Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Computational insights into the reaction mechanism of methanol-to-olefins conversion in H-ZSM-5: nature of hydrocarbon pool

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Fig. S1. Two adsorption structures and their adsorption enthalpies of methanol in H-ZSM-5 at T12 site.

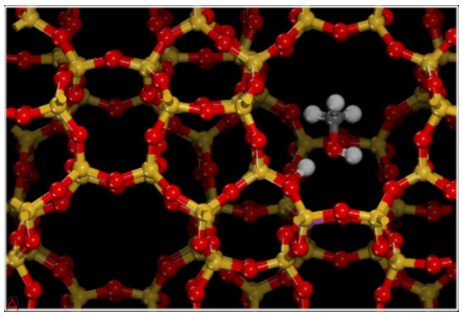
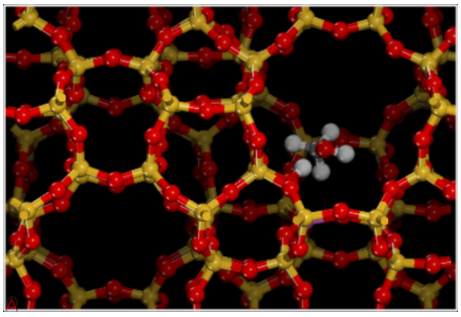
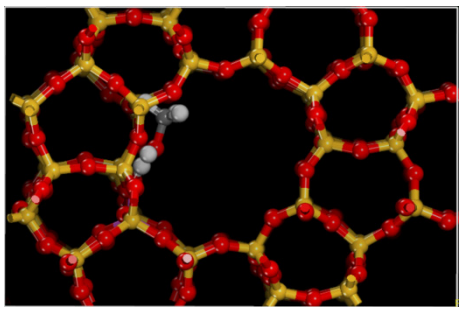
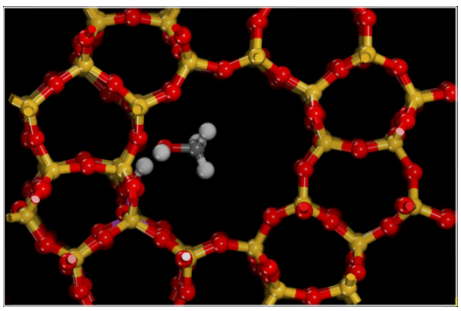
