

Electronic supplementary information

Propane dehydrogenation catalysis of group IIIB and IVB metal hydrides

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Preparation of PtSn and CrO_x catalysts

SiO₂-supported PtSn bimetallic catalyst was prepared by the pore-filling co-impregnation method using SiO₂ as the support (PtSn/SiO₂, Pt: 1 wt%, Pt:Sn = 1:1). Mixed aqueous solution of Pt(NH₃)₂(NO₂)₂ and SnCl₂ was added dropwise to ground dried SiO₂ (CARiACT G-6, Fuji Silysia) so that the solutions just filled the pores of the SiO₂. The mixture was kept in a sealed round-bottom flask overnight at room temperature, followed by quick freezing with liquid nitrogen, freeze-drying in vacuum at -5 °C. The resulting powder was further dried in an oven at 90 °C overnight, calcined in dry air at 400 °C for 1 h, and finally reduced by H₂ (50 mL/min) at 700 °C for 1 h.^{S1}

Al₂O₃-supported PtSn-K catalyst was prepared according to the previous report.^{S2} Al₂O₃ (SASOL, PURALOX SBa 200) was added into the mixed aqueous solution containing Pt(NH₃)₂(NO₂)₂, SnCl₂, and KNO₃. The water was removed by evaporation from the above mixture. The obtained solid was dried in an oven at 90 °C overnight, calcined in dry air at 750 °C for 2 h, and finally reduced by H₂ (50 mL/min) at 700 °C for 1 h.²

Al₂O₃ supported Cr-oxide catalysts (CrO_x/Al₂O₃, (Cr: 20 wt%)) was prepared according to the previous papers.^{S3} Al₂O₃ (purity: >99.99%, powder 2-3 μm, Kojundo Chemical Co.,Ltd.), was used as support material, and Cr(NO₃)₃·9H₂O (purity: >99.99%, powder, SIGMA-ALDRICH Co.,Ltd.) was used as a chromium source. Cr(NO₃)₃·9H₂O aqueous solution and Al₂O₃ were mixed by a magnetic stirrer at room temperature for 3 h. The mixture was evaporated at 50 °C to remove water. The resulting solid was dried in the oven at 100 °C for 1 h and then calcined for 6 h at 600 °C. After grinding in a mortar, the powder can be used in the experiment.

Characterization

XRD measurements were conducted using a Rigaku MiniFlex II/AP diffractometer with Cu Kα radiation (Rigaku Corporation, Japan). The samples were transferred to the chamber without exposure to air. The detail analysis was performed using indexing program TREOR97⁴ and least-squares refinement of lattice constant program PIRUM⁵. N₂ adsorption measurements were conducted by using an AUTOSOBB 6AG (Yuasa Ionics Co.). The samples used in this measurement were 0.2 g. For H₂ TPD and isotope experiments, the generated gases a mass spectrometer (BELMass, MicrotracBEL Corp.) was utilized to monitor m/z = 2 (H₂), 3 (HD), 4 (D₂), 42 (C₃H₆), 43 (C₃H₇⁺), 44 (C₃H₈), and 45 (C₃H₉⁺).

Figures

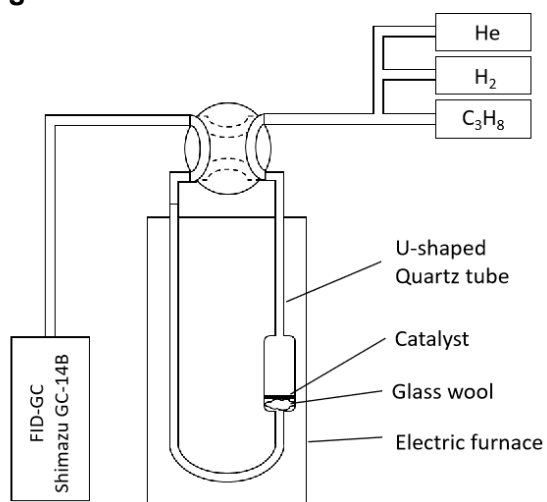


Fig. S1 Illustration of reactor systems for PDH reaction. Metal hydrides were loaded into a U-shaped quartz reactor connecting with 4-way valve in glove box, and then transfer to the reactor without exposure to air.

