

Support Information

Table S1. Unit cell parameters for HZSM-5/Al₂O₃ material and Zr- and Mg- modified samples.

No	Samples	a, Å	b, Å	c, Å	Volume, Å ³
1	HZSM-5/Al ₂ O ₃	20.162	20.002	13.432	5416.8
2	Zr-HZSM-5/Al ₂ O ₃	20.123	19.942	13.466	5431.3
3	Mg-HZSM-5/Al ₂ O ₃	20.176	19.991	13.392	5374.3

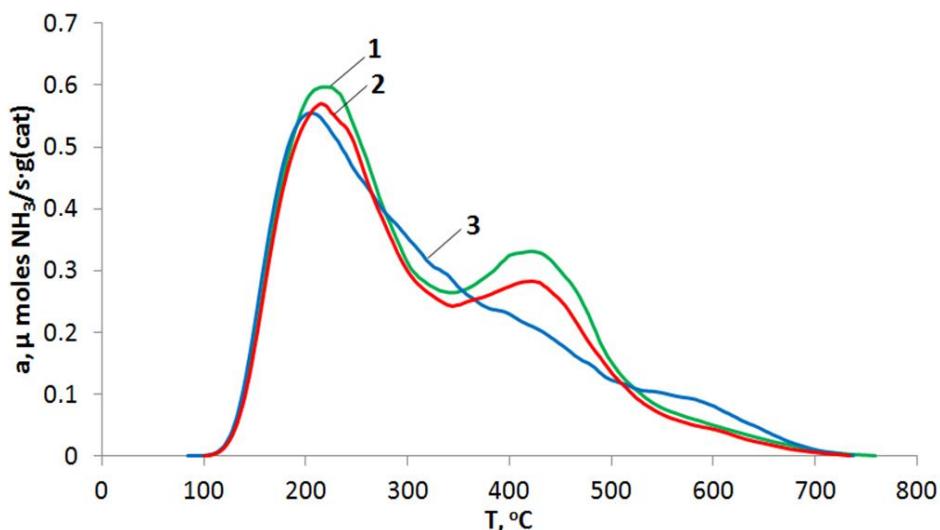


Fig. S1. NH₃ TPD profiles of the fresh HZSM-5/Al₂O₃, Zr- and Mg-modified samples.

1 – HZSM-5/Al₂O₃, 2 – Zr-HZSM-5/Al₂O₃, 3 – Mg-HZSM-5/Al₂O₃.

Total Acidity, μmol NH₃/ g (cat): 1 – 1005, 2 – 924, 3 – 952.

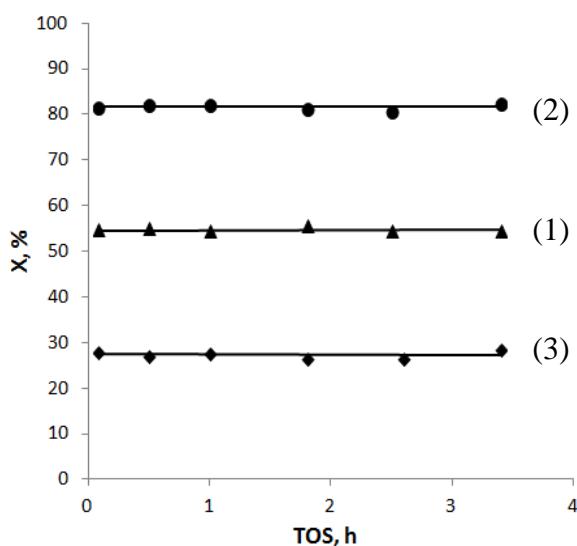


Fig. S2. Conversion of DME (X(DME)) as a function of time on stream (TOS).

1 – HZSM-5/Al₂O₃, 2 – Zr-HZSM-5/Al₂O₃, 3 – Mg-HZSM-5/Al₂O₃.

T = 320°C, P = 0.1 MPa, τ = 0.82

g(cat)/g(C)*h.

