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

Supporting Information

Transition-state scaling relations in zeolite catalysis: influence of framework topology and acid-site reactivity

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Table S1. Optimized lattice constants for zeolites and zeotypes. The units are Å and ° for length and angle.

	a	***b***	***c***	***α***	***β***	***γ***
AlPO-34	13.90	13.90	15.11	90	90	120
CHA	13.80	13.80	14.84	90	90	120
AlPO-18	13.83	12.73	18.72	90	90	90
AEI	13.82	12.66	18.61	90	90	90
AlPO-5	13.92	13.92	8.61	90	90	120
AFI	13.88	13.88	8.65	90	90	120

Note. The optimized lattice constants of the isomorphic substitution Me-AlPO-34/CHA are listed as below for comparison. The substitution brings negligible change of the cell.

	a/Å	b/Å	c/Å
AlPO-34	13.900	13.900	15.112
Si-AlPO-34	13.933	13.933	15.145
Ge-AlPO-34	13.928	13.928	15.156
Ti-AlPO-34	13.941	13.941	15.142
Mg-AlPO-34	13.941	13.941	15.151
Zn-AlPO-34	13.934	13.934	15.156
CHA	13.805	13.805	14.836
Al-CHA	13.837	13.837	14.856
Ga-CHA	13.835	13.835	14.873

Table S2. Relative stabilities of different acid sites in Si-AlPO-18 zeotype.

Relative energies/ kJ/mol	T1	T2	T3
O1	6	3	3
O2	7	0	2
O3	13	10	10
O4	6	3	3

Note. The definition of T sites is from IZA database. see:

http://izasc-mirror.la.asu.edu/fmi/xsl/IZA-SC/ftc_fw.xsl?-db=Atlas_main&-lay=fw&-max=25&STC=AEI&-find.

The acid sites are defined as follows. The sites T1O4, T2O1, and T3O3 are not shown as they connect to other cavities.

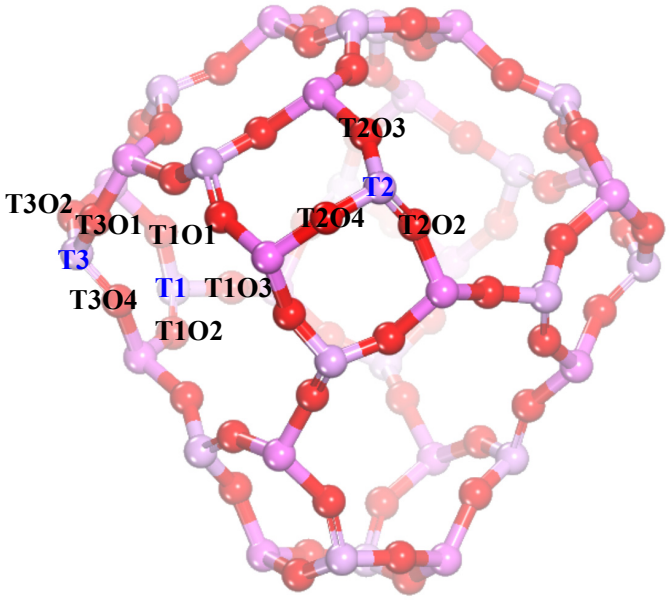


Table S3. Calculated ammonia adsorption enthalpy in metal isomorphically substituted zeolites and zeotype materials. The unit is kJ/mol.

Me	AlPO-34/CHA	AlPO-18/AEI	AlPO-5/AFI
Si	-98	-101	-92
Ge	-90	-94	-83
Ti	-73	-81	-67
Mg	-134	-132	-119
Zn	-118	-115	-113
Al	-118	-116	-101
Ga	-109	-107	-95

Table S4. Calculated adsorption energies of propene in concerted pathway in metal isomorphically substituted zeolites and zeotype materials. The unit is kJ/mol.

Me	AlPO-34/CHA	AlPO-18/AEI	AlPO-5/AFI
Si	-48	-40	-39
Ge	-48	-41	-40
Ti	-46	-41	-38
Mg	-48	-41	-41
Zn	-48	-41	-41
Al	-51	-46	-40
Ga	-51	-45	-38
Average	-49±2	-42±3	-39±1

Table S5. Calculated adsorption energies of ethene in concerted pathway in metal isomorphically substituted zeolites and zeotype materials. The unit is kJ/mol.

