

# **SUPPORTING INFORMATION**

## The Reaction Dynamics of Zeolite Catalyzed Alkene Methylation by Methanol

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## I. QM/MM methodology

### a. QM region

The Brønsted-acid site was modeled using a QM region of 5 tetrahedral atoms of stoichiometry  $\text{AlH}(\text{OSiH}_3)_4$ . Terminal Si-O bonds created during the separation of the QM region from the full zeolite model are converted to Si-H link-atom bonds in a manner prescribed elsewhere.<sup>1</sup>

### b. QM/MM energy breakdown for selected structures

The QM/MM electronic energy is obtained by the sum of the QM electronic energy (in the presence of MM point charges) with the MM energy obtained from a force field of the CHARMM variety. In a previous study<sup>2</sup> we have shown that a T5 QM region is sufficient for obtaining chemical accurate heats of adsorption and activation barriers, and that there is little advantage to using a larger QM region when using an electrostatic embedding QM/MM method. Since most zeolite T-atoms are present only in the MM calculation, many zeolite-guest interactions are calculated with the MM force field. A breakdown of all contributions to the QM/MM electronic energy for the methanol (ads) structure is provided below.

	QM	LJ	TOTAL	
Zeolite (s)	-1816.721497	109.0237186	-1707.697779	[Hartree]
Methanol (ads)	-1932.489718	109.014909	-1823.474809	[Hartree]
Methanol (g)	-115.7307241	0	-115.7307241	[Hartree]
$\Delta E$ (ads)	-23.52940044	-5.528149191	-29.05754963	[kcal mol <sup>-1</sup> ]

## II. Calculation of thermodynamic quantities

Electronic energies obtained from QM/MM calculations are zero-point corrected and converted to thermodynamic quantities using a rigid-rotor harmonic oscillator (RRHO)-type partition function. The HO vibrational partition function has been replaced by the weighted vibrational partition function of Grimme.<sup>3</sup> A feature of this method is a more physically-realistic treatment of vibrational modes resembling frustrated translational and rotational motion exhibited by the guest molecule in the zeolite lattice. The total partition function for each vibrational mode is a weighted sum of a free rotor partition function and a standard harmonic-oscillator partition function such that modes with a vibrational frequency below a certain threshold ( $200\text{ cm}^{-1}$ ) are treated primarily as free rotations. The individual partition functions are weighted with a switching function such that the total partition function is a smooth, continuous function of vibrational frequency. A comparison of this method with the traditional RRHO method is given in SI Section IV. Molecules adsorbed from the gas phase into the zeolite are treated as immobile.

## III. Comparison between step-wise and concerted mechanism

Two mechanisms have been proposed for alkene methylation. The first is the concerted mechanism. In this case, methanol adsorbs molecularly at a Brønsted acid site and then reacts with adsorbed alkene to produce the next higher alkene and water. The alternative is the stepwise mechanism. The first step in this scheme is the same as that for the concerted mechanism; however, in this case, the adsorbed methanol next undergoes reaction to form methoxide species and water. Methylation occurs by reaction of the methoxide species with adsorbed alkene to form the next highest alkene. A comparison

between the enthalpy and free energy profiles of concerted and stepwise methylation mechanisms at 623 K and 1 bar total pressure are given in figures S1 and S2. In figure S1, we observe that the rate-determining dehydration reaction responsible for methoxide formation in the stepwise mechanism has a significantly higher activation enthalpy compared with the rate-determining methylation step of the concerted mechanism. The loss of entropy associated with adsorbing molecules from the gas phase increases the free energy of activation for both mechanisms, although it has a smaller effect on the stepwise mechanism since there is only one molecule of gas adsorbed before methoxide formation. At these conditions, it is predicted that both mechanism operate competitively since the apparent activation free energy values are calculated to be within  $0.1 \text{ kcal mol}^{-1}$ . Figure S3 shows the effects of pressure on the free energy of activation of the methoxide formation step (stepwise mechanism), the free energy of activation of methylation (concerted), and the free energy of adsorption of methanol. There is a logarithmic term describing the pressure dependence present in the RRHO translational entropy correction. At higher pressure, the desorption of water to the gas-phase is disfavored due to this term such that the difference in apparent activation free energy is now approximately  $4 \text{ kcal mol}^{-1}$  in favor of the concerted pathway and a 25X difference in turnover frequency.

