

Supplementary Material

Effects of ZSM-5 morphology and Fe promoter for dimethyl ether conversion to gasoline-range hydrocarbons

Mansoor Ali, Jong Jin Kim, Faisal Zafar, Dong Ming Shen, Xu Wang, Jong Wook Bae*

Figure S1. Schematic diagram of catalytic activity measurement system.

Figure S2. (A) Original chromatograph peaks of the measurable products and (B) temperature program for GC analysis.

Figure. S3. PXRD patterns: (A) PXRD patterns of fresh ZSM-5 in the range of (1) $2\theta = 7 - 10^\circ$ and (2) $2\theta = 22.5 - 25.0^\circ$, (B) pore size distribution of fresh ZSM-5, and (C) pore size distribution of fresh Fe/N-ZSM-5.

Figure. S4. FT-IR spectra of the adsorbed pyridine (Py-IR) at two different desorption temperatures of (A) 150°C and (2) 250°C on fresh ZSM-5.

Figure S5. Proposed reaction pathways for DTG over HZSM-5 catalyst, where the labels over arrows represents each reaction step [S1].

Table S1. Catalytic activity for DME conversion to gasoline-range hydrocarbons (mol%) on ZSM-5 catalysts with their different morphologies.

Table S2. Catalytic activity for DME conversion to gasoline-range hydrocarbons (mol%) on Fe/N-ZSM-5 catalysts.

Catalyst preparations

The preparation of nano-structured ZSM-5 (N-ZSM-5) and hierarchically structured nano-ZSM-5 (H-ZSM-5) was carried out by using a silicalite-1 seed suspension. The silicalite-1 seed suspension was prepared by mixing tetraethyl orthosilicate (TEOS, corresponding to 0.2 mol SiO_2), 71.72 mmol of tetrapropyl ammonium hydroxide (TPAOH, 40 wt% in water), and 14.58 ml of water in a Teflon-lined stainless steel autoclave reactor, and kept stirring for 24 h at room temperature, followed by heating at 80 °C for 72 h. Then, the obtained suspension was utilized without any further treatment. For the further preparation of these two different ZSM-5 zeolites, 1.2 mmol of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ was dissolved in 80 ml of deionized water (DIW), followed by adding 0.75 mol of ammonium hydroxide (25 - 28 wt%). The mixture was stirred for several minutes before adding 0.2 mol SiO_2 of deionized colloidal silica (Ludox TMA) and 30 mmol SiO_2 of the silicalite-1 seed suspension. For the synthesis of N-ZSM-5, the solution was prepared for a hydrothermal treatment.

For the separate synthesis of H-ZSM-5, the mixture was mixed with 4.2 mmol of cetyltrimethylammonium bromide (CTAB) and 12 ml of ethanol after the addition of the seed suspension. Then, the solution was stirred for 1 h at room temperature and then transferred into a Teflon-lined stainless steel autoclave reactor for further crystallization. N-ZSM-5 was heated at 175 °C for 24 h, and H-ZSM-5 was treated at 150 °C for 60 h. Subsequently, the white-colored solid powders were collected with additional water, separated by centrifuge at 9000 rpm for 10 min, and washed with DIW until the pH approached 7. Then, the obtained powders were dried overnight at 110 °C and calcined at 550 °C for 7 h at a ramp rate of 2 °C/min to obtain H-form ZSM-5 zeolites. The finally synthesized zeolites are denoted as N-ZSM-5 and H-ZSM-5, respectively.

