Supporting Information

Hollow mesoporous organosilica spheres encapsulating PdAg nanoparticles and poly(ethyleneimine) as reusable catalysts for CO_2 hydrogenation to formate

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Experimental Procedures

Materials. Tetraethoxy orthosilicate (TEOS, 95%), disodium tetrachloropalladate(II) (Na_2PdCl_4, >95%), silver(I) nitrate ($AgNO_3$, 99.8%), sodium borohydride ($NaBH_4$, >95%), fumed silica (SiO_2), aqueous ammonia solution (28%), ammonium nitrate (99%) and ethanol (99.5%) were purchased from Nacalai Tesque Inc. 1,4-Bis(triethoxysilyl)benzene (BTEB, 98%) was purchased from Sigma-Aldrich. Branched poly(ethylenimine) (PEI, M_w = 1,800, 99%) was purchased from Alfa Aesar. Cetyltrimethylammonium bromide (CTAB, 98%) was purchased from Wako Pure Chemical Industries, Ltd. Titanium dioxide P25® as a catalyst support was purchased from Evonik. Activated carbon Shirasagi® as a catalyst support was supplied from Osaka Gas Chemicals Co., Ltd. All regents were used as received without further purification. Deionized water was used in all synthetic and catalytic experiments.

Synthesis of supported PdAg NP catalysts. Supported PdAg NP catalysts (PdAg/fumed SiO_2, PdAg/AC and PdAg/TiO_2) were prepared by the conventional wet impregnation method; briefly, 1.0 g of support was impregnated with 100 mL of water containing Na_2PdCl_4 (0.047 mmol) and $AgNO_3$ (0.047 mmol), followed by stirring for 3 h at room temperature and vacuum dry. Subsequently, the solid was re-dispersed in 50 mL of water, then reduced with 1.7 mL of freshly-prepared aqueous $NaBH_4$ solution (20 mg/mL) (approximately 10 equiv. of metals), washed with distilled water and dried under vacuum to yield supported PdAg NPs catalysts (Pd: 0.5 wt%, Pd/Ag molar ratio = 1/1). PEI-supported PdAg NP catalyst (denoted as PdAg/PEI) was synthesized by evaporating ethanol/water from the brownish suspension obtained in step 2 in the synthesis procedure for PdAg+PEI@HMOS.

Gas-phase CO_2 adsorption measurement. CO_2 gas adsorption experiments were performed under dry conditions using TG-DTA system (Rigaku, Thermo plus EVO II). The sample (10 mg) was loaded into a platinum pan and heated at 130 °C for 180 min under a N_2 flow (100 mL/min) to remove the physisorbed water. The temperature was then lowered to 40 °C and kept for 120 min in a flow of N_2 (100 mL/min) to stabilize the sample weight and temperature. The amount of adsorbed CO_2 was monitored for 7 h under a flow of water-saturated 10% CO_2/N_2 (100 mL/min).

Liquid-phase adsorption measurement. Liquid-phase adsorption experiments for HCO_3^- and $HCOO^-$ anions in water were performed in sealed quartz vessels for up to 20 h at room temperature (25±3 °C). A dried sample (ca. 100 mg) was dispersed in a glass beaker containing designated amount of either $NaHCO_3$ aqueous solution (0.06 mol/L, 50 mL) or HCOONa aqueous solution (0.08 mol/L, 50 mL) and was magnetically stirred at 300 rpm. A portion of the solution was collected at predetermined time intervals by filtration, and the residual concentration was determined by a titration method using methyl orange as an indicator for HCO_3^- anion and by using HPLC for $HCOO^-$ anion.

