pd-NCs/LDH catalysts with different morphologies and exposed facets for Pd NCs in the catalytic performances of Suzuki cross-coupling reactions. The plausible heterogeneous reaction mechanism can be put forward, where the Pd nanocubes surface undergoes oxidative addition with Ph-Br and Ph-B$(OH)_3^-$ to form Ph-Pd-Br and Ph-Pd-B$(OH)_3^-$ as possible transition states, which is similar to the reaction pathways described for the homogeneous catalysts.

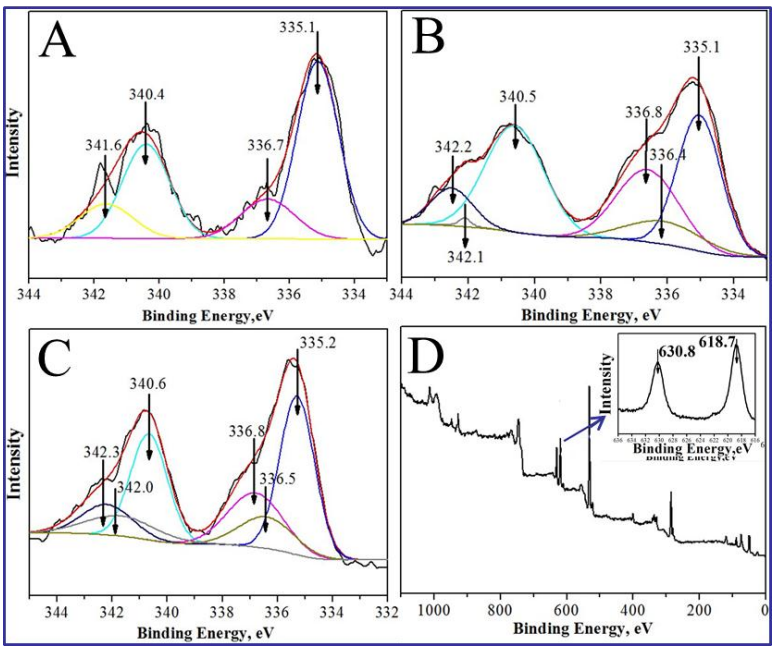


Figure S5. Pd 3d XPS spectra of the samples: (A) pristine Pd-CUs/LDH, (B) sample 1 and (C) sample 2. (D) XPS survey scan of pristine Pd-CUs/LDH along with I $3d_{5/2}$ and $3d_{3/2}$ (chemically adsorbed I^- ions).

References:

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