Synthesis of conventional C-ZSM-5 and S-ZSM-5 zeolites

The conventional ZSM-5 zeolite was prepared by a hydrothermal synthesis method with the precursor molar composition of (2TEOS:0.68TPAOH:8ethanol:120H₂O:xAl₂O₃). The mixture was prepared by adding DIW and ethanol to TPAOH. After their complete mixing, aluminum isopropoxide (AIP) was added as a Al source; finally, TEOS as a Si source was added dropwise, and the solution was stirred overnight. For the synthesis of conventional ZSM-5, the mixture was ready for a hydrothermal synthesis, whereas for the synthesis of sheet-like ZSM-5 after the addition of TEOS, urea was added to the solution and aged overnight. In addition, the solution was sealed in an autoclave and heated to 180 °C for 24 h for conventional ZSM-5 and treated at 180 °C for 48 h for sheet-like ZSM-5 at a rotation speed of 5 rpm. After the crystallization step, the white solid powders were collected, and the mother solution was washed with deionized water until the solution pH reached 7, then the sample was dried overnight at 110 °C. Finally, the H-form ZSM-5 zeolite was obtained after calcination at 550 °C for 6 h at a heating rate of 1 °C/min. The obtained final conventional ZSM-5 and sheet-like ZSM-5 zeolites are denoted as C-ZSM-5 and S-ZSM-5, respectively.

Equation of DME conversion calculation

$$\text{DME conversion (\%)} = \left(1 - \frac{A_{\text{DME}}/A_{\text{N}_2}}{A_{\text{DME}}^0/A_{\text{N}_2}^0} \right) * 100$$

where, A_{DME}^0 and $A_{\text{N}_2}^0$ are the measured peak area of CO₂ and N₂ before the reaction and A_{DME} and A_{N_2} are the measured peak area of CO₂ and N₂ during the reaction, respectively.

