Supporting Information

Cyclopropane Hydrogenation vs. Isomerization over Pt and Pt-Sn Intermetallic Nanoparticle Catalysts: A Parahydrogen Spin Labelling Study

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1. Catalyst Synthesis and Characterization

1.1 Catalyst Synthesis

Synthesis of Pt@mSiO₂ Silica encapsulated Pt nanoparticles (Pt@mSiO₂) were synthesized by previously reported method with minor modifications.¹⁻² In a typical synthesis, 104 mg K₂PtCl₄ (Acros Organics, 46–47% Pt) dissolved in 25 mL DI water (10 mM solution) was added to a previously prepared aqueous solution of 8.4 g tetradecyltrimethylammonium bromide (TTAB, \geq 99%, Sigma-Aldrich) in 200 mL DI water. The mixture was stirred for 10 minutes at room temperature to obtain a cloudy solution and then moved to an oil bath at 50 °C and stirred for another 10 minutes until the cloudy solution became clear. To this an aqueous solution of NaBH₄ (284 mg NaBH₄ in 25 mL ice-cold DI water, 300 mM solution, Alfa Aesar, 98%) was added. After the solution was stirred for another 20 hours at 50 °C, a dark brown colloidal solution of Pt nanoparticles was formed. This solution was first centrifuged at 3000 rpm for 30 minutes, four times. After each centrifuge, the residue was discarded, and the supernatant solution was collected for subsequent centrifugation. Finally, the collected supernatant solution was

centrifuged at 14000 rpm for 15 min, twice to collect all the Pt nanoparticles. This Pt nanoparticle solution was redispersed in around 200 mL DI water. About 1 mL of a 0.05 M sodium hydroxide solution was added to obtain a pH between 11 and 12. Under stirring, 3 mL of a 10% tetraethylorthosilicate (TEOS, Sigma-Aldrich, reagent grade, 98%) solution in methanol was added dropwise to this solution using a syringe. After 24 h, the sample was centrifuged at 14000 rpm for 20 minutes twice, and the silica-coated Pt nanoparticles (Pt@mSiO₂) were redispersed in 200 mL of methanol. To this 10 mL of concentrated HCI (36% assay, Fisher Chemicals) was added and the solution was refluxed at 90 °C for 24 h.

Synthesis of Pt₃Sn@mSiO₂ and PtSn@mSiO₂ iNPs To synthesize silica encapsulated intermetallic Pt₃Sn@mSiO₂ and PtSn@mSiO₂ nanoparticles, the above methanol-dispersed Pt@mSiO₂ solution was centrifuged at 14000 rpm for 20 minutes. The Pt@mSiO₂ sample in the residue was collected and redispersed in around 80 mL tetraethylene glycol (TEG, Alfa Aesar, 99%) in a 250 mL two-neck round bottomed flask. Before the intermetallic synthesis, the Pt content in Pt@mSiO₂ sample was identified using inductively coupled plasma mass spectrometry (ICP-MS). SnCl₂·2H₂O was used as the Sn precursor. Pt to Sn ratio was kept 1:1 and 3:1 for PtSn and Pt₃Sn intermetallic nanoparticles respectively. The solution was heated at 280 °C under argon to form the Pt-Sn alloys. After synthesis, the solution was mixed with acetone, sonicated and finally centrifuged to obtain the silica encapsulated Pt-Sn alloy nanoparticles. Both the samples were calcined in air at 500 °C for 4 hours to remove remaining organic residues. Finally, the calcined samples were reduced in a tube furnace under 10% H₂/Ar flow at 300 °C for 4 hours (Pt₃Sn@mSiO₂).