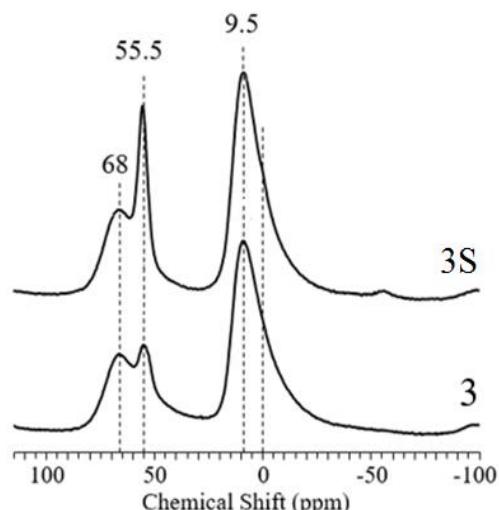


Fig. S3. ²⁷Al MAS NMR spectra of Mg-HZSM-5/Al₂O₃. 3 - hydrothermally treated sample, 3S - fresh sample.

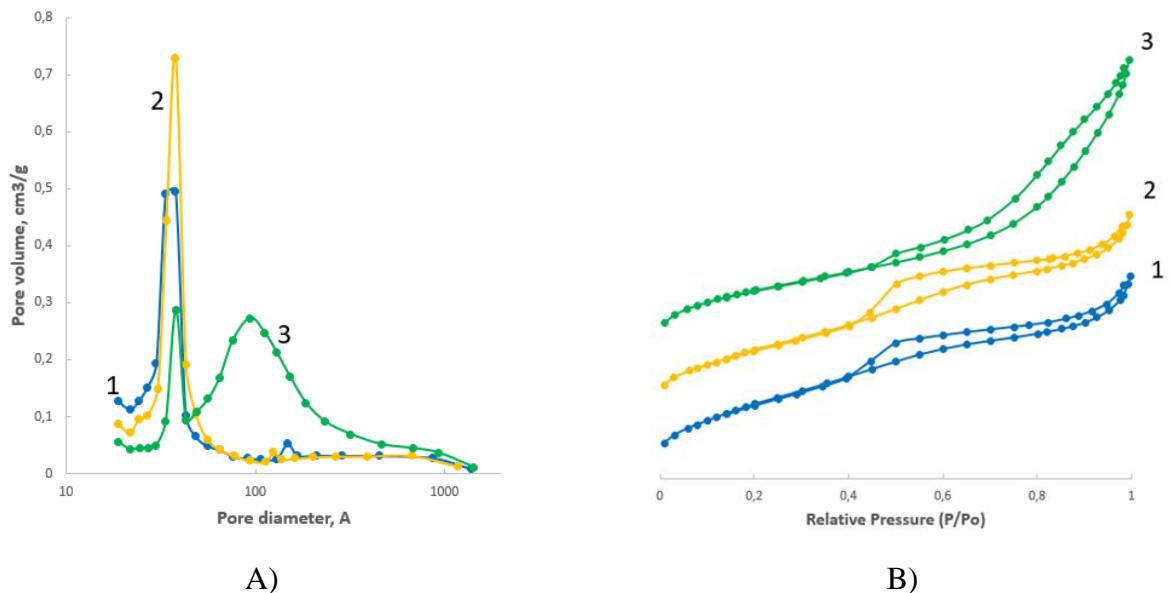


Fig. S4. The pore size distribution (A) (BJH method) and BET isotherms (B).
1 – HZSM-5/Al₂O₃, 2 – Zr-HZSM-5/Al₂O₃, 3 – Mg-HZSM-5/Al₂O₃.

