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Supplementary Information

Mechanistic Kinetic Modeling for Catalytic Conversion of DME to Gasoline-range Hydrocarbons over Nanostructured ZSM-5

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Table S1. Experimental conditions for DTH reaction on the nano-structured ZSM-5

Run	T [K]	P_{total} [bar]	GHSV [L/(kg_{cat}·h]	DME/N_2 [Molar ratio%]
1	573	1	4400	5/95
2	553	1	4400	5/95
3	533	1	4400	5/95
4	523	1	4400	5/95
5	513	1	4400	5/95
6	573	3	4400	5/95
7	553	3	4400	5/95
8	533	3	4400	5/95
9	523	3	4400	5/95
10	513	3	4400	5/95
11	573	5	4400	5/95
12	553	5	4400	5/95
13	533	5	4400	5/95
14	523	5	4400	5/95
15	513	5	4400	5/95
16	533	1	2200	5/95
17	533	1	8800	5/95
18	533	1	10000	5/95

Table S2. Textural and surface properties of nano-structured ZSM-5 zeolite

XRF[a]	N_2 sorption[b]			XRD[c]	NH_3-TPD[d]			Py-IR[e]	dTBPy-IR[f]
Si/Al	S_g	P_V	P_D	d_P	S_W	S_S	S_T	B/L	AF
72	373	0.27	3.9	35	0.19	0.27	0.46	22.1	0.05

[a] Si/Al molar ratio on the fresh nano-structured ZSM-5 was determined by XRF analysis.

[b] S_g (sirface area, m^2/g), P_V (pore volume, cm^3/g) and P_D (averge pore diameter, nm) were determiced by N_2-sorption analysis with the help of BET equation.

[c] Average crystallite size of ZSM-5 were measured by Scherrer equation from the most intense XRD peak at $2\theta = 7 – 9^o$.

[d] Quantities of weak (S_W, mmol/g) and strong (S_S, mmol/g) acid sites as well as total acid sites (S_T, mmol/g) were determined by the integrated areas of NH_3-TPD peaks located at 393 − 523 and 523 − 823 K, respectively.

[e] Quantities of Brønsted (B) and Lewis (L) acid sites and ratio of B/L were calculated from the Py-IR spectra obtained at a desorption temperature of 523 K.

[f] Accessibility factor (AF) correpsonding to the percentage of outer surface acidic sites (external acidic sites) were calculated by the adsorption sites for 2,6-di-tert-butylpyridine (dTBPy) divided by total amount of acid sites measured by Py-IR analysis.

Table S3. Detailed products distributions and DME conversions at 18 different reaction conditions such as temperatures, space velocities, and pressures