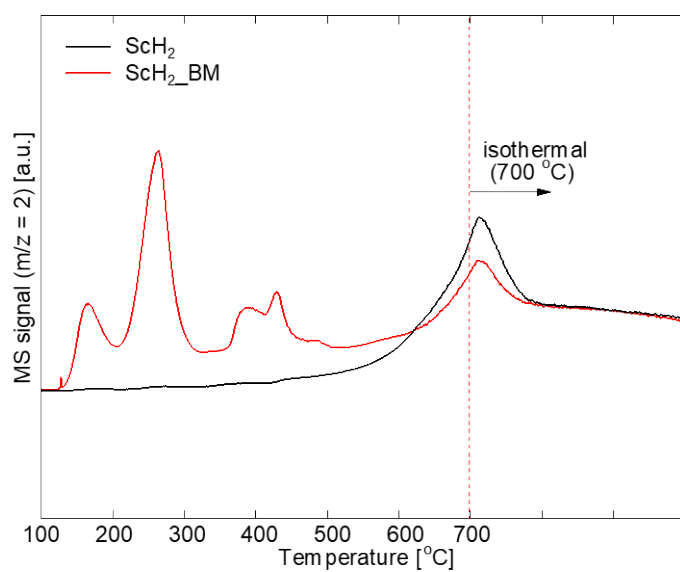


Fig. S2 H₂ TPD profile of the ScH₂ and ScH₂_BM under He flow (m/z = 2).

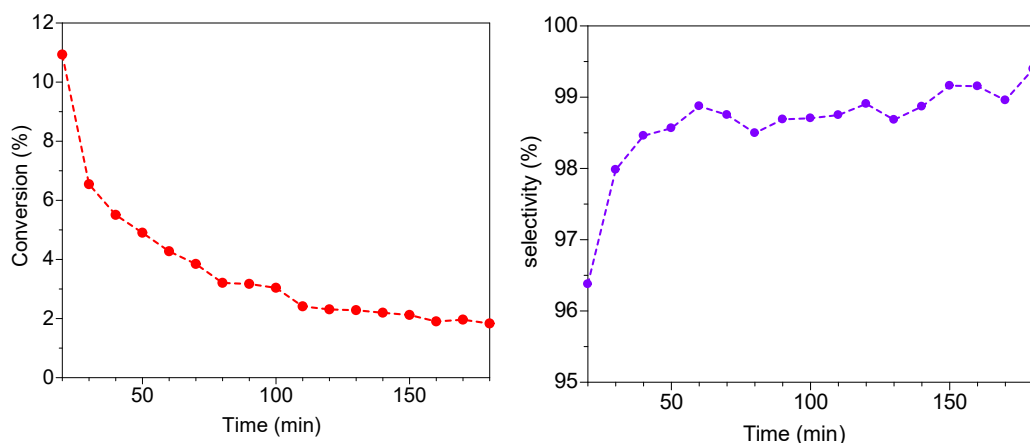


Fig. S3 Conversion and propylene selectivity of PDH reaction using $\text{LaH}_3\text{-BM}$ at 450 °C.

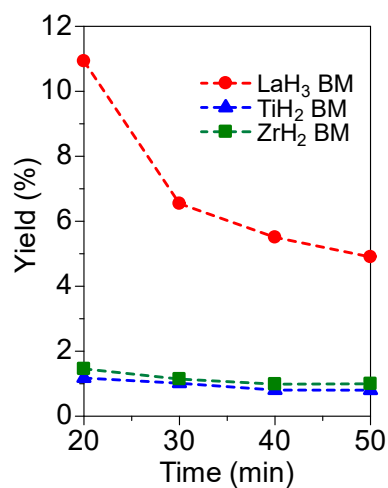


Fig. S4 Comparison of conversion values of PDH reaction using different ball-illed metal hydrides at 450 °C.