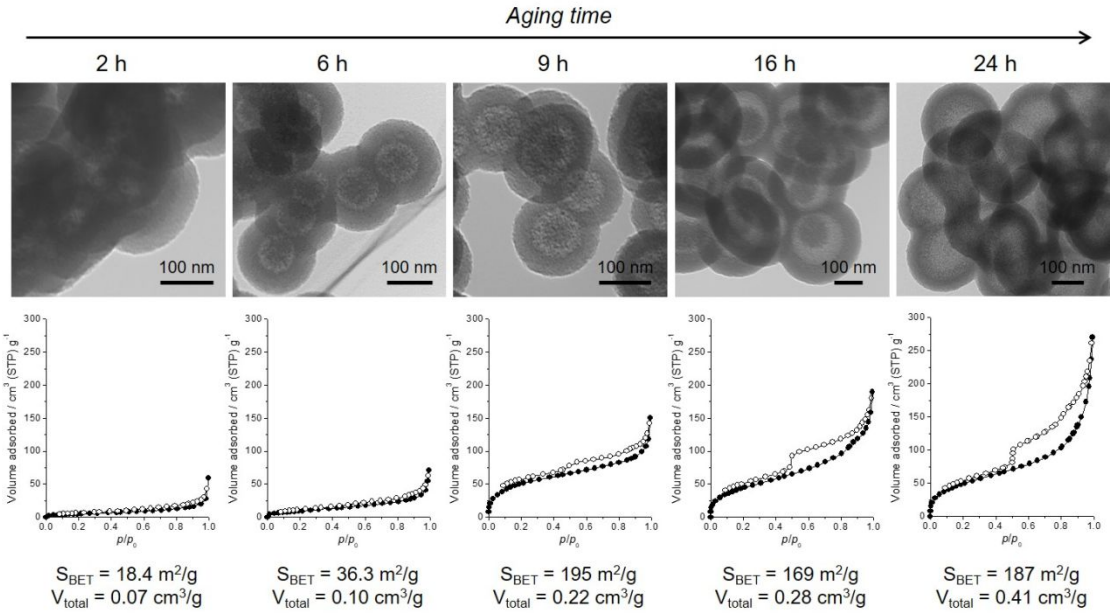

Figure S1 (Above) TEM images and (Below) the corresponding N_2 adsorption-desorption isotherms of as-synthesized PdAg+PEI@HMOS (without CTAB extraction) along with the aging time (2−24 h) at 35°C. Filled and empty symbols show adsorption and desorption isotherm data, respectively.

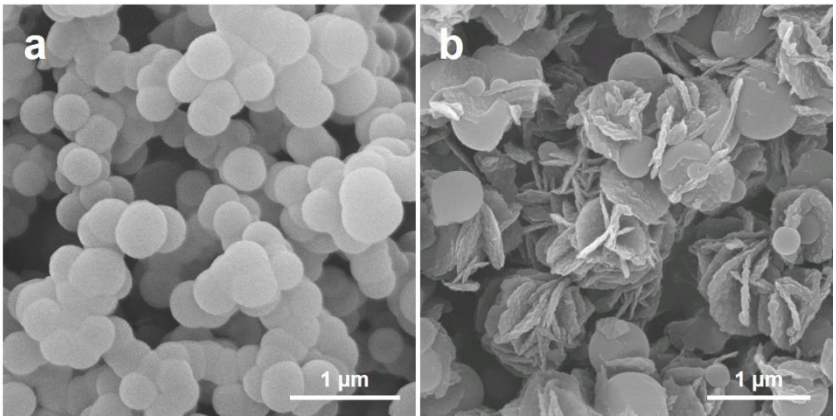

Figure S2 FE-SEM images of PdAg+PEI@HMOS samples synthesized with (a) branched PEI (M_w = 1,800) and (b) linear PEI (M_w = 2,500) as a template.

