Electronic Supplementary information (ESI)

Kinetics and thermodynamics of polymethylbenzenes formation over zeolites in different pore sizes for understanding the mechanisms of methanol to olefins conversion – A computational study

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Table S1. The adsorption energy without dispersion correction (E_{ads}') using ωB97X/6-311+G(2df,2p)

H-SAPO-34	H-BEA	H-ZSM-5	H-ZSM-22	H-FAU
-0.51	-0.54	-0.57	-0.66	-0.54
-0.51	-0.61	-0.67	-0.74	-0.61
-0.65	-0.69	-0.74	-0.82	-0.66
-0.71	-0.68	-0.72	-0.63	-0.70
-0.82	-0.72	-0.83	-0.29	-0.74
-0.62	-0.79	-0.13	0.23	-0.75
-0.67	-0.77	-0.14	0.70	-0.77
-0.20	-0.62	0.90	2.60	-0.74

Table S2. Adsorption enthalpies ($\Delta H_{ads\text{-}d}$, eV) of hexamethylbenzene (6MB) in H-FAU and H-ZSM-5 at 525K using different models and methods

Model	method	$\Delta H_{ads\text{-}d}$
H-FAU	Exp.	-1.30
(1) H-FAU-8T/61T (in this work)	ωB97X-D/6-311+G(2df,2p)// B3LYP /6-31G(d,p)	-1.24
(2) H-FAU-8T/61T	ωB97X-D /6-311+G(2df,2p)// ωB97X-D /6-31G(d,p)	-1.72
(3) H-FAU-8T/61T	B3LYP -D3/6-311+G(2df,2p)// B3LYP -D3/6-31G(d,p)	-1.62
(4) H-FAU-12T/61T-ONIOM (a)	ωB97X-D /6-311+G(2df,2p)// B3LYP /6-31G(d,p):mp6	-1.23
(5) H-FAU-8T/92T	ωB97X-D /6-311+G(2df,2p)// B3LYP /6-31G(d,p)	-1.42
(6) H-FAU-8T/92T	ωB97X-D /6-311+G(2df,2p)// ωB97X-D /6-31G(d,p)	-1.48
(7) H-FAU-12T/92T-ONIOM (a)	ωB97X-D /6-311+G(2df,2p)// B3LYP /6-31G(d,p):mp6	-1.39
(8) H-FAU-12T/92T-ONIOM (b)	ωB97X-D /6-311+G(2df,2p)// B3LYP /6-31G(d,p):mp6	-1.48
H-ZSM-5		
(9) H-ZSM-5-5T/49T (in this work)	ωB97X-D/6-311+G(2df,2p)// B3LYP /6-31G(d,p)	-0.09
(10) H-ZSM-5-8T/49T	ωB97X-D /6-311+G(2df,2p)// B3LYP /6-31G(d,p)	-0.13
(11) H-ZSM-5-8T/49T –ONIOM (a)	ωB97X-D /6-311+G(2df,2p)// B3LYP /6-31G(d,p):mp6	-0.11
(12) H-ZSM-5-8T/68T –ONIOM (a)	ωB97X-D /6-311+G(2df,2p)// B3LYP /6-31G(d,p):mp6	-0.23

(a) The outer hydrogen atoms of the cluster were constrained in space to prevent unphysical deformations, and all the other atoms are relaxed.

(b) The low layer atoms of the cluster were constrained, and the high layer and reactive atoms are relaxed.

Table S3. Intrinsic free energy barriers ($\Delta G^{\neq}$, eV) and enthalpies ($\Delta H^{\neq}$, eV) of the reaction of 4MB → 5MB in H-ZSM-5 at 725K using different models and methods.

model	method	$\Delta G^{\neq}$	$\Delta H^{\neq}$
(1) H-ZSM-5-5T/49T (in this work)	ωB97X-D/6-311+G(2df,2p)// B3LYP /6-31G(d,p)	1.59	1.27
(2) H-ZSM-5-8T/49T-ONIOM (a)	ωB97X-D /6-311+G(2df,2p)// B3LYP /6-31G(d,p):mp6	1.59	1.09
(3) H-ZSM-5-5T/68T	ωB97X-D /6-311+G(2df,2p)// B3LYP /6-31G(d,p)	1.65	1.26
(4) H-ZSM-5-8T/68T –ONIOM (a)	ωB97X-D /6-311+G(2df,2p)// B3LYP /6-31G(d,p):mp6	1.52	1.12

(a) The outer hydrogen atoms of the cluster were constrained in space to prevent unphysical deformations, and all the other atoms are relaxed.

