

## Electronic Supplementary Information

### Palladium silica nanosphere-catalyzed decomposition of formic acid for chemical hydrogen storage

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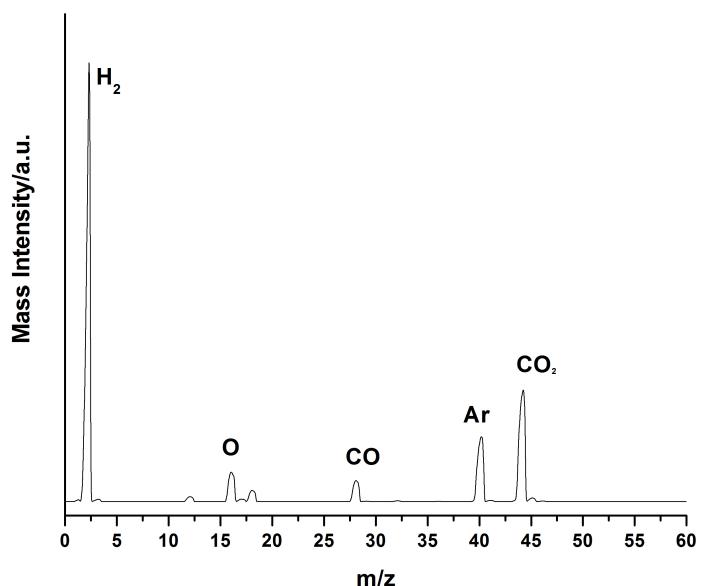


Fig. S1 Mass spectral profile for physical mixture of  $\text{H}_2$  and  $\text{CO}_2$  (1:1) as a reference gas sample.

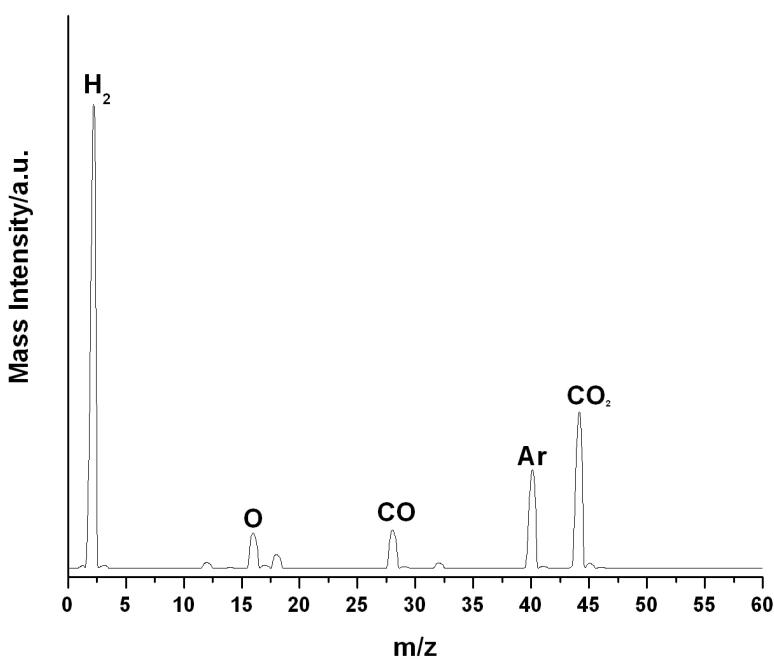


Fig. S2 Mass spectral profile of the released gas from the aqueous solution (5.0 mL) of formic acid (9.94 M) and sodium formate (3.33 M) in the presence of Pd@SiO<sub>2</sub> catalyst (240 mg) at 90°C.

