

Electronic Supplementary Information

Controllable integration of ultrasmall noble metal nanoparticles into mesoporous silica matrixes by a self-assembly method

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Experimental Section

Materials and reagents

The following chemicals were used as received without any further purification: absolute ethanol (Fisher, analytical reagent grade), tetraethyl orthosilicate (TEOS, Aldrich, $\geq 99.0\%$), hexadecyltrimethylammonium chloride solution (CTACl, 25 wt.% in H₂O, Sigma-Aldrich), ammonia solution (Merck, $\sim 35\%$), ethylene glycol (C₂H₆O₂, $\geq 99.5\%$, Merck), ruthenium chloride hydrate (RuCl₃·xH₂O, Sigma-Aldrich, reagentplus), chloroplatinic acid hydrate (H₂PtCl₆·xH₂O, Sigma-Aldrich), Rhodium (II) acetate dimer (Rh₂(OOCCH₃)₄, 99.99%, Sigma-Aldrich). Deionized water was generated by Elga Micromeg Purified Water system.

Preparation of Pt (~1 nm) nanoparticles

Pt nanoparticles were synthesized by a polyol reduction method according to the literature.^{1,2} Typically, NaOH (5 mL, 0.5 M) in ethylene glycol was added to a solution of H₂PtCl₆·xH₂O in 5 mL of ethylene glycol. The Pt concentration was 0.5 mM. The mixture was heated at 433 K for 3 h under N₂ flow. After the reaction, the mixture was cooled to room temperature and stored for further use.

Preparation of Ru (~1 nm) nanoparticles

The procedures were similar to the preparation section of Pt nanoparticles except that RuCl₃·xH₂O was used as metal precursor instead.

Preparation of Rh (~1 nm) nanoparticles

The procedures were similar to the preparation section of Pt nanoparticles except that Rh₂(OOCCH₃)₄ was used as metal precursor instead.

Preparation of Pt-Ru (~1 nm) alloy nanoparticles

The procedures were similar to the preparation section of Pt nanoparticles except that H₂PtCl₆·xH₂O and RuCl₃·xH₂O with a molar ratio of 1:1 was used as metal precursors instead.

Preparation of Pt nanoparticles (4.4 nm)

Pt nanoparticles were synthesized by a reduction method with some modification.³ 133 mg of PVP was dissolved in a mixture of 20 mL of 6.0 mM H₂PtCl₆ aqueous solution and 180 mL of methanol. The nanoparticles were obtained after the mixture was refluxed for 3 h at 110 °C.

Preparation of noble metal integrated mesoporous silica

13 mL of DI water was mixed with 50 μ L noble metal colloidal suspension, 2 mL of CTACl solution, 1 to 3 mL of ethanol, and 0.1 mL of 1.0 M ammonia solution. The resulting mixture was stirred at room temperature for 30 min. After that, 0.5 mL of TEOS, was added to the above mixture. The mixture was further stirred for another 30 min, followed by heating at 60 °C in an electric oven for 2 h. The final product was collected by centrifuging, washed with ethanol and dried at 60 °C overnight. Then the samples were calcined at 400 °C for 5 h in 30 mL/min of Ar flow.

Hydrogenation of CO₂

Hydrogenation of CO₂ was carried out in a fixed bed stainless steel reactor (inner diameter = 7 mm, length = 50 cm) loading with 100 mg of the prepared catalysts. Catalyst bed at the center of the reactor was supported by glass wool at both ends, while the remaining space was filled with 2 mm glass beads. Temperature was measured by a type K thermocouple inserted into the reactor and near the catalyst bed. In situ activation was carried out at 400°C for 1 h with a heating rate of 5°C/min under a constant flow of 50 mL/min of H₂/N₂ (10%/90%) at 1 atm. A gas mixture of H₂ and CO₂ (H₂:CO₂ = 4:1) at a total flow rate of 20 mL/min was fed into the reactor. The reaction temperature was increased from 100 to 400 °C with 25 °C intervals. Reactants and products were measured online by gas chromatography (GC, Agilent-7890A) coupled with thermal conductivity detector (TCD). Unless otherwise mentioned, all the data were measured at steady state, e.g., after 60 min to 90 min on stream. The data presented at each temperature were the averaged values of three measurements.