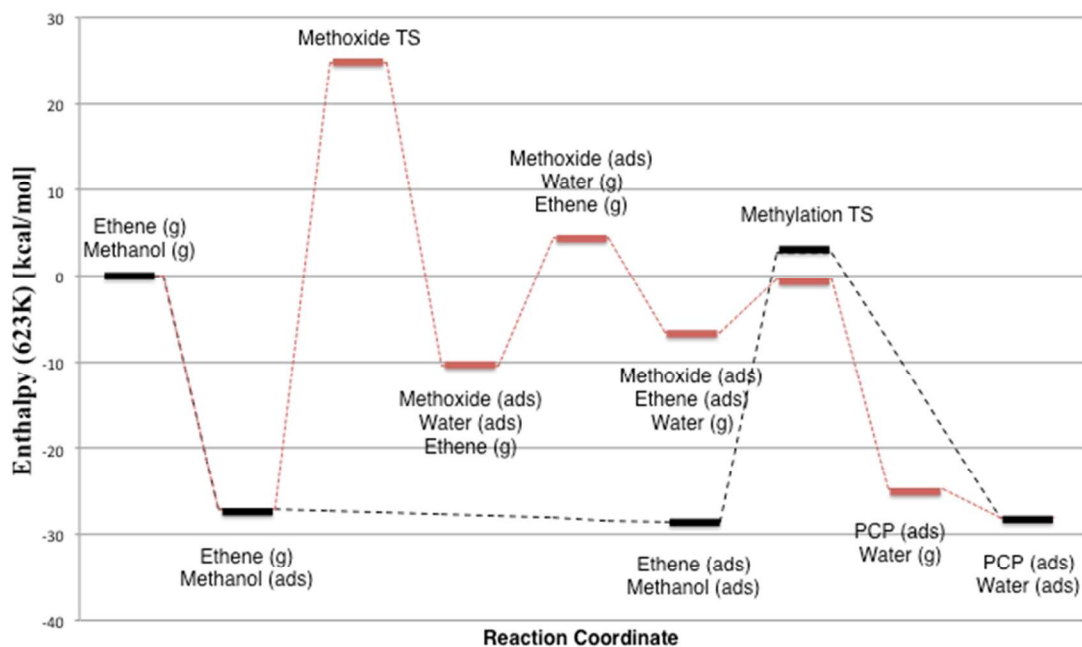


Figure S1. Enthalpy (623K) [kcal mol<sup>-1</sup>] diagram calculated at the  $\omega$ B97X-D/6-31G(d,p)// $\omega$ B97X-D/6-311++G(3df,3pd) level of theory describing the concerted (black) and stepwise (red) pathways of ethene methylation by methanol in H-MFI.