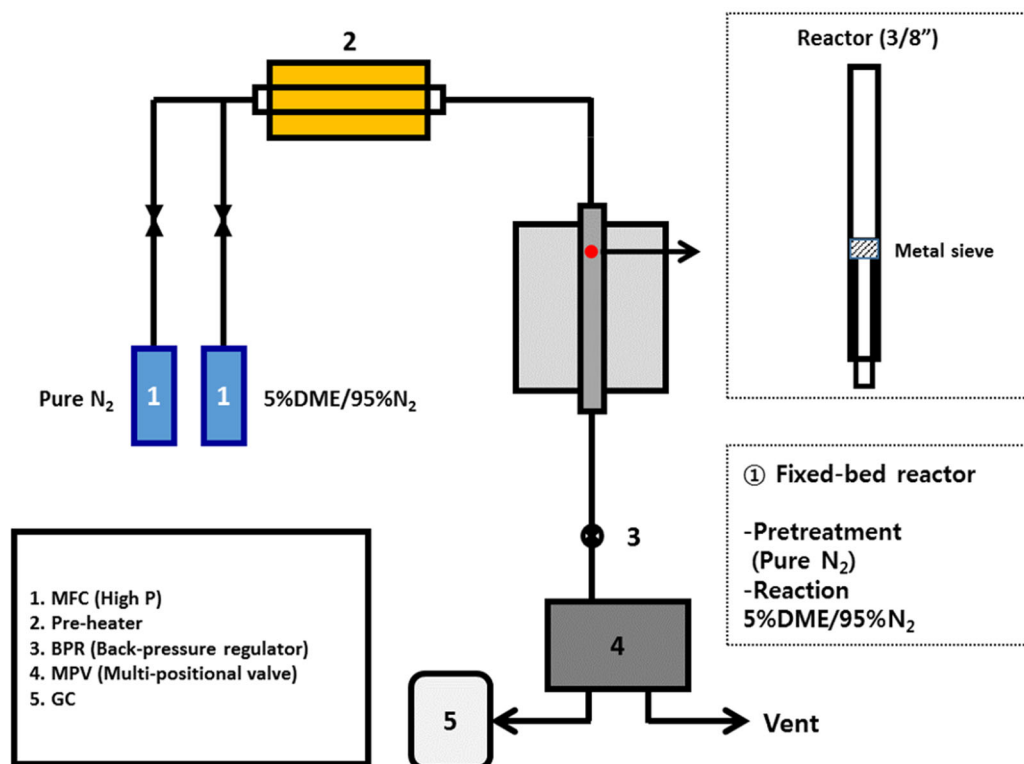


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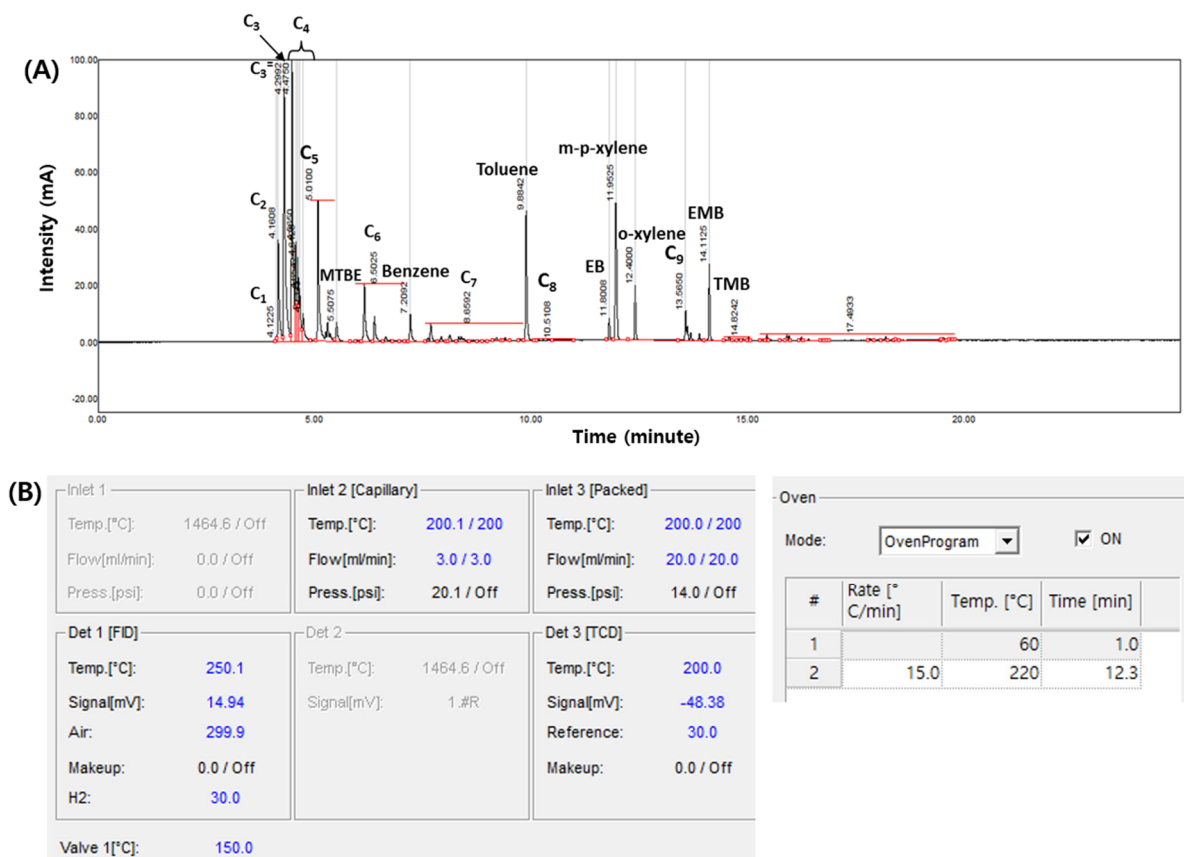