Characterization techniques

Morphologies of samples were characterized by scanning electron microscopy (SEM, JEOL-6700F), transmission electron microscopy (TEM, JEM-2010, 200 kV) and high-resolution transmission electron microscopy (HRTEM, JEM-2100F, 200 kV). The crystallographic information was analyzed by X-ray diffraction (XRD, Bruker D8 Advance) equipped with a Cu K_α radiation source. Specific surface areas and average pore size of samples were determined using N₂ physisorption isotherms at 77 K (Quantachrome NOVA-3000 system). Metal content in the catalysts was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 7300DV, Perkin Elmer, USA).

Supplementary Figures (Figure S1 to Figure S12)

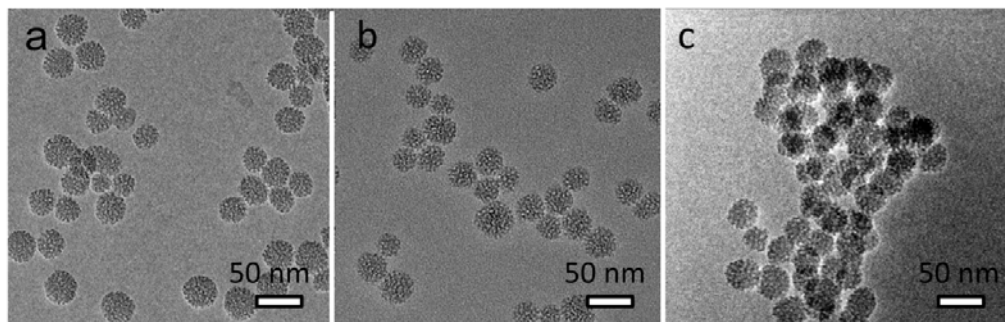


Figure S1. TEM images of Pt/*m*SiO₂ using different volumes of Pt colloidal suspension: (a) 10 μ L, (b) 20 μ L, and (c) 100 μ L.

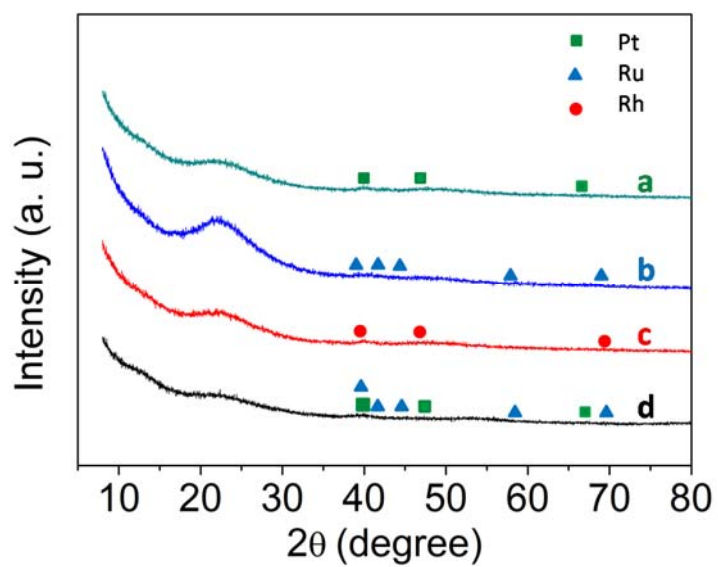


Figure S2. XRD patterns of (a) Pt/*m*SiO₂, (b) Ru/*m*SiO₂, (c) Rh/*m*SiO₂, and (d) Pt-Ru/*m*SiO₂.

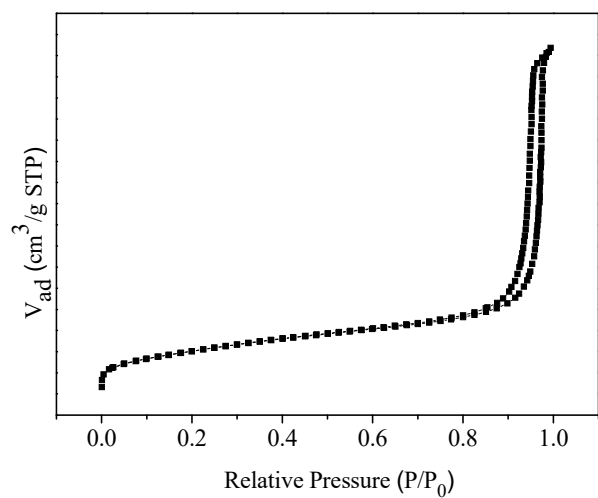


Figure S3. N₂ sorption isotherm of Pt/*m*SiO₂.