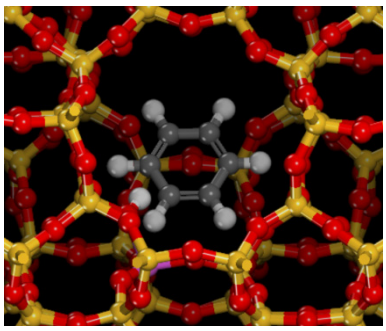
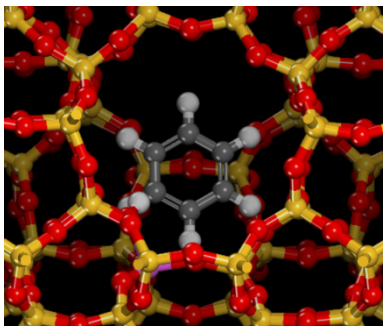
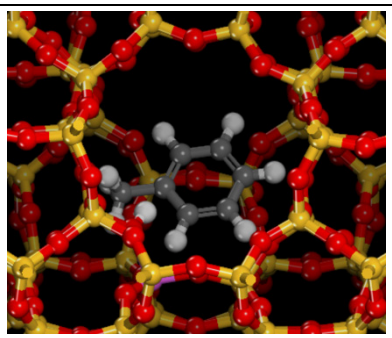
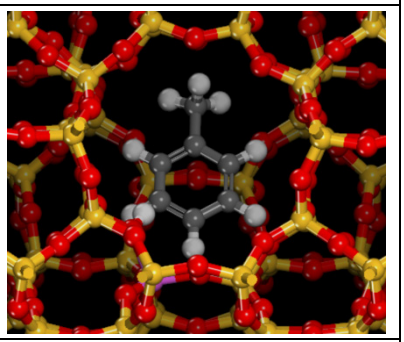
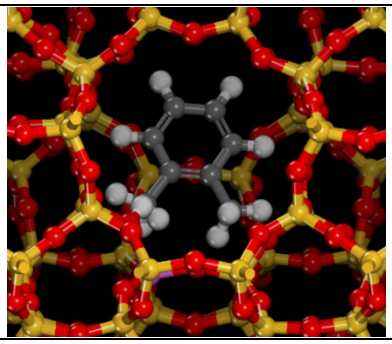
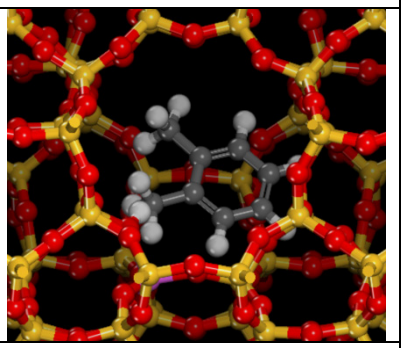
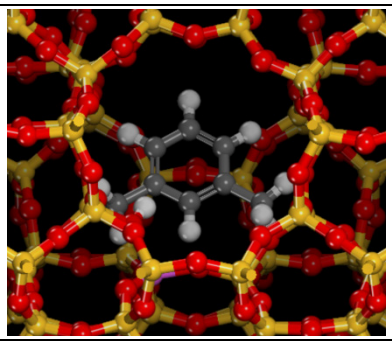
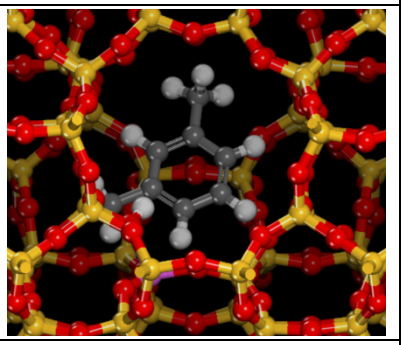
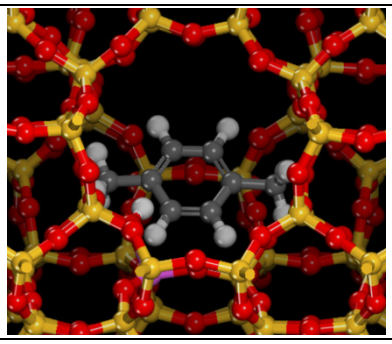
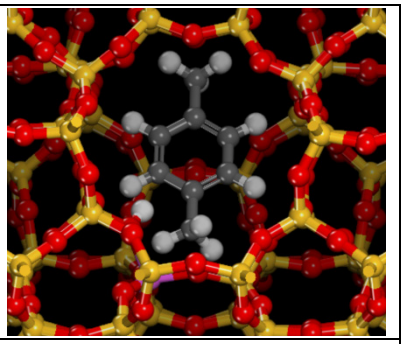
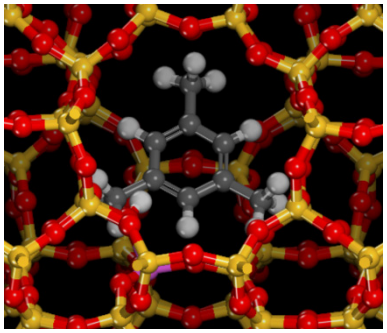
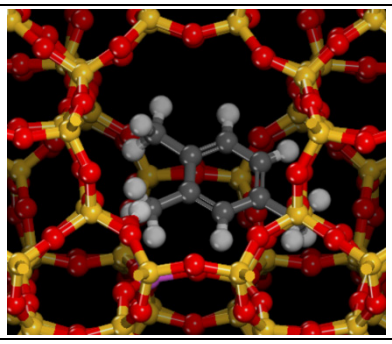