T [K]	SV [L/kg$_{cat}$/h]	P [bar]	DME Conv. (mol%)	Mole fractions of effluent gases (%)[a]																		
				C1	C2	C3	C4	C5	MTBE	C6	Benzene	C7	Toluene	C8	Ethyl benzene	m,p-X	o-X	C9	EMB	TMB	etc	Carbon balance(%)
573	4400	1	100.0	0.1	3.3	18.7	14.7	12.3	2.9	12.9	0.9	8.5	1.0	4.4	0.2	2.7	1.0	3.0	6.6	1.1	5.7	102.4
553	4400	1	100.0	0.1	4.5	14.7	11.9	11.1	2.8	14.3	0.6	11.0	0.5	7.3	0.1	2.5	1.2	2.7	6.9	0.9	7.1	100.6
533	4400	1	57.8	0.1	5.4	29.9	10.5	6.1	1.3	10.3	0.5	9.6	0.3	6.8	0.0	2.1	0.9	2.2	6.5	1.1	6.2	102.2
523	4400	1	44.6	0.3	7.1	31.4	10.0	5.9	0.7	9.1	0.2	9.2	1.6	3.7	0.0	1.7	1.2	0.8	7.2	1.0	9.0	101.1
513	4400	1	28.8	0.3	5.8	36.1	11.8	5.0	0.8	8.0	0.3	8.5	1.7	3.3	0.1	1.6	1.1	0.8	6.4	0.9	7.4	98.2
573	4400	3	100.0	0.2	1.9	17.1	8.3	14.4	1.2	14.3	1.0	8.7	1.1	4.3	0.2	3.0	1.1	3.1	7.8	1.1	11.3	97.8
553	4400	3	100.0	0.3	3.7	12.1	6.9	12.6	1.3	15.8	0.6	11.9	0.5	6.8	0.1	2.3	1.2	2.7	7.5	0.9	12.8	102.2
533	4400	3	62.0	0.4	8.5	22.2	6.1	7.5	0.5	10.9	0.3	9.9	0.3	6.7	0.0	2.1	1.0	2.2	8.5	1.0	12.0	104.1
523	4400	3	46.0	0.6	9.2	27.0	7.9	6.7	0.2	8.8	0.2	8.3	1.5	3.5	0.0	1.7	1.2	1.0	8.2	1.3	12.8	100.9
513	4400	3	20.0	0.6	6.3	38.8	11.3	3.7	0.4	4.7	0.5	5.4	0.2	4.3	0.0	1.6	0.7	2.1	6.9	1.0	11.1	102.4
573	4400	5	100.0	0.2	1.2	16.9	7.4	14.8	0.8	14.9	0.9	9.4	1.5	4.3	0.3	3.2	1.2	3.5	7.1	1.4	11.0	97.7
553	4400	5	100.0	0.3	3.0	12.2	6.2	13.5	1.0	16.2	0.6	12.1	0.6	6.9	0.1	2.3	1.0	2.8	7.4	0.9	13.0	100.7
533	4400	5	64.5	0.4	8.1	19.2	6.0	7.2	0.4	9.7	0.4	8.8	0.3	6.0	0.0	2.0	1.0	2.4	8.7	1.2	18.1	105.1
523	4400	5	52.9	0.6	9.6	25.7	7.5	7.2	0.3	9.0	0.2	8.4	1.5	3.5	0.0	1.7	1.1	1.0	8.2	1.3	13.2	103.1
513	4400	5	20.9	0.7	6.4	35.8	10.9	3.7	0.5	4.2	0.4	4.5	0.2	3.5	0.0	1.5	0.6	1.7	7.1	1.1	17.2	99.2
533	2200	1	92.9	0.2	5.6	14.1	8.4	9.4	1.5	14.4	0.5	12.0	0.4	7.5	2.3	0.3	1.1	2.6	7.4	1.1	11.2	98.5
533	8800	1	38.6	0.2	4.1	36.1	14.3	5.3	1.6	8.4	0.6	8.1	0.2	5.3	1.4	0.3	0.5	2.4	4.4	1.2	5.6	101.2
533	10000	1	33.5	0.2	4.1	41.4	14.0	4.1	1.5	7.6	0.6	7.5	0.2	5.4	0.0	2.0	0.4	1.6	4.8	0.8	4.0	98.8

[a]Products distributions were verified by using the gaseous effluent chemicals at the reaction conditions of T = 573–513 K, P = 1–5 bar and GHSV = 4400–10000 L/(kg$_{cat}$·h) with DME/N_2 = 5/95 (mol%), and the abbreviations of m,p,o-X, EMB and TMB stand for m,p,o-Xylene, ethylmethylbenzene and tetramethylbenzene, respectively.

