Supplementary information for:

# Ultrasmall palladium nanoparticles supported on amine-functionalized nanoporous silica efficiently catalyze hydrogen evolution from formic acid

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## Contents

This file contains:

- Detailed experimental procedures, TEM image of Pd NPs synthesized without SBA-15 template (Figure S1),
- XPS spectra of SBA-15/Pd and SBA-15-Amine/Pd (Figure S2 and Figure S3),
- Experimental setup used for formic acid dehydrogenation catalytic reaction (Figure S4),
- Detailed TOF calculations (Eq.1 and Eq.2) and comparison of TOFs (Figure S5 and Table S1),
- FT-IR results (Figure S6), and
- XPS results of the catalyst SBA-15-Amine/Pd after 0th and 6th cycle (Figure S7 and Table S2).

### 1. Detailed Experimental Section

**Materials and Reagents:** Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*poly(ethylene glycol) copolymer (Pluronic® 123, with an average molecular mass of 5800 Da) was purchased from BASF. (3-Aminopropyl)triethyoxysilane (APTES), ammonium hydroxide (NH<sub>4</sub>OH), formic acid (HCOOH), anhydrous toluene, tetraethyl orthosilicate (TEOS), *n*-propylamine, and palladium chloride (PdCl<sub>2</sub>) were obtained from Sigma-Aldrich. Hydrochloric acid (36.5%) was purchased from Fischer Scientific. Anhydrous ethanol was purchased from Pharmco-Aaper. All the reagents were used as received without further purification.

**Instrumentation:** Transmission electron microscopy (TEM) and scanning transmission electron microscope (STEM) were performed with a FEI Tecnai<sup>TM</sup> F20 instrument equipped with Schottkey FEG electron gun and operating at 200 kV. FA dehydrogenation experiments were performed using a laboratory-made customized system (please see the procedure above for details). Gaseous products were identified using an in situ FT-IR spectrometer (Nicolet iS10, Thermo Scientific) equipped with an MCT detector and a customized gas cell. Spectral data were collected using a scan rate of 8 scans min<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. Elemental analysis (EA) and inductively coupled plasma atomic emission spectrometer (ICP-AES) were done at Korea Institute of Science and Technology Advanced Analysis center. ICP-AES analyses of all samples were done using a Varian 710-ES (Varian, Australia). X-ray Photoelectron spectroscopy (XPS) were performed using a PHI 5000 VersaProbe (Ulvac-PHI) instrument, equipped with Al K $\alpha$  (1486.6 eV) monochromator, Anode (25W, 15kV), operating at background pressure is 6.7x10<sup>-8</sup> Pa and has 100 µm x 100 µm sample size.

#### **Experimental Section**

Synthesis of SBA-15 Mesoporous Silica: SBA-15 was synthesized using Pluronic® 123 as templating agent in acidic solution, as reported previously by Zhao et al.<sup>[1]</sup> Typically, a solution of Pluronic® 123 / 12 M HCl / tetraethyl orthosilicate (TEOS) / H<sub>2</sub>O (2:12:4.3:26, mass ratio in grams) was prepared and stirred at 40 °C for 24 h. The solution was then aged at 65 °C for another 24 h. The resulting solution was filtered, and the solid material was washed with copious amount of water and dried, giving a white powder labeled as "as-synthesized

SBA-15". As-synthesized SBA-15 (1 g) was then dispersed in ethanol (100 mL) and diethyl ether (100 mL) and stirred at 50 °C for 5 h to remove Pluronic®123. After filtration and washing with ethanol, the final solid material was dried in oven, giving the template extracted SBA-15 mesoporous silica, denoted as "SBA-15."

Synthesis of ultrasmall Pd nanoparticles-loaded amine-functionalized SBA-15: 100 mg of SBA-15 was mixed and stirred with 1.37 mmol of (3-amonopropyl)triethoxysilane (APTES) in 50 mL of anhydrous toluene for 6 h at 80 °C to graft the mesoporous channel surfaces of SBA-15 with primary amine groups. After filtration the mixture, the solid product was washed with toluene and ethanol and let to dry at ambient condition, producing amine-functionalized SBA-15 that was denoted as "SBA-15-Amine".