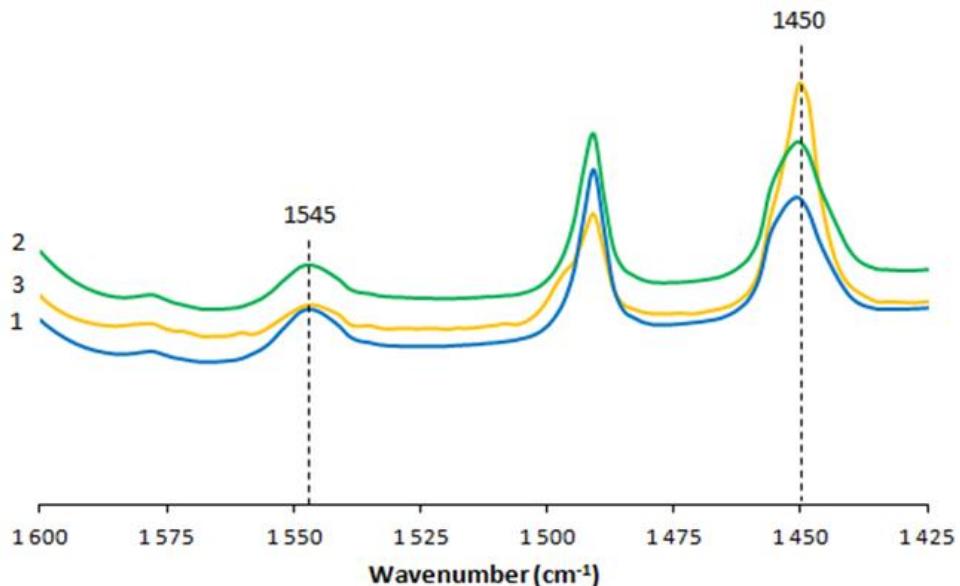


Fig. S5. IR spectra of pyridine adsorbed at 150°C.
1 – HZSM-5/Al₂O₃, 2 – Zr-HZSM-5/Al₂O₃, 3 – Mg-HZSM-5/Al₂O₃.

