Electronic Supplementary Information

Strong metal-support interaction between Pt and SiO$_2$ following high-temperature reduction: a catalytic interface for propane dehydrogenation

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Fig. S1 XRD patterns of Pt/SiO$_2$ treated in H$_2$ (a) at 1073 K, N$_2$ (b) at 1073 K, O$_2$ (c) at 1073 K, (d) O$_2$ firstly at 773 K followed by H$_2$ 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 H$_2$. 
Figure S4  TPO spectra of fresh catalyst (a) and the calcination of coke deposited on spent Pt/SiO$_2$$_{1073}$ K H$_2$ catalyst after running the reaction for 3 h (b): (a) fresh Pt/SiO$_2$$_{1073}$K, (b) spent Pt/SiO$_2$$_{1073}$ K H$_2$. Reaction condition: the flow rate of air = 50 ml/min, heating rate=10 K / min.
Figure S5  TEM images of fresh Pt/SiO$_2$-1073 K and spent one after 7 h of reaction as well as their corresponding histograms.
Fig. S6 XRD patterns of Pt/SiO$_2$ precursor and the catalysts reduced at (a) 773 K, (b) 1073 K, (c) 1273 K. ▼: Pt metal.
Fig. S7  TEM images of Pt/SiO₂ reduced at (A) 773 K, (B) 1073 K, (C) 1273 K as well as their corresponding histograms.
Figure S8  HRTEM images of Pt/SiO$_2$ reduced at (A) 773 K, (B) 1073 K, (C) 1273 K.
Fig. S9 XPS profiles of Pt level for (a) Pt/SiO$_2$-773 K H$_2$, (b) Pt/SiO$_2$-1073 K H$_2$, (c) Pt/SiO$_2$-1273 K H$_2$. 
Figure S10 $k^3$-weighted EXAFS oscillation at Pt L₃-edge (A) and their Fourier transforms (B) of the catalysts and the reference samples (Pt foil and PtCl₂): (a) Pt/SiO₂ precursor, (b) Pt/SiO₂_773 K H₂, (c) Pt/SiO₂_1073 K H₂, (d) Pt/SiO₂_1273 K H₂, (e) Pt foil, (f) PtCl₂.
Figure S11 XANES spectra at Pt L$_2$-edge of the catalysts and the reference samples: (a) Pt/SiO$_2$$_773$ K H$_2$, (b) Pt/SiO$_2$$_{1073}$ K H$_2$, (c) Pt/SiO$_2$$_{1273}$ K H$_2$, (d) Pt foil.
Table S1 The lattice parameters of Pt.

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Table S2 The lattice parameters of Pt$_3$Si.

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1. Catalyst Preparation

Silica (JRC-SIO-9, 334 m$^2$ g$^{-1}$) was used as support for the Pt/SiO$_2$ catalysts. Prior to impregnation, the SiO$_2$ support was calcined in air at 773 K for 3 h. Pt/SiO$_2$ was prepared by impregnating the SiO$_2$ support with an adequate volume of aqueous H$_2$PtCl$_6$$\cdot$6H$_2$O (3 wt% Pt), stirring at 353 K for 3 h, and then drying at 353 K for 20 h. The precipitate was noted as Pt/SiO$_2$ precursor. Prior to catalytic experiments, the catalyst precursor was *in situ* reduced in 20 vol% H$_2$ diluted with N$_2$ (total flow rate 50 ml min$^{-1}$) at temperatures ranged from 773K to 1273K. Finally, the catalyst was cooled to 773 K in N$_2$ (100 ml min$^{-1}$). The obtained catalysts were denoted as Pt/SiO$_2$-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 Kα 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 L₃ and L₂-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 Kα 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 N\textsubscript{2} was taken as the background.

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

The number of unfilled d states (h\textsubscript{Tr}) 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/SiO\textsubscript{2} (reduced in H\textsubscript{2} at 773 K) compared to the reference platinum foil (f\textsubscript{d}) was calculated using equation (1).

\[
\frac{\sigma_3 \Delta A_3 + (1.11 \sigma_2 \Delta A_2)}{\sigma_3 A_{3r} + (1.11 \sigma_2 A_{2r})} \quad (1)
\]

Here, A\textsubscript{3r} and A\textsubscript{2r} are the areas corresponding to electronic transitions to unfilled d-states in the XANES spectra for the reference Pt foil for L\textsubscript{3}- and L\textsubscript{2}- edges, respectively. A\textsubscript{3} and A\textsubscript{2} are the areas corresponding to electronic transitions to unfilled d-states in the XANES spectra between Pt/SiO\textsubscript{2} and the reference Pt foil for L\textsubscript{3}- and L\textsubscript{2}- edges, respectively. \Delta A\textsubscript{3} and \Delta A\textsubscript{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 L\textsubscript{3}- and L\textsubscript{2} edges.

All the areas (\Delta A\textsubscript{3}, \Delta A\textsubscript{2}, A\textsubscript{3r}, A\textsubscript{2r}) were normalized by multiplying with the X-ray absorption cross section (\sigma) at the respective edge jump. Values of 117.1 and 54.2 cm\textsuperscript{2} g\textsuperscript{-1} were used for the \sigma at the Pt L\textsubscript{3}- and L\textsubscript{2}- edges, respectively.

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

\[
h_{Tr} = (1 + f_d) h_{Tr} \quad (2)
\]