

Supporting information

Title: Theoretical Insight on How the First C-C Bond Forms in the Methanol-to-Olefin Process Catalysed by HSAPO-34

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1. The active $\text{CH}_3\text{OCH}_2^+$ and C2 species formation

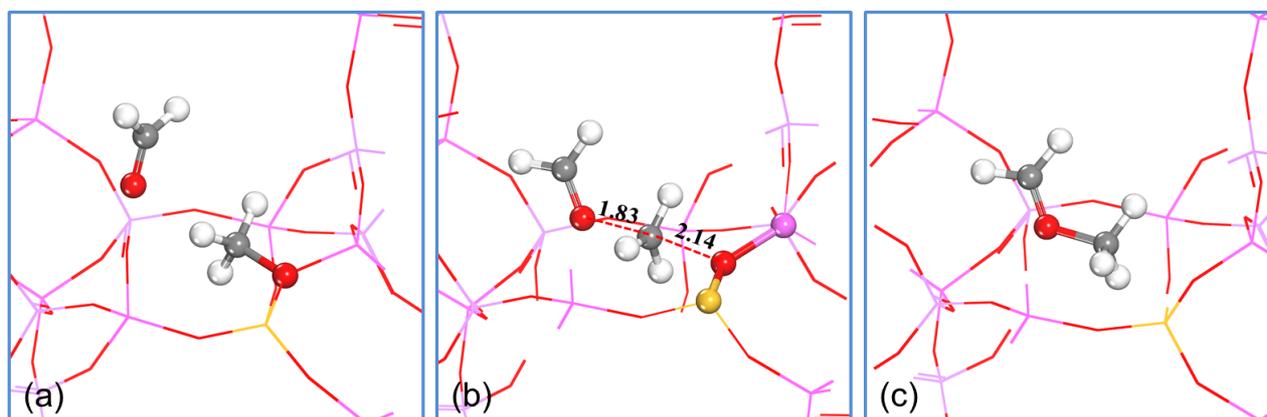


Fig. S1 The active $\text{CH}_3\text{OCH}_2^+$ obtained from the reaction between formaldehyde and $\text{Z}(\text{O})\text{-CH}_3$. (a) The structure of the initial state; (b) The structure of the transition state, in which the distances between C atom and two oxygen atoms are 1.83 and 2.14 Å, respectively; (c) The optimized $\text{CH}_3\text{OCH}_2^+$ in the final state.

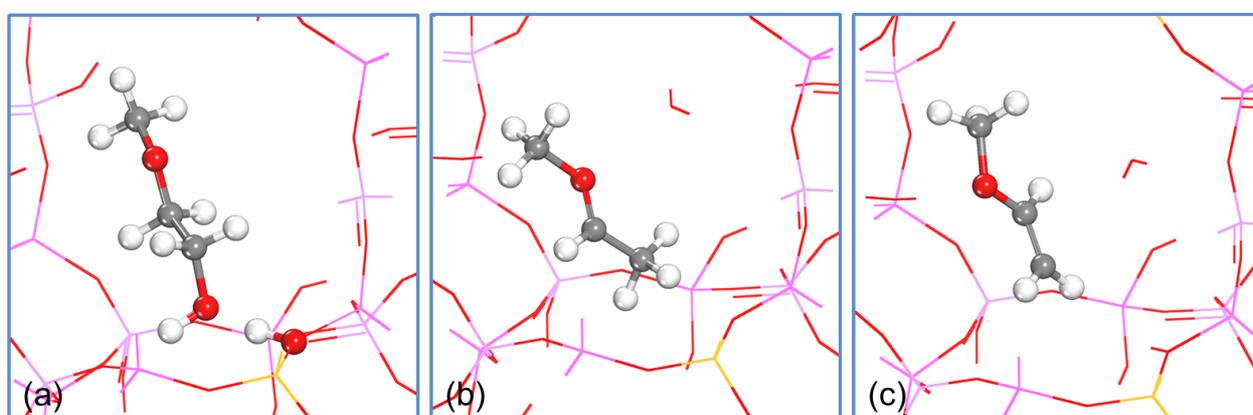


Fig. S2 The optimized structures of different C2 intermediates. (a) $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, formed from the reaction of $\text{CH}_3\text{OCH}_2^+$ and CH_3OH . (b) $\text{CH}_3\text{OCH}^+\text{CH}_3$, which was produced from the dehydration of the protonated

CH₃OCH₂CH₂OH. (c) Methyl vinyl ether (CH₃OCH=CH₂), generated from the deprotonation of CH₃OCH⁺CH₃.