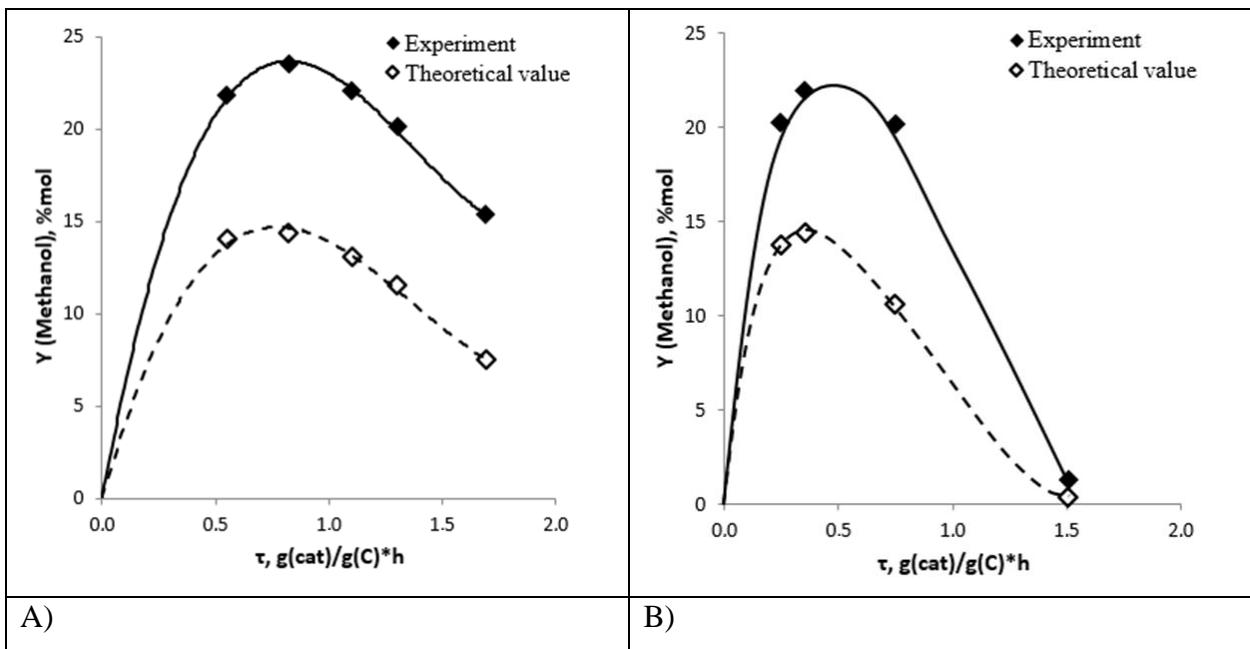


Fig. S6. The experimental and equilibrium yield of methanol for HZSM-5/Al₂O₃ (A) and Zr-HZSM-5/Al₂O₃ (B).

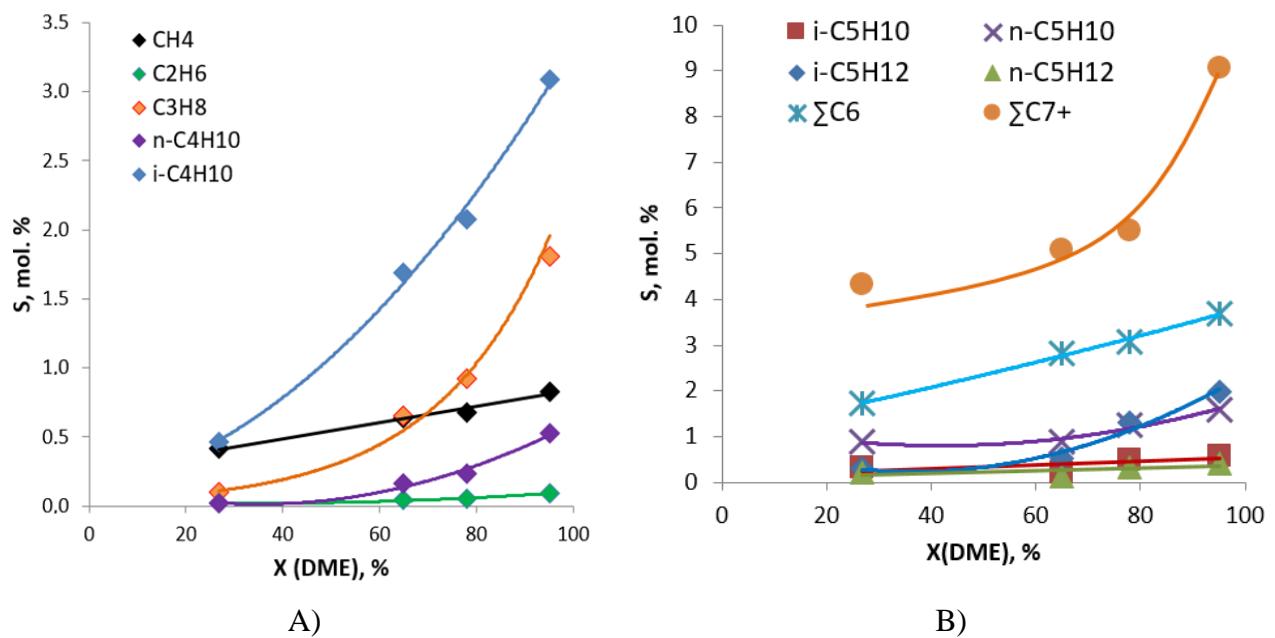


Fig. S7. The product distribution of C₁–C₄ alkanes (A) and C₅–C₈ hydrocarbons (B) over Mg-HZSM-5/Al₂O₃.

