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Supporting Information

Phenylamine-functionalized mesoporous silica supported PdAg nanoparticle: a dual heterogeneous catalyst for the formic acid/CO_2-mediated chemical hydrogen delivery/storage

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Experimental Section

Materials: $Pd(NH_3)_4Cl_2$ and Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) were obtained from were obtained from Aldrich Chemical Co. $AgNO_3$, formic acid, and tetraethyl orthosilicate (TEOS) were purchased from Nacarai tesque. Aminophenyltrimethoxysilane was obtained from Manchester organic. All commercially available chemicals were used as received.

Synthesis of SBA-15: 4.0 g of Pluronic P123 was dissolved in 30 g of deionized water and 120 ml of 2 M HCl solution with stirring at 313 K. 8.5 g of TEOS was added into the above solution with stirring for 24 h. The mixture was aged at 353 K overnight without stirring, and then the product was recovered by vacuum filtration and washed with deionized water. The resulting white powder was dried at 383 K overnight and calcined at 823 K for 10 h.

Synthesis of SBA-15-Amine-*x*: To remove physisorbed water before surface modification, SBA-15 was dried at 403 K for 3 h under vacuum. 100 ml of toluene mixture containing 1.0 g of SBA-15 and appropriate amount of amine-functionalized silane coupling reagents were stirred at 373 K for 24 h. The product was recovered by vacuum filtration, washed with toluene and diethylether, and dried under vacuum overnight.

Synthesis of PdAg/SBA-15-Amine-*x*: Modified SBA-15 (0.5 g) was mixed with 50 mL of an aqueous solution containing $Pd(NH_3)_4Cl_2$ (10 mM, 4.75 ml) and $AgNO_3$ (5 mM, 9.49 ml) and stirred at room temperature for 1 h. The suspension was evaporated under vacuum and the obtained powder was dried overnight. Subsequently, the samples were pre-reduced with $NaBH_4$, giving PdAg/SBA-15-Amine-*x* (Pd 3wt%; molar ratio of Pd:Ag =1:1). ICP analysis clearly indicated that the desired amount of metal species is successfully loaded onto each supports.

Characterization: Powder X-ray diffraction patterns were recorded using a Rigaku Ultima IV diffractometer with Cu K_α radiation (λ = 1.5406 Å). BET surface area measurements were performed using a BEL-SORP max (Bel Japan, Inc.) at 77 K. The sample was degassed in vacuum at 373 K for 2 h prior to data collection. Inductively coupled plasma optical emission spectrometry (ICP-OES) measurements were performed using a Nippon Jarrell-Ash ICAP-575 Mark II. TEM micrographs were obtained with a Hitachi Hf-2000 FE-TEM equipped with a Kevex energy-dispersive X-ray detector operated at 200 kV. Infrared spectra were obtained with a JASCO FTIR-6100. Samples were diluted with KBr and compressed into thin disk-shaped pellets. XPS spectra were measured by Shimadzu AXIS-ULTRA DLD. All binding energies were calibrated by using the contaminant carbon (C 1s=284.6 eV) as a reference. Pd K-edge and Ag K-edge XAFS spectra were recorded using a fluorescence-yield collection technique at the beam line 01B1 station with an attached Si (111) monochromator at SPring-8, JASRI, Harima, Japan (prop. No. 2016A1095, 2016B1104). The data reduction was performed by the REX2000 program (Rigaku).

Decomposition of formic acid: The catalyst (0.1 g) was placed into a reaction vessel (30 mL) with a reflux condenser and equipped with gas burette. After the purging with Ar, HCOOH/HCOONa = 9/1 aqueous solution (1.0 M, 10 mL) was added to the reaction vessel and reacted at 348 K with magnetic stirring. TOFs (h^{-1}) were determined according to the following equation.

$$TOF = \frac{P_{atm}V_{H2}/RT}{N_{Pd} \cdot t} \quad \text{equation S1}$$

Where P_{atm} is the atmospheric pressure, V_{H2} is the generated volume of H_2, R is the gas constant, T is reaction temperature, N_{Pd} is the mol number of Pd, and t is the reaction time.

Hydrogenation of CO_2: The catalyst (0.05 g) and 1 M $NaHCO_3$ aqueous solution (10 ml) were loaded into an autoclave, and the pressure was increased to 1.0 MPa of CO_2 and then increased to 2.0 MPa with H_2. The system was heated to 373 K and stirred for 24 h. The yield of formic acid was determined by HPLC using a Shimazu HPLC instrument equipped with a Bio-rad Aminerganic Analysis Column and an Aminex HPX-87H Ion Exclusion Column. 5 mM H_2SO_4 (0.500 mL/min) was used as mobile phase at 313 K. TON was determined by the formed formic acid (mol)/employed Pd in catalyst (mol) after 24 h.

Measurement of CO_2 adsorption capacity: CO_2 adsorption was determined using TG-DTA (Rigaku, Thermo Plus EVO II). The sample (0.03 g) was heated to 383 K, and this temperature was maintained for 3 h under a N_2 flow (100 mL/min) to remove the physically adsorbed water. The sample was then cooled down to 303 K, and this temperature was held for 60 min to stabilize the sample weight and temperature. The amount of adsorbed CO_2 was monitored for 3 h under a flow of CO_2 (50 mL/min). This adsorption time was sufficient to allow consideration of the amount of adsorbed CO_2 in a pseudo-equilibrium capacity. TON was determined by the formed formic acid (mol)/employed Pd in catalyst (mol) after 24 h.

