Electronic Supplementary Information

Strong metal-support interaction between Pt and SiO₂ following

high-temperature reduction: a catalytic interface for propane dehydrogenation

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Fig. S1 XRD patterns of Pt/SiO₂ treated in H₂ (a) at 1073 K, N₂ (b) at 1073 K, O₂ (c) at 1073 K, (d) O₂ firstly at 773 K followed by H₂ treatment at 1073 K. ▼: Pt metal.



Fig. S2 The effect of treatment atmosphere on the conversion of propane over Pt/SiO_2 catalysts.



Fig. S3 Time course of propane dehydrogenation over Pt/SiO_2_{1073} K H₂.



Figure S4 TPO spectra of fresh catalyst (a) and the calcination of coke deposited on spent Pt/SiO₂_1073 K H₂ catalyst after running the reaction for 3 h (b): (a) fresh Pt/SiO₂_1073K, (b) spent Pt/SiO₂_1073 K H₂. Reaction condition: the flow rate of air = 50 ml/min, heating rate=10 K / min.



Figure S5 TEM images of fresh Pt/SiO₂_1073 K and spent one after 7 h of reaction as well as their corresponding histograms.



Fig. S6 XRD patterns of Pt/SiO₂ precursor and the catalysts reduced at (a) 773 K, (b) 1073 K, (c) 1273 K. ▼: Pt metal.



Fig. S7 TEM images of Pt/SiO₂ reduced at (A) 773 K, (B) 1073 K, (C) 1273 K as well as their corresponding histograms.



Figure S8 HRTEM images of Pt/SiO₂ reduced at (A) 773 K, (B) 1073 K, (C) 1273 K.



Fig. S9 XPS profiles of Pt level for (a) Pt/SiO₂_773 K H₂, (b) Pt/SiO₂_1073 K H₂, (c) Pt/SiO₂_1273 K H₂.



Figure S10 k³-weighted EXAFS oscillation at Pt L₃-edge (A) and their Fourier transforms (B) of the catalysts and the reference samples (Pt foil and PtCl₂): (a) Pt/SiO₂ precursor, (b) Pt/SiO₂_773 K H₂, (c) Pt/SiO₂_1073 K H₂, (d) Pt/SiO₂_1273 K H₂, (e) Pt foil, (f) P tCl₂.



Figure S11 XANES spectra at Pt L₂-edge of the catalysts and the reference samples: (a) Pt/SiO₂_773 K H₂, (b) Pt/SiO₂_1073 K H₂, (c) Pt/SiO₂_1273 K H₂, (d) Pt foil.

2 θ	d	Ι	(h k l)
39.67	2.27	100	(1 1 1)
46.28	1.96	86	(2 0 0)
67.31	1.39	86	(2 2 0)
81.51	1.18	100	(3 1 1)
85.95	1.13	57	(2 2 2)
103.63	0.98	28	(4 0 0)
117.72	0.9	71	(3 3 1)
122.17	0.88	71	(4 2 0)
148.68	0.8	57	(4 2 2)
180	0.75	43	(5 1 1)

Table S1 The lattice parameters of Pt.

2 θ	d	Ι	(h k l)
19.49	4.55	20	(1 1 1)
22.9	3.88	50	(0 0 2)
23.08	3.85	40	(200)
32.18	2.779	50	(2 0 2)
32.77	2.731	60	(2 2 0)
33.27	2.691	60	(-2 0 2)
38.12	2.359	60	(1 1 3)
38.39	2.343	50	(3 1 1)
38.63	2.329	80	(-1 3 1)
38.84	2.317	50	(-1 1 3)
39.78	2.264	100	(2 2 2)
40.8	2.21	80	(-2 2 2)
46.81	1.939	60	(0 0 4)
47.18	1.925	60	(4 0 0)
50.61	1.802	30	(3 1 3)
51.22	1.782	40	(3 3 1)
51.78	1.764	40	(-3 3 1)
52.29	1.748	40	(4 0 2)
52.75	1.734	50	(2 4 0)
53.08	1.724	5	(4 2 0)
53.61	1.708	5	(-2 0 4)
57.64	1.598	5	(2 2 4)
57.91	1.591	20	(2 4 2)
61.71	1.502	10	(1 1 5)
62.31	1.489	20	(5 1 1)
63.06	1.473	10	(-5 1 1)
67.36	1.389	5	(4 0 4)
68.37	1.371	5	(0 4 4)
68.71	1.365	40	(2 2 5)
69.88	1.345	20	(-4 0 4)

Table S2 The lattice parameters of Pt_3Si .

1. Catalyst Preparation

Silica (JRC-SIO-9, 334 m² g⁻¹) was used as support for the Pt/SiO₂ catalysts. Prior to impregnation, the SiO₂ support was calcined in air at 773 K for 3 h. Pt/SiO₂ was prepared by impregnating the SiO₂ support with an adequate volume of aqueous H₂PtCl₆•6H₂O (3wt% Pt), stirring at 353 K for 3 h, and then drying at 353 K for 20 h. The precipitate was noted as Pt/SiO₂ precursor. Prior to catalytic experiments, the catalyst precursor was *in situ* reduced in 20 vol% H₂ diluted with N₂ (total flow rate 50 ml min⁻¹) at temperatures ranged from 773K to 1273K. Finally, the catalyst was cooled to 773 K in N₂ (100 ml min⁻¹). The obtained catalysts were denoted as Pt/SiO₂_x K, where x indicates the reduction temperature.

