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Electronic Supplementary Information

Dehydrogenative Coupling of Methane over Pt/Al_2O_3 Catalysts: Effect of Hydrogen Co-feeding

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Experimental Section

CH_4 conversion was calculated based on Eq. (S1).

$$CH_4 conversion\ /\ \% = \frac{r(converted\ CH_4)}{r(CH_{4\ in})} \times 100$$
$$= \frac{\begin{array}{c}(r(C_2H_6) \times 2 + r(C_2H_4) \times 2 + r(C_3H_8) \times 3 \\ + r(C_3H_6) \times 3 + r(C_6H_6) \times 6 + r(C_7H_8) \times 7 + r(coke))\end{array}}{CH_{4\ in}} \times 100 \cdots (S1)$$

The formation rate of coke was estimated based on Eq. (S2)

$$r(coke)/\mu mol\ min^{-1}\ g_{cat}^{-1} = \frac{\begin{array}{c}(r(H_2) - r(C_2H_6) - r(C_2H_4) \times 2 - r(C_3H_8) \times 2 \\ - r(C_3H_6) \times 3 - r(C_6H_6) \times 9 - r(C_7H_8) \times 10)\end{array}}{2} \cdots (S2)$$

The selectivity of the products was calculated on a carbon basis. For example, the equation for the selectivity of ethane is shown below.

$$Selectivity/\% = \frac{2 \times r(C_2H_6)}{\begin{array}{c}(r(C_2H_6) \times 2 + r(C_2H_4) \times 2 + r(C_3H_8) \times 3 \\ + r(C_3H_6) \times 3 + r(C_6H_6) \times 6 + r(C_7H_8) \times 7 + r(coke))\end{array}} \times 100 \cdots (S3)$$

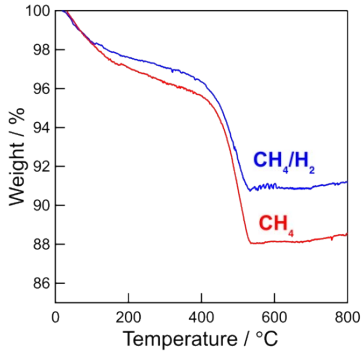

Fig. S1 TG profiles of spent Pt(1)/Al_2O_3 catalysts. T: 600 °C, flow rate: 20 (CH_4) and 20+1 (CH_4+H_2) mL min^{-1}, and catalyst mass: 0.10 g.

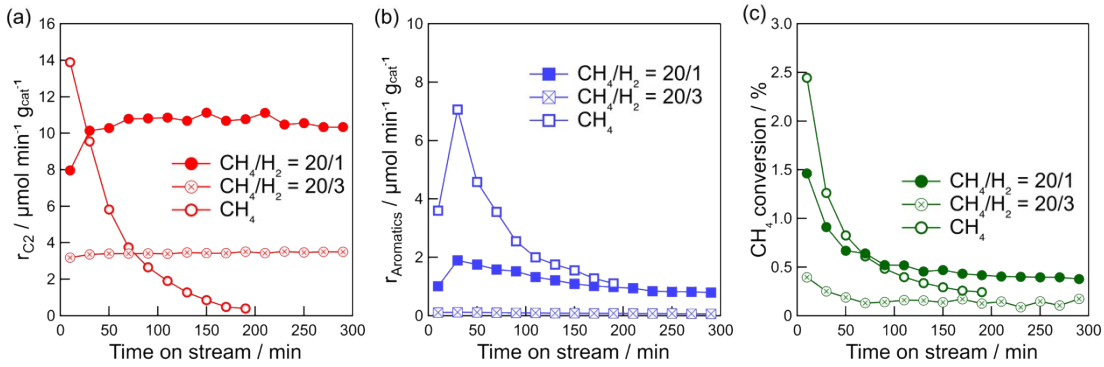

Fig. S2 Time course of formation rate of (a) C_2 hydrocarbons and (b) aromatics, and (c) methane conversion for DCM reaction. Catalyst: Pt(1)/Al_2O_3, T: 600 °C, flow rate: 20 (CH_4), 20+1 (CH_4+H_2), and 20+3 (CH_4+H_2) mL min^{-1}, and catalyst mass: 0.10 g.