Computational method: All DFT calculations were performed with the DMol^3 program in Materials Studio 6.1.[24] The generalized gradient approximation (GGA) exchange-correlation functional proposed by Perdew, Burke, and Ernzerhof (PBE)[25] was combined with the double numerical basis set plus polarization functions (DNP). The inner electrons of Pd atoms are replaced by DFT semi-core pseudopotentials. Brillouin zone integrations were performed on a Monkhorst-Pack[26] k-point grid with a k-point spacing of 0.04 Å. The Pd nanoparticles experimentally prepared were modelled by a supercell slab consisting of a 4 × 4 surface unit cell with four atomic (111) surface layers, where the bottom two layers were fixed at the corresponding bulk position and the top two layers were allowed to relax during geometry optimizations. The slab was separated by a vacuum space with a height of 20 Å. Geometry optimizations were carried out by considering solvent effects of water (ε = 78.54) with COSMO.[27] The dipole slab correction[28] was then applied for the optimized structures. The adsorption energy E_{ad} is defined as $E_{\mathrm{ad}} = E_{\mathrm{adsorbate}} + E_{\mathrm{slab}} - E_{\mathrm{adsorbate/slab}}$, where $E_{\mathrm{adsorbate}}$ is the total energy of free adsorbate, E_{slab} is the total energy of the bare slab, and $E_{\mathrm{adsorbate/slab}}$ is the total energy of the adsorbate–slab system.

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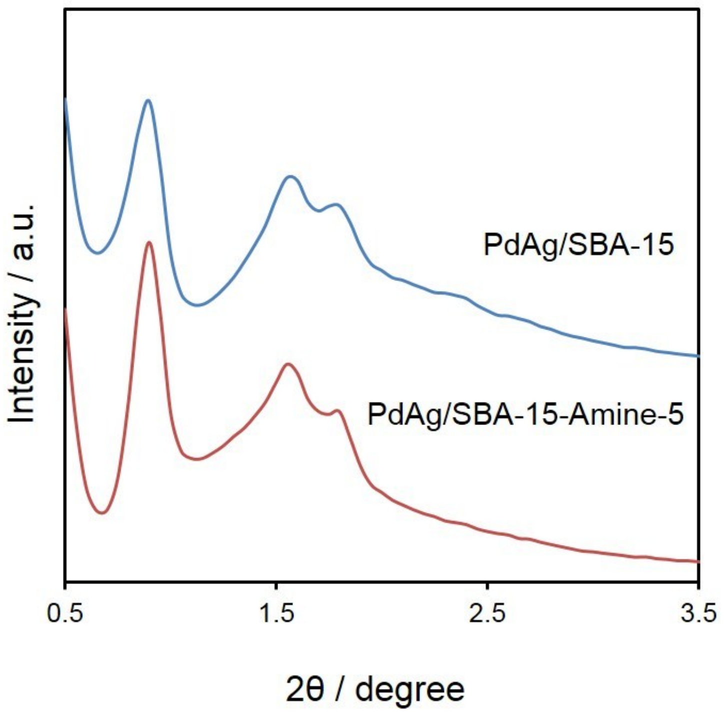