1.2 Characterization

Characterization details of silica-encapsulated Pt-Sn nanoparticles were already reported.¹⁻² Monometallic phase of Pt and intermetallic phases of Pt₃Sn and PtSn were confirmed by the Powder X-ray diffraction (PXRD) patterns and Transmission Electron Microscope (TEM)

S3

micrographs. Pt/Sn stoichiometries of three nanoparticles were examined by the Pt and Sn metal loadings in the nanoparticles as measured by inductively coupled plasma mass spectroscopy (ICP-MS). Average diameters of the metal cores (Table S1) for Pt@mSiO₂, Pt₃Sn@mSiO₂, and PtSn@mSiO₂ were measured as 14.3 ± 0.8 , 16.6 ± 0.9 , and 20.6 ± 0.9 nm respectively by TEM, indicating the incorporation of Sn into the Pt nanoparticles. The pore size of the mesoporous silica shell (mSiO₂) is determined as ~2.7 nm and shell thickness are 10.9 to 8.3 nm going from monometallic Pt to intermetallic Pt₃Sn, and PtSn nanoparticles. Pt dispersions measured by CO adsorption in Pt@mSiO₂, Pt₃Sn@mSiO₂, and PtSn@mSiO₂ are 6.5%, 2.8%, and 1.8% respectively, proving the formation of Pt-Sn alloys. Surface Pt sites per gram of catalysts were estimated from the Pt loadings and dispersion.

NPs	Pt	Sn	Core Size ^(b)	Pt	Surface Pt
	Loading ^(a)	Loading	(nm)	Dispersion	Sites (/gram)
Pt@mSiO ₂	44.5%	0%	14.3 ± 0.8	6.5%	8.9×10 ¹⁹
Pt ₃ Sn@mSiO ₂	52.0%	9.0%	16.6 ± 0.9	2.8%	4.5×10 ¹⁹
PtSn@mSiO ₂	36.6%	22.4%	206+09	1.8%	2 0×10 ¹⁹
FIGHIGHO2	50.078	22.470	20.0 ± 0.9	1.070	2.0×10

2. Supplementary Tables and Figures

(a) Metal loadings were measured based on weight percentage.

(b) Diameter of the metal core.

Table S1. Metal loadings, particle size, Pt dispersion, and surface Pt sites of the mesoporous silica-encapsulated Pt, Pt₃Sn, and PtSn nanoparticles. Table is adapted from the previous report Ref 2.



Figure S1. 400 MHz ALTADENA proton NMR difference spectra of gas effluent after passing the 15 mg of (A) PtSn@mSiO₂ (B)Pt₃Sn@mSiO₂ and (C) Pt@mSiO₂ at different temperatures with 120/70/210 mL/min of H_2/N_2 /cyclopropane. 32 number of scans and recycle delay of 2 s were used for all spectra.



Figure S2. 400 MHz thermally polarized proton spectra of gas effluent sealed in the NMR tube after passing the 15 mg of (A) PtSn@mSiO₂ (B)Pt₃Sn@mSiO₂ and (C) Pt@mSiO₂ at different temperatures with 120/70/210 mL/min of H₂/N₂/cyclopropane. 512 number of scans and recycle delay of 6 s were used for all spectra.

NPs	Conversion (%)	150 °C	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C
Pt	$arphi_{PE}$	0	0	0	0.05 ± 0.02	N/A	N/A	N/A
	$arphi_{PA}$	3.29 ± 0.21	3.15 ± 0.29	2.31 ± 0.28	0.54 ± 0.02	N/A	N/A	N/A
	$arphi_{total}$	3.29 ± 0.21	3.15 ± 0.29	2.31 ± 0.28	0.59 ± 0.01	N/A	N/A	N/A
Pt₃Sn	$arphi_{PE}$	0	0	0	0.28 ± 0.03	0.63 ± 0.10	1.88 ± 0.26	N/A
	$arphi_{PA}$	0.14 ± 0.01	0.09 ± 0.02	0.10 ± 0.01	0.08 ± 0.02	0.09 ± 0.01	0.19 ± 0.06	N/A
	$arphi_{total}$	0.14 ± 0.01	0.09 ± 0.02	0.10 ± 0.01	0.36 ± 0.05	0.72 ± 0.10	2.08 ± 0.32	N/A
PtSn	$arphi_{PE}$	0.17 ± 0.05	0.20 ± 0.03	0.20 ± 0.04	0.21 ± 0.06	0.49 ± 0.05	1.30 ± 0.16	1.98 ± 0.11
	$arphi_{PA}$	0	0	0	0.04 ± 0.01	0.08 ± 0.01	0.11 ± 0.01	0.16 ± 0.05
	$arphi_{total}$	0.17 ± 0.05	0.20 ± 0.03	0.20 ± 0.04	0.25 ± 0.07	0.57 ± 0.07	1.41 ± 0.17	2.14 ± 0.07