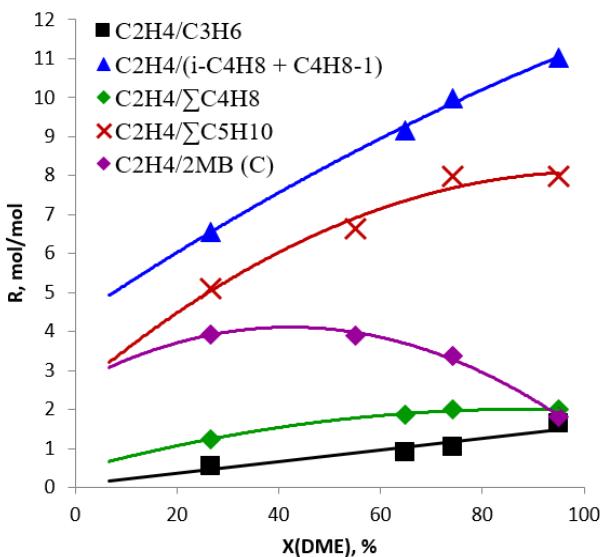


Fig. S8. The ratio of ethylene/alkenes C₃-C₅ (R) as a function of DME conversion (X(DME)) for the Mg-HZSM-5/Al₂O₃.

C₂H₄/2MB is the ratio of ethylene to sum of 2-methylbutane and 2-methyl-2-butene yield in carbon basis.

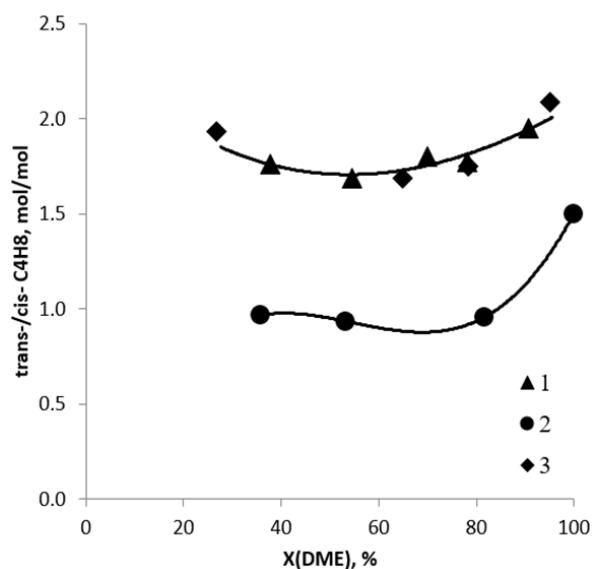


Fig. S9. Molar ratio of trans-/cis- C₄H₈ as a function of DME conversion (X(DME)).
1 – HZSM-5/Al₂O₃, 2 – Zr-HZSM-5/Al₂O₃, 3 – Mg-HZSM-5/Al₂O₃.

The isomerization rate was too high for Zr-modified sample, and the catalysts worked in the kinetic control zone of reaction. Therefore, butenes formed did not have time enough for isomerization into the trans-configuration.

Table S2. Products distribution for HZSM-5/Al₂O₃, Zr- and Mg- modified samples. Experimental data.

Product	S, % mol.			
	HZSM-5/Al ₂ O ₃		Zr-HZSM-5/Al ₂ O ₃	Mg-HZSM-5/Al ₂ O ₃
	X=55%	X=78%	X=53%	X=82%
				X=78%

CH ₃ OH	51.2	38.0	49.9	37.9	37.5
C ₂ H ₄	12.7	17.5	13.1	17.8	18.5
C ₃ H ₆	17.4	18.6	18.5	18.9	17.7
ΣC ₄ H ₈	7.7	10.5	7.0	9.3	9.6
ΣC ₅ H ₁₀	0.9	1.2	0.8	1.3	1.8
CH ₄	0.5	0.6	0.4	0.5	0.8
C ₂ H ₆	0.1	0.1	0.1	0.1	0.1
C ₃ H ₈	0.3	0.8	0.3	0.6	0.8
ΣC ₄ H ₁₀	1.0	2.7	1.0	2.6	2.4
ΣC ₅ H ₁₂	0.5	1.3	0.8	1.6	1.7
ΣC ₆	2.8	3.2	2.9	3.5	3.4
ΣC ₇₊	5.0	5.5	5.2	5.8	5.6

Table S3. The activation energy for the methylation reaction of olefins C₂ – C₄ and aromatics. Zeolite HZSM-5 (SiO₂ / Al₂O₃ = 45). Experimental data.