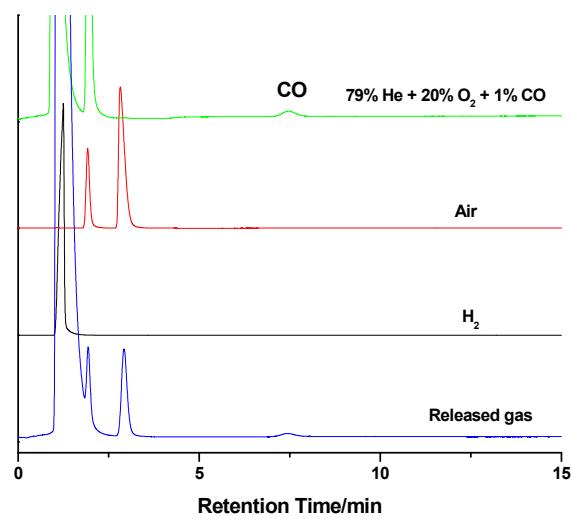


Fig. S3 Gas chromatograms of H<sub>2</sub>, air and CO as reference gases and the released gas from the aqueous solution (5.0 mL) of formic acid (9.94 M) and sodium formate (3.33 M) in the presence of Pd@SiO<sub>2</sub> catalyst (240 mg) at 90°C.

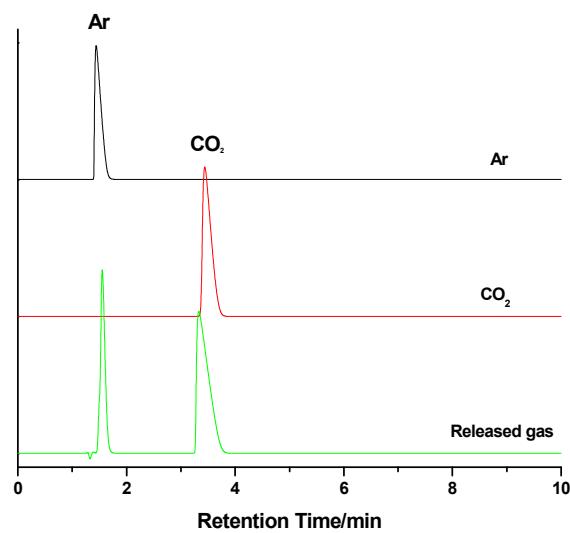


Fig. S4 Gas chromatograms of generated gas from the aqueous solution (5.0 mL) of formic acid (9.94 M) and sodium formate (3.33 M) in the presence of Pd@SiO<sub>2</sub> catalyst (240 mg) at 90°C.

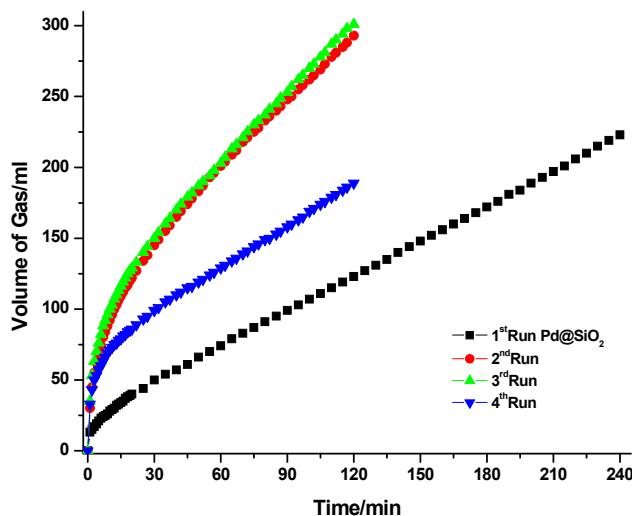


Fig. S5 Time-course plots for hydrogen generation from the aqueous solution (5.0 mL) of formic acid (9.94 M) and sodium formate (3.33 M) in the presence of Pd@SiO<sub>2</sub> catalyst (240 mg, 2 wt% Pd) at 90°C.

