Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Nanocavity effects of various zeolite frameworks on *n*-pentane cracking to light olefins: Combination studies of DFT calculations and experiments

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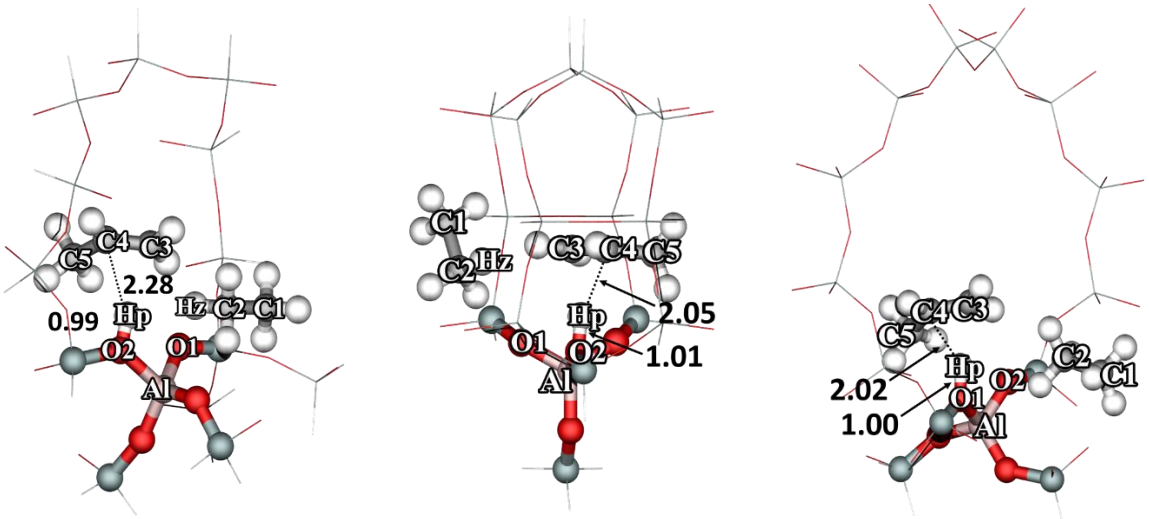
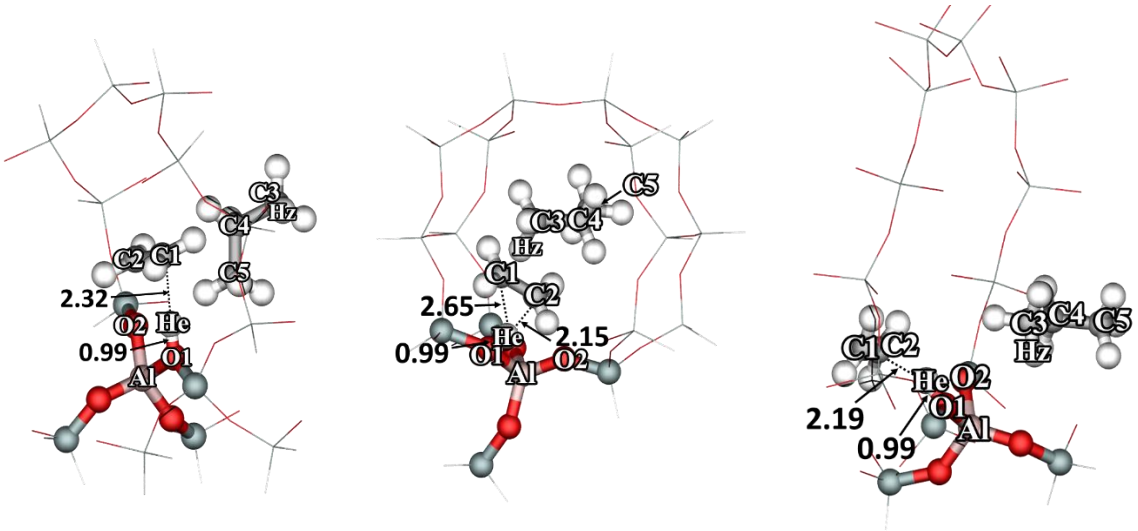


(a) (b) (c)

Figure S1. Optimized structures of the ethane-propylene products adsorbed on various zeolite frameworks: (a) H-ZSM-5 34T, (b) H-FER 37T, and (c) H-FAU 36T.



(a) (b) (c)

Figure S2. Optimized structures of the ethylene-propane products adsorbed on various zeolite frameworks: (a) H-ZSM-5 34T, (b) H-FER 37T, and (c) H-FAU 36T.