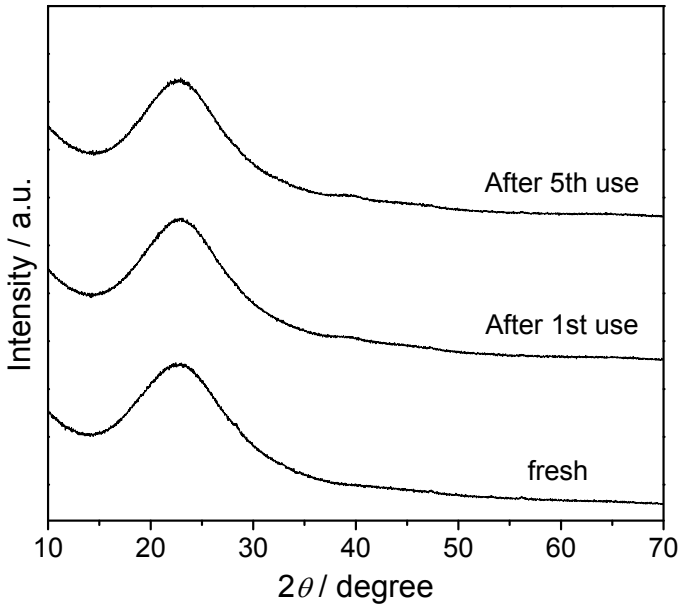

Figure S3 Powder XRD patterns of PdAg+PEI@HMOS catalyst upon catalytic use.

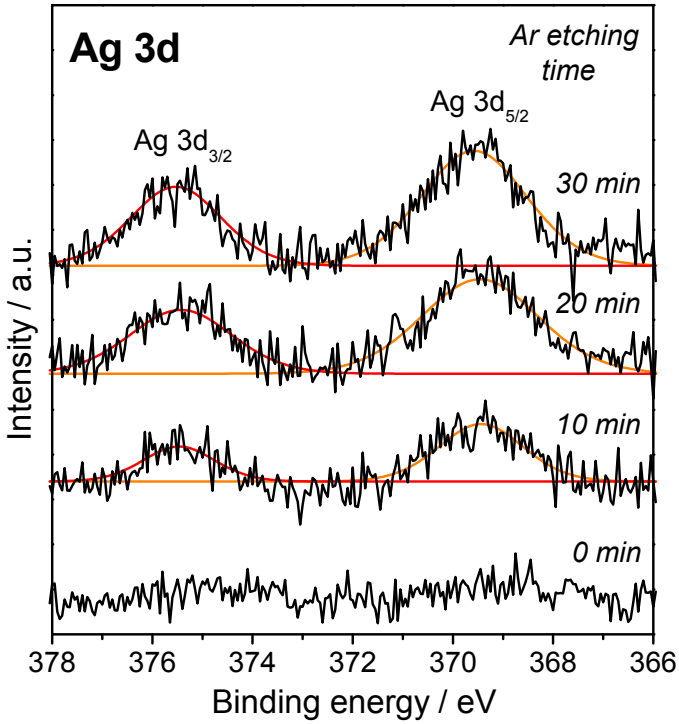

Figure S4 Ag 3d XPS spectra for PdAg+PEI@HMOS along with Ar etching time (0-30 min).