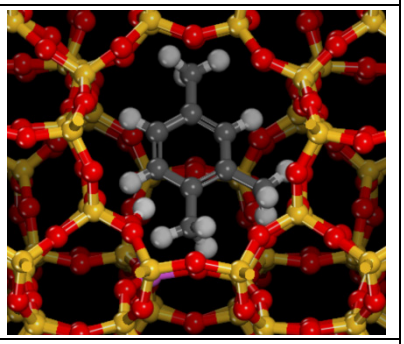
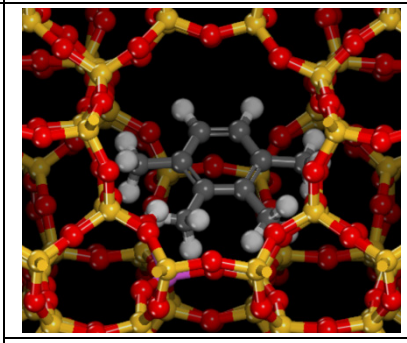
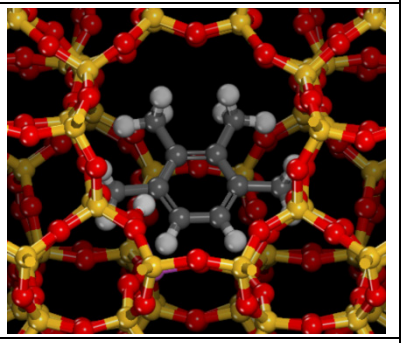
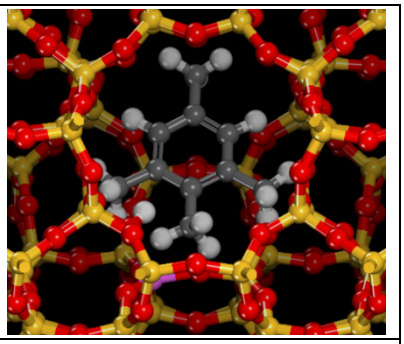
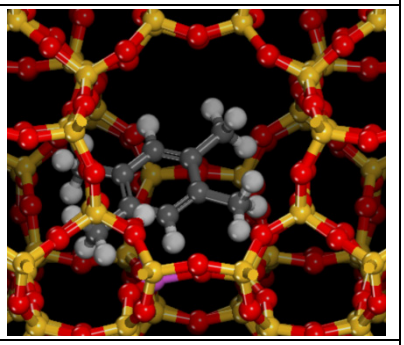
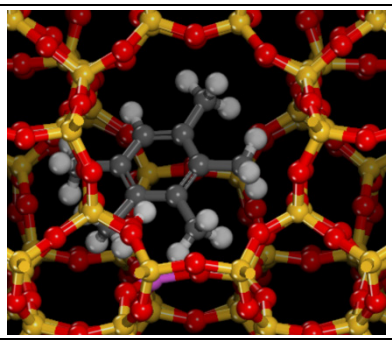
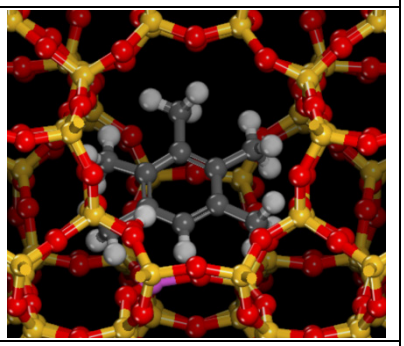
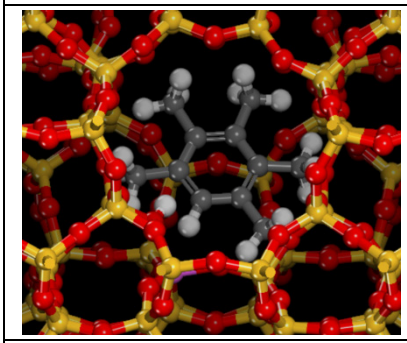
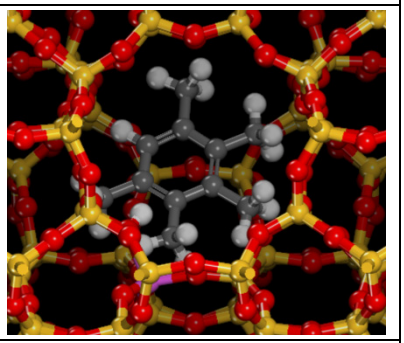
	Adsorption structure: most stable	Adsorption structure: less stable
A-axis view		
B-axis view		
Adsorption enthalpy	**-102 kJ/mol**	-87 kJ/mol