Figure S1. Low angle XRD pattern

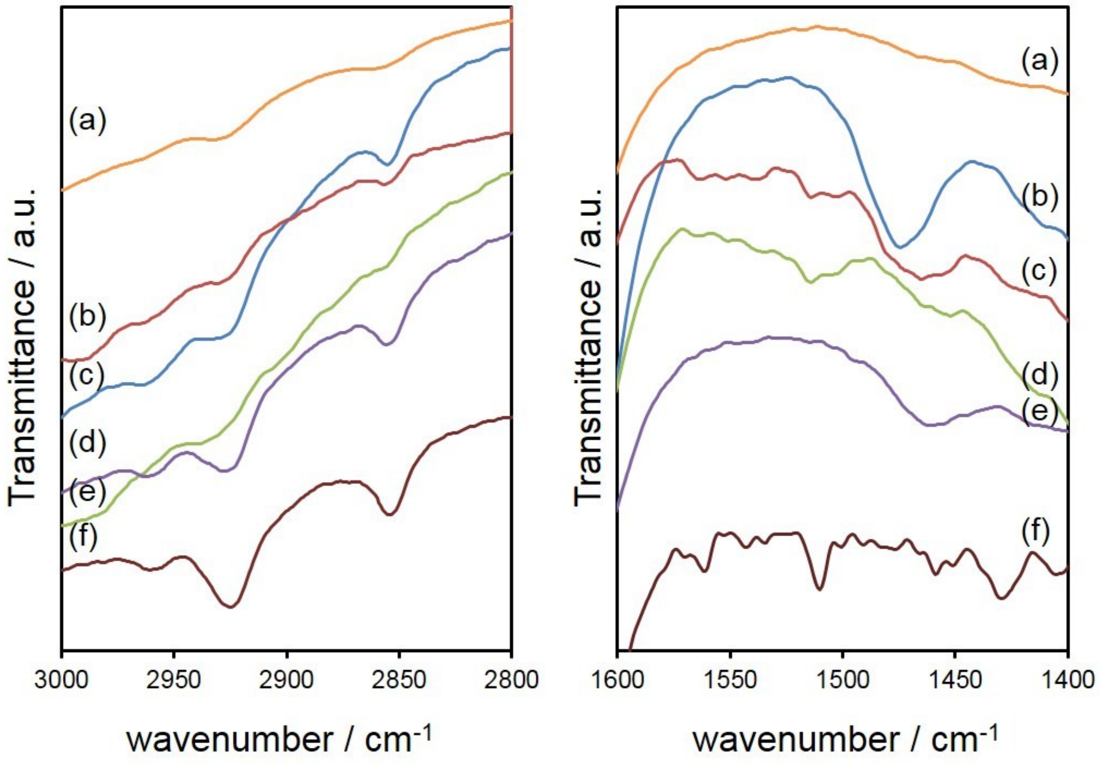

Figure S2. FT-IR spectra of (a) parent SBA-15 and (b-f) SBA-15-amine-x (x= 1-5).

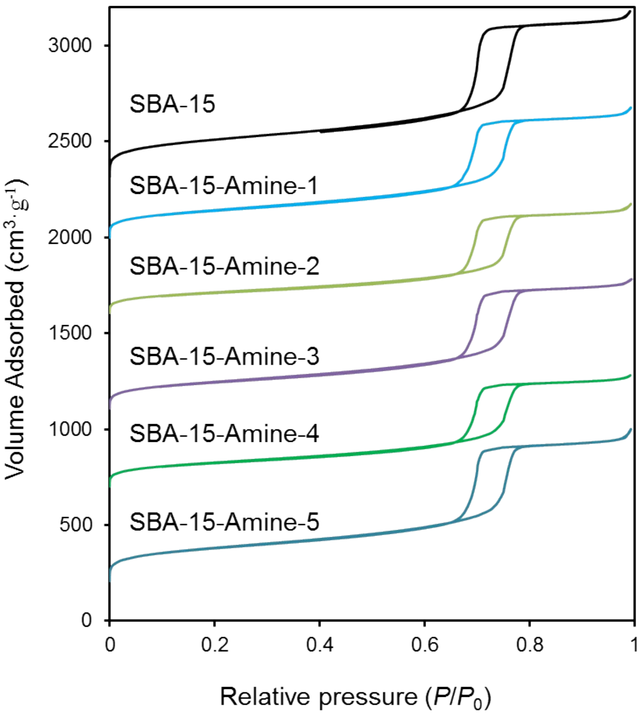

Figure S3. N_2 adsorption-desorption isotherm.

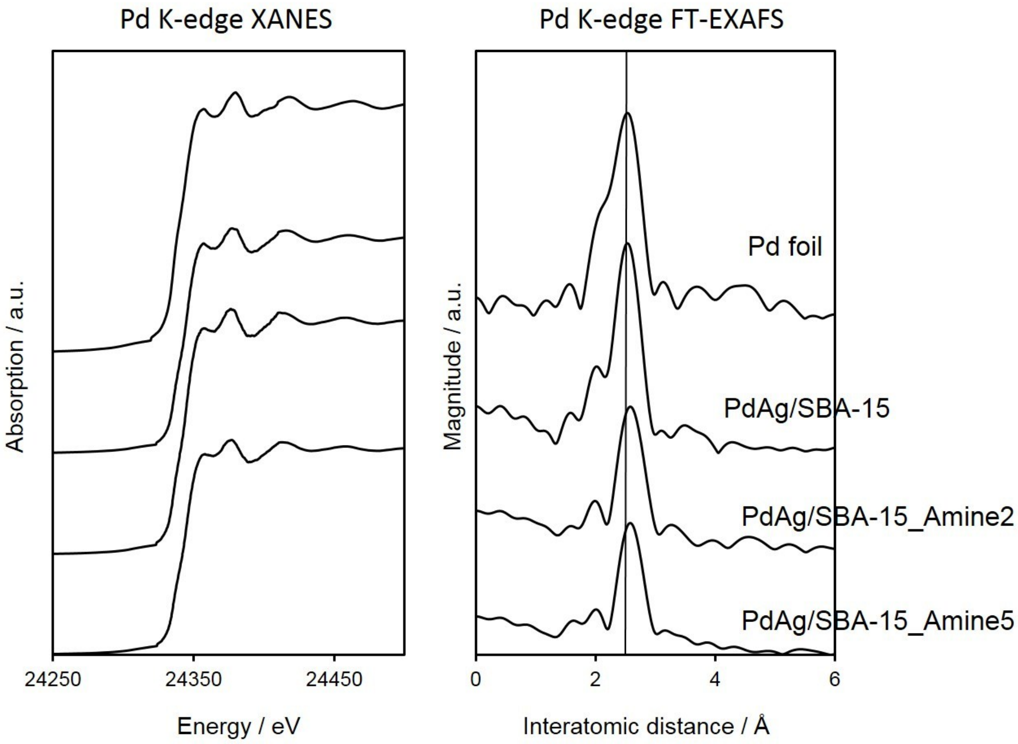

Figure S4. Pd K-edge XAFS spectra.