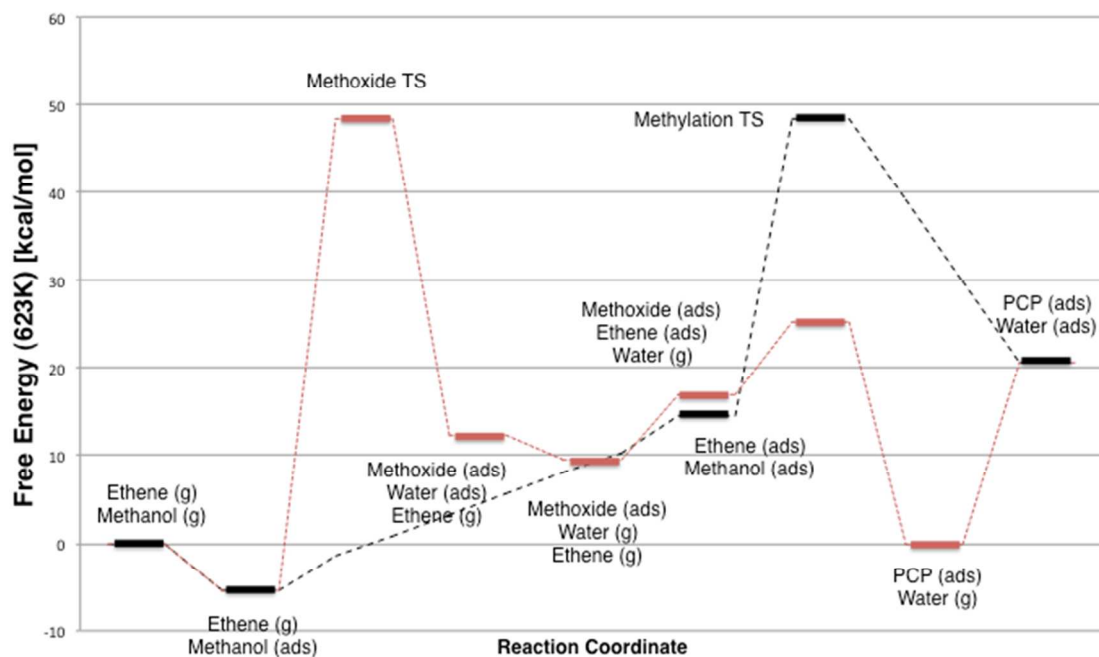


Figure S2. Free Energy (623K) [kcal mol<sup>-1</sup>] diagram calculated at the  $\omega$ B97X-D/6-31G(d,p)// $\omega$ B97X-D/6-311++G(3df,3pd) level of theory describing the concerted (black) and stepwise (red) pathways of ethene methylation by methanol in H-MFI.

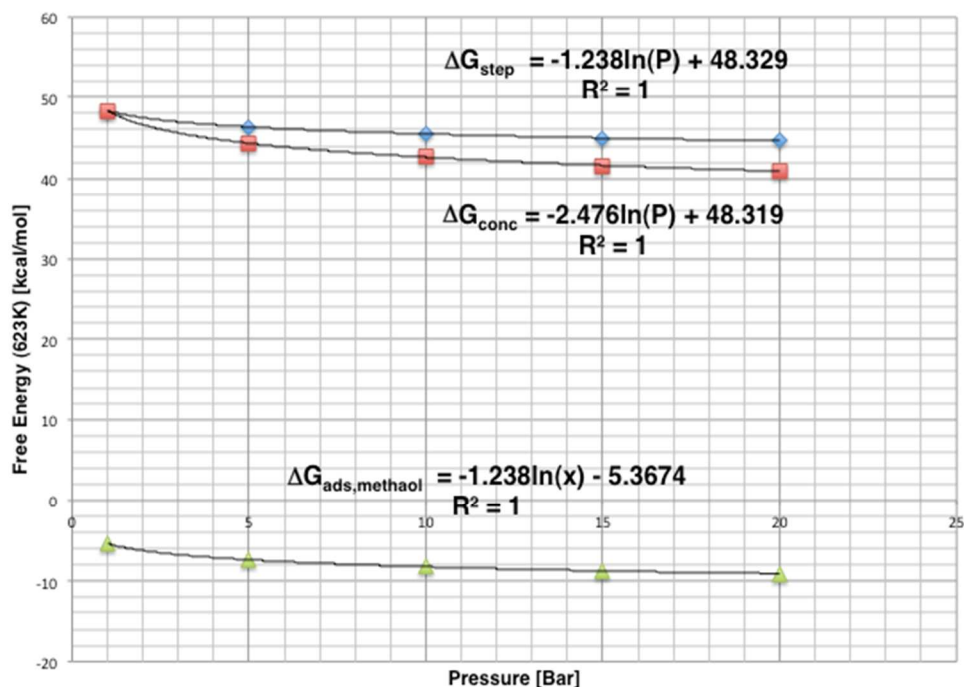


Figure S3. Free Energy (623K) [kcal mol<sup>-1</sup>] of activation as calculated at various pressures, at the  $\omega$ B97X-D/6-31G(d,p)// $\omega$ B97X-D/6-311++G(3df,3pd) level of theory for the concerted mechanism (red square) and stepwise mechanism (blue triangle) of ethene methylation by methanol in H-MFI. Also shown is the free energy of adsorption of methanol (green triangle) calculated at various pressures.