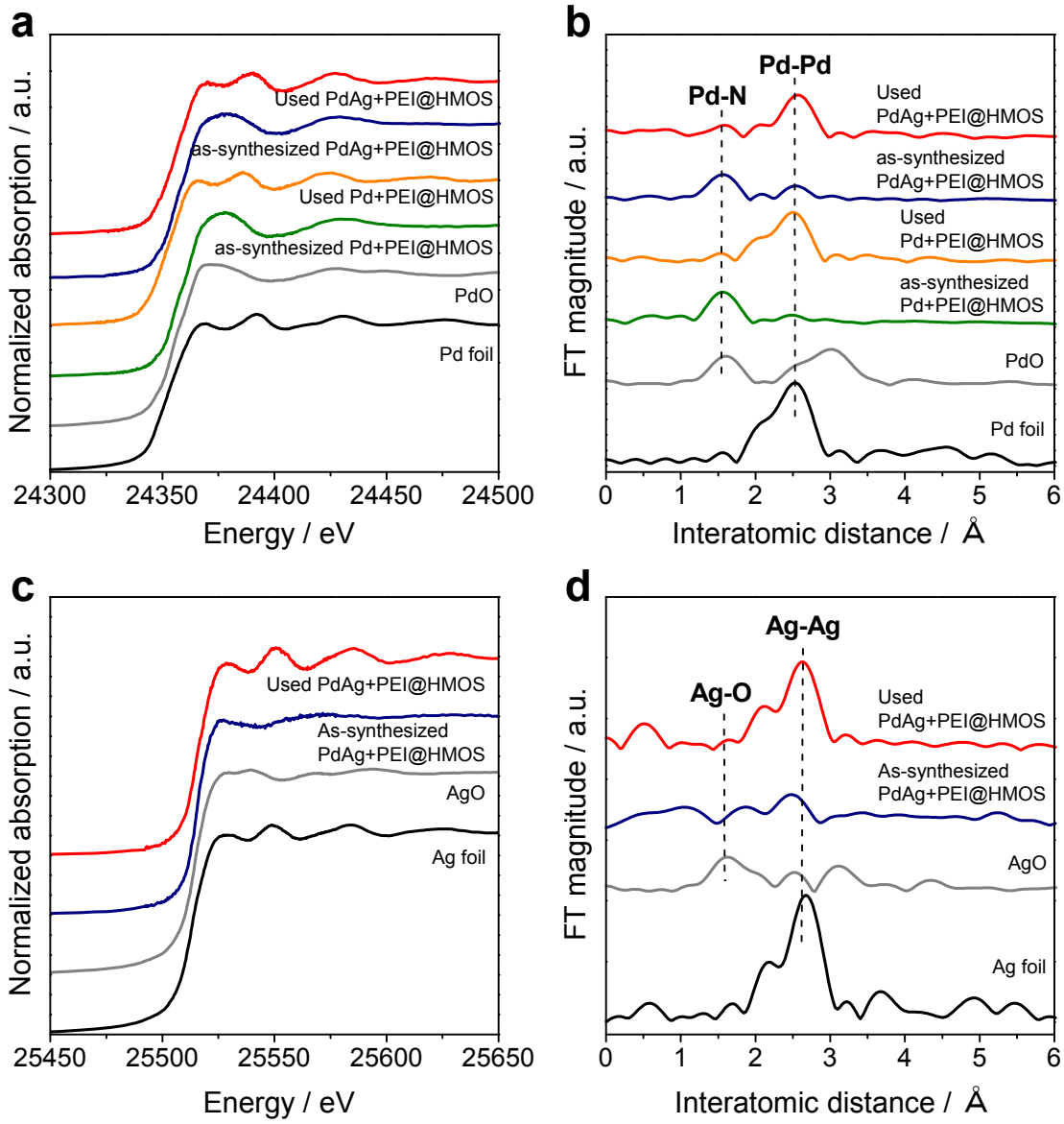

Figure S5 (a) Pd K-edge XANES spectra and (b) fourier transforms of EXAFS spectra for Pd K-edge of as-synthesized/used PdAg+PEI@HMOS, as-synthesized/used Pd+PEI@HMOS and some Pd references (Pd foil and PdO). (c) Ag K-edge XANES spectra and (d) fourier transforms of EXAFS spectra for Ag K-edge of as-synthesized/used PdAg+PEI@HMOS and some Ag references (Ag foil and AgO).