Fig. S2. Adsorption structures and calculated enthalpies of different MBs in H-ZSM-5.

MBs	Orientation-I	Orientation-II
benzene		
	-81 kJ/mol	**-84 kJ/mol**
toluene		
	-98 kJ/mol	**-99 kJ/mol**
o-xylene		
	-87 kJ/mol	**-94 kJ/mol**
m-xylene		
	-104 kJ/mol	**-112 kJ/mol**

p-xylene		
	-107 kJ/mol	-87 kJ/mol
1,3,5-TriMB		
		-118 kJ/mol
1,2,4-TriMB		
	-101 kJ/mol	**-101 kJ/mol**
1,2,3,4-TMB		
	-60 kJ/mol	**-94 kJ/mol**

1,2,3,5-TMB		
		-112 kJ/mol
1,2,4,5-TMB		
		-95 kJ/mol
PMB		
	-77 kJ/mol	-71 kJ/mol
		
	-32 kJ/mol	-63 kJ/mol

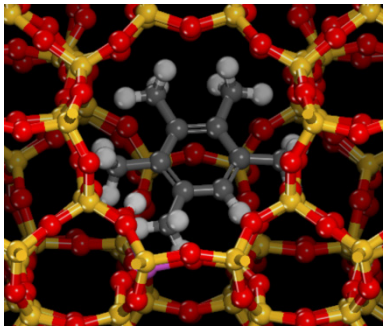
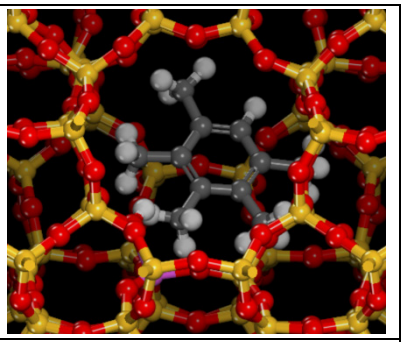
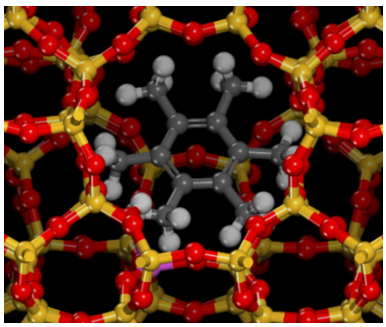
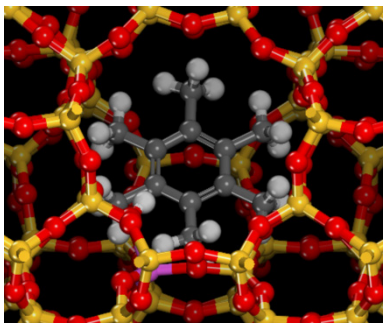
		
	-24 kJ/mol	-69 kJ/mol
HMB		
	-7 kJ/mol	12 kJ/mol

Fig. S3. Schematic enthalpy, entropy, and Gibbs free energy diagrams of ethyl side chain propagation in 1,2,3,5-TMB-based, 1,2,4,5-TMB-based, and PX-based side chain cycles in H-ZSM-5.