#### IV. Tabulated enthalpy and free energy values

##### a. Ethene Methylation (concerted) – Grimme-corrected RRHO

	$\Delta E$ (0 K)	$\Delta H(623K)$	$\Delta G(623K)$	Imaginary Freq
Zeolite (s)	0.00	0.00	0.00	
Methanol (ads)	-29.06	-28.12	-4.20	
Methanol + Ethene (ads)	-33.64	-33.67	14.50	
Ethene Methylation TS	-2.69	-2.44	48.22	-435 cm <sup>-1</sup>
PCP (ads)	-33.46	-33.23	20.52	
PCProt TS	-28.32	-26.29	30.61	-72 cm <sup>-1</sup>
PCProt (ads)	-32.00	-28.40	26.76	
Elimination TS	-30.51	-27.13	30.39	-179 cm <sup>-1</sup>
Propene + Water (ads)	-57.31	-54.55	2.42	
PCP (ads)	-33.46	-33.23	20.52	
2PCC TS	-26.67	-24.91	33.89	
2PCC (ads)	-46.89	-44.91	10.09	
Elimination TS	-30.91	-29.16	28.09	-118 cm <sup>-1</sup>
Propene + Water (ads)	-57.31	-54.55	2.42	
PCP (ads)	-33.46	-33.23	20.52	
Elimination TS	-25.50	-25.22	31.32	-1096 cm <sup>-1</sup>
Cyclopropane + Water (ads)	-48.47	-45.22	11.91	
PCProt (ads)	-32.00	-28.40	26.76	
Alkoxide Formation TS	-33.97	-31.40	31.19	-235 cm <sup>-1</sup>
1-Propoxide + Water (ads)	-40.03	-34.90	21.39	
PCProt (ads)	-32.00	-28.40	26.76	
Alcohol Formation TS	-24.51	-22.12	34.29	-163 cm <sup>-1</sup>
1-Propanol (ads)	-69.68	-64.68	-4.77	
1-Propanol (g)	-30.56	-27.25	-4.32	
Cyclopropane + Water (g)	-10.20	-9.57	-7.54	
Propene + Water (g)	-15.80	-15.49	-15.64	

Table S1. Relative Electronic Energy, Enthalpy, and Free Energy values (kcal mol<sup>-1</sup>) calculated at the  $\omega$ B97X-D/6-31G(d,p)// $\omega$ B97X-D/6-311++G(3df,3pd) level of theory for intermediates and transition states formed during Ethene Methylation in H-MFI.

**b. Ethene Methylation (concerted) – RRHO**

	$\Delta E$ (0 K)	$\Delta H(623K)$	$\Delta G(623K)$	Imaginary Freq
Zeolite (s)	0.00	0.00	0.00	
Methanol (ads)	-29.06	-27.63	-3.80	
Methanol + Ethene (ads)	-33.64	-29.11	12.69	
Ethene Methylation TS	-2.69	1.45	45.51	-435 cm <sup>-1</sup>
PCP (ads)	-33.46	-28.66	12.87	
PCProt TS	-28.32	-25.30	18.68	-72 cm <sup>-1</sup>
PCProt (ads)	-32.00	-26.75	14.66	
Elimination TS	-30.51	-28.15	19.44	-179 cm <sup>-1</sup>
Propene + Water (ads)	-57.31	-53.25	-9.63	
PCP (ads)	-33.46	-28.66	12.87	
2PCC TS	-26.67	-23.65	20.34	
2PCC (ads)	-46.89	-43.51	-0.50	
Elimination TS	-30.91	-28.17	20.09	-118 cm <sup>-1</sup>
Propene + Water (ads)	-57.31	-53.25	-9.63	
PCP (ads)	-33.46	-28.66	12.87	
Elimination TS	-25.50	-23.71	20.38	-1096 cm <sup>-1</sup>
Cyclopropane + Water (ads)	-48.47	-43.35	-0.24	
PCProt (ads)	-32.00	-26.75	14.66	
Alkoxide Formation TS	-27.69	-23.55	21.12	-235 cm <sup>-1</sup>
1-Propoxide + Water (ads)	-40.03	-34.80	12.86	
PCProt (ads)	-32.00	-26.75	14.66	
Alcohol Formation TS	-24.51	-20.44	22.59	-163 cm <sup>-1</sup>
1-Propanol (ads)	-69.68	-63.76	-12.80	
1-Propanol (g)	-30.56	-27.25	-4.32	
Cyclopropane + Water (g)	-10.20	-9.57	-7.54	
Propene + Water (g)	-15.80	-15.49	-15.64	