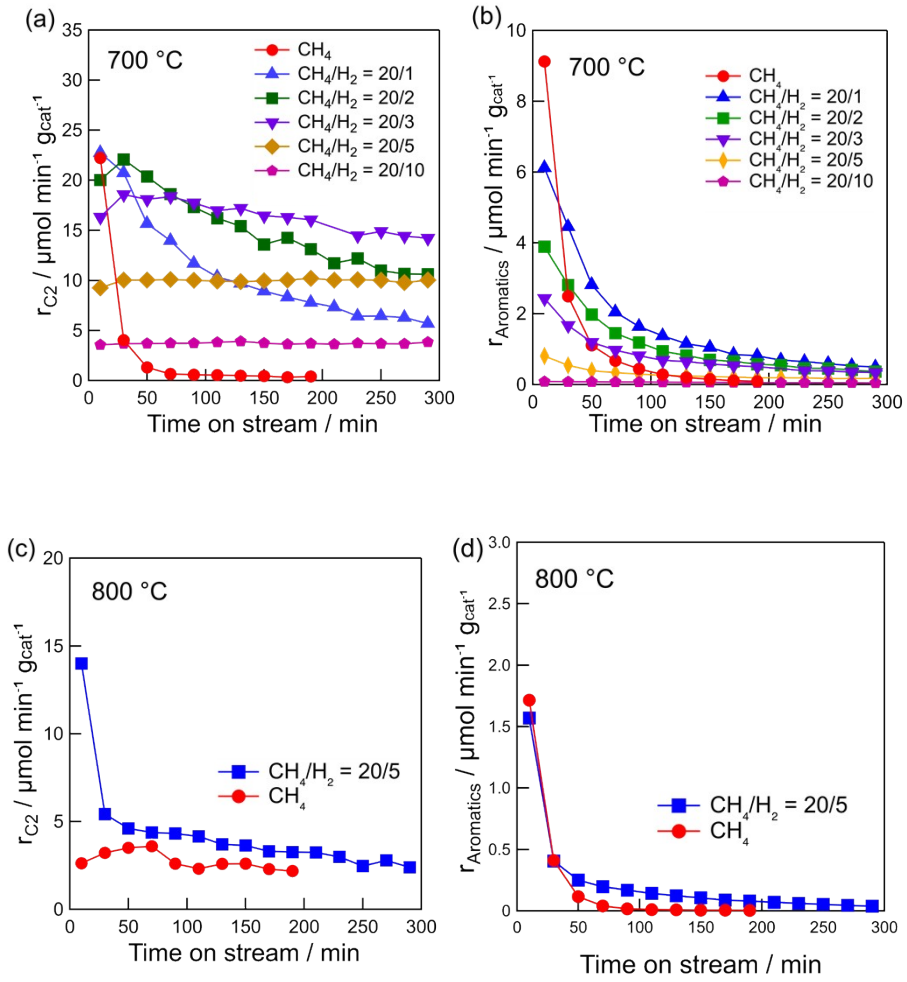

Fig. S3 Time course of formation rate of C2 hydrocarbons and aromatics for DCM reaction. Catalyst: Pt(1)/Al_2O_3, T: 700 (a, b) or 800 (c, d) °C, flow rate: 20 (CH_4) and 20+X (CH_4+H_2) mL min^{-1}, and catalyst mass: 0.10 g.

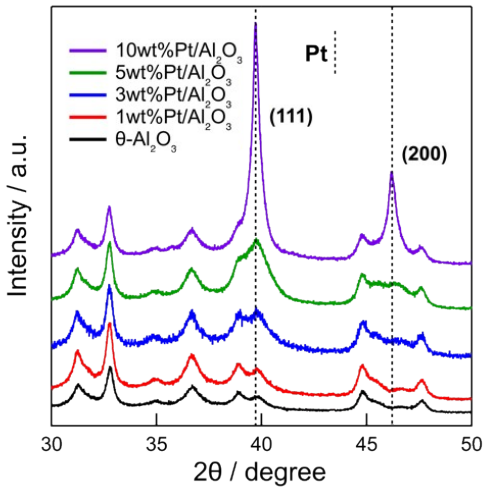

Fig. S4 XRD patterns of Pt(1, 3, 5, and 10)/Al_2O_3 and θ-Al_2O_3.