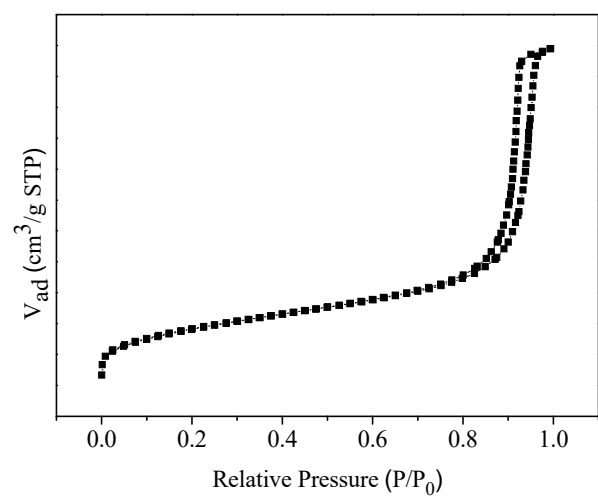


Figure S4. N₂ sorption isotherm of Ru/*m*SiO₂.

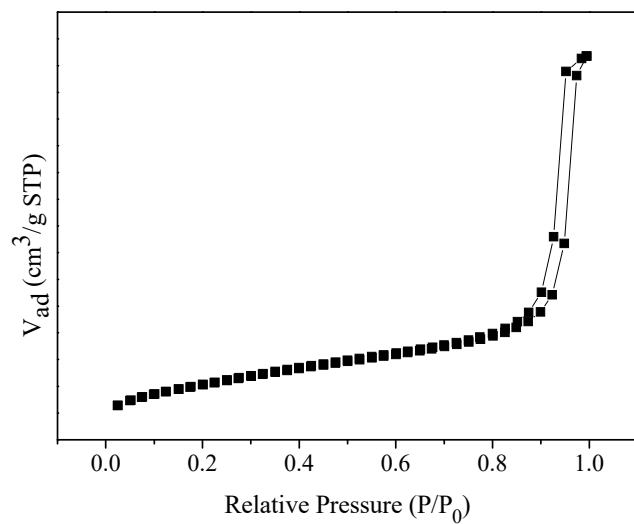


Figure S5. N₂ sorption isotherm of Rh/mSiO₂.

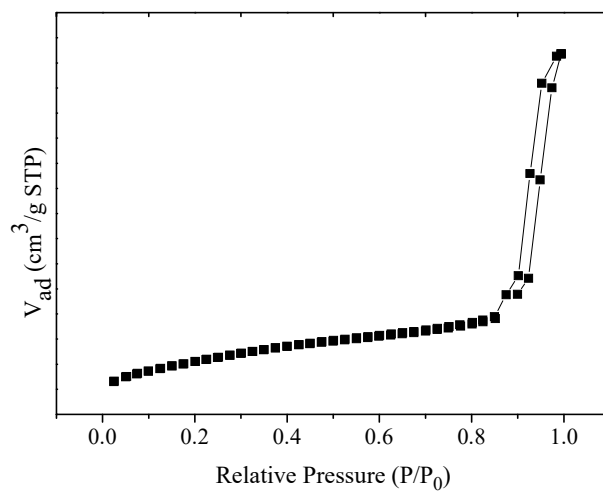


Figure S6. N₂ sorption isotherm of Pt-Ru/mSiO₂.