	Methylation agent	Ea, kJ/mol	References
Ethylene	Methanol	103-109	[50, 51]
	DME	94±3	[39]
Propylene	Methanol	69	[50, 51]
	DME	63±3	[39]
Butenes	Methanol	45	[50, 51]
	DME	44-56	[39]
Toluene	Methanol*	57-79	[52]
	DME	52±4	[53]
Xylene	Methanol*	25±5	[52]
	DME	62±4	[55]

*) for HZSM-5 with SiO₂/Al₂O₃=30

Table S4. Chemical reaction equations of conversion DME into hydrocarbons.

Nº	Reaction
Hydrocarbon pool formation	
1	n(CH ₃) ₂ O → hydrocarbon pool (cyclopentenyl cations + methylbenzenes cations)
Methylation by DME	
2	2(CH ₃) ₂ O → CH ₃ OH + C ₃ H ₆ + H ₂ O
3	(CH ₃) ₂ O + C ₃ H ₆ → C ₄ H ₈ + CH ₃ OH
4	(CH ₃) ₂ O + C ₄ H ₈ → C ₅ H ₁₀ + CH ₃ OH
5	(CH ₃) ₂ O + C ₅ H ₁₀ → C ₆ H ₁₂ + CH ₃ OH
6	(CH ₃) ₂ O + C ₆ H ₁₂ → C ₇ H ₁₄ + CH ₃ OH
7	(CH ₃) ₂ O + C ₇ H ₁₄ → C ₈ H ₁₆ + CH ₃ OH
Breaking of higher olefins	
8	C ₈ H ₁₆ → C ₃ H ₆ + C ₅ H ₁₀
9	C ₈ H ₁₆ → 2C ₄ H ₈
10	C ₇ H ₁₄ → C ₃ H ₆ + C ₄ H ₈
Methylation polymethylbenzenes by methanol and subsequent dealkilation	
11	n(CH ₃)-C ₆ H _{6-n} + CH ₃ OH → n-1(CH ₃)-C ₆ H _{6-n} -(C ₂ H ₅) + H ₂ O
12	n-1(CH ₃)-C ₆ H _{6-n} -(C ₂ H ₅) → n-1(CH ₃)-C ₆ H _{7-n} + C ₂ H ₄
H-transfer	

13	$2C_4H_8 \rightarrow C_4H_6 + C_4H_{10}$
14	$C_3H_6 + C_4H_8 \rightarrow C_3H_8 + C_4H_6$
15	$2C_4H_6 \rightarrow \text{cyclo-}C_6H_9-(C_2H_3) + 2\text{Zeolite} \rightarrow C_6H_5-(C_2H_5) + 2\text{Zeolite-H}$
16	$C_4H_6 + C_3H_6 \rightarrow \text{cyclo-}C_6H_9-(CH_3) + 4\text{Zeolite} \rightarrow C_6H_5-(CH_3) + 4\text{Zeolite-H}$
17	$C_3H_6 + 2\text{Zeolite-H} \rightarrow C_3H_8 + 2\text{Zeolite}$
18	$C_4H_8 + 2\text{Zeolite-H} \rightarrow C_4H_{10} + 2\text{Zeolite}$
19	$C_5H_{10} + 2\text{Zeolite-H} \rightarrow C_5H_{12} + 2\text{Zeolite}$
20	$C_6H_{12} + 2\text{Zeolite-H} \rightarrow C_6H_{14} + 2\text{Zeolite}$
21	$C_7H_{14} + 2\text{Zeolite-H} \rightarrow C_7H_{16} + 2\text{Zeolite}$
Isomerization	
22	$n-C_4H_8 \rightarrow i-C_4H_8$
23	$n-C_5H_{10} \rightarrow i-C_5H_{10}$
24	$n-C_6H_{12} \rightarrow i-C_6H_{12}$
25	$n-C_7H_{14} \rightarrow i-C_7H_{14}$