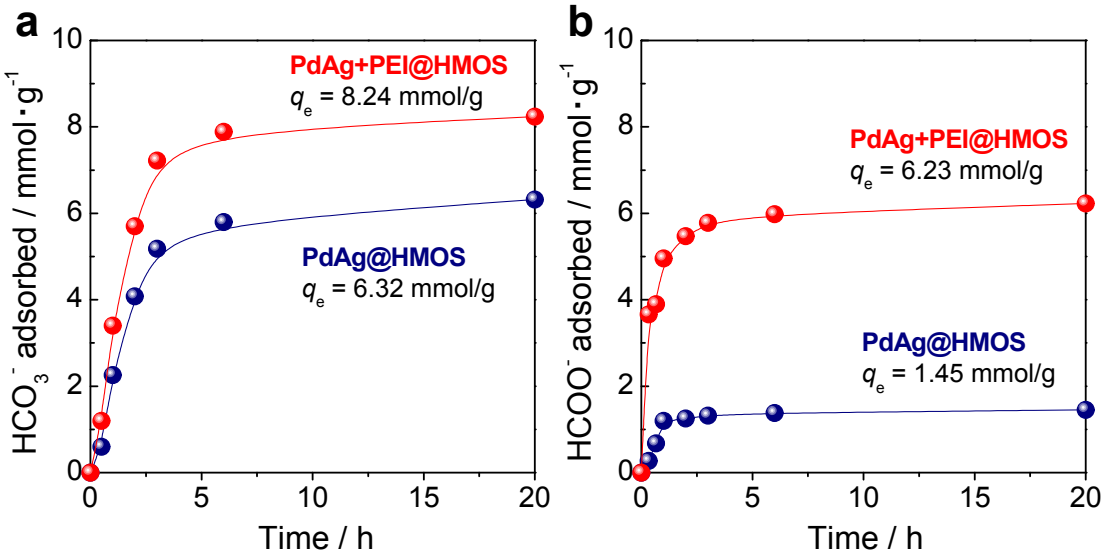

Figure S6 Kinetics in adsorption of (a) bicarbonate (HCO_3^-) and (b) formate ($HCOO^-$) at room temperature in water using PdAg+PEI@HMOS and PdAg@HMOS catalysts. *Adsorption conditions for bicarbonate*: sample (100 mg), $NaHCO_3$ aq. (0.06 M, 50 mL), room temperature, 300 rpm. *Adsorption conditions for formate*: sample (100 mg), HCOONa aq. (0.08 M, 50 mL), room temperature, 300 rpm.

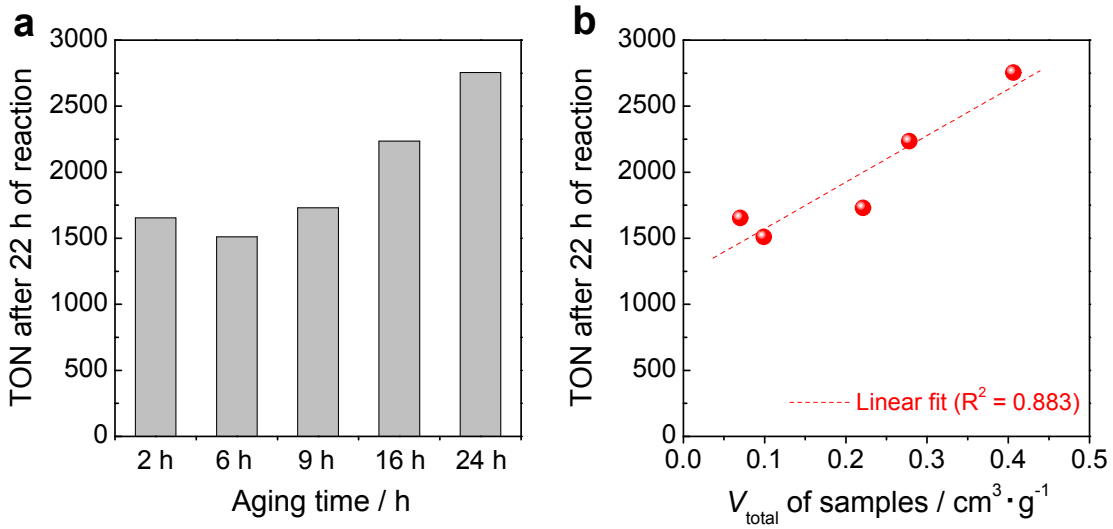

Figure S7 (a) TON after 22 h reaction in the CO_2 hydrogenation and (b) the relationship between TON in the CO_2 hydrogenation and the total volume (V_{total}) over the series of PdAg+PEI@HMOS catalysts synthesized with different aging period of time (2−24 h). *Reaction conditions*: catalyst (10 mg, Pd 0.38 μmol), solvent (0.1 M NaOH aq., 15 mL), H_2 (1.0 MPa), CO_2 (1.0 MPa), Temp. = 100 °C, t = 22 h.

Table S1 Textural properties of PdAg+PEI@HMOS catalysts synthesized with different aging period of time (2−24 h)[a].