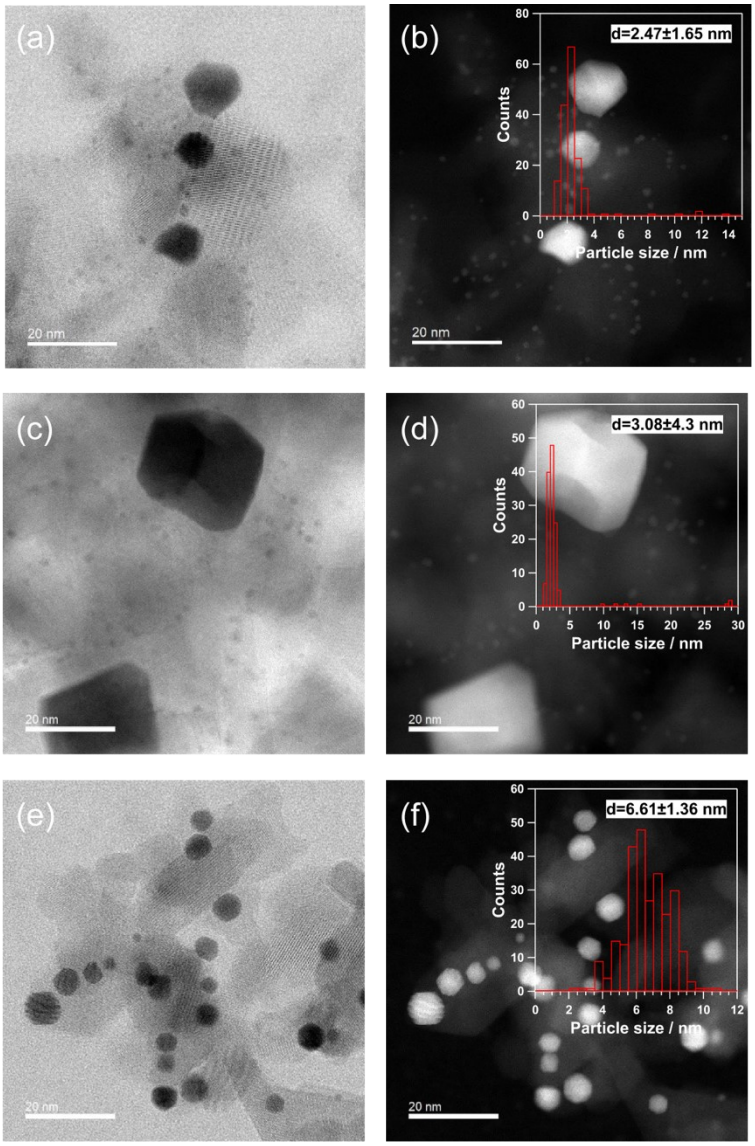

Fig. S5 BF- and HAADF-STEM images and particle size distribution of fresh (a, b) Pt(3)/Al_2O_3, (c, d) Pt(5)/Al_2O_3, and (e, f) Pt(10)/Al_2O_3.

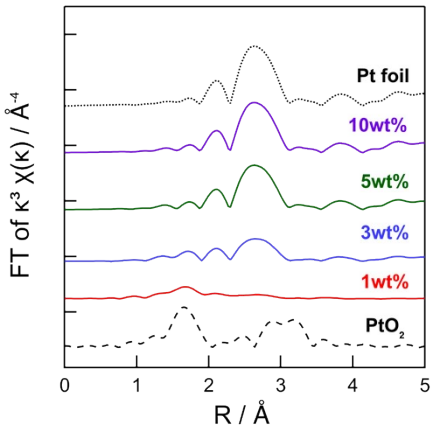

Fig. S6 Pt L_3-edge Fourier transforms (FT) of k^3-weighted EXAFS oscillations.

Table S1 EXAFS fitting results for Pt(X)/Al_2O_3 catalysts

sample	path	R / Å	CN	σ^2 / Å	ΔE_0 / eV	R-factor
1wt%Pt/Al_2O_3	Pt-Pt	2.73±0.01	4.22±0.83	0.012±0.001	10±2	0.0014
	Pt-O	2.00±0.01	2.69±0.35	0.007±0.001	13±2	
3wt%Pt/Al_2O_3	Pt-Pt	2.77±0.003	5.62±0.44	0.006±0.0003	10±1	0.0044
	Pt-O	2.02±0.02	1.42±0.38	0.005±0.002	13±3	
5wt%Pt/Al_2O_3	Pt-Pt	2.76±0.001	9.63±0.30	0.005±0.0001	8±0.4	0.0007
	Pt-O	2.01±0.05	0.19±0.15	-0.0005±0.004	13±12	
10wt%Pt/Al_2O_3	Pt-Pt	2.77±0.0009	10.22±0.25	0.005±0.0001	9±0.3	0.0007

The range in k was 3.0−14.0 $Å^{-1}$, and the fit range in distance r was 1.0−3.1 Å. Notation: R, scattering path length between the absorber and the scattering atom; CN, coordination number; σ^2, mean square relative displacement; ΔE_0, inner potential correction.