Table S4. Calculated intrinsic free energy barriers ($\Delta G^{\neq}$, eV at 725 K) of methylation and gem-methylation of polyMBs in the four zeolites using surface methoxy species as methylating agent

Elementary steps	H-SAPO-34	H-BEA	H-ZSM-5	H-ZSM-22
2MB → 3MB	1.71	1.43	1.25	1.21; 1.08[3]
2MB → $3MB^+$	1.71; 1.37[4]	1.43	1.23; 1.37[5]	1.15; 1.47[3]
3MB → 4MB	1.68	1.23	1.32	0.82; 1.35[3]
3MB → $4MB^+$	1.59	1.31	1.09; 0.82[5]	1.71; 1.42[3]
4MB → 5MB	1.74; 1.33[2]	1.17	1.59	1.09; 1.62[3]
4MB → $5MB^+$	1.84; 1.37[2]; 1.21[4]	1.61	1.17; 1.54[1]; 1.24[6]; 0.94[5]	1.20; 2.15[3]
5MB → 6MB	1.71; 1.23[2]	1.07	1.39	1.60
5MB → $6MB^+$	1.81; 1.36[2]	1.50	0.99; 0.84[5]	0.90
6MB → $7MB^+$	1.51; 1.08[2]; 1.16[4]	1.23; 1.49[5]	1.04; 1.31[5]	1.02

References	**Model and Method**
1. Wang, C. et al. *Chem. Eur .J.*, 2014, *20*, 1-13.	$\Delta E^{\neq}$ (0K), 72T, ωB97XD/6–31G(d,p)//ONIOM(ωB97XD/6–31G(d,p):MNDO)
2. Van Speybroeck, V. et al. *chemcatchem*, 2013, *5*, 173-184.	$\Delta E^{\neq}$ (0K), 6T/44T, B3LYP/DGTZVP-D//ONIOM(B3LYP/DGTZVP:MNDO)
3. Wang, C. M. et al. *Catal. Sci. Technol*.,2015, *5*, 3507–3517.	$\Delta E^{\neq}$ (0K), 22T/66T,ωB97XD/6–31G(d,p):MNDO
4. Wang, C. M. et al. *Catal. Sci. Technol*., 2015, *5*, 4354–4364.	$\Delta G^{\neq}$ (673K), 36T/PBC,BEEF-vdW
5. Lesthaeghe, D. et al. *Angew. Chem. Int. Ed*. 2007, *46*, 1311 –1314.	$\Delta E^{\neq}$ (0K), 5T/44T, without dispersion interactions, B3LYP/6-31+g(d):HF/6-31+g(d))//ONIOM(B3LYP/6-31+g(d):MNDO),
6. McCann, D. M. et al. *Angew. Chem. Int. Ed*. 2008, *47*, 5179 –5182.	$\Delta E^{\neq}$ (0K), 8T:46T, without dispersion interactions, ONIOM(B3LYP/6-31g(d):HF/6-31g(d))//ONIOM(B3LYP/6-31g(d):MNDO), Outer hydrogen atoms were fixed.

The differences are mainly caused by the models and methods, such as functional, basis set, dispersion correction, thermal correction and entropy contribution; on the other hand, the methylation pathways might be also different, such as concerted or stepwise. These differences indicate that the computed method shows significant effect on the results of zeolite system. The effect of calculated method is not illustrated in detail because it is not our aim in this work. It further indicates that it is not reasonable and rigorous to discuss a reaction rate only by intrinsic free energy barriers.

Table S5. The computed critical distances (A) in the transition states of the methylation and gem-methylation steps. O-C means the distance between O atom in ZO^- and C atom in CH_3, and C-C means the distance between C atom in CH_3 and C atom of benzene ring in nMB.

Elementary steps	H-SAPO-34		H-BEA		H-ZSM-5		H-ZSM-22	
	O-C	C-C	O-C	C-C	O-C	C-C	O-C	C-C
2MB → 3MB	2.18	2.21	2.13	2.22	2.15	2.20	2.07	2.18
2MB → $3MB^+$	2.20	2.21	2.16	2.21	2.12	2.19	2.12	2.17
3MB → 4MB	2.15	2.23	2.09	2.25	2.12	2.22	2.08	2.21
3MB → $4MB^+$	2.19	2.25	2.11	2.24	2.12	2.23	2.11	2.27
4MB → 5MB	2.11	2.23	2.06	2.26	2.07	2.19	1.97	2.17
4MB → $5MB^+$	2.12	2.29	2.09	2.30	2.06	2.18	2.11	2.30
5MB → 6MB	2.10	2.24	2.05	2.26	2.08	2.26	2.05	2.24
5MB → $6MB^+$	2.19	2.30	2.07	2.29	2.04	2.20	1.97	2.15
6MB → $7MB^+$	2.14	2.32	2.09	2.32	2.04	2.20	2.03	2.23

Table S6. Each term of reaction free energy (eV) of polyMBs formation over the four zeolites under 725 K (4MB is denoted 1,2,3,5-4MB for SAPO-34, BEA and ZSM-5, while 1,2,4,5-4MB for ZSM-22)