Sample	S_{BET}[b] (°C)	V_{total}[c] (cm^3/g)	D_{pore}[d] (nm)
PdAg+PEI@HMOS (aging 2 h)	18.4	0.070	2.1
PdAg+PEI@HMOS (aging 6 h)	36.3	0.100	2.0
PdAg+PEI@HMOS (aging 9 h)	195	0.221	1.6
PdAg+PEI@HMOS (aging 16 h)	169	0.278	1.6
PdAg+PEI@HMOS (aging 24 h)	187	0.406	1.6

[a] Samples prepared without the CTAB extraction process (see the Experimental procedures). [b] Surface area calculated by the BET method. [c] Total pore volume reported at $p/p_0 = 0.99$. [d] Peak pore size determined by the BJH method.

Table S2 Summary of reaction conditions and catalytic activities for hydrogenation of CO_2 to formic acid/formate over supported metal NPs catalysts recently reported.

Catalyst	Temp (°C)	Base/Solvent	$P(H_2/CO_2)$ (MPa)	Time (h)	TON	TOF (h^{-1})	Ref.
PdAg+PEI@HMOS	100	0.1 M NaOH aq.	1/1	22	2754	125	This work
Pd+PEI@HMOS	100	0.1 M NaOH aq.	1/1	22	455	21	This work
PdAg/TiO_2	100	0.1 M NaOH aq.	1/1	22	519	24	This work
PdAg/AC	100	0.1 M NaOH aq.	1/1	22	71	3.2	This work
PdAg/fumed SiO_2	100	0.1 M NaOH aq.	1/1	22	63	2.9	This work
Pd/mpg-C_3N_4	100	20 vol.% NEt_3 aq.	2/2	24	38	1.6	Ref. 1
$Pd_{0.8}Co_{0.2}$@MSN	100	1 M $NaHCO_3$ aq.	1/1	10	4082	408	Ref. 2
PdAg/SBA-15-phenylamine	100	1 M $NaHCO_3$ aq.	1/1	24	874	36	Ref. 3
PdAg/amine-modified mesoporous carbon	100	1 M $NaHCO_3$ aq.	1/1	24	839	35	Ref. 4
PdAg/amine-modified resorcinol−formaldehyde polymers	100	1 M $NaHCO_3$ aq.	1/1	24	867	36	Ref. 5
PdAg@mesoporous hollow carbon sphere	100	1 M $NaHCO_3$ aq.	1/1	24	2680	112	Ref. 6
PdAg/TiO_2	100	1 M $NaHCO_3$ aq.	1/1	24	748	31	Ref. 7
Pd@Ag/TiO_2	100	1 M $NaHCO_3$ aq.	1/1	24	2496	104	Ref. 7
Ru/LDH (Mg^{2+}/Al^{3+}=5)	100	1 M NaOH aq.	1/1	24	698	29	Ref. 8
Ru NPs	80	67 vol.% NEt_3 aq.	5/8	3	6351	2117	Ref. 9
Ir/AP-POP	120	1 M NEt_3 aq.	3/3	24	6784	283	Ref. 10
Au NPs/Al_2O_3	70	14 vol.% NEt_3/EtOH	2/2	20	215	11	Ref. 11
Au NPs/TiO_2	70	14 vol.% NEt_3/EtOH	2/2	20	111	5.5	Ref. 11
AURO*lite*	80	20 vol.% NEt_3 aq.	9/9	37 days	18040	28	Ref. 12

Au/SiO_2-Schiff	90	1.5 M NEt_3 in H_2O/MeOH (20/80 v/v%)	5/3	12	14470	1206	Ref. 13

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Table S3 Textural properties of PdAg+PEI@HMOS catalysts after calcination and after catalytic use.

Sample	S_{BET}[c] (°C)	V_{total}[d] (cm^3/g)	D_{pore}[e] (nm)
PdAg+PEI@HMOS[a]	401	0.500	1.8
PdAg@HMOS[b]	464	0.422	1.3
PdAg+PEI@HMOS (after 1st use)	438	0.673	1.6
PdAg+PEI@HMOS (after 5th use)	326	0.549	1.8

[a] Samples after the CTAB extraction process (see the Experimental procedure). [b] Prepared from PdAg+PEI@HMOS by calcination in air at 500 °C, followed by H_2 reduction at 200 °C [c] Surface area calculated by the BET method. [d] Total pore volume reported at $p/p_0 = 0.99$. [e] Peak pore size determined by the BJH method.