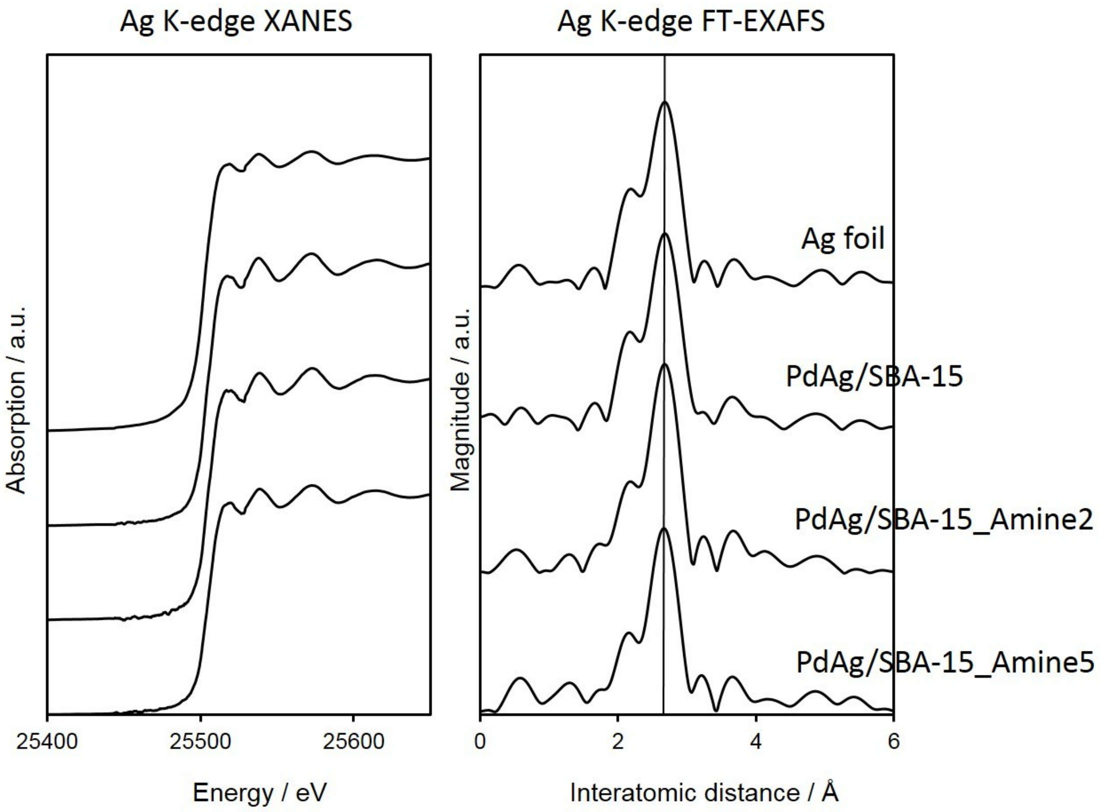

Figure S5. Ag K-edge XAFS spectra.