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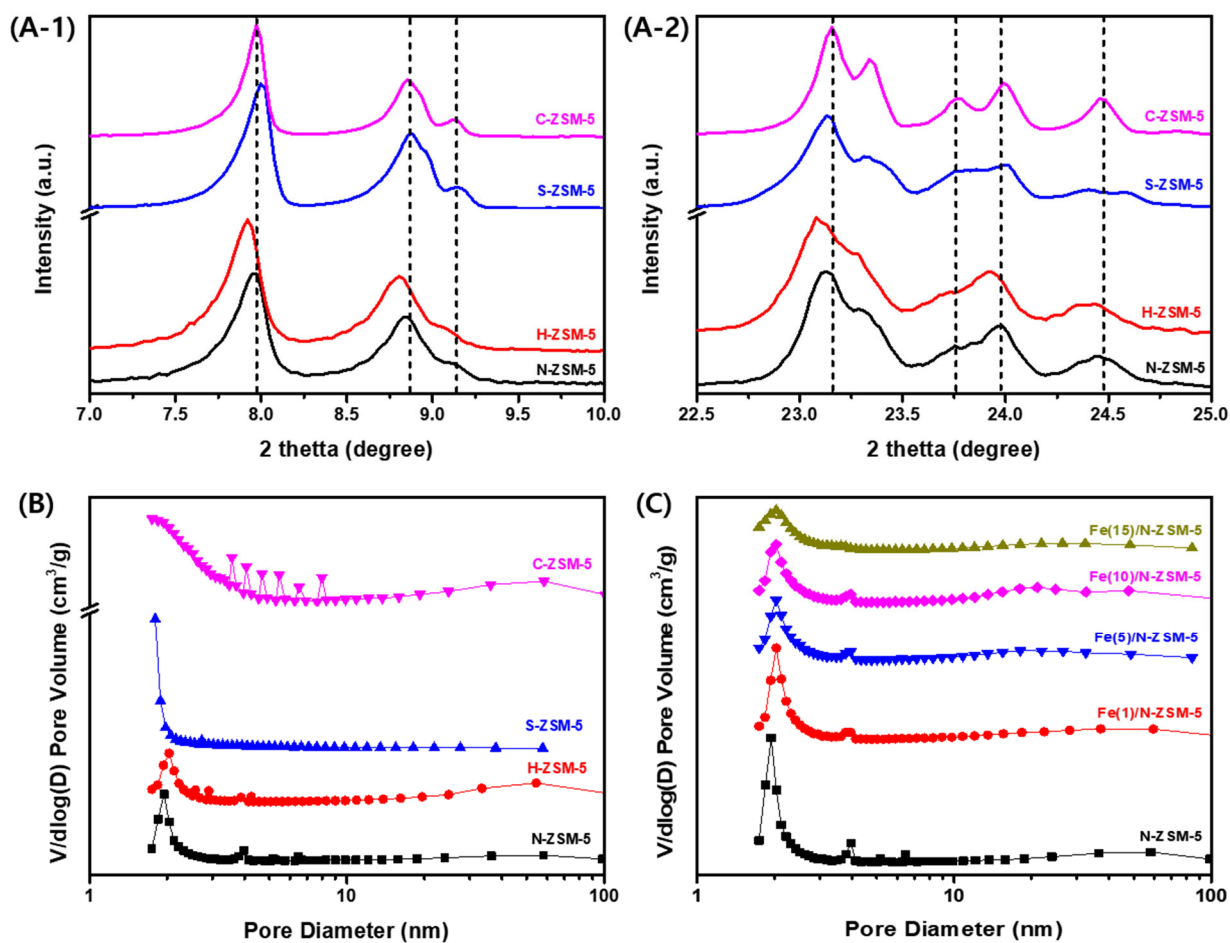