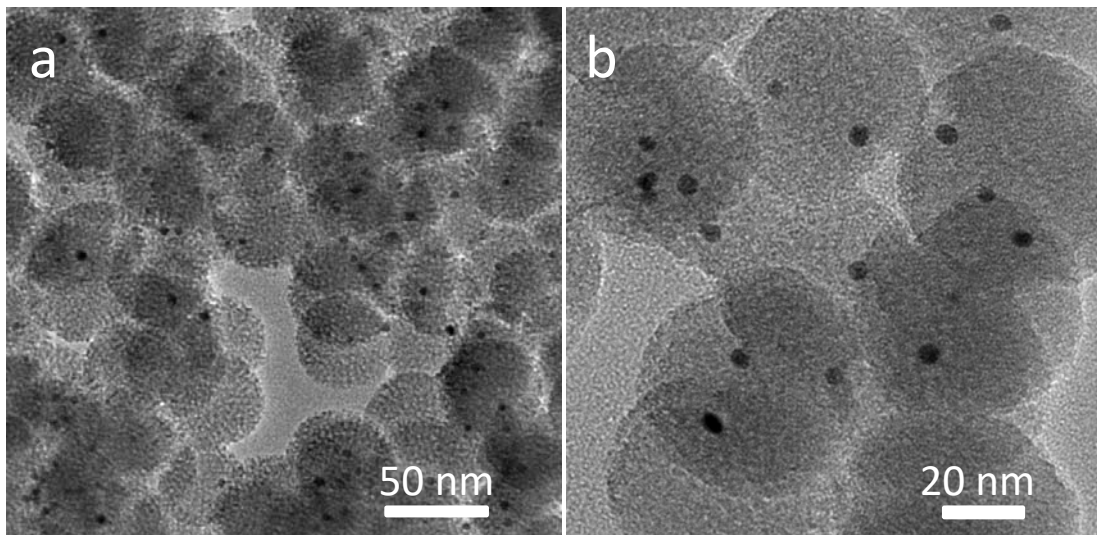


Figure S7. TEM images of Pt(4.4 nm)/*m*SiO₂ sample.

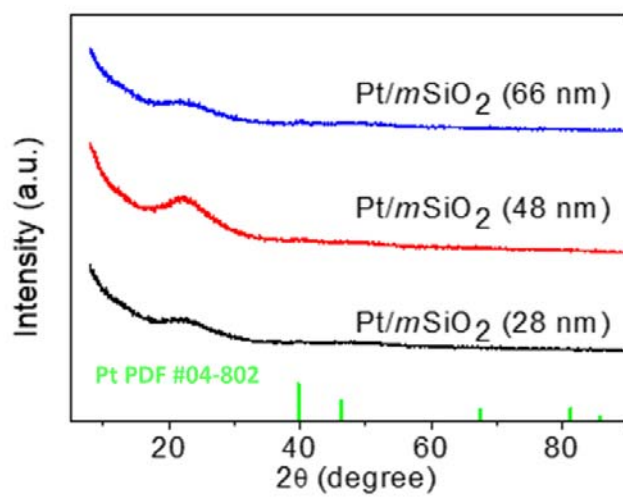


Figure S8. XRD patterns of the three Pt based nanocatalysts with different matrix sizes of *m*SiO₂: Pt/*m*SiO₂ (28 nm), Pt/*m*SiO₂ (48 nm), and Pt/*m*SiO₂ (66 nm).

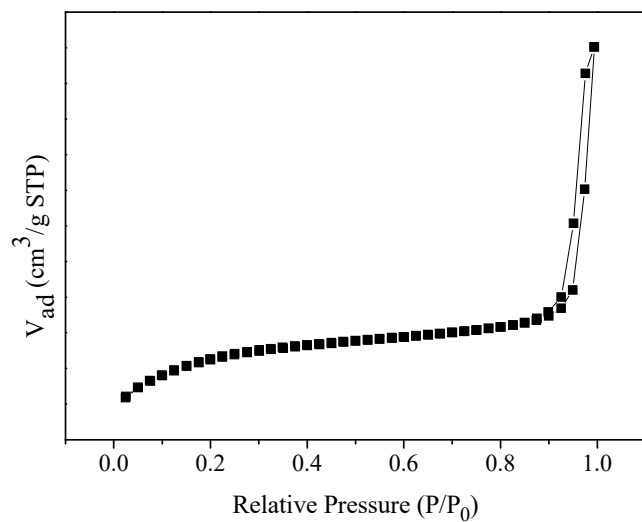


Figure S9. N₂ sorption isotherm of Pt/*m*SiO₂ (48 nm).

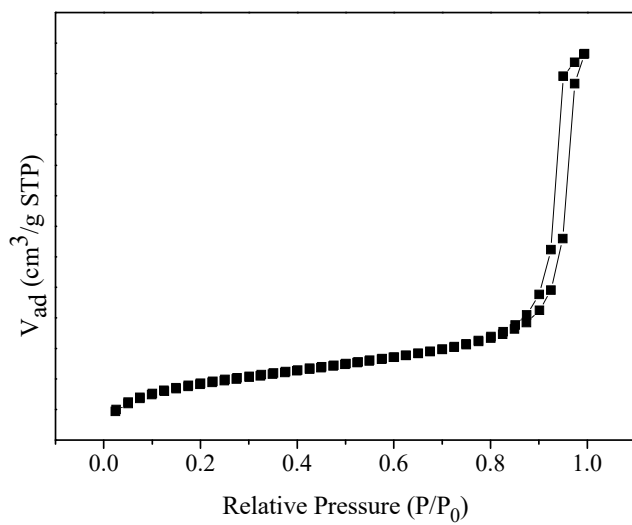


Figure S10. N₂ sorption isotherm of Pt/*m*SiO₂ (66 nm).