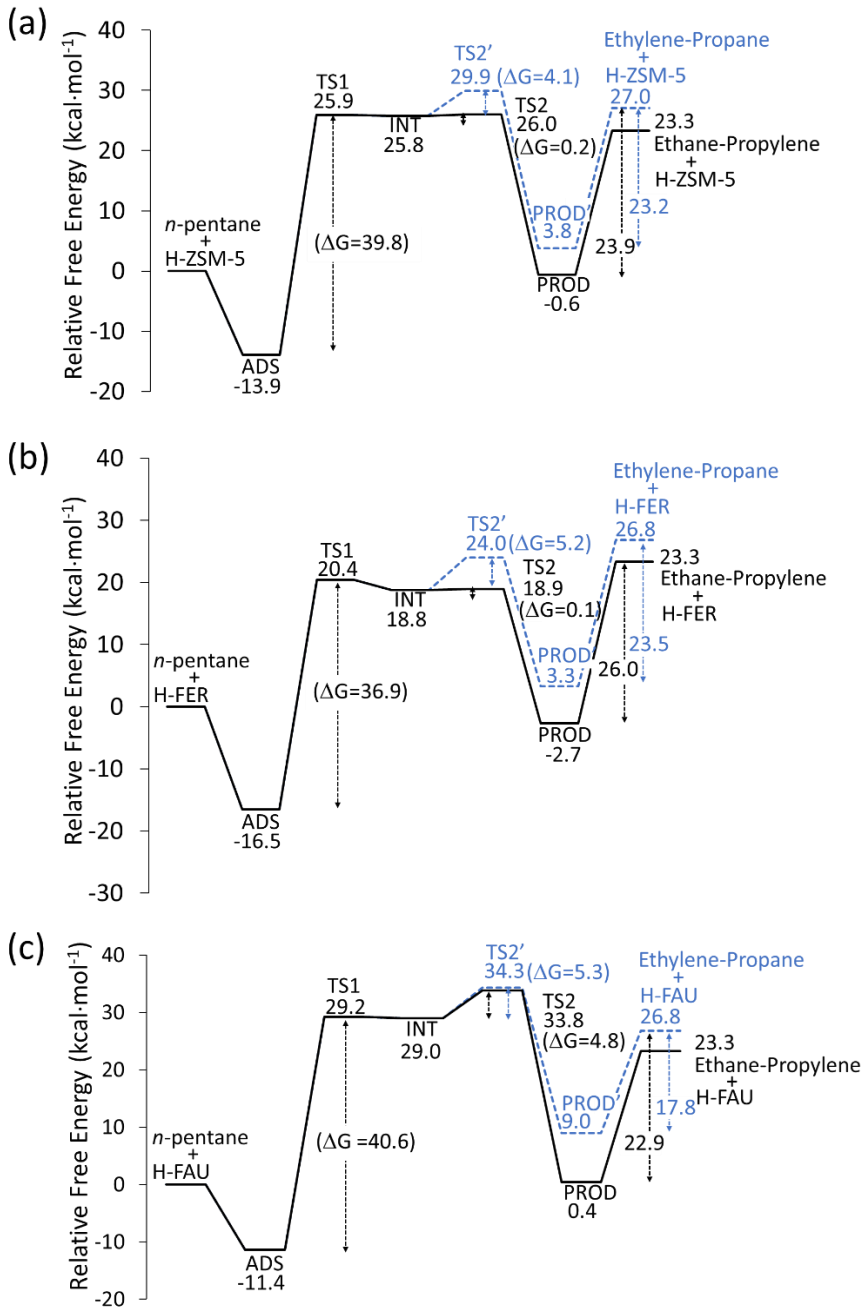


Figure S3. Schematic free energy profiles ($\Delta G_{298.15}$) of overall steps of *n*-pentane catalytic cracking via ethane-propylene and ethylene-propane production over various zeolite frameworks: (a) H-ZSM-5 34T, (b) H-FER 37T, and (c) H-FAU 36T (black line and blue dash line demonstrating the mechanisms through ethane-propylene pathway and ethylene-propane pathway, respectively).

Rates of reaction

$$k(T) = \frac{k_B T}{hc} e^{-\Delta G/RT} \qquad (1)$$

Where *k(T)* is reaction rate at temperature T, k_B is Boltzmann constant = 1.380662 × 10^{-23} J/K, *T* is temperature, *h* is Planck's constant = 6.626176 ×10^{-34} J·s, c is concentration (taken to be 1), ΔG is activation free energy and *R* is gas constant = 8.31441 J/(mol·K).

Table S1 Product selectivity of *n*-pentane catalytic cracking over various zeolites obtained at the reaction condition of: T = 823 K, WHSV = 5 h^{-1}, *n*-pentane feed = 0.025 mL.min^{-1}.

Zeolites	Product selectivity (wt.%)											
	C_1	C_2	C_3	C_4	Iso-C_5	C_6	$C_2^=$	$C_3^=$	$C_4^=$	BTX	$\frac{C_3^=}{C_2^=}$	$\frac{C_2 + C_3^=}{C_2^= + C_3}$
H-ZSM-5	5.2	17.0	17.9	3.3	2.8	2.3	17.8	30.1	2.9	0.7	1.7	1.3
H-FER	5.1	26.4	8.3	0.2	2.5	2.0	13.2	40.7	0.2	1.5	3.1	3.1
H-FAU	4.4	7.8	27.5	16.9	1.3	3.5	10.9	13.3	10.0	4.4	1.2	0.5

*C_1, C_2, C_3, C_4, C_5, C_6: Methane, ethane, propane, butane, pentane, and hexane.