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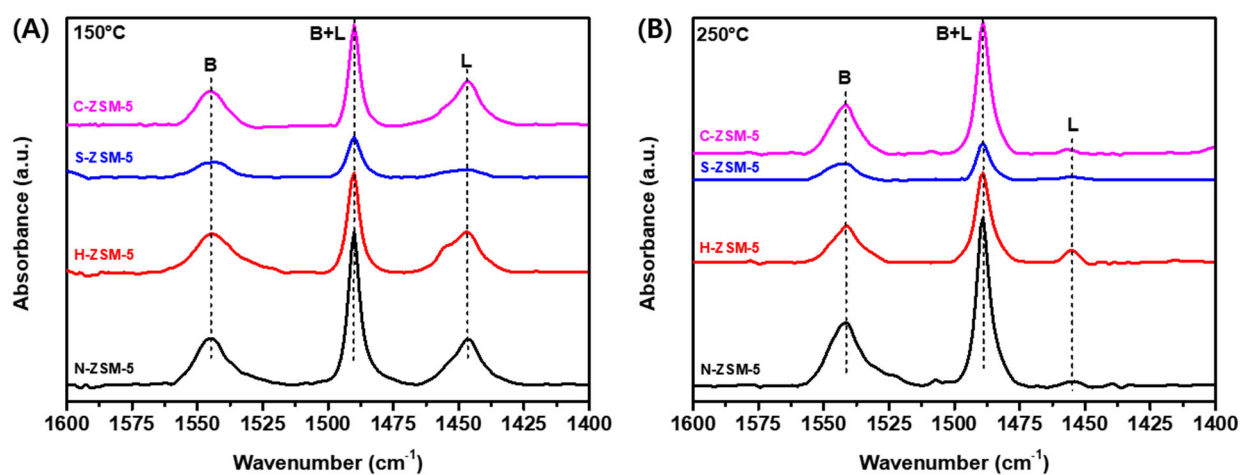


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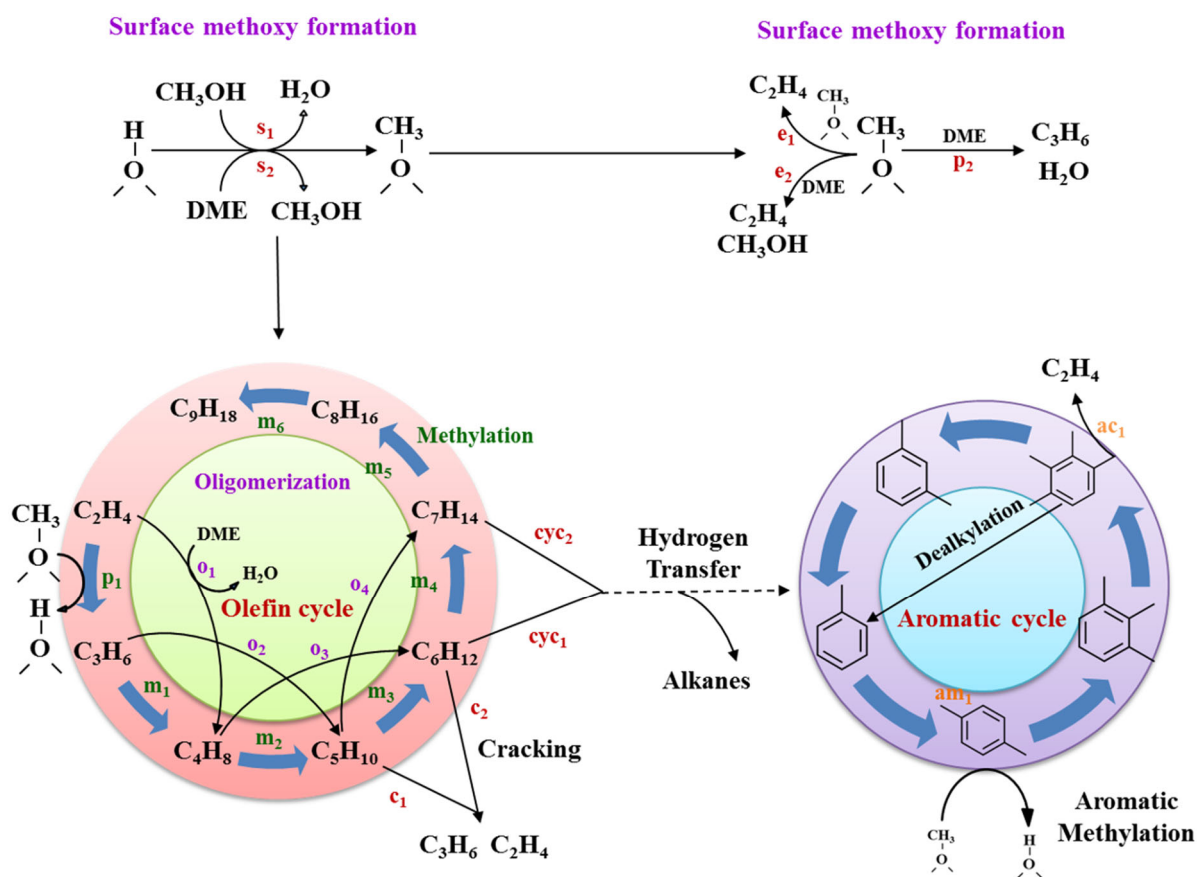