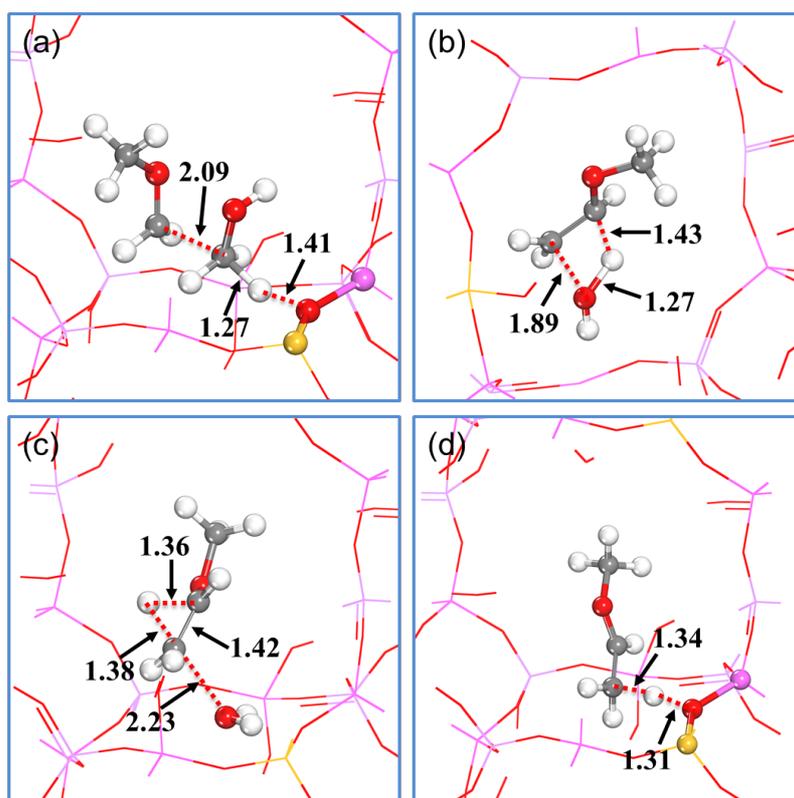


Fig. S3 Structures of some important transition state. (a) CH₃OCH₂CH₂OH formation from the reaction of CH₃OCH₂⁺, CH₃OH and Z(O)-H. (b) The transition state of the direct dehydration of CH₃OCH₂CH₂OH. (c) The transition state of CH₃OCH⁺CH₃ formation from the indirect dehydration of the protonated CH₃OCH₂CH₂OH₂. (d) Methyl vinyl ether (CH₃OCH=CH₂), generated from the deprotonation of CH₃OCH⁺CH₃.

2. The Brønsted acid site

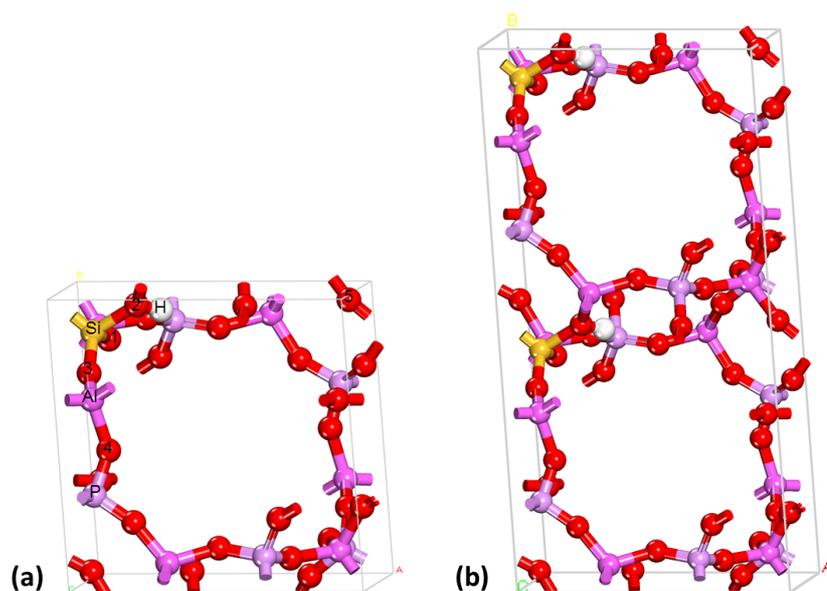


Fig. S4 (a) The optimized structure of HSAPO-34 unit cell. The numbers represent different adsorption sites of hydrogen. (b) Structure of the supercell (1 × 2 × 1) that was used in our simulation.