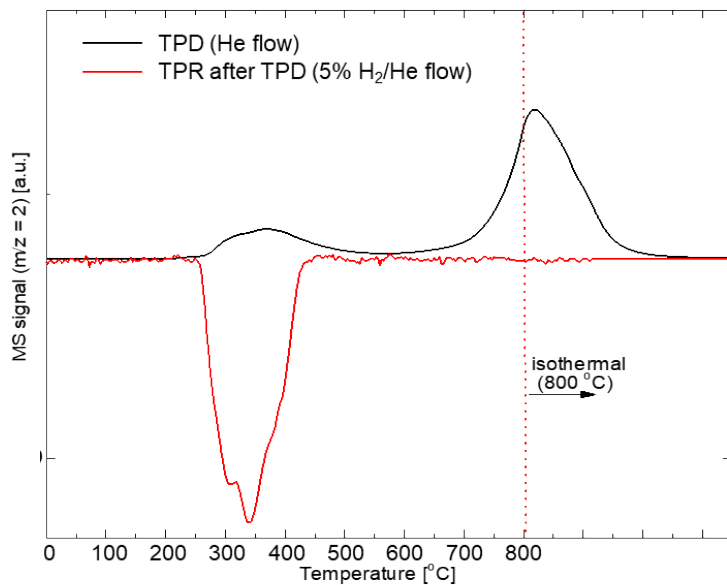


Fig. S5 H₂ TPD profile of LaH₃ under He flow and successive H₂ TPR profile under H₂/He flow (m/z = 2).

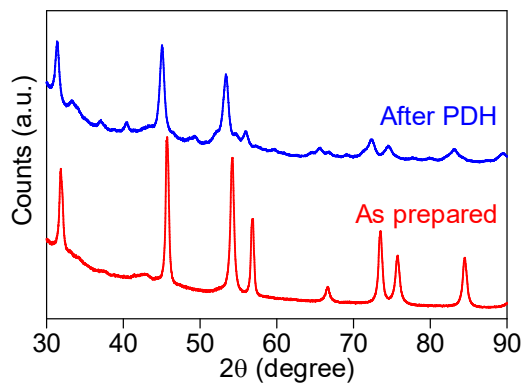


Fig. S6 XRD pattern of as-prepared LaH₃ and the LaH₃ after PDH reaction for 3 h. The sample was transfer to the XRD chamber without exposure to air.

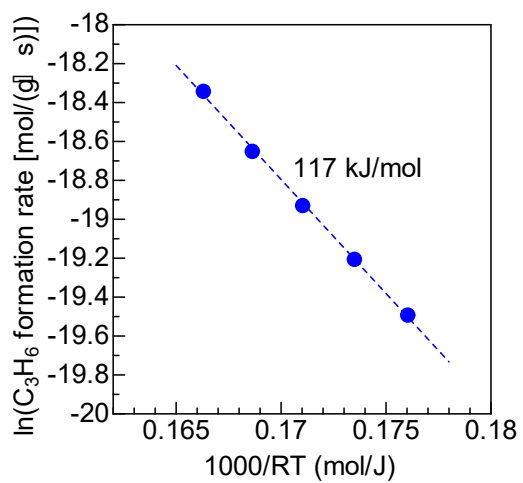


Fig. S7 Temperature dependence of propylene formation rate in PDH using K-PtSn/Al₂O₃.