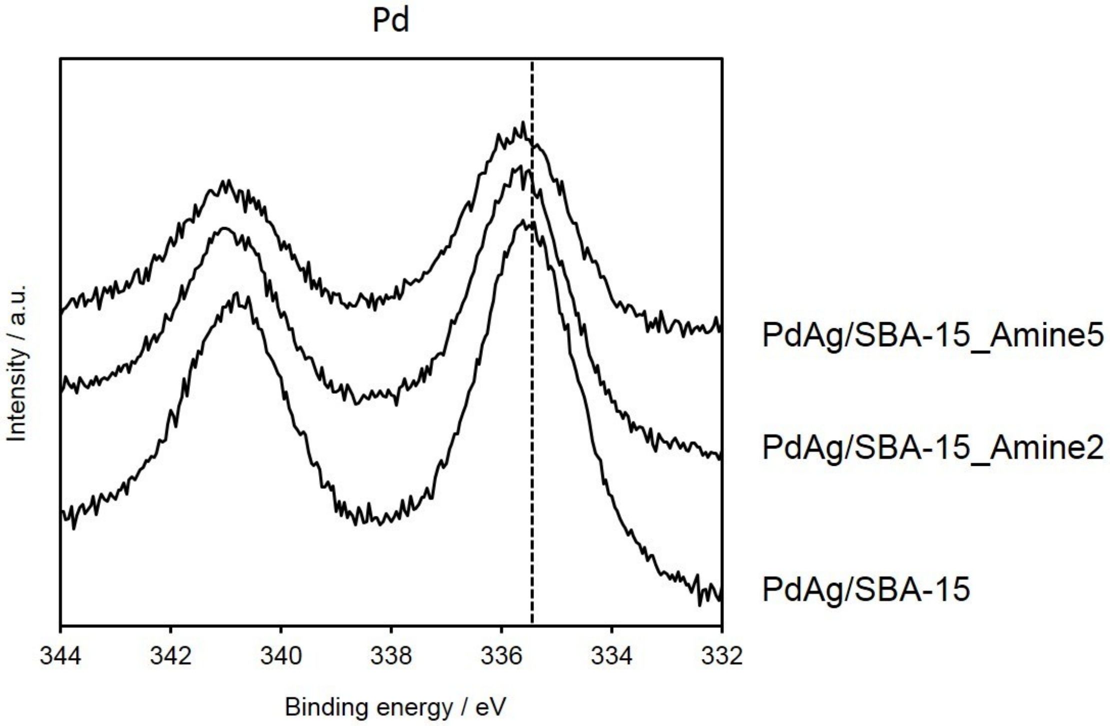

Figure S6. Pd 3d XPS spectra.

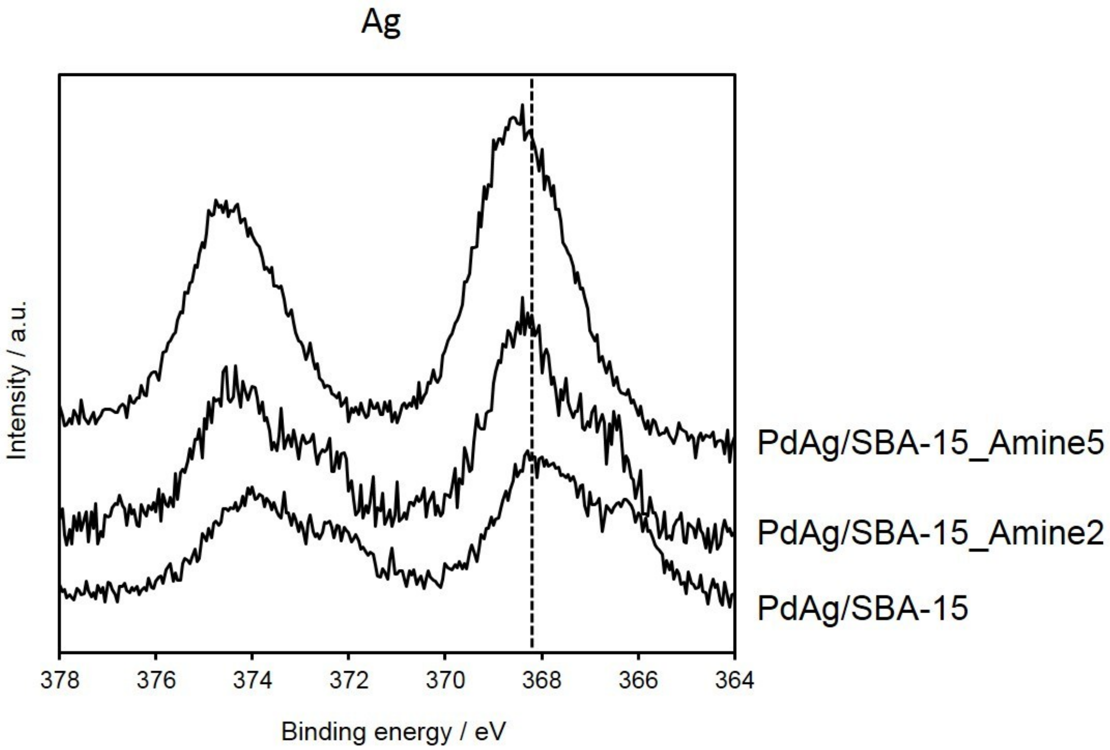

Figure S7. Ag 3d XPS spectra

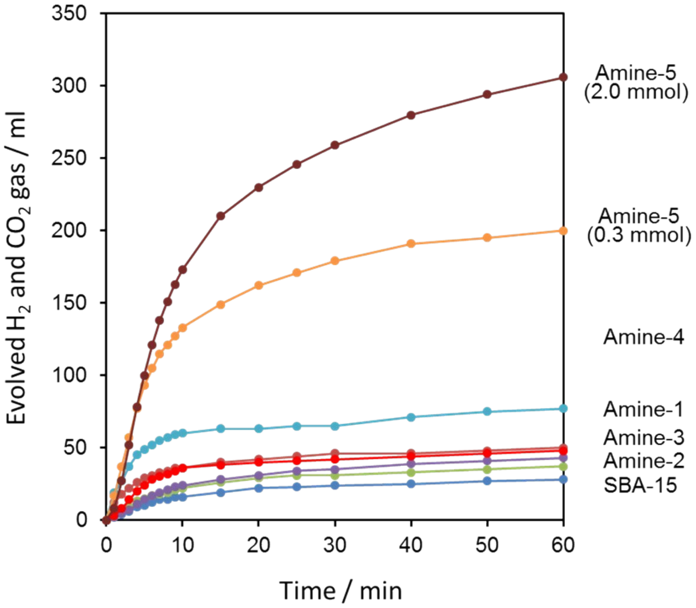

Figure S8. Time profile for the decomposition of formic acid.