Table S1 Comparison between the total energy results and those from the free energies for the reactions listed on the left column; the free energies were obtained at 670 K. ΔH and E_a represent the enthalpy changes and the energy barriers of the reactions from the total energy calculations, respectively. ΔG_1 and G_{a1} stand for the free energy changes and free energy barriers of the reactions, respectively, which were obtained from the enthalpies with the vibrational entropies and the corrections of internal energies and ZPE.¹⁻⁴ ΔG_2 are the free energy changes of the reactions with the corrections of internal energies and ZPE, which include the translational, rotational and vibrational entropies for the gas-phase molecules and the vibrational entropies for the adsorbates. G_{a2} are the free energy barriers from the enthalpies with the entropies and the corrections of internal energies and ZPE, in which the entropy of each transition state was approximately obtained from its vibrational entropy, as well as 2/3 of the translational entropy and full rotational entropy of the corresponding initial state.⁵ The unit is eV.

Reactions	ΔH	E_a	ΔG_1	G_{a1}	ΔG_2	G_{a2}
$Z\text{-CH}_3 + \text{CH}_3\text{OCH}_3 \rightarrow Z^- + \text{CH}_4 + \text{CH}_3\text{OCH}_2^+$	0.92	1.66	1.03	1.38	-0.58	1.79
$Z\text{-CH}_3 + \text{CH}_3\text{OH} \rightarrow Z\text{-H} + \text{CH}_4 + \text{HCHO}$	-0.37	1.31	-0.37	1.35	-1.94	1.75
$Z\text{-CH}_3 + \text{HCHO} \rightarrow Z^- + \text{CH}_3\text{OCH}_2^+$	0.71	1.17	0.24	0.84	0.08	1.23
$\text{CH}_4 + \text{HCHO} \rightarrow \text{CH}_3\text{CH}_2\text{OH}$	-1.04	1.83	-1.18	1.96	-0.52	1.94
$Z^- + \text{CH}_3\text{OCH}_2^+ + \text{CH}_3\text{OH} \rightarrow Z\text{-H} + \text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$	-3.03	0.56	-2.79	0.65	-0.50	1.44
$Z\text{-CH}_3 + \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \rightarrow Z^- + \text{CH}_3\text{OCH}_2\text{CH}_3 + \text{H}_3\text{O}^+$	0.38	2.73	0.64	2.78	0.57	3.55
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{OCH}=\text{CH}_2 + \text{H}_2\text{O}$		3.84		3.34		3.76
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}_2^+ \rightarrow \text{CH}_3\text{OC}^+\text{HCH}_3 + \text{H}_2\text{O}$	-0.45	1.01	-1.00	0.76	-2.42	1.18
$Z^- + \text{CH}_3\text{OC}^+\text{HCH}_3 \rightarrow Z\text{-H} + \text{CH}_3\text{OCH}=\text{CH}_2$	-0.35	0.26	-0.42	0.23	-0.41	1.01
$\text{CH}_3\text{OCH}_2\text{CH}_2^+ \rightarrow \text{CH}_2\text{OC}^+\text{HCH}_3$	-1.77		-1.90		-1.89	
$Z^- + \text{CH}_3\text{OC}^+\text{HCH}_3 + \text{CH}_3\text{OCH}=\text{CH}_2 \rightarrow Z\text{-H} + \text{CH}_3\text{OCH}(\text{CH}_3)\text{CH}_2\text{C}^+\text{HOCH}_3$		0.14		0.15		0.97
$Z\text{-CH}_3 + \text{CH}_3\text{OH} \rightarrow Z^- + \text{CH}_4 + \text{}^+\text{CH}_2\text{OH}$	1.98		1.61		0.02	
$Z\cdot + \text{CH}_3\text{OCH}_2\cdot \rightarrow Z^- + \text{CH}_3\text{OCH}_2^+$	-3.59		-3.55		-3.55	
$Z\text{-CH}_3 \rightarrow Z^- + \text{CH}_3^+$	3.35		3.07		1.48	

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