A solution of PdCl<sub>2</sub> (56.3 µmol) in 100 µL of 14 M of ammonium hydroxide (NH<sub>4</sub>OH) and 5 mL ethanol:DI water (1:4 v/v) was prepared. After mixing this solution with SBA-15-Amine, the mixture was stirred at 80 °C for 3 h. The solid material was recovered by filtration, washed with water and ethanol, and finally dried, yielding Pd(II)-functionalized SBA-15-Amine. The resulting material was then treated at 250 °C for 3 h with 10% H<sub>2</sub> : 90% N<sub>2</sub> affording ultrasmall Pd-NPs-containing SBA-15-Amine, denoted as SBA-15-Amine/Pd.

Synthesis of palladium nanoparticles (control sample):  $PdCl_2$  (56.3 µmol) of Palladium chloride ( $PdCl_2$ ) was dissolved in 100 µL of 14 M of ammonium hydroxide ( $NH_4OH$ ) and sonicated until a colorless solution was obtained. The resulting solution was allowed to undergo reduction under the same conditions as above, i.e., at 250 °C for 3 h with 10% H<sub>2</sub>: 90% N<sub>2</sub>, yielding palladium nanoparticles, denoted as "Pd NPs".

*Catalytic formic acid dehydrogenations:* Formic acid dehydrogenation reactions in the presence of the materials synthesized above were conducted in a modified glass reactor (volume, 40 mL) possessing two necks (one for inlet and another for outlet). The inlet was employed to purge the reactor with N<sub>2</sub> gas. During consecutive H<sub>2</sub> generation tests, the outlet goes directly to gas burette system for real-time measurement of the rate of H<sub>2</sub> + CO<sub>2</sub> release as well as the accumulative amount of H<sub>2</sub>, as we have demonstrated previously. The overall experimental apparatus for H<sub>2</sub> measurement is shown in **Figure S5**. The reactions were performed using 10 mL of 1 M formic acid at room temperature. 50 mg of catalyst was used in each reaction. The reactor was stirred at room temperature (299K) with vigorous stirring at

a rate of 300 rpm. The gases evolved from the reaction were directly delivered into a gas burette system and their volumes were quantified.

*Recyclability Studies of Catalysts:* After the initial catalytic test involving 50 mg of SBA-15-Amine/Pd and 10 mL of 1 M FA was performed, the catalyst was recovered and washed with copious D.I water and dried under vacuum for 4 h. It was then used in the next reaction cycle in the same way as above and by keeping the same ratio of substrate to catalyst.

*Leaching Studies in Catalysis*: To determine whether or not palladium nanoparticles or some palladium species leach into the reaction mixture during the catalytic reaction or not, the supernatant was taken 50 min after FA dehydrogenation reaction started. The recovered SBA-15-Amine/Pd catalyst was analyzed for the amount of palladium in it using ICP-AES.



**Figure S1.** TEM image of Pd NPs synthesized using any support materials such as SBA-15 and SBA-15-NH<sub>2</sub>.

#### **Additional XPS Results and Discussion**

C1s normalization is needed and commonly applied on XPS spectra. But the situation in our case is a bit different, where some spectra did not allow us to apply C1s normalization and we had to thus rely on a different approach. Whereas there is distinct C1s signal in the XPS spectrum for SBA-Amine/Pd that can be used for normalization, there is no strong enough C1s signal in the corresponding spectrum of SBA-15/Pd (because the sample has no carbon) (Figure S2A, below), limiting our ability to do the same in the latter case. So, we used the signal associated with Si2p signal (at ~103. 30 eV) as a reference instead (Figure S2B below). Because Si is abundant in these materials (as they are predominantly silicabased), the Si signal is so strong and reasonably distinct that it can safely be used as a reference in the spectra (Figure S3 below).

We have tried to explain the difference in the XPS signals of Pd 3d in the two materials, which the reviewer seems to refer to, as follows. In case of SBA-15/Pd, the Pd nanoparticles (Pd NPs) are attached to the support material by coordinating only with the oxygen atoms of either the free silanol or siloxane groups present on the silica-network. On the other hand, in the case of SBA-15-Amine/Pd, the attachment of the Pd NPs with the support material involves mainly Pd-N type linkages. As oxygen is more electronegative than nitrogen, we believe that oxygen atoms draw more electron-density from the Pd-NPs, resulting in higher binding energy for the Pd atoms of SBA-15/Pd. Though, thorough knowledge of the environment of our supported catalysts is beyond the scope of our current manuscript, apart from the above-mentioned factor, we also believe that the extent/nature of functionalization and the size of the nanoparticles might have also played some roles in determining the binding energy of the 3d electrons of the Pd NPs in the two materials.