Table S2. Percent conversions in the hydrogenation of cyclopropane to propane. φ_{PE} , φ_{PA} , and φ_{total} represents the conversions of cyclopropane to propene, propane, and total conversion, respectively. N/A means data not available due to either extremely low conversion or data not acquired at these temperatures.

NPs	150 °C	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C
Pt	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Pt₃Sn	251.6 ± 32.9	286.6 ± 50.6	188.7 ± 14.3	196.2 ± 41.7	88.2 ± 12.2	22.7 ± 9.9	N/A
PtSn	N/A	N/A	N/A	73.7 ± 10.7	103.6 ± 17.7	66.8 ± 7.6	31.4 ± 8.4

Table S3. Signal enhancement factor of propane -CH₃ peak in the hydrogenation of cyclopropane to propane. N/A means data not available due to either extremely low conversion or data not acquired at these temperatures.

NPs	150 °C	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C
Pt	N/A						
Pt₃Sn	2.43% ± 0.31%	2.77% ± 0.49%	1.82% ± 0.14%	1.90% ± 0.40%	0.85% ± 0.12%	0.22% ± 0.10%	N/A
PtSn	N/A	N/A	N/A	0.71% ± 0.10%	1.00% ± 0.17%	0.65% ± 0.07%	0.30% ± 0.08%

Table S4. Pairwise selectively (i.e. polarization level) in the hydrogenation of cyclopropane to propane. N/A means data not available due to either extremely low conversion or data not acquired at these temperatures.

NPs	150 °C	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C
Pt	2.11 ± 0.13 s ⁻¹	2.02 ± 0.19 s ⁻¹	1.48 ± 0.18 s ⁻¹	0.38 ± 0.01 s ⁻¹	N/A	N/A	N/A
Pt₃Sn	0.18 ± 0.01 s ⁻¹	0.11 ± 0.03 s ⁻¹	0.13 ± 0.01 s ⁻¹	2.11 ± 0.13 s ⁻¹	0.92 ± 0.13 s ⁻¹	2.65 ± 0.41 s ⁻¹	N/A
PtSn	0.48 ± 0.14 s ⁻¹	0.56 ± 0.08 s ⁻¹	0.56 ± 0.11 s ⁻¹	0.70 ± 0.20 s ⁻¹	1.61 ± 0.20 s ⁻¹	3.98 ± 0.48 s ⁻¹	6.03 ± 0.20 s ⁻¹

Table S5. Turnover frequencies (TOFs) in the hydrogenation of cyclopropane to propane for Pt, Pt₃Sn, and PtSn@mSiO₂ nanoparticles at temperatures from 150 °C to 450 °C. N/A means data not available due to either extremely low conversion or data not acquired at these temperatures.

3. Hydrogenation Reactor and Catalyst Treatment

Details of our hydrogenation reactor have been well described before.²⁻³ Before hydrogenation reactions, all solid catalysts (15 mg) were firmly packed in a U-shaped glass tube (1/4" O.D.) mounted in a ceramic heating element where the temperature can be adjusted accordingly. All catalysts were first oxidized with 50 mL/min air at 400 °C for 2 hours then reduced with 10% H₂ in N₂ at 300 °C at a total flow rate of 100 mL/min for another 2 hours. After the treatments, the hydrogenation reactor was cooled down to room temperature to start the hydrogenation reactions immediately.