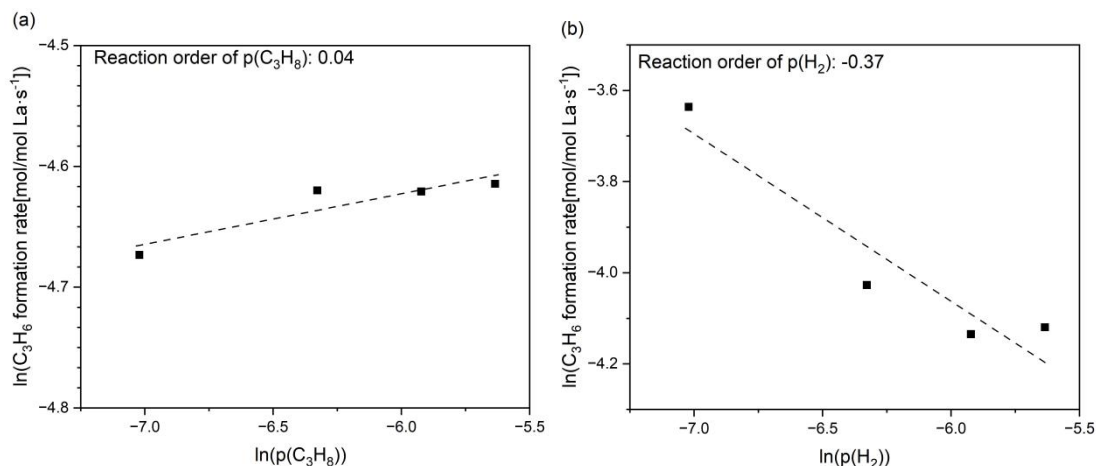


Fig. S8 Effects of the partial pressures of C₃H₈ and H₂ ($p(\text{C}_3\text{H}_8)$ and $p(\text{H}_2)$) on PDH using ZrH₂. (a) Effect of $p(\text{C}_3\text{H}_8)$ (C₃H₈ concentration: 2% – 8%, H₂ concentration: zero (without H₂ co-feeding)). (b) Effect of $p(\text{H}_2)$ (C₃H₈ concentration: 10% (fixed), H₂ concentration: 2%–8%). 100 mg of as-prepared ZrH₂ was utilized, and the total flow rate was fixed at 50 mL/min.

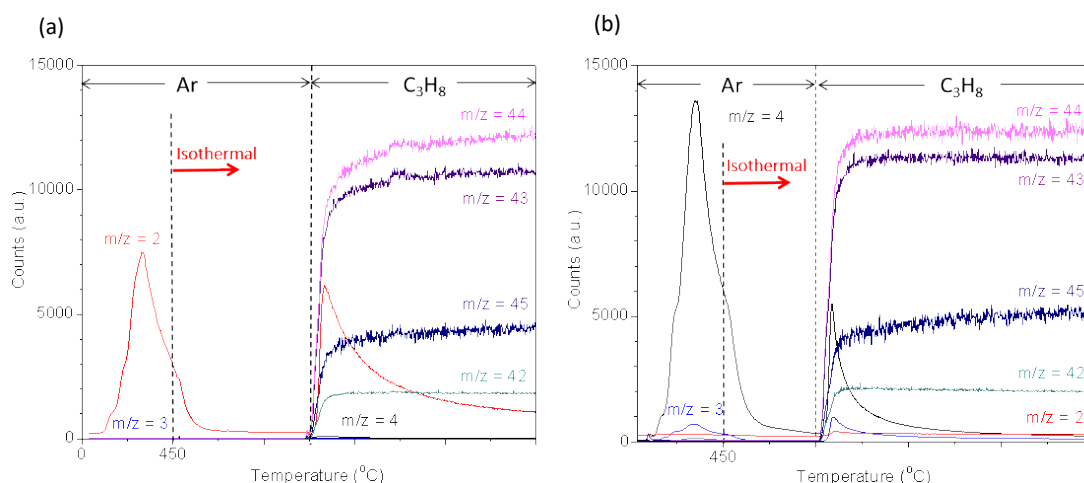


Fig. S9 The gas products in PDH using (a) LaH₃ and (b) LaD₃ including Ar pre-treatment. The temperature was isothermal after being increased from 30 to 450 °C. After the signals for H₂ or D₂ were stabilized, propane was introduced at a concentration of 10%. The total flow rate was 10 mL/min, and the carrier gas was Ar. The mass numbers of the gases shown are $m/z = 2$ (H₂), 3 (HD), 4 (D₂), 42 (C₃H₆), 43 (C₃H₇⁺), 44 (C₃H₈), and 45 (C₃H₉⁺).