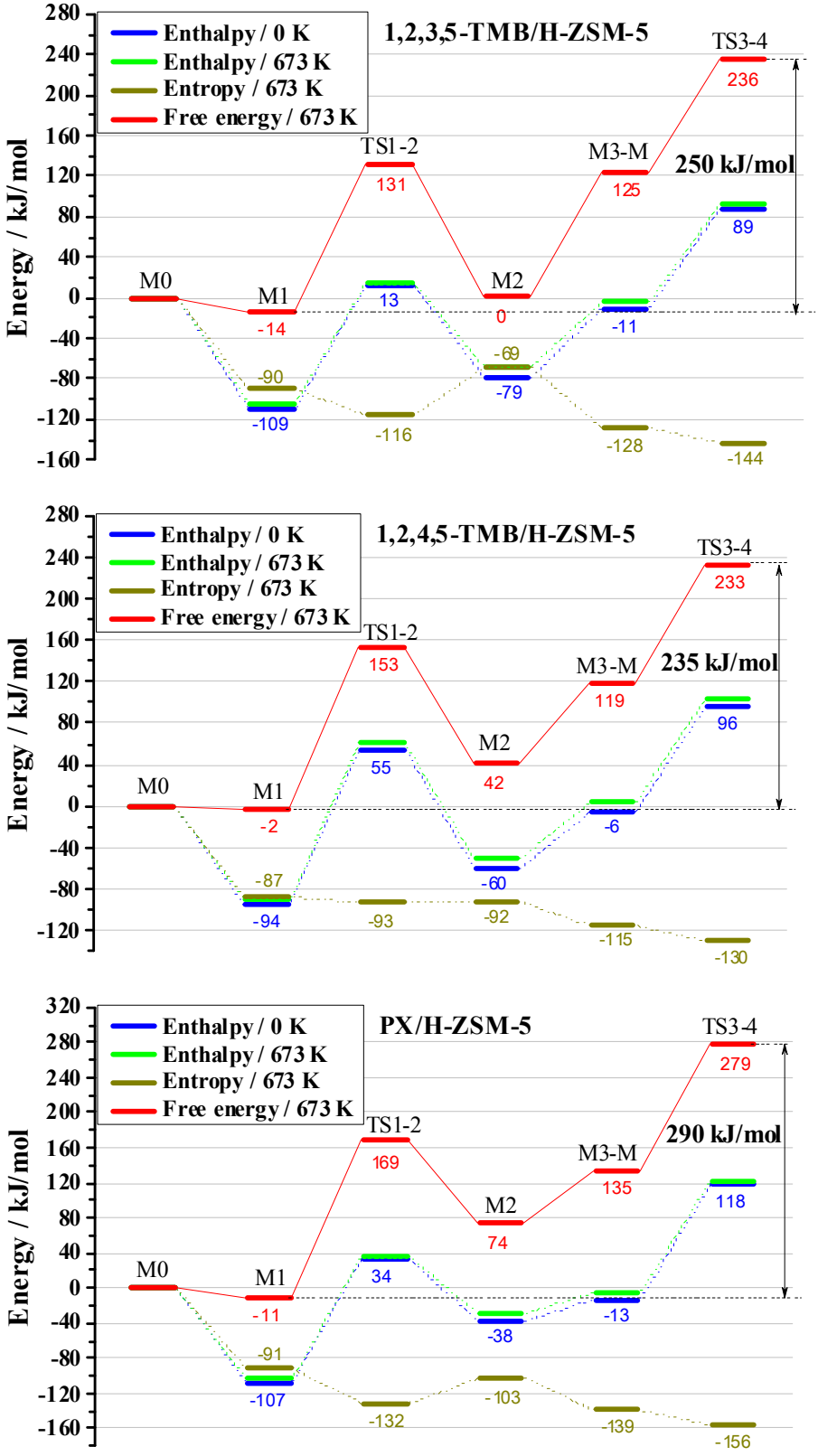


Fig. S4. Optimized transition state structures in aromatic-based side chain cycle in H-ZSM-5. The relative enthalpies of the transition states are listed for comparison.