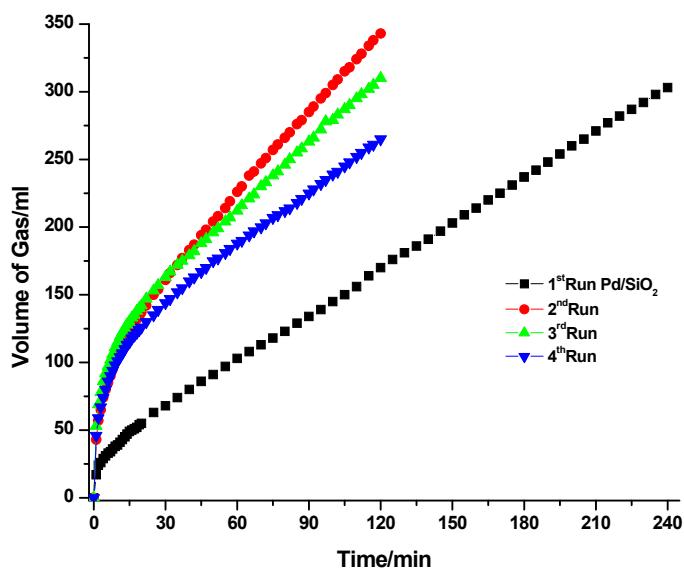


Fig. S6 Time-course plots for hydrogen generation from the aqueous solution (5.0 mL) of formic acid (9.94 M) and sodium formate (3.33 M) in the presence of Pd/SiO<sub>2</sub> catalyst (240 mg, 2 wt% Pd) at 90°C.

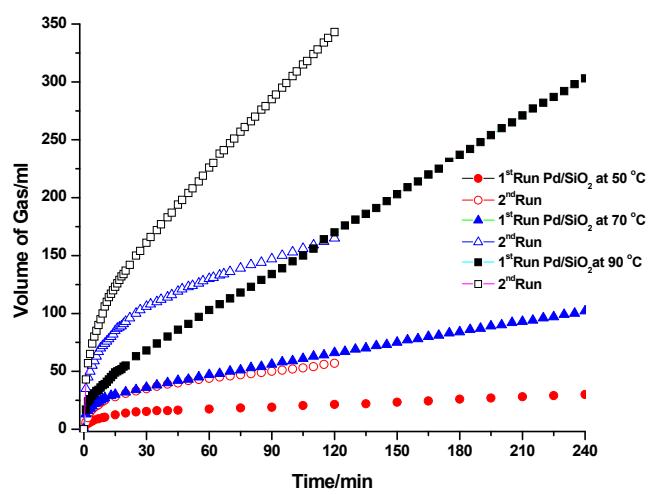


Fig. S7 Time-course plots for hydrogen generation from the aqueous solution (5.0 mL) of formic acid (9.94 M) and sodium formate (3.33 M) in the presence of Pd/SiO<sub>2</sub> catalysts (240 mg, 2 wt% Pd) at 50, 70 and 90 °C.