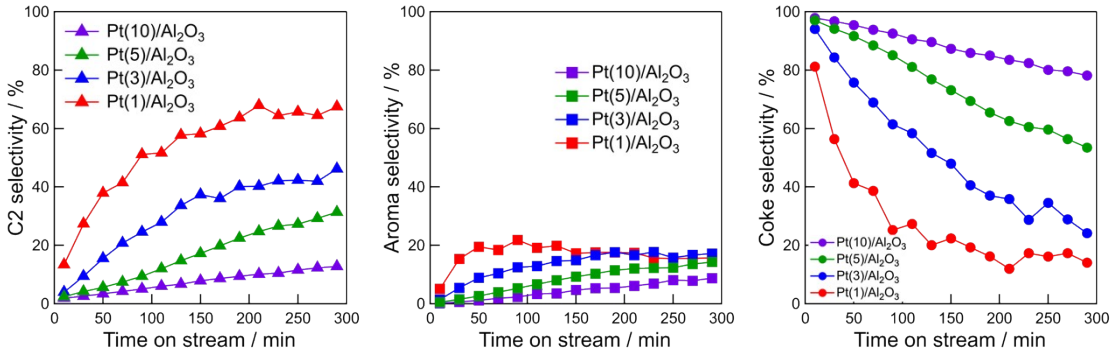

Fig. S7 Time course of selectivity of (a) C_2 hydrocarbons, (b) aromatics, and (c) coke for DCM reaction. Catalyst: Pt(1, 3, 5, and 10)/Al_2O_3, T: 600 °C, flow rate: 20+1 (CH_4+H_2) mL min^{-1}, and catalyst mass: 0.10 g.

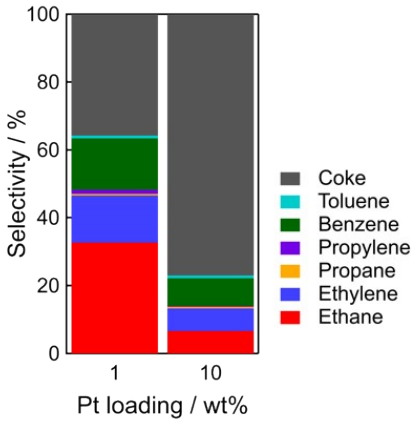

Fig. S8 Product selectivity for DCM reaction Catalyst: Pt(1 and 10)/Al_2O_3, T: 600 °C, flow rate: 20+1 (CH_4+H_2) mL min^{-1}, and catalyst mass: 0.10 g (for Pt(1)/Al_2O_3) and 0.694 g (for Pt(10)/Al_2O_3).

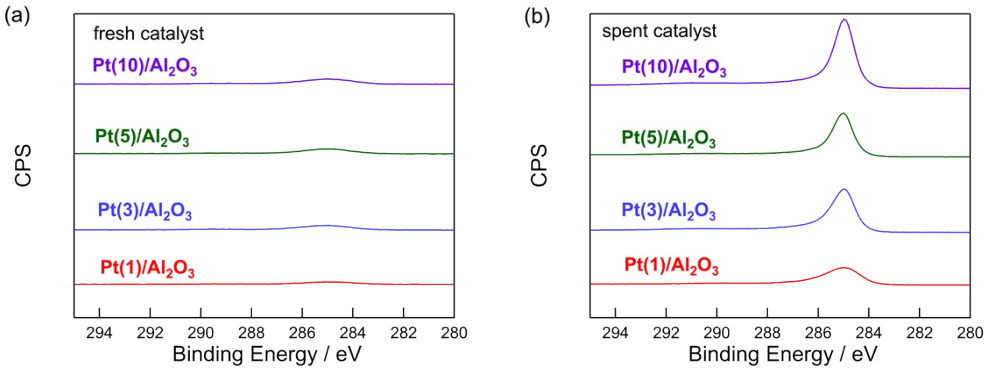

Fig. S9 C 1s XPS of (a) fresh and (b) spent Pt(1, 3, 5, and 10)/Al_2O_3 catalysts. DCM conditions: T = 600 °C, flow rate = 20+1 (CH_4+H_2) mL min^{-1}, and catalyst mass = 0.10 g.