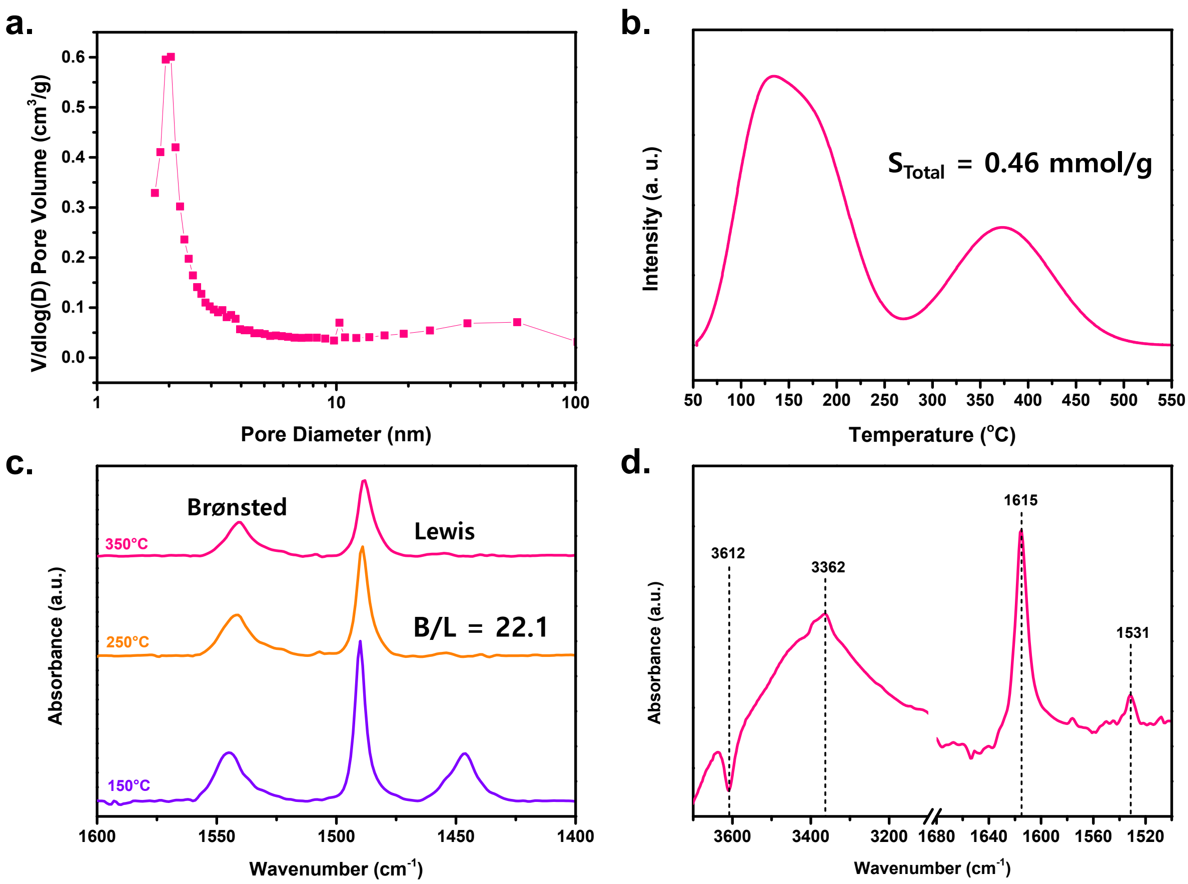

Figure S1. Bulk and surface properties of the fresh nano-structured ZSM-5; **(a)** Pore size distribution measured by N_2 adsorption-desorption analysis, **(b)** NH_3 TPD patterns, **(c)** Characteristic Py-IR spectra at three different desorption temperatures of 423, 523, 623 K and **(d)** characteristic DTBPy-IR spectra.