4. Calculations

Conversions The gas impurities in the stock cyclopropane (CPA) cylinder are negligible. φ_{PE} and φ_{PA} , representing conversion of cyclopropane to propene (PE) and propane (PA), were

reported in the manuscript, respectively. The total conversion φ_{total} is the summation of φ_{PE} and φ_{PA} . φ_{PE} , φ_{PA} and φ_{total} were calculated by solving the Eq (S1)-(S4).

$$\frac{S_{CPA,CH_2}^{*,thermal}}{6} \times \varphi_{PE} = S_{PE,CH}^{thermal}$$
(S1)

$$\frac{S_{CPA,CH_2}^{*,thermal}}{6} \times \varphi_{PA} = \frac{S_{PA,CH_3}^{thermal}}{6}$$
(S2)

$$\frac{S_{CPA,CH_2}^{*,thermal}}{6} = \frac{S_{CPA,CH_2}^{thermal}}{6} + S_{PE,CH}^{thermal} + \frac{S_{PA,CH_3}^{thermal}}{6}$$
(S3)

$$\varphi_{total} = \varphi_{PE} + \varphi_{PA} \tag{S4}$$

where

 φ_{PE} = conversion of cyclopropane to propene, calculated.

 φ_{PA} = conversion of cyclopropane to propane, calculated.

 φ_{total} = total conversion, summation of φ_{PE} and φ_{PA} , calculated.

 $S_{CPA,CH_2}^{*,thermal}$ = thermally polarized NMR signal integral of the cyclopropane methylene group before hydrogenation reaction, representing moles of cyclopropane before reaction, calculated.

 $S_{CPA,CH_2}^{thermal}$ = thermally polarized NMR signal integral of the cyclopropane methylene group after hydrogenation reaction, representing moles of cyclopropane after reaction, measured.

 $S_{PE,CH}^{thermal}$ = thermally polarized NMR signal integral of the propene methine group, measured.

 $S_{PA,CH_3}^{thermal}$ = thermally polarized NMR signal integral of the propane methyl group, measured.

Signal Enhancement Factor The signal enhancement factor of cyclopropane (CPA) hydrogenation was determined by solving the Eq (S5).

$$\eta_{CPA}^{exp} = \frac{\frac{C^{PHIP} \times S_{PA,CH_3}^{PHIP,CPA}}{N^{NPHIP,CPA}}{\frac{S_{PA,CH_3}^{thermal,CPA}}{6}}$$
(S5)

where

 η_{CPA}^{exp} = NMR signal enhancement factor for the cyclopropane hydrogenation reaction, calculated.

 C^{PHIP} = Relaxation correction factor for gas signal loss due to the transportation from Utube reactor to NMR coil, which is 1.25 at the total flow rate of 400 mL/min.⁴

 $S_{PA,CH_3}^{PHIP,CPA}$ = NMR signal integral of the propane methyl group in ALTADENA difference spectrum, measured.

 $S_{PA,CH_3}^{thermal,CPA}$ = thermally polarized NMR signal integral of the propane methyl group, measured.

 $N^{PHIP,CPA}$ = Number of scans that applied when acquiring the ALTADENA spectra. $N^{PHIP,CPA}$ = 32 in the manuscript.

 $N^{thermal,CPA}$ = Number of scans that applied when acquiring the thermally polarized spectra. $N^{thermal,CPA}$ = 512 in the manuscript.

Pairwise Selectivity & polarization Level. The theoretical NMR signal enhancement factor in the ALTADENA hyperpolarization was calculated using Eq (S6).

$$\eta^{theory} = \frac{1}{3} \times (4\chi_p - 1) \times \frac{2k_B T}{\gamma \hbar B_0}$$
(S6)

 χ_p is the parahydrogen enrichment, which is 50% in the manuscript. At T= 298 K and B₀ = 9.4 T, the theoretical enhancement factor is calculated as 10349. The pairwise selectivity or polarization level in the cyclopropane hydrogenation was calculated using Eq (S7).

$$\delta_{CPA} = \frac{\eta_{CPA}^{exp}}{\eta^{theory}} \times 100\%$$
(S7)

Catalyst Turn Over Frequencies (TOFs) Example calculations of the TOF using the measured conversion for each catalyst type is presented here.