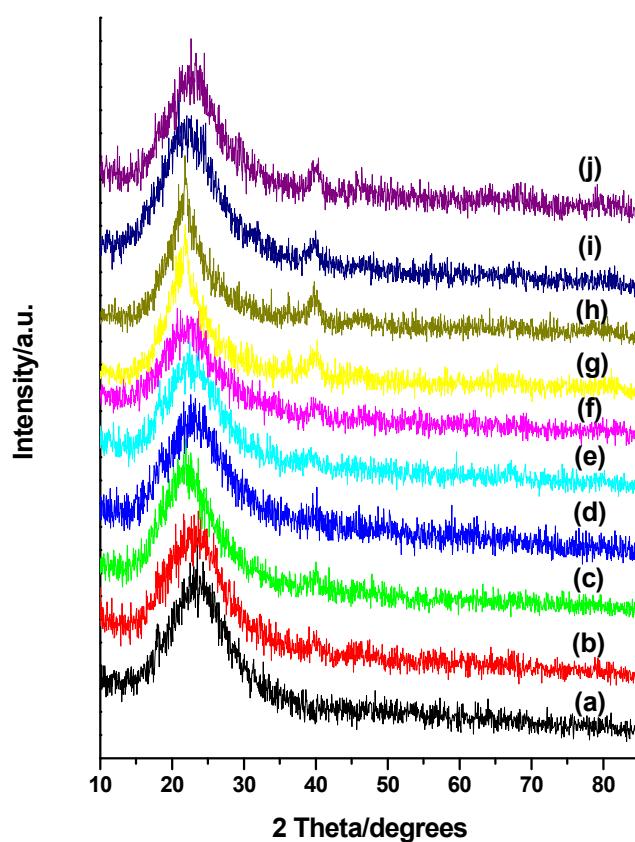


Fig. S8 Powder XRD profiles for Pd@SiO<sub>2</sub> (a) before and (b) after catalysis, Pd@SiO<sub>2</sub>(C\_560) (c) after catalysis, Pd/SiO<sub>2</sub> (d) before and (e) after catalysis, Pd/SiO<sub>2</sub>(C\_560) (f) after catalysis, Pd/SiO<sub>2</sub>(calcined silica nanosphere) (g) before and (h) after catalysis, and Pd/SiO<sub>2</sub>(commercial) (i) before and (j) after catalysis.

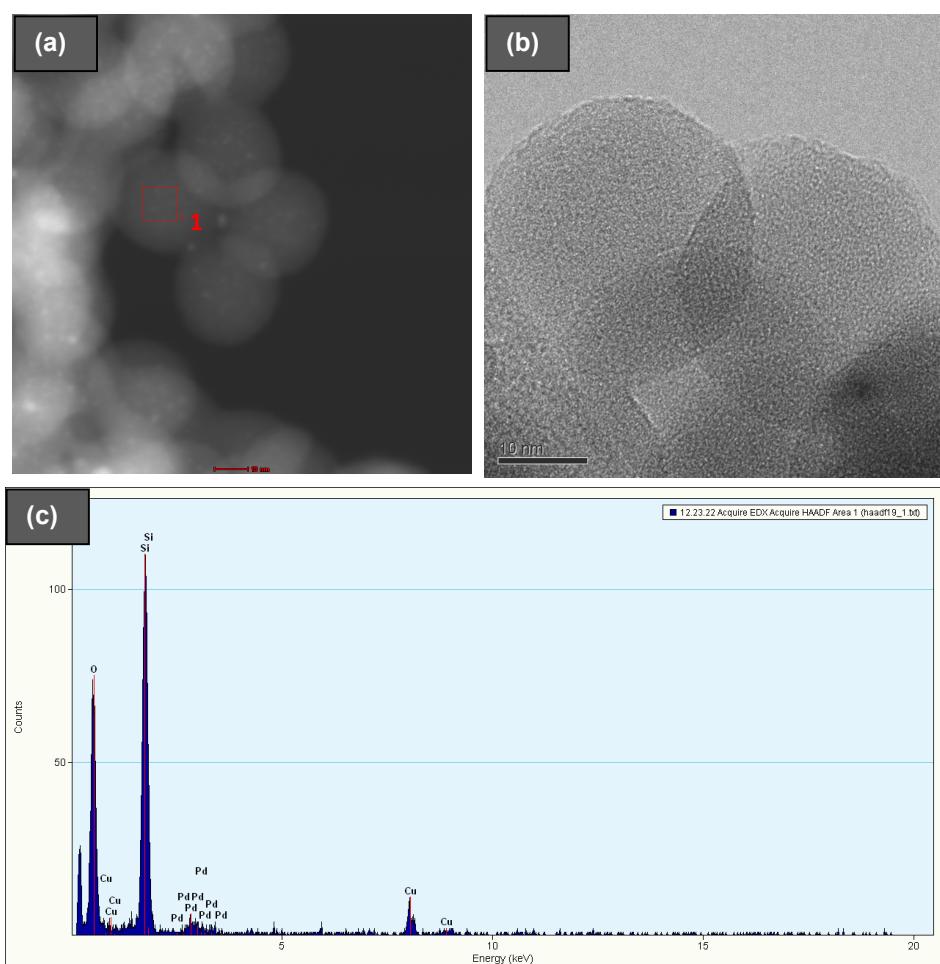


Fig. S9 Representative (a) HAADF-STEM image, (b) TEM image and (c) corresponding EDX spectrum (area 1 in (a)) of Pd@SiO<sub>2</sub>(C\_560) after catalytic reaction.