Figure S5. Proposed reaction pathways for DTG over HZSM-5 catalyst, where the labels over arrows represents each reaction steps [S1]. [surface methoxy formation (s), DME-methanol dehydration (md), ethylene from direct mechanism (e), propylene from direct mechanism (p), methylation with surface methoxy (m), oligomerization with DME (o), olefin cracking (c) and aromatic cyclization (cyc, am, ac)]

Reference

[S1] Lee, D.; Kim, J.J.; Ali, M.; Choung, J.W.; Lee, W.B.; Bae, J.W.; Park, M.J. Mechanistic kinetic modeling for catalytic conversion of DME to gasoline-range hydrocarbons over nanostructured ZSM-5. *Catal. Sci. Technol.* **2022**, *12*, 4798-4810.

Table S1. Catalytic activity for DME conversion to gasoline-range hydrocarbons (mol%) on ZSM-5 catalysts with their different morphology ^a

Temperature (°C)	280			290			300			310			320		
Catalyst	C ₁ –C ₄	C ₅ +	Aro	C ₁ –C ₄	C ₅ +	Aro	C ₁ –C ₄	C ₅ +	Aro	C ₁ –C ₄	C ₅ +	Aro	C ₁ –C ₄	C ₅ +	Aro
N-ZSM-5	33.1	43.8	23.1	34.7	41.7	23.6	35.4	40.8	23.8	38.7	37.2	24.1	39.3	36.2	24.5
H-ZSM-5	34.8	43.9	21.3	37.1	41.0	21.9	37.6	39.5	22.9	40.6	36.9	22.5	43.5	34.4	22.1
S-ZSM-5	42.8	38.3	18.9	43.4	38.1	18.5	44.7	37.1	18.2	46.4	35.6	18.0	48.4	33.8	17.8
C-ZSM-5	37.9	42.2	19.9	39.5	40.5	20.0	42.0	38.9	19.1	44.8	36.0	19.2	48.3	33.3	18.4

^a DTG reaction (DME to gasoline-range hydrocarbons) activity was measured at T = 280–320 °C, P = 0.1 MPa and space velocity (SV) = 4400 L/(kg_{cat}·h) with a feed reactant of DME/N₂ = 5/95 (mol%).

Table S2. Catalytic activity for DME conversion to gasoline-range hydrocarbons (mol%) on Fe/N-ZSM-5 catalysts^a

Catalyst	DME Conversion (mol%)	Product distribution (mol%)			Liquid product distribution (mol%)			
		C ₁ –C ₄	C ₅ +	Aromatics	C ₅	C ₆ +	Aromatics	Aliphatics
N-ZSM-5	100	34.7	41.7	23.6	19.6	44.2	36.2	63.8
Fe(1)/N-ZSM-5	100	38.2	41.5	20.3	18.6	48.5	32.9	67.1
Fe(5)/N-ZSM-5	91.7	38.3	43.4	18.3	15.1	51.9	29.6	68.4
Fe(10)/N-ZSM-5	100	21.9	60.6	17.5	14.9	54.9	30.2	69.8
Fe(15)/N-ZSM-5	83.5	44.5	38.5	17	14.1	56.8	29.1	70.9

^a DTG reaction (DME to gasoline-range hydrocarbons) activity was measured at T = 290 °C, P = 0.1 MPa and space velocity (SV) = 4400 L/(kg_{cat}·h) with a feed reactant of DME/N₂ = 5/95 (mol%).