Table S2. Relative Electronic Energy, Enthalpy, and Free Energy values (kcal mol<sup>-1</sup>) calculated at the  $\omega$ B97X-D/6-31G(d,p)// $\omega$ B97X-D/6-311++G(3df,3pd) level of theory for intermediates and transition states formed during Ethene Methylation in H-MFI. PCP = protonated cyclopropane carbocation and 2PCC = 2-propyl carbocation. Imaginary frequencies characterizing each transition state are given.

**c. Propene Methylation (concerted) - Grimme-corrected RRHO**

	$\Delta E$ (0K)	$\Delta H(623K)$	$\Delta G(623K)$	Imaginary Freq
Zeolite (s)	0.00	0.00	0.00	
Methanol (ads)	-29.06	-28.12	-4.12	
Methanol + Propene (ads)	-40.41	-38.53	14.16	
Propene Methylation TS	-12.14	-9.60	42.31	-483 cm <sup>-1</sup>
mPCP (ads)	-39.55	-37.47	15.53	
2BCC TS	-31.55	-31.48	19.20	-71 cm <sup>-1</sup>
2BCC (ads)	-33.38	-33.04	18.13	
Elimination TS	-27.47	-26.70	25.26	-165 cm <sup>-1</sup>
trans-Butene + Water (ads)	-60.16	-57.79	-5.95	
trans-Butene + Water (g)	-15.06	-15.07	-13.34	

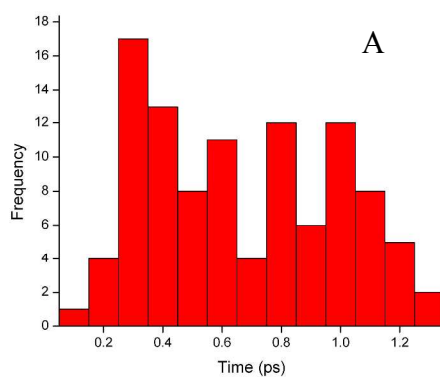
Table S3. Relative Electronic Energy, Enthalpy, and Free Energy values (kcal mol<sup>-1</sup>) calculated at the  $\omega$ B97X-D/6-31G(d,p)// $\omega$ B97X-D/6-311++G(3df,3pd) level of theory for intermediates and transition states formed during Propene Methylation in H-MFI. mPCP = protonated methyl-cyclopropane carbocation and 2BCC = 2-butyl carbocation. Imaginary frequencies characterizing each transition state are given.

**d. Propene Methylation (concerted) – RRHO**

	$\Delta E$ (0K)	$\Delta H(623K)$	$\Delta G(623K)$	Imaginary Freq
Zeolite (s)	0.00	0.00	0.00	
Methanol (ads)	-29.06	-27.72	-3.80	
Methanol + Propene (ads)	-40.41	-36.23	9.10	
Propene Methylation TS	-12.14	-8.22	41.40	-483 cm <sup>-1</sup>
mPCP (ads)	-39.55	-36.87	12.56	
2BCC TS	-31.55	-27.48	14.52	-71 cm <sup>-1</sup>
2BCC (ads)	-33.38	-30.94	12.43	
Elimination TS	-27.47	-24.68	28.29	-165 cm <sup>-1</sup>
trans-Butene + Water (ads)	-60.16	-56.28	-9.82	
trans-Butene + Water (g)	-15.06	-15.07	-13.34	

Table S4. Relative Electronic Energy, Enthalpy, and Free Energy values (kcal mol<sup>-1</sup>) calculated at the  $\omega$ B97X-D/6-31G(d,p)// $\omega$ B97X-D/6-311++G(3df,3pd) level of theory for intermediates and transition states formed during Propene Methylation in H-MFI. mPCP = protonated methyl-cyclopropane carbocation and 2BCC = 2-butyl carbocation. Imaginary frequencies characterizing each transition state are given.

