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Electronic Supplementary Information

Adsorption and Dehydrogenation of C_2–C_6 *N*-alkanes over Pt catalyst: Theoretical Study on Size Effects of Alkane Molecule and Pt Substrate

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Table S1. Adsorption Energies (ΔE_{ads}, eV) and average C–H bond lengths (Å) of CH_4 on Pt(111) and Pt_{55}.

	Pt Substrates	ΔE_{ads}	d_{C-H}
CH_4(g)	-	-	1.098
CH_4	Pt(111)	–0.28	1.098
	Pt_{55}	–1.18	1.101

Table S2. ZPE-corrected reaction energies (ΔE_r, eV) and energy barriers (E_a, eV) for the dehydrogenation reactions of C_2–C_6 *n*-alkanes on Pt(111), Pt_{55}, and Pt_{38}.

Reactions	Pt(111)		Pt_{55}		Pt_{38}	
	ΔE_r	E_a	ΔE_r	E_a	ΔE_r	E_a
$C_2H_6 \rightarrow C_2H_5 + H$	–0.11	0.71	–0.50	0.46	–0.73	0.22
$C_2H_5 \rightarrow C_2H_4 + H$	–0.47	0.51	–0.67	0.38	–0.76	0.41
$C_3H_8 \rightarrow C_3H_7 + H$	0.06	0.72	–0.55	0.52	–0.70	0.29
$C_3H_7 \rightarrow C_3H_6 + H$	–0.23	0.63	–0.85	0.54	–0.78	0.46
$C_4H_{10} \rightarrow C_4H_9 + H$	–0.13	0.78	–0.51	0.46	–0.83	0.27
$C_4H_9 \rightarrow C_4H_8 + H$	–0.31	0.30	–0.85	0.54	–0.71	0.63
$C_5H_{12} \rightarrow C_5H_{11} + H$	–0.07	0.87	–0.33	0.51	–0.67	0.35
$C_5H_{11} \rightarrow C_5H_{10} + H$	–0.27	0.54	–0.79	0.54	–0.72	0.63
$C_6H_{14} \rightarrow C_6H_{13} + H$	–0.02	0.93	–0.37	0.31	–0.67	0.37
$C_6H_{13} \rightarrow C_6H_{12} + H$	–0.31	0.57	–1.10	0.37	–0.74	0.65

Table S3. Calculated reaction energies (ΔE_r, eV) and energy barriers (E_a, eV) for the dehydrogenation reactions of C_2–C_6 *n*-alkanes on Pt_{38}.

Reactions	Pt_{38}	
	ΔE_r	E_a
$C_2H_6 \rightarrow C_2H_5 + H$	–0.58	0.33
$C_2H_5 \rightarrow C_2H_4 + H$	–0.60	0.58
$C_3H_8 \rightarrow C_3H_7 + H$	–0.51	0.39
$C_3H_7 \rightarrow C_3H_6 + H$	–0.64	0.61
$C_4H_{10} \rightarrow C_4H_9 + H$	–0.60	0.39
$C_4H_9 \rightarrow C_4H_8 + H$	–0.57	0.78
$C_5H_{12} \rightarrow C_5H_{11} + H$	–0.49	0.45
$C_5H_{11} \rightarrow C_5H_{10} + H$	–0.56	0.80
$C_6H_{14} \rightarrow C_6H_{13} + H$	–0.49	0.47
$C_6H_{13} \rightarrow C_6H_{12} + H$	–0.55	0.83

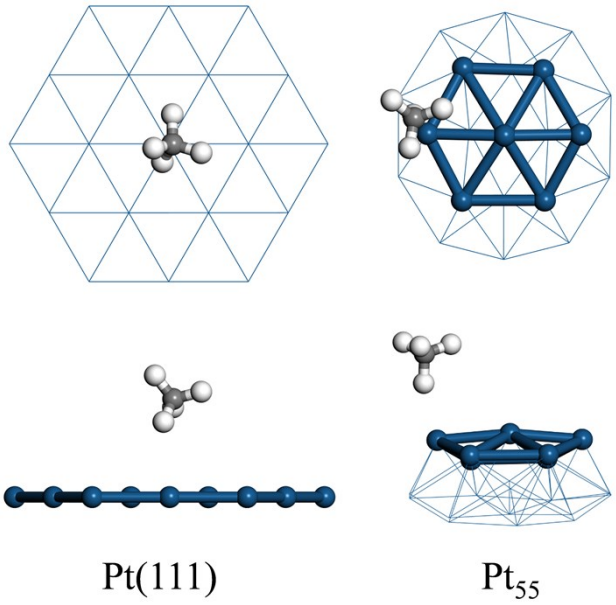

Figure S1. Adsorption configurations of CH_4 on Pt(111) and Pt_{55}.