	SAPO-34	BEA	ZSM-5	ZSM-22	FAU
			-TΔS		
B	-2.59	-2.60	-2.62	-2.42	-2.66
MB	-2.67	-2.57	-2.52	-2.38	-2.66
2MB-p	-2.68	-2.55	-2.49	-2.42	-2.61
3MB-1,2,4	-2.54	-2.52	-2.39	-2.12	-2.55
4MB	-2.38	-2.47	-2.25	-1.94	-2.49
5MB	-2.17	-2.45	-1.86	-1.74	-2.29
6MB	-1.99	-2.23	-1.60	-1.21	-2.32
			ΔH_{corr}		
B	-0.56	-0.57	-0.57	-0.56	-0.57
MB	-0.55	-0.56	-0.56	-0.56	-0.57
2MB-p	-0.54	-0.56	-0.55	-0.54	-0.56
3MB-1,2,4	-0.53	-0.55	-0.54	-0.52	-0.55
4MB	-0.53	-0.54	-0.50	-0.48	-0.55
5MB	-0.49	-0.53	-0.45	-0.42	-0.52
6MB	-0.45	-0.49	-0.38	-0.43	-0.49
			ΔE_{dis}		
B	-0.61	-0.60	-0.65	-0.68	-0.54
MB	-0.75	-0.68	-0.75	-0.79	-0.61
2MB-p	-0.79	-0.77	-0.84	-0.89	-0.68
3MB-1,2,4	-0.89	-0.87	-0.93	-0.99	-0.76
4MB	-1.01	-0.96	-1.09	-1.15	-0.87
5MB	-1.12	-1.05	-1.20	-1.29	-0.92
6MB	-1.24	-1.08	-1.36	-1.47	-0.99
			ΔE_e		
B	-0.26	-0.29	-0.32	-0.42	-0.30
MB	-0.91	-1.00	-1.06	-1.13	-1.01
2MB-p	-1.68	-1.72	-1.77	-1.84	-1.69
3MB-1,2,4	-2.39	-2.37	-2.40	-2.31	-2.38
4MB	-3.12	-3.04	-3.09	-2.59	-2.99
5MB	-3.44	-3.55	-2.92	-2.08	-3.54
6MB	-3.39	-3.81	-2.54	-0.59	-3.93

Figure S1. Computed Gibbs free reaction energies of the polyMBs formation at 525K and 725K.

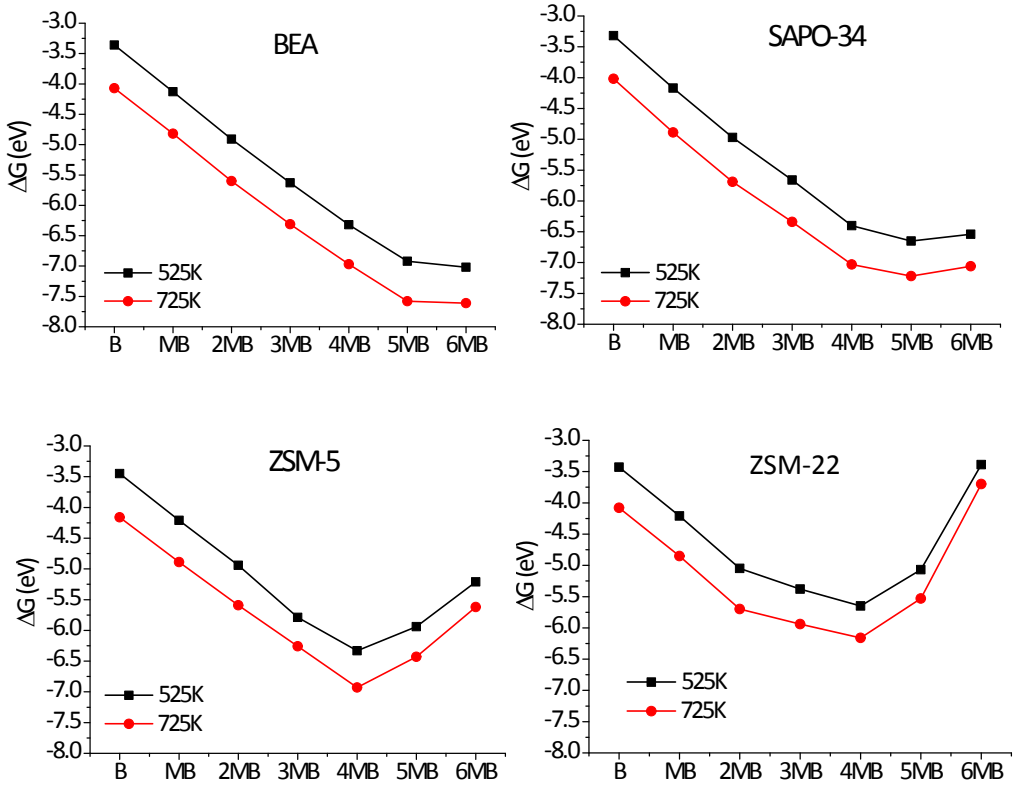

Figure S2. Computed Gibbs free reaction energies of the polyMBs formation at 725K.