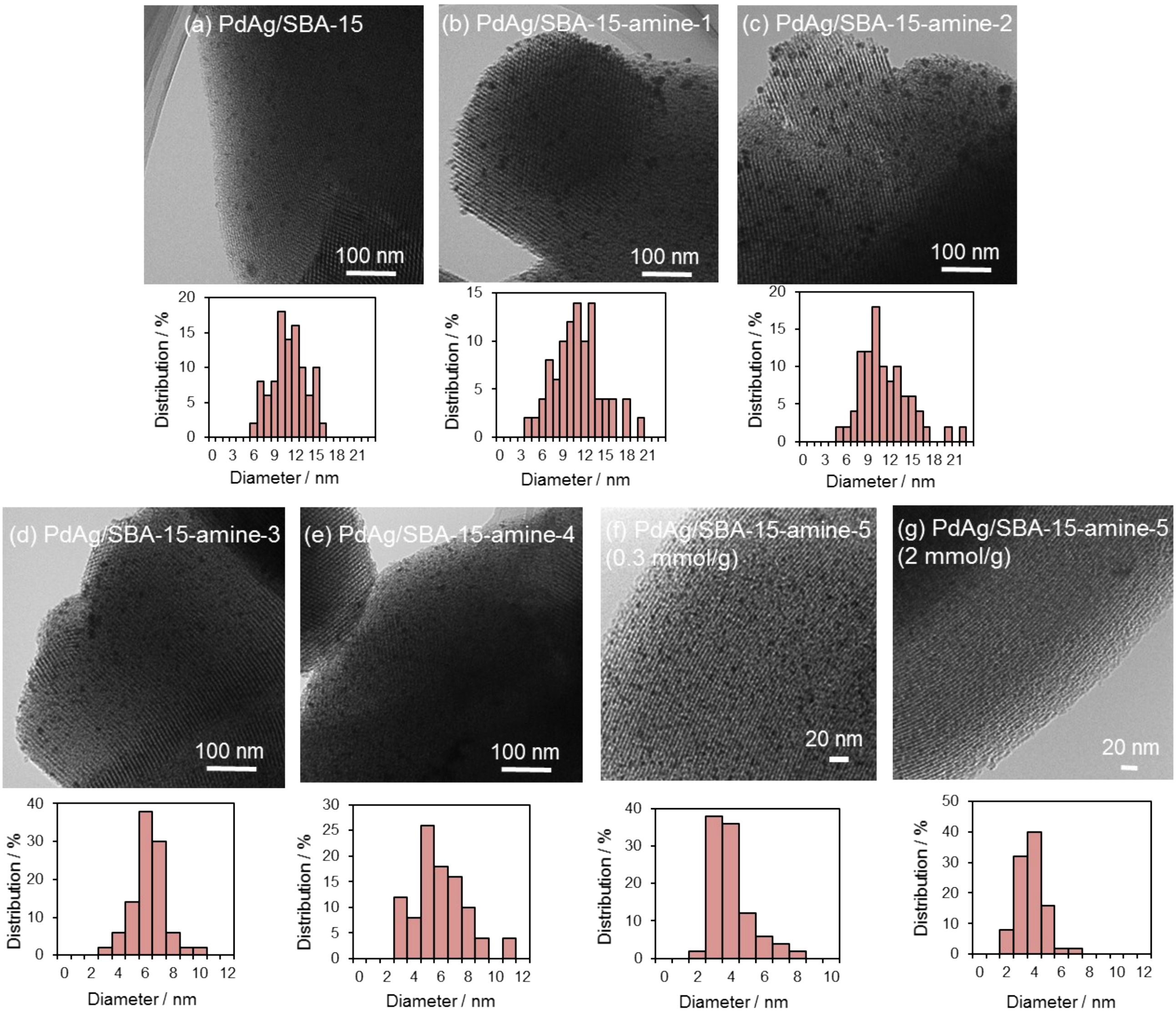

Figure S9. (A) TEM images and size distribution diagrams of PdAg/SBA-15-amine-x.