**Figure S2.** The high-resolution C1s peaks (A) and Si2p (B) in the XPS spectra of SBA-15-/Pd and SBA-15-Amine/Pd.



**Figure S3**. XPS survey spectra of (a) SBA-15-Amine/Pd and SBA-15/Pd. Enlarged (b) Pd3d peaks and (c) Si2s peaks of the survey spectra. The peaks are assigned using Si 2p peak as reference. (d) Enlarged XPS survey spectra of the materials with some of the important peaks.

# Calculation and Comparison of Turn Over Frequency (TOF)

Initial TOF was calculated by total amount of gas volume  $(H_2 + CO_2)$  at 10 min by using the following equations (Eqns. 1 and 2).

Moles of HCOOH at 10 min (n) = 
$$\frac{PV}{RT} = \frac{1 \times Total \, Volume \, at \, 10min}{0.082 \times Temperature} X \frac{1}{2}$$
 Eqn. 1  
 $TOF(h^{-1}) = \frac{moles \, of \, HCOOH \, at \, 10 \, min}{moles \, of \, metal \, used \, X \, time}$  Eqn. 2



Figure S4. An experimental set up used for measuring volume of  $H_2 + CO_2 (mL)$ .



**Figure S5**. Comparison of TOFs at 10 min of SBA-15-Amine/Pd catalyst with other recently reported catalysts.

| Entry      | Catalyst                             | Temperature        | Volume | TOF                | Additives              | Reference |
|------------|--------------------------------------|--------------------|--------|--------------------|------------------------|-----------|
|            |                                      | [K]                | [mL]   | [h <sup>-1</sup> ] |                        |           |
| <b>1</b> a | SBA-15-                              | 299                | 38.5   | 300                | None                   | This work |
|            | Amine/Pd                             |                    |        |                    |                        |           |
| 1b         | SBA-15-                              | 299                | 38.5   | 377                | None                   | This work |
|            | Amine/Pd <sup>[b]</sup>              |                    |        |                    |                        |           |
| 2          | AgPd/C                               | 298                | 80     | 309                | None                   | [S2]      |
| 3          | Pd/mpg-C <sub>3</sub> N <sub>4</sub> | 298                | 52     | 144                | None                   | [\$3]     |
| 4          | PdAu/C                               | 298                | 30     | 63                 | None                   | [S4]      |
| 5          | $Pd/C_3N_4 (+ hv)$                   | 288 <sup>[c]</sup> | 8      | 68                 | None                   | [85]      |
| 6          | CoAuPd/C                             | 298                | 50     | 61                 | None                   | [86]      |
| 7          | Pd/MSC-30                            | 298                | 440    | 600                | Sodium                 | [S7]      |
|            |                                      |                    |        |                    | formate <sup>[d]</sup> |           |

**Table S1.** Comparison of TOFs at 10 min of SBA-15-Amine/Pd catalyst with other recently reported catalysts without additives.<sup>[a]</sup>

<sup>[a]</sup> The TOFs of some of the materials were calculated based on information provided in the manuscripts with Eqns. 1 and 2 above. <sup>[b]</sup> For recycled catalyst (activity increased due to its treatment with H<sub>2</sub>, see discussion). <sup>[c]</sup> Please note that the temperature is different from others. <sup>[d]</sup> The ratio of formic acid : sodium formate was 1:1.



**Figure S6.** *In situ* FT-IR spectra of gases generated during FA dehydrogenation over SBA-15-Amine/Pd after 50 min: (a)  $CO_2$  and CO stretch ranges (3000-1800 cm<sup>-1</sup>). (b) Enlarged area of CO stretching range (2200-2000 cm<sup>-1</sup>).



**Figure S7.** N1s XPS results of SBA-15-Amine/Pd catalysts after 0<sup>th</sup> and 6<sup>th</sup> recycle after reactions in formic acid dehydrogenation.

**Table S2.** XPS results of the catalyst SBA-15-Amine/Pd after 0<sup>th</sup> and 6<sup>th</sup> cycle.

| No. of Reaction | C 1s  | N 1s | O 1s  | Si 2p | Pd 3d |
|-----------------|-------|------|-------|-------|-------|
| Cycle           |       |      |       |       |       |
| 0 <sup>th</sup> | 30.24 | 2.40 | 47.44 | 19.48 | 0.44  |
|                 |       |      |       |       |       |
| 6 <sup>th</sup> | 22.25 | 2.98 | 52.37 | 21.87 | 0.54  |
|                 |       |      |       |       |       |

## **References for Supporting Information**

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