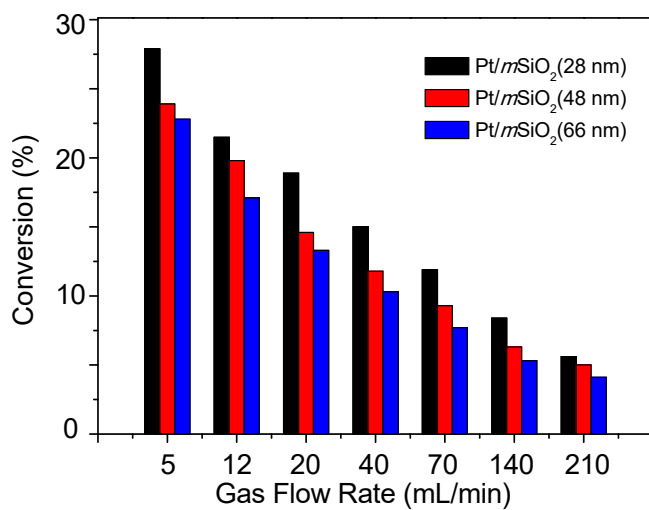


Figure S11. Effect of gas flow rate on the performance of the three Pt/mSiO₂ nanocatalysts: Pt/mSiO₂ (28 nm), Pt/mSiO₂ (48 nm), and Pt/mSiO₂ (66 nm).

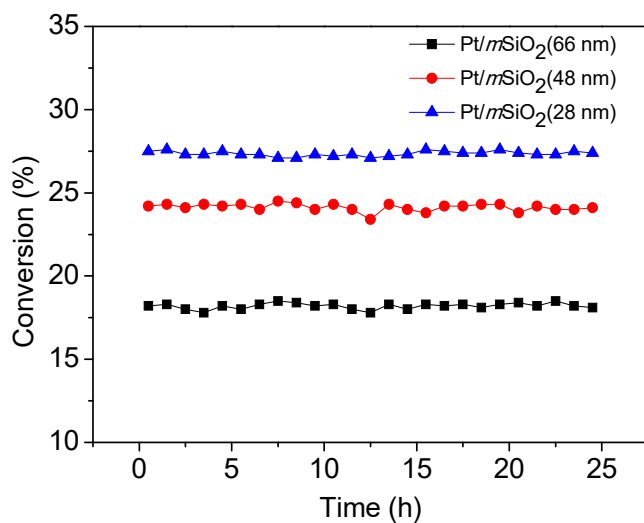


Figure S12. Stability tests of the three Pt/mSiO₂ nanocatalysts at 400 °C and 1 atm.

Supplementary Tables

sample	Metal Content (wt%)	BET (m ² ·g ⁻¹)
Pt/ <i>m</i> SiO ₂ (28 nm)	1.73 %	747.2
Ru/ <i>m</i> SiO ₂ (27 nm)	1.70%	750.2
Rh/ <i>m</i> SiO ₂ (29 nm)	1.67%	772.6
Pt-Ru/ <i>m</i> SiO ₂ (30 nm)	0.84% (Pt) + 0.81% (Ru)	745.0
Pt/ <i>m</i> SiO ₂ (48 nm)	1.75%	751.2
Pt/ <i>m</i> SiO ₂ (66 nm)	1.71%	754.3

Table S1 Noble metal contents and BET specific surface areas of integrated M/*m*SiO₂ nanocatalysts prepared *via* this self-assembly method, where M = Pt, Ru, Rh and Pt-Ru.

sample	TOF (min ⁻¹)
Pt/ <i>m</i> SiO ₂ (28 nm)	9.8
Pt/ <i>m</i> SiO ₂ (48 nm)	8.6
Pt/ <i>m</i> SiO ₂ (66 nm)	6.1

Table S2 Comparison of TOF calculated from data achieved at 400 °C. TOF values were defined as mole of CO₂ converted per mole of Pt metal per minute.

References

1. Y. Wang, J. W. Ren, K. Deng, L. L. Gui, and Y. Q. Tang, *Chem. Mater.*, 2000, **12**, 1622-1627.
2. H. S. R. M. Rioux, J. D. Hoefelmeyer, P. Yang, and G. A. Somorjai, *J. Phys. Chem. B* 2005, **109**, 2192-2202.
3. L. M. Baldyga, S. O. Blavo, C.-H. Kuo, C.-K. Tsung and J. N. Kuhn, *ACS Catal.* 2012, **2**, 2626-2629.