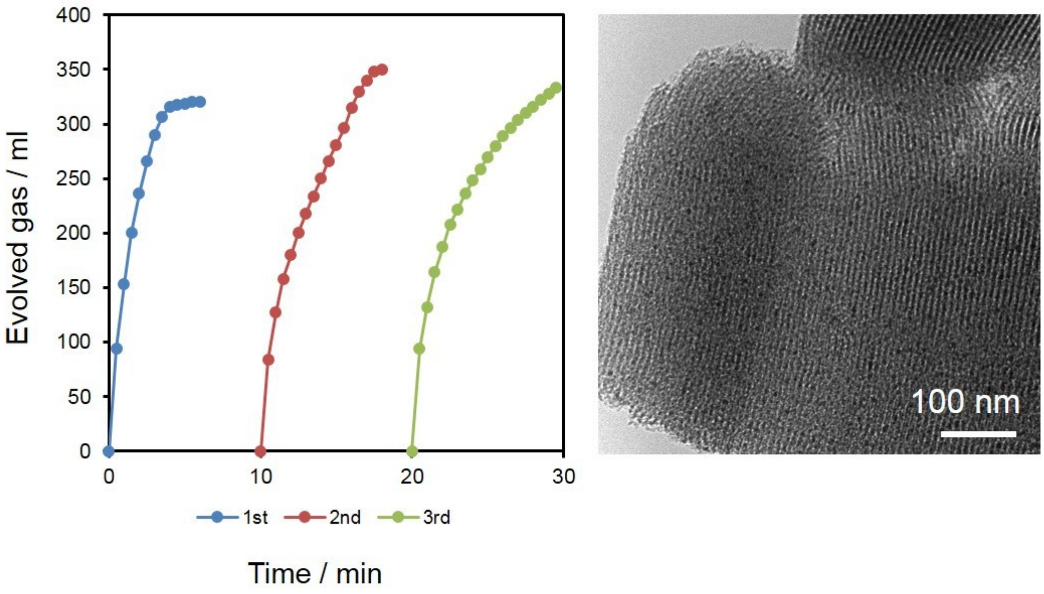

Figure S10. (A) Recycling experiment and (B) TEM images of the recovered PdAg/SBA-15-amine-5 (amine: 0.3 mmol) after 3rd dehydrogenation reaction from formic acid. Reaction conditions: catalyst (0.3 g) HCOOH/HCOONa = 9/1 (0.65 M, 10 mL), Ar, at 348 K.

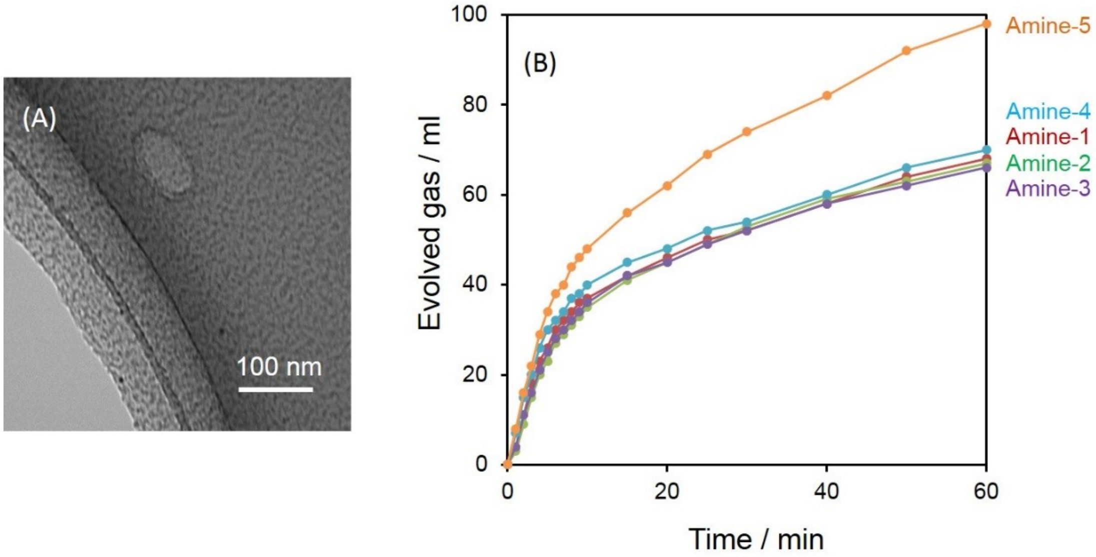

Figure S11. (A) TEM image of the as-synthesized PdAg nanoparticles and (B) time profiles for the hydrogen production from formic acid using PdAg deposited SBA-15-amine-x.

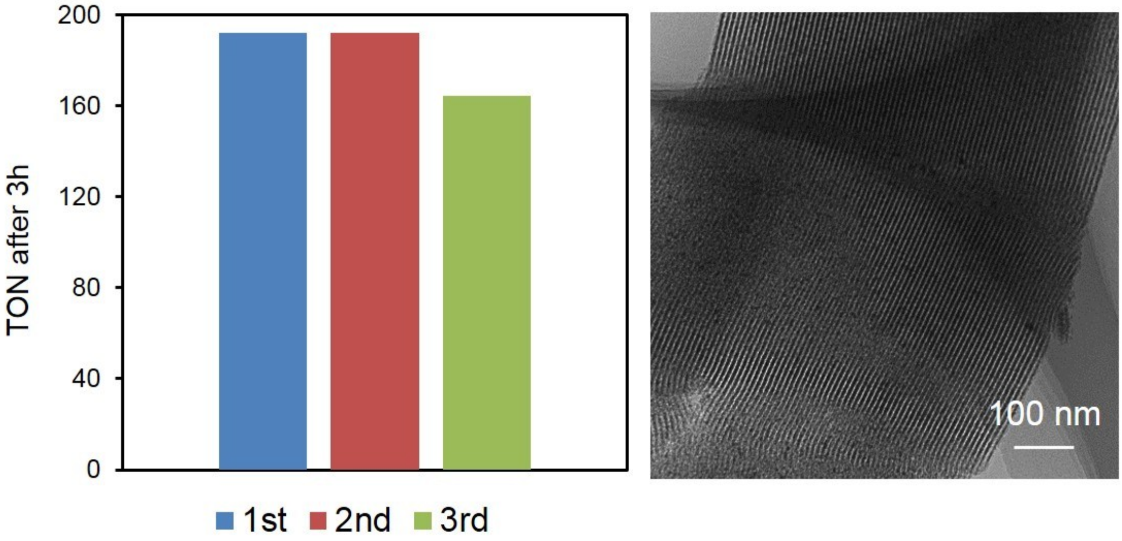

Figure S12. (A) Recycling experiment and (B) TEM images of the recovered PdAg/SBA-15-amine-5 (amine: 0.3mmol) after 3rd hydrogenation reaction of CO_2 to form formic acid. Reaction conditions: catalyst (0.05 g), 1 M $NaHCO_3$ aqueous solution (10 ml), CO_2/H2 =1.0 MPa/10MPa, at 373 K, 3 h.