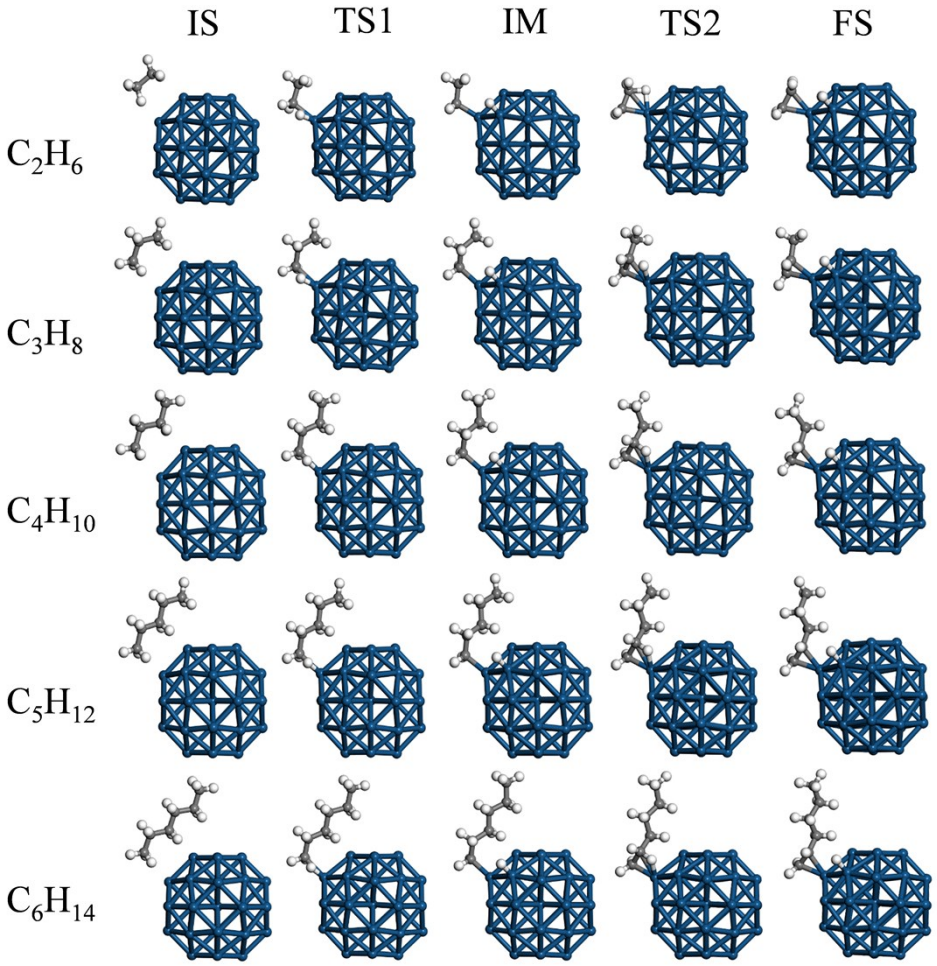

Figure S2. Dehydrogenation reactions of C_2–C_6 *n*-alkanes on Pt_{38}. IM denotes the alkyl groups generated from the first dehydrogenation step of alkanes, and the atomic H's co-adsorbed with the alkyls are omitted in the second dehydrogenation step for simplicity.

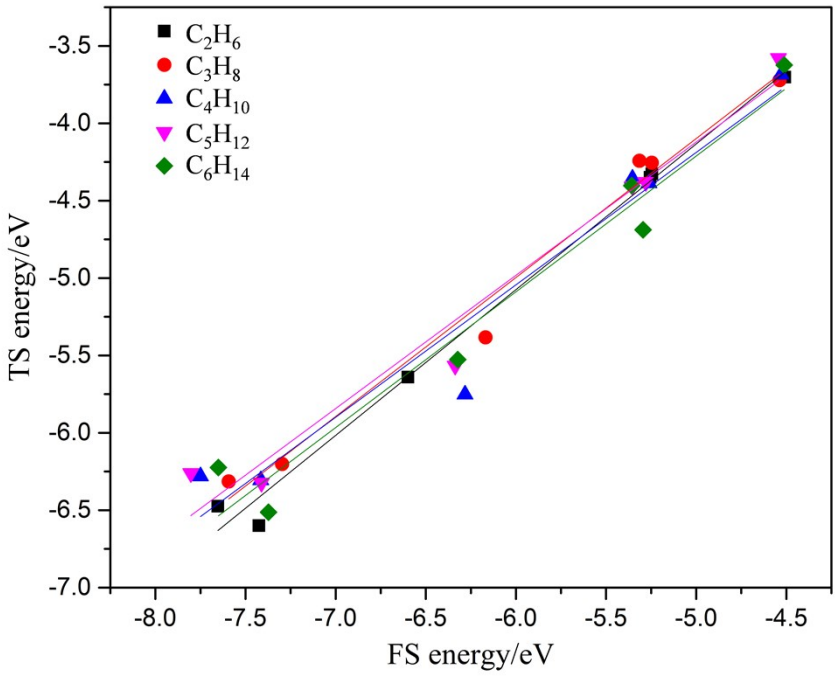

Figure S3. Linear fittings for the BEP relation based on the C–H bond-scission reactions of each alkane over Pt(111), Pt_{55}, and Pt_{38}. The fitted values of R2 are 0.99, 0.98, 0.98, 0.97, and 0.96 for C_2–C_6 *n*-alkanes, respectively.