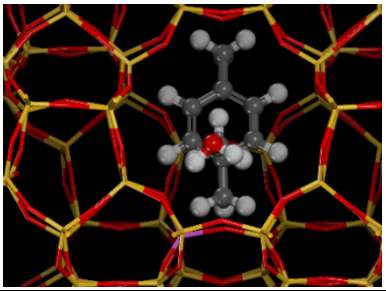
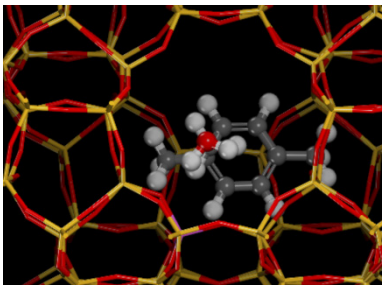
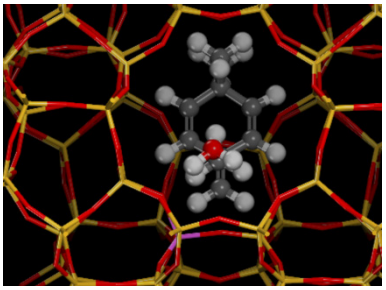
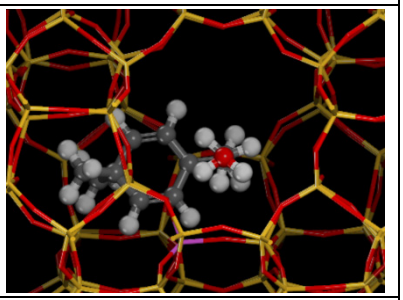
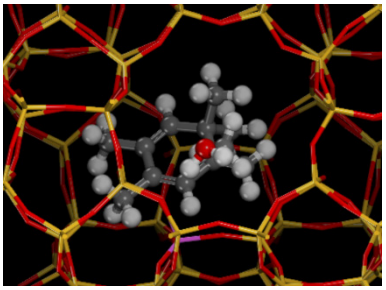
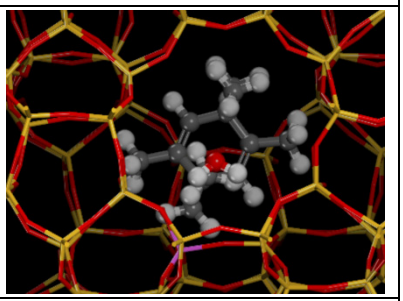
PX-based cycle	TS1-2		
		50 kJ/mol	**34 kJ/mol**
	TS3-4		
		118 kJ/mol	140 kJ/mol
1,2,4,5-TMB -based cycle	TS3-4		
		96 kJ/mol	123 kJ/mol

Fig. S5. Structures of intermediates in iso-C6-based cycle in H-ZSM-5.