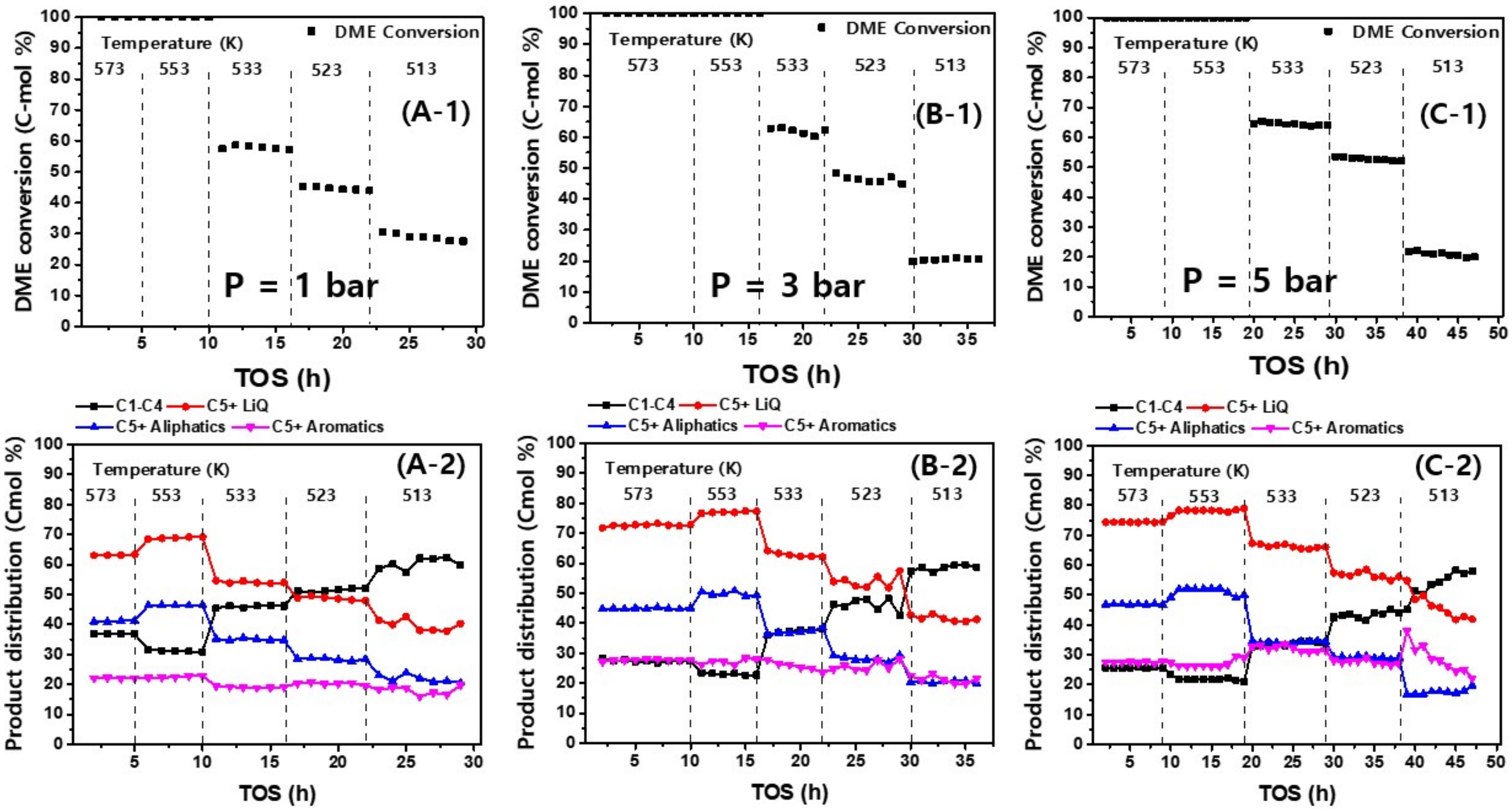

Figure S2. Representative reaction results of (1) DME conversion and (2) product distributions of gaseous and liquid products at different temperatures and pressures such as (A) 1 bar, (B) 3 bar, and (C) 5 bar.

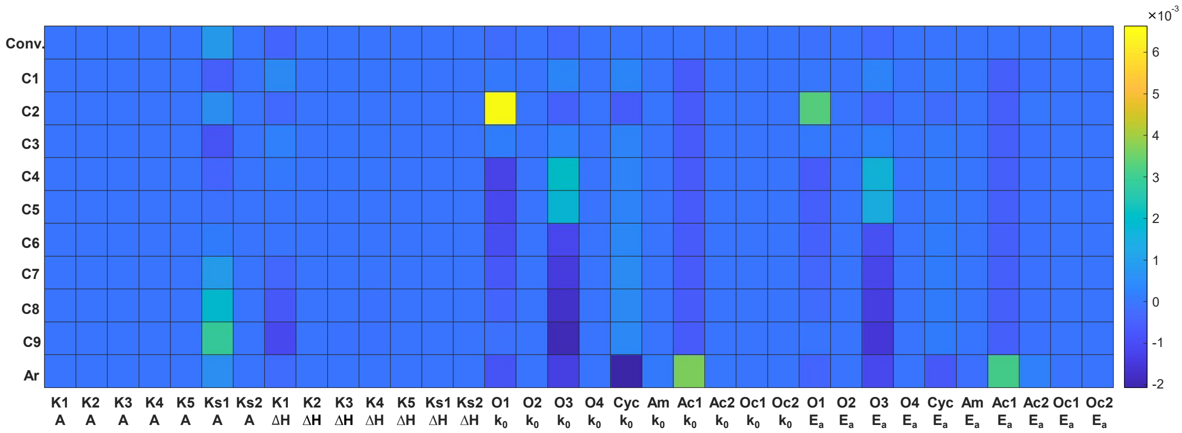

Figure S3. Sensitivity analysis of the conversion and product selectivities to the estimated parameters of the model.