2. Dehydrogenation of propane

Propane dehydrogenation was carried out by in a quartz reactor (i.d. 8 mm) at atmospheric pressure with 20 vol. % of propane diluted with N_2 at 773 K. Total flow rate was 100 ml min⁻¹. The catalyst precursor (50 mg) was placed between glass-wool. The composition of gas was analyzed with an on-line gas chromatographs (Shimadzu GC-8A, Japan) equipped with a TCD (5A Molecular Sives column) and methanizer FID (Porapak-Q column) detectors.

3. Characterization

All characterization was carried out on catalysts after *in situ* reduction in H_2 atmosphere. Brunauer—Emmett—Teller (BET) specific surface areas were estimated from N_2 isotherms obtained using a BELSORP 28SA (BEL Japan, Osaka, Japan) at 77 K. The analyzed samples were evacuated at 573 K for 3 h prior to the measurements.

The metal content of the catalysts was determined by X-ray fluorescence spectrometer (XRF). For this analysis, the catalyst pellet (~20 mg) was made and XRF measurements were performed on a X-ray diffractometer (Rigaku ZSX 100 e).

The amount of adsorbed CO on the catalysts at room temperature was determined by the CO pulse method with an Okura BP-2 instrument (Okura Riken, Japan) interfaced with a TCD.

X-ray diffraction (XRD) patterns were obtained using a MultiFlex DR powder X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu K α radiation (λ = 1.5405 Å).

Transmission electron microscope (TEM) images were obtained using a JEOL JEM-3200FS transmission electron microscope. The samples were prepared by depositing drops of ethanol suspensions containing small amounts of the powders onto a carbon-coated copper grid (Okenshoji Co. Ltd.), followed by evaporation of the ethanol in air.

X-ray absorption experiments were carried out at the BL01B1 at SPring-8 (Hyogo, Japan). The ring energy was 8 GeV, and the stored current was 99.5 mA. The Pt L_3 and L_2 -edge (11.56 and 13.27 keV) X-ray absorption spectra were recorded in air at room temperature using a Si(111) monochromator in transmission mode. The data processing was performed using the REX2000 Ver.2.5.9 (Rigaku) and FEFF8.40 programs.

X-ray photoelectron spectra (XPS) were acquired using an ULVAC PHI 5500MT. The spectra were measured using Mg K α radiation (15 kV, 400 W) in a chamber with the base pressure of ~ 10⁻⁷ Pa.

The temperature programmed oxidation (TPO) analysis of the coke deposited on the catalysts in the dehydrogenation of propane was conducted by combustion with air in a Okura BP-2 instrument (Okura Riken, Japan), coupled to a BELmass (BEL JAPAN, INC) for monitoring the signal corresponding to CO₂.

CO-Drifts experiments were performed on a FT/IR-600 JASCO spectrometer with a liquid N₂ cooled detector (MCT). The samples (~20 mg) will be firstly prepared with the reactor at high temperature in a gas flow at 50 mL min⁻¹ of a 20:80 mixture of H₂ in N₂ and then placed in a ceramic crucible in an in situ Drifts cell which allowed heating (up to 300 °C) under 5% H₂/Ar (50 mL min⁻¹) for 0.5 h. During the Drifts studies, the spectrum of

the sample at 323 K under flowing N₂ was taken as the background.

4. Calculation the number of unfilled d states (h_{Ts}) (ref. V. Ho, *et al. J. Am. Chem. Soc.*, 2011, 133, 11716-11724):

The number of unfilled d states (h_{Ts}) was calculated following these steps (J. Am. Chem. Soc. 2011, 133, 11716–11724): Briefly, in the first step, the fractional change in the total number of unfilled d-band states of the sample Pt/SiO₂ (reduced in H₂ at 773 K) compared to the reference platinum foil (f_d) was calculated using equation (1).

$$f_d = \frac{\sigma_3 \Delta A_3 + (1.11\sigma_2 \Delta A_2)}{\sigma_3 A_{3r} + (1.11\sigma_2 A_{2r})}$$
(1)

Here, A_{3r} and A_{2r} are the areas corresponding to electronic transitions to unfilled d-states in the XANES spectra for the reference Pt foil for L₃- and L₂- edges, respectively. A₃ and A₂ are the areas corresponding to electronic transitions to unfilled d-states in the XANES spectra between Pt/SiO₂ and the reference Pt foil for L₃- and L₂- edges, respectively. ΔA_3 and ΔA_2 were calculated by subtracting the reference platinum foil data from the catalyst data and then numerically integrating the resulting curves between -10 and +14 eV for L₃- and L₂ edges.

All the areas (ΔA_3 , ΔA_2 , A_{3r} , A_{2r}) were normalized by multiplying with the X-ray absorption cross section (σ) at the respective edge jump. Values of 117.1 and 54.2 cm² g⁻¹ were used for the σ at the Pt L₃- and L₂- edges, respectively.

Once the f_d value was evaluated, h_{Ts} was able to be calculated from equation (2), where h_{Tr} is the number of unfilled d states in the Pt foil reference sample, which is a known quantity equal to 1.60.

$$h_{Ts} = (1 + f_d) h_{Tr} \tag{2}$$