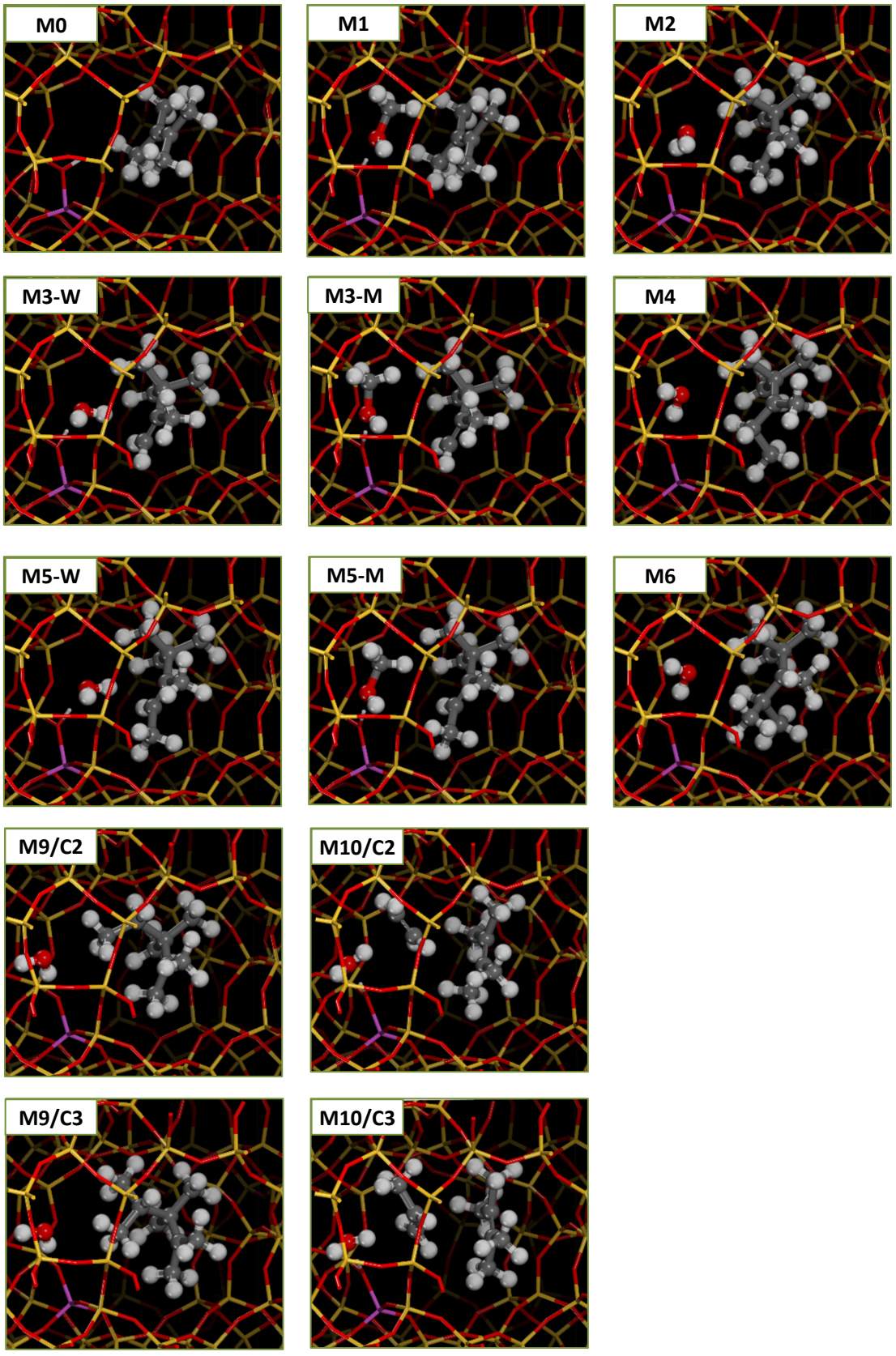


Fig. S6. Optimized transition state structure in the cracking of C8+ ion into propene and pentene in H-ZSM-5. All distances are in Å.

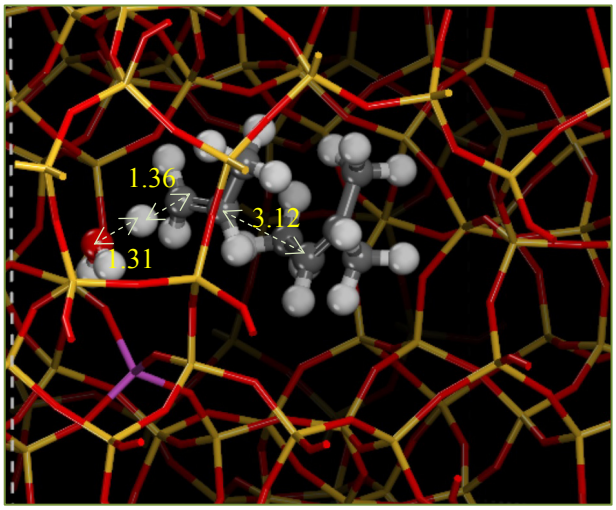


Table S1. Adsorption enthalpies (kJ/mol) of MBs in H-ZSM-5 calculated using different XC functionals with/without vdW correction.

MBs	BEEF-vdW	vdW-DF	vdW-DF2	DFT-D2	DFT-D3	PBE
benzene	-84	-106	-95	-96	-104	-19
toluene	-99	-125	-102	-96	-106	-20
o-xylene	-94	-121	-103	-89	-101	2
m-xylene	-112	-143	-122	-111	-123	-19
p-xylene	-107	-137	-115	-101	-112	-8
1,3,5-TriMB	-118	-150	-126	-104	-121	-1
1,2,4-TriMB	-101	-135	-113	-97	-110	10
1,2,3,4-TMB	-94	-127	-112	-110	-114	25
1,2,3,5-TMB	-112	-151	-129	-111	-123	12
1,2,4,5-TMB	-95	-138	-124	-120	-121	23
PMB	-77	-124	-112	-110	-107	52
HMB	-7	-50	-42	-60	-51	125