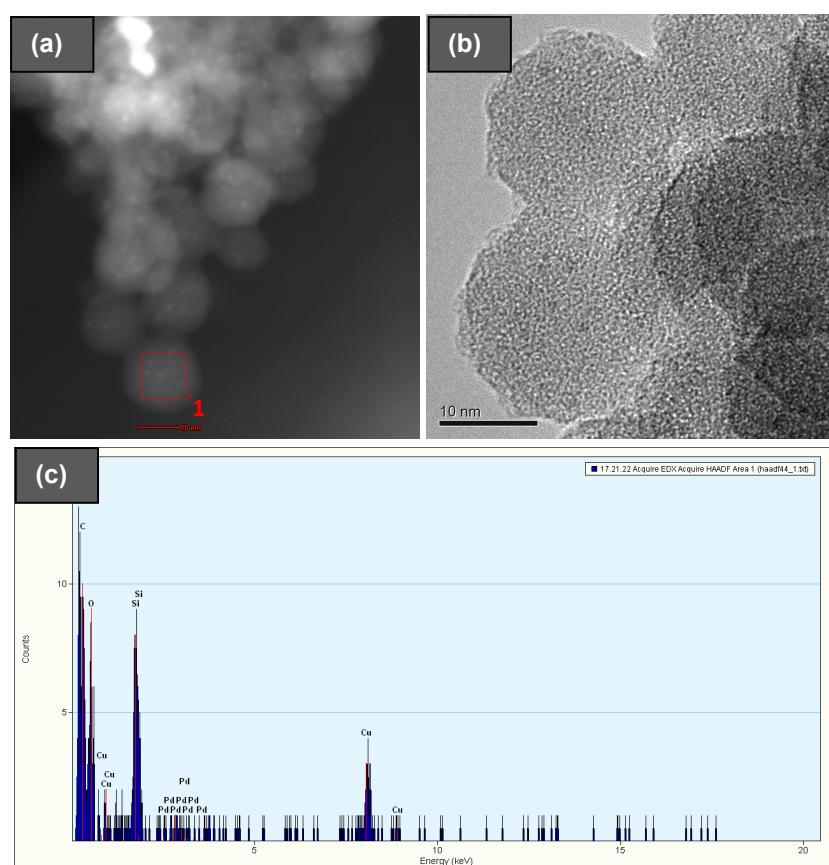


Fig. S10 Representative (a) HAADF-STEM image, (b) TEM image and (c) corresponding EDX spectrum (area 1 in (a)) of Pd/SiO<sub>2</sub>(C\_560) after catalytic reaction.

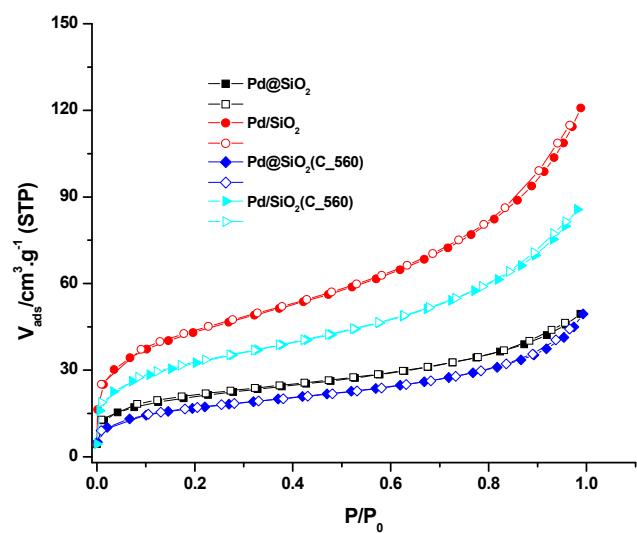


Fig. S11 Nitrogen adsorption isotherms of Pd@SiO<sub>2</sub>, Pd/SiO<sub>2</sub>, Pd@SiO<sub>2</sub>(C\_560) and Pd/SiO<sub>2</sub>(C\_560) at 77 K.