## V. Quasiclassical trajectory reactive event statistics



VI.

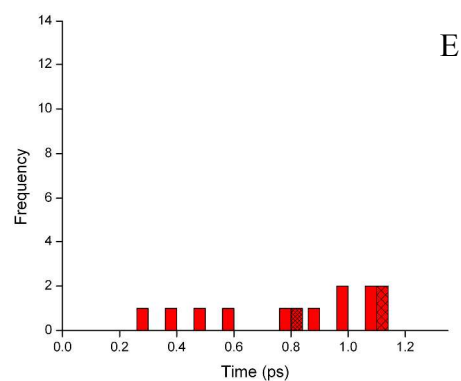
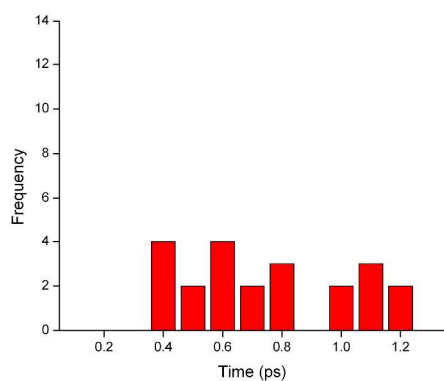
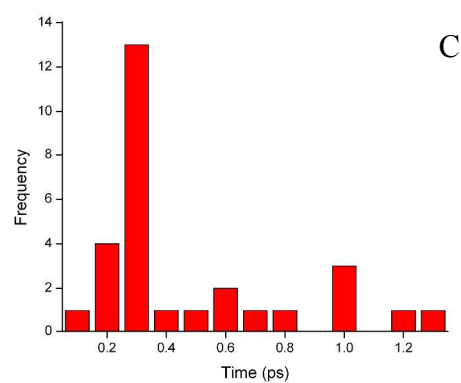
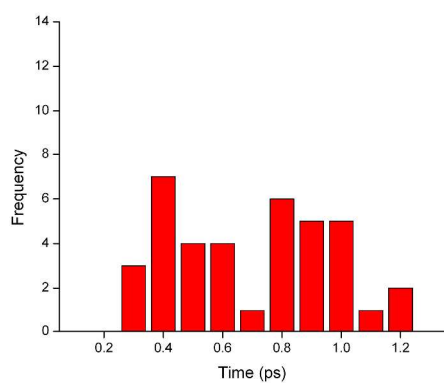


Figure S4. Frequency of reaction events observed during QCT trajectories launched at the Ethene Methylation transition state. (a) All  $\text{PCP}^+$  decomposition events (b) 1-Propanol (c) Cyclopropane (d) 1-Propoxide and (e) Propene (solid) and 2-Propanol (thatched).