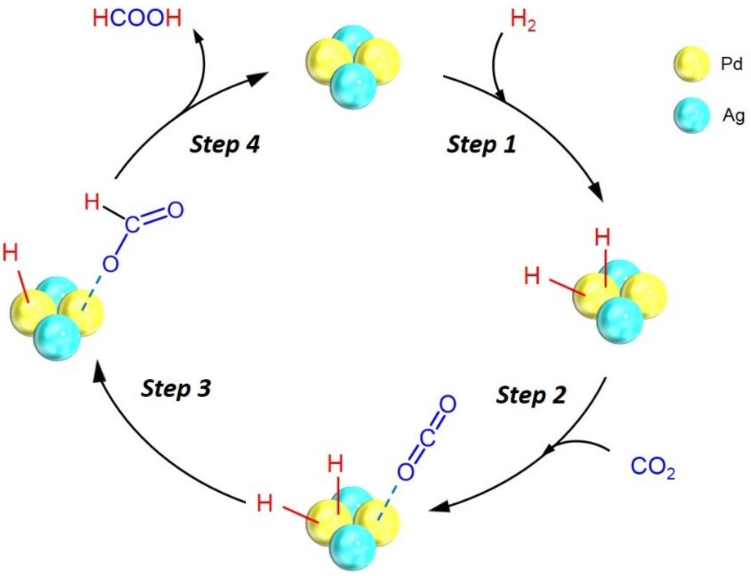

Figure S13. A possible reaction pathway for the CO_2 hydrogenation to produce formic acid on PdAg alloy catalyst

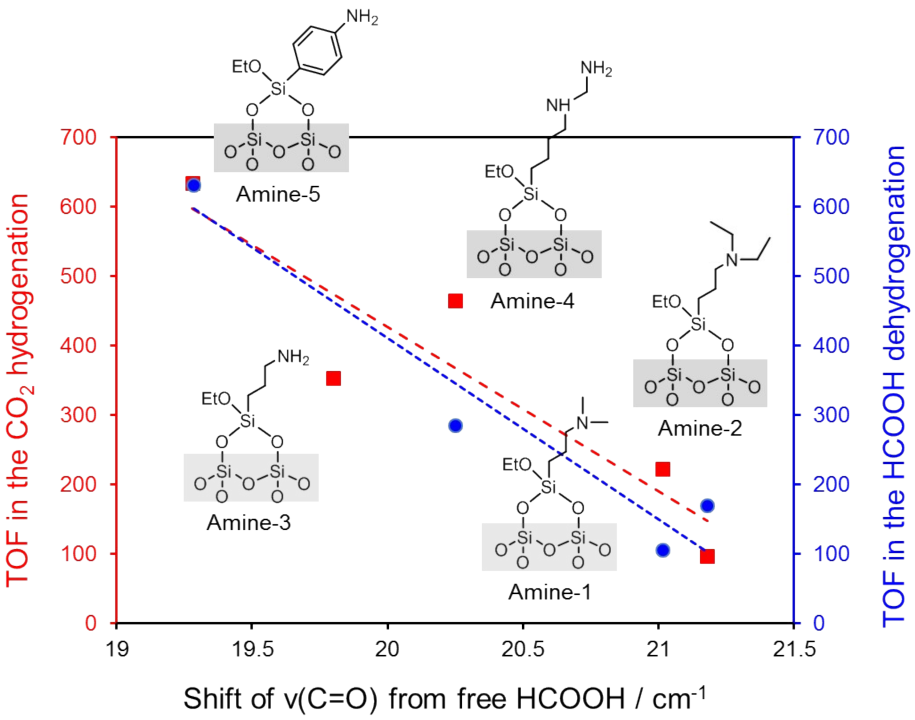

Figure S14. The relationship between catalytic activity in the CO_2 hydrogenation and shift of the *v*(C=O) band from free HCOOH determined by FT-IR spectra.

Table S1. Textural properties of the SBA-15 and SBA-15-amine-x

	Surface-grafted Amine [mmol g^{-1}]	Surface area [m^2g^{-1}]	Average pore diameter [nm]	Pore volume [cm^3g^{-1}]
SBA-15	-	733	8.86	1.35
Amine-1	0.3	517	8.32	1.04
Amine-2	0.3	406	8.86	0.87
Amine-3	0.3	522	8.86	1.05
Amine-4	0.3	447	8.86	0.89
Amine-5	0.3	635	8.32	1.22
Amine-5	2.0	530	7.79	0.83