Pt@mSiO₂ For 1 gram of Pt@mSiO₂, moles of Pt in surface is

$$\frac{1 g \times 44.5\% \times 6.5\%}{195.08 g/mole} = 1.483 \times 10^{-4} mole$$

For 1 gram of Pt@mSiO₂, surface Pt sites is

$$1.483 \times 10^{-4} mole \times 6.022 \times 10^{23} / mole = 8.93 \times 10^{19}$$

For 15 mg of Pt@mSiO₂ sample that used in our experiments, surface Pt sites is

$$8.93 \times 10^{19} \times \frac{15 \, mg}{1 \, g} = 1.34 \times 10^{18}$$

At 150°C, the total conversion in the hydrogenation reaction of $H_2/N_2/cyclopropane$ (120/70/210 mL/min) is 3.29% for 15 mg Pt@mSiO₂. 24.5 L/mole molar volume of gas is used at 25°C and 1.01×10^5 Pa.

$$TOF = \frac{\text{cyclopropane} \times \text{conversion}}{\text{surface Pt sites} \times \text{time}}$$

moles of cyclopropane in 1 min = $\frac{0.4 L/min \times 1 min}{24.5 L/mole} \times \frac{210}{400} = 8.57 \times 10^{-3}$

of cyclopropane molecules in $1 \min = 8.57 \times 10^{-3} \times 6.022 \times 10^{23} / mole = 5.16 \times 10^{21}$

$$TOF = \frac{5.16 \times 10^{21} \times 3.29\%}{1.34 \times 10^{18} \times 60s} = 2.11 \, s^{-1}$$

Pt₃Sn@mSiO₂ For 1 gram of Pt₃Sn@mSiO₂, moles of Pt in surface is

$$\frac{1 g \times 52.0\% \times 2.8\%}{195.08 g/mole} = 7.46 \times 10^{-5} mole$$

For 1 gram of Pt₃Sn@mSiO₂, surface Pt sites is

$$7.46 \times 10^{-5} mole \times 6.022 \times 10^{23} / mole = 4.49 \times 10^{19}$$

For 15 mg of Pt₃Sn@mSiO₂ sample that used in our experiments, surface Pt sites is

$$4.49 \times 10^{19} \times \frac{15 \, mg}{1 \, g} = 6.74 \times 10^{17}$$

PtSn@mSiO₂ For 1 gram of PtSn@mSiO₂, moles of Pt in surface is

$$\frac{1 g \times 36.6\% \times 1.8\%}{195.08 \, g/mole} = 3.38 \times 10^{-5} \, mole$$

For 1 gram of PtSn@mSiO₂, surface Pt sites is

$$3.38 \times 10^{-5} mole \times 6.022 \times 10^{23} / mole = 2.03 \times 10^{19}$$

For 15 mg PtSn@mSiO₂ sample that used in our experiments, surface Pt sites is

$$2.03 \times 10^{19} \times \frac{15 \ mg}{1 \ g} = 3.05 \times 10^{17}$$

5. References

1. Maligal-Ganesh, R. V., et al., A Ship-in-a-Bottle Strategy to Synthesize Encapsulated Intermetallic Nanoparticle Catalysts: Exemplified for Furfural Hydrogenation. *ACS Catal.* **2016**, *6*, 1754-1763.

2. Zhao, E. W.; Maligal-Ganesh, R.; Xiao, C.; Goh, T.-W.; Qi, Z.; Pei, Y.; Hagelin-Weaver, H. E.; Huang, W.; Bowers, C. R., Silica-Encapsulated Pt-Sn Intermetallic Nanoparticles: A Robust Catalytic Platform for Parahydrogen-Induced Polarization of Gases and Liquids. *Angew. Chem. Int. Ed.* **2017**, *56*, 3925-3929.

3. Zhou, R.; Zhao, E. W.; Cheng, W.; Neal, L. M.; Zheng, H.; Quinones, R. E.; Hagelin-Weaver, H. E.; Bowers, C. R., Parahydrogen-Induced Polarization by Pairwise Replacement Catalysis on Pt and Ir Nanoparticles. *J. Am. Chem. Soc.* **2015**, *137*, 1938-46.

4. Zhou, R. PhD Thesis. University of Florida, **2014**.