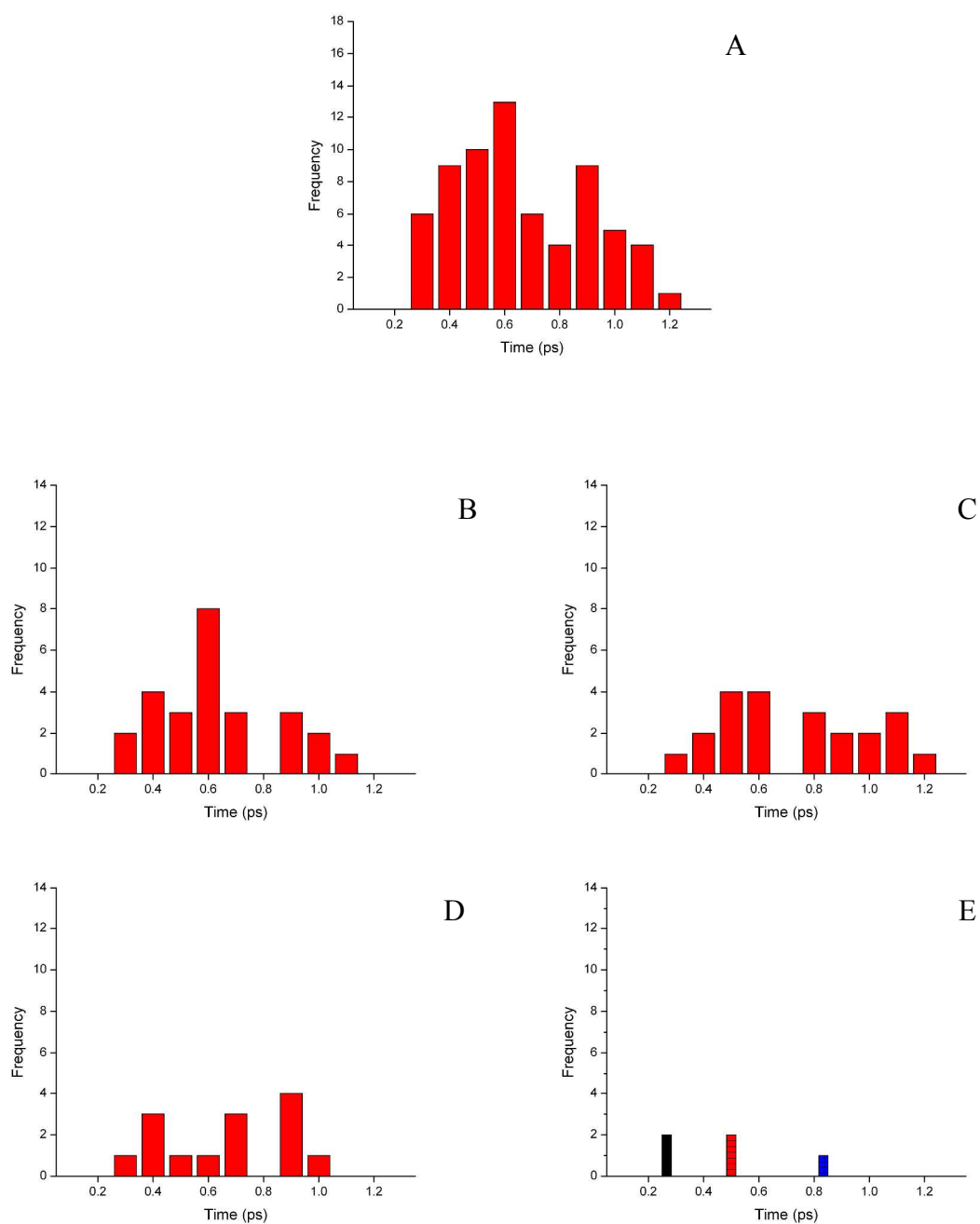


Figure S5. Frequency of reaction events observed during QCT trajectories launched at the Propene Methylation transition state. (A) Total m-PCP<sup>+</sup> decomposition events (B) 1-Butene (C) (cis+trans)-2-Butene (D) 2-Butanol and (E) m-CP (0.25 ps), 1-Butoxide (0.5 ps), and 1-Butanol (0.8 ps).

## Supporting Information References

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<sup>1</sup> Zimmerman, P.M.; Head-Gordon, M.; Bell, A.T. Selection and Validation of Charge and Lennard-Jones Parameters for QM/MM Simulations of Hydrocarbon Interactions with Zeolites. *J. Chem. Theor. Comp.* **2011**, 7, 1695-1703.

<sup>2</sup> Gomes, J.; Zimmerman, P.M.; Head-Gordon, M.; Bell, A.T. Accurate Prediction of Hydrocarbon Interactions with Zeolites Utilizing Improved Exchange-Correlation Functionals and QM/MM Methods: Benchmark Calculations of Adsorption Enthalpies and Application to Ethene Methylation by Methanol. *J. Phys. Chem. C* **2012**, 116, 15406-15414.

<sup>3</sup> Grimme, S. Supramolecular binding thermodynamics by dispersion-corrected density functional theory. *Chem. Eur. J.* **2012**, 18, 9955-9964.