Me	AlPO-34/CHA	AlPO-18/AEI	AlPO-5/AFI
Si	-36	-27	-26
Ge	-36	-28	-27
Ti	-34	-31	-26
Mg	-36	-26	-29
Zn	-36	-26	-28
Al	-37	-34	-27
Ga	-37	-33	-25
Average	-36±1	-29±3	-27±1

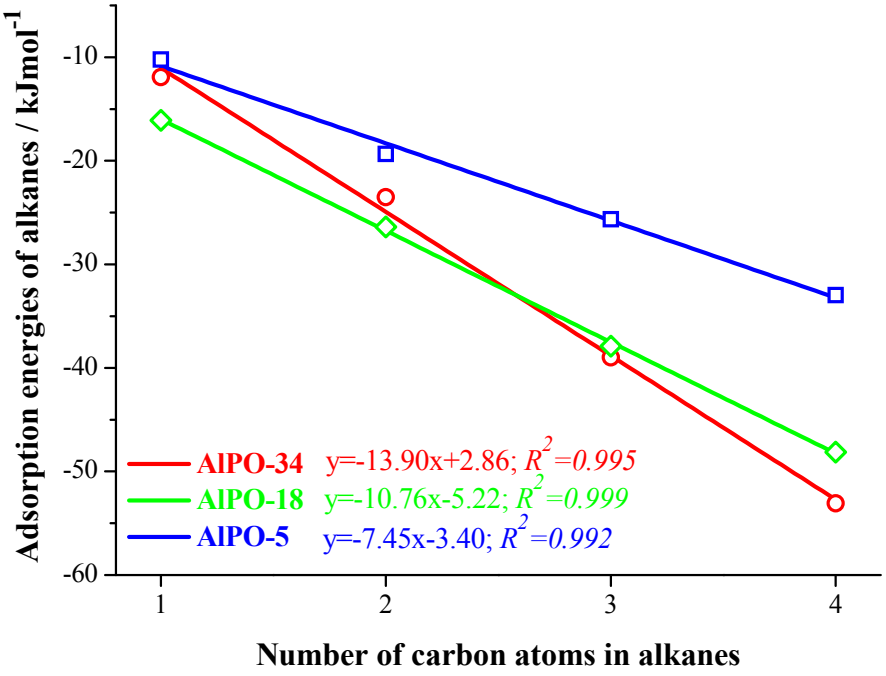
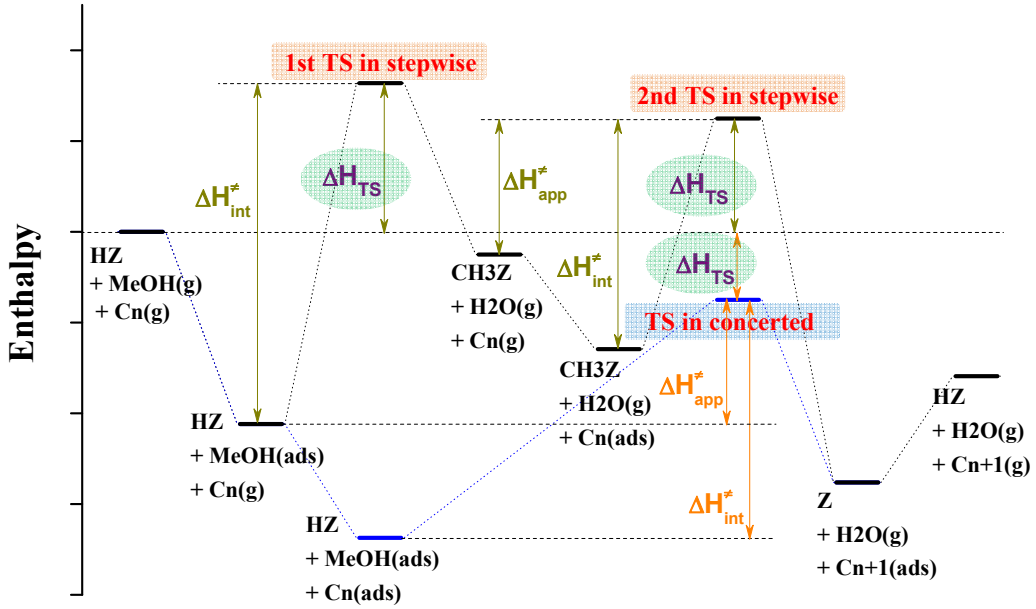


Figure S1. Adsorption energies of alkanes (methane, ethane, propane, butane) in different zeotypes.



Scheme S1. Schematic enthalpy diagram for the methylation of olefins through concerted or stepwise pathways. The transition state energies (ΔH_{TS}) is relative to gaseous methanol, olefins, and zeotypes (HZ). The definitation of apparent barrier ($\Delta H_{app}^{\neq}$), and intrinsic barrier ($\Delta H_{int}^{\neq}$) is also depicted.