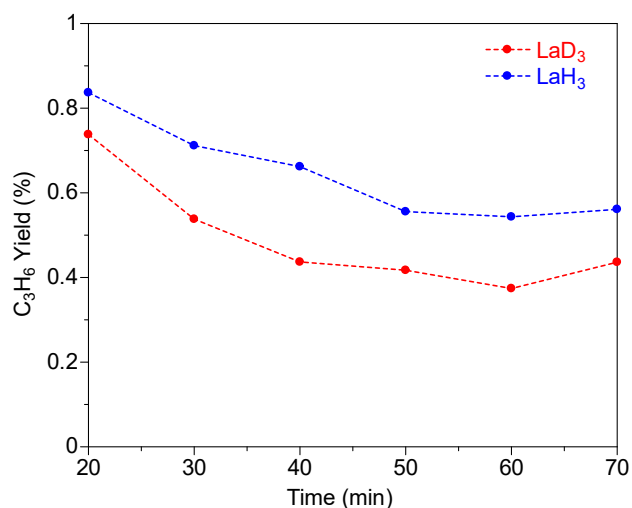


Fig. S10 C₃H₆ yield in PDH reaction (10 mL/min of 10% C₃H₈/Ar) of 450 °C using 100 mg of LaH₃ or LaD₃.

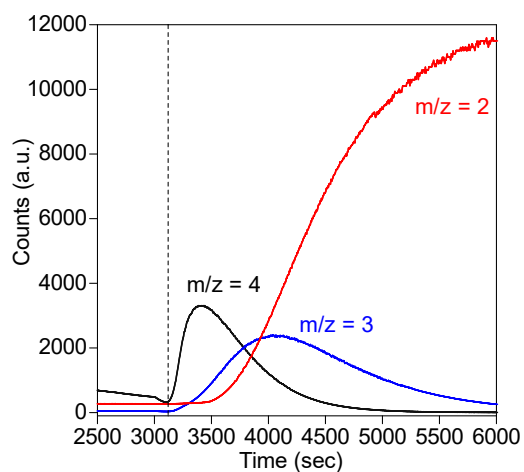


Fig. S11 The gas products in the reaction of LaD₃ with H₂. The temperature was isothermal after being increased from 30 to 450 °C. After the signals for D₂ were stabilized, H₂ was introduced at a concentration of 10%. The total flow rate was 10 mL/min, and the carrier gas was Ar. The mass numbers of the gases shown are m/z = 2 (H₂), 3 (HD), and 4 (D₂).

Calculation of normalized formation rate

The normalized formation rate was calculated using the following equation.

$$\text{Normalized formation rate} \left[\frac{\mu\text{mol}}{\text{h} \cdot \text{m}^2} \right] = \frac{\text{Propane molar flow rate} \left[\frac{\mu\text{mol}}{\text{min}} \right] \times 60 \left[\frac{\text{min}}{\text{h}} \right] \times \text{Propylene yield}}{\text{Catalyst amount} [\text{g}] \times \text{Specific surface area} [\text{m}^2/\text{g}]}$$

Table S1. Detail results of PDH reaction using LaH₃_BM.

Time (min)	Conversion (%)	Yield (%)	Selectivity (%)				Carbon balance
			CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₆	
0	15.4	0.7	94.7	0.3	0.2	4.8	0.60
10	3.0	2.9	1.7	0.4	0.9	97.0	0.98
20	2.7	2.6	1.0	0.0	0.9	98.1	0.98
30	2.5	2.5	0.8	0.0	0.8	98.4	0.98
40	2.4	2.4	0.7	0.0	0.9	98.4	0.98
50	2.3	2.3	0.0	0.0	0.0	100	0.98

Reaction conditions: 100 mg of LaH₃_BM(1h), 100 mL/min of 10% C₃H₈/Ar flow, 450 °C. The conversion, yield and selectivity values were determined by FID GC.

Table S2. Detail results of regeneration test in PDH reaction using LaH₃_BM. The used LaH₃_BM for PDH was treated with H₂ (100 mL/min of 10% H₂/Ar) at 300 °C to investigate the regeneration.

Time (min)	Conversion (%)	Yield (%)	Selectivity (%)				c.balance
			CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₆	
0	0.2	0.2	0.9	0.0	0.0	99.1	1.0
10	0.5	0.5	0.0	0.0	0.0	100	1.0
30	<0.1	<0.1	0.0	0.0	0.0	100	1.0
40	0.6	0.6	0.0	0.0	0.0	100	1.0
50	0.7	0.7	0.0	0.0	0.0	100	1.0

Reaction conditions: 100 mg of the H₂ treated LaH₃_BM(1h) after PDH, 100 mL/min of 10% C₃H₈/Ar flow, 450 °C. The conversion, yield and selectivity values were determined by FID GC.

References

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