$C_2^=$, $C_3^=$, $C_4^=$, BTX: Ethylene, propylene, butene, and benzene toluene and xylene.

Table S2 Optimized geometrical parameters of related compounds according to *n*-pentane cracking to light olefins over the H-ZSM-5.

Parameters	Isolated	ADS	TS1	INT1	TS2	PROD	TS2'	PROD'
Distances (Å)								
O1-Hz	0.97	0.97	1.70	2.21	3.32	3.78	3.68	5.52
Al-O1	1.82	1.82	1.73	1.71	1.69	1.68	1.72	1.81
Al-O2	1.68	1.68	1.70	1.71	1.75	1.82	1.69	1.68
Hz-C2	-	2.88	1.38	1.25	1.09	1.10	3.90	4.86
Hz-C3	-	2.62	1.29	1.24	3.21	3.31	1.09	1.10
C2-C3	1.53	1.53	1.74	1.98	3.91	4.19	4.99	4.59
C1-C2	1.53	1.53	1.52	1.50	1.52	1.52	1.39	1.33
C3-C4	1.53	1.53	1.52	1.51	1.35	1.34	1.52	1.52
O2-Hp	-	-	-	-	1.28	0.99	-	-
Hp-C4	-	-	-	-	1.30	2.28	-	-
O1-He	-	-	-	-	-	-	1.50	0.99
He-C1	-	-	-	-	-	-	1.24	2.32
Angle (°)								
O1-Al-O2	90.3	90.5	94.0	95.2	95.4	91.0	94.7	92.2
C2-Hz-C3	-	-	81.2	104.8	-	-	-	-

Table S3 Optimized geometrical parameters of related compounds according to *n*-pentane catalytic cracking to light olefins over H-FER.

Parameters	Isolated	ADS	TS1	INT1	TS2	PROD	TS2'	PROD'
Distances (Å)								
O1-Hz	0.98	0.98	1.68	2.18	5.61	2.69	6.45	3.43
Al-O1	1.88	1.87	1.76	1.73	1.70	1.69	1.76	1.86
Al-O2	1.67	1.67	1.70	1.71	1.78	1.82	1.70	1.67
Hz-C2	-	3.40	1.34	1.25	1.09	1.10	4.10	3.78
Hz-C3	-	2.62	1.39	1.25	3.66	3.20	1.10	1.09
C2-C3	1.53	1.53	1.71	1.93	4.38	3.62	4.35	3.62
C1-C2	1.53	1.53	1.52	1.51	1.53	1.53	1.38	1.33
C3-C4	1.53	1.53	1.53	1.51	1.35	1.34	1.53	1.53
O2-Hp	-	-	-	-	1.17	2.05	-	-
Hp-C4	-	-	-	-	1.47	1.01	-	-
O1-He	-	-	-	-	-	-	1.52	0.99
He-C1	-	-	-	-	-	-	1.25	2.65
Angle (°)								
O1-Al-O2	91.6	92.1	96.2	98.6	97.4	98.5	97.3	92.7
C2-Hz-C3	-	-	77.5	100.7	-	-	-	-

Table S4 Optimized geometrical parameters of related compounds according to *n*-pentane catalytic cracking to light olefins over H-FAU.

Parameters	Isolated	ADS	TS1	INT1	TS2	PROD	TS2’	PROD’
Distances (Å)								
O1-Hz	0.97	0.98	2.34	2.26	4.02	2.67	5.61	3.29
Al-O1	1.92	1.91	1.77	1.76	1.75	1.88	1.84	1.72
Al-O2	1.71	1.70	1.76	1.76	1.79	1.71	1.74	1.88
Hz-C2	-	2.40	1.24	1.25	1.10	1.10	4.25	5.09
Hz-C3	-	3.11	1.25	1.25	2.91	3.51	1.10	1.10
C2-C3	1.53	1.53	2.00	2.01	3.82	3.61	3.94	4.88
C1-C2	1.53	1.53	1.50	1.50	1.52	1.52	1.44	1.33
C3-C4	1.53	1.53	1.52	1.52	1.42	1.34	1.52	1.52
O1-Hp	-	-	-	-	1.79	1.00	-	-
Hp-C4	-	-	-	-	1.13	2.02	-	-
O2-He	-	-	-	-	-	-	1.53	0.99
He-C1	-	-	-	-	-	-	1.13	2.19
Angle (°)								
O1-Al-O2	98.6	99.2	101.0	101.2	101.0			
C2-Hz-C3	-	-	106.4	107.1	-	-	-	-