Supplementary Information

Methanol-to-Hydrocarbon Initiation Reactions over a Zeolite Catalyst: Reactive Molecular Dynamics Simulations

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Force Field Errors in the Estimation of Zeolite Framework Parameters

Table S1. Percentage errors of lattice parameters determined using the force field developed in this work. Reference values are from the International Zeolite Association database [1].

	% Error					
Framework	**Length a**	**Length b**	**Length c**	**Angle α**	**Angle β**	**Angle γ**
FER	2.36	2.36	2.36	0.00	0.00	0.00
IFR	0.16	0.16	2.36	0.00	0.00	0.00
MFI	1.90	1.90	1.91	0.00	0.00	0.00
TON	0.52	0.52	0.52	0.00	0.00	0.00

Water-assisted Proton Transfer

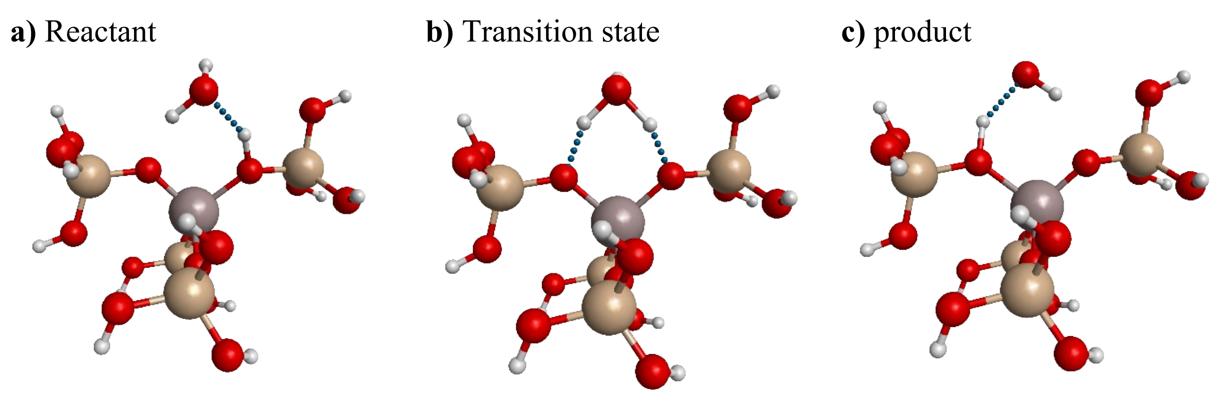

Figure S1. Water-assisted proton transport in the first coordination sphere of an aluminum atom. This reaction was found significant in the reactive simulation of the initiation reactions of the methanol-to-hydrocarbon process, and the force field well reproduced the potential energy barrier

(7.63 kcal·mol^{-1}) estimated using density functional theory (7.28 kcal·mol^{-1}) at the ωB97X-D/6-311G(d,p) level, as shown in Figure S2. This system is built upon the works of Ryder et al. [2] and Joshi et al. [3]. White, red, brown, and dark pink spheres represent hydrogen, oxygen, silicon, and aluminum atoms, respectively.

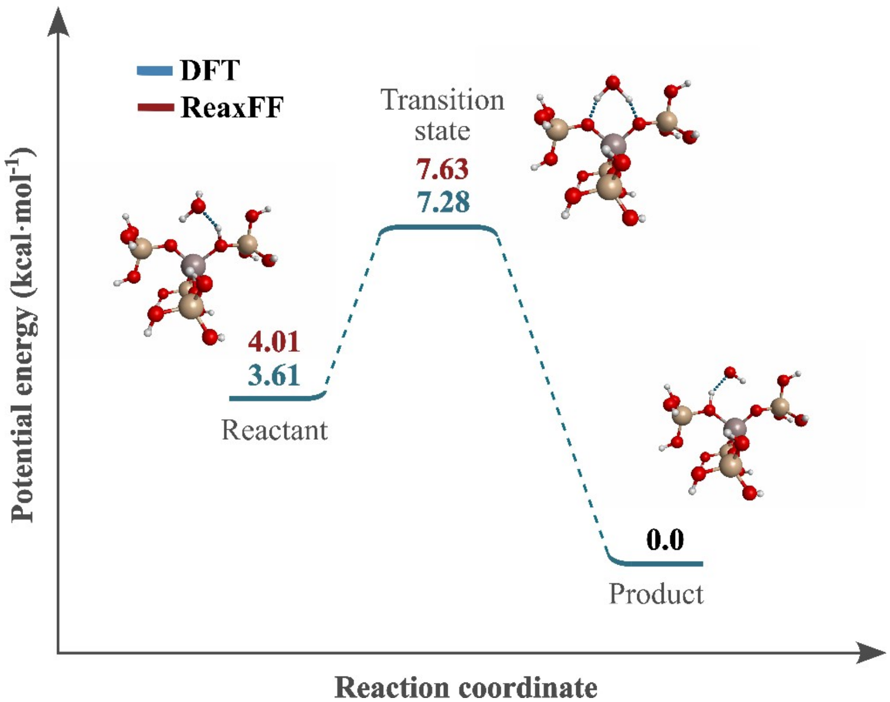

Figure S2. Density functional theory (DFT) and ReaxFF potential energy diagram of the water-mediated proton transport as a function of the forming ZO-H bond length. The transition state energy is 7.28 and 7.63 kcal·mol^{-1} for DFT and ReaxFF, respectively. The asymmetry of the reaction pathway is attributed to the differences of the binding energies in the reactant and product [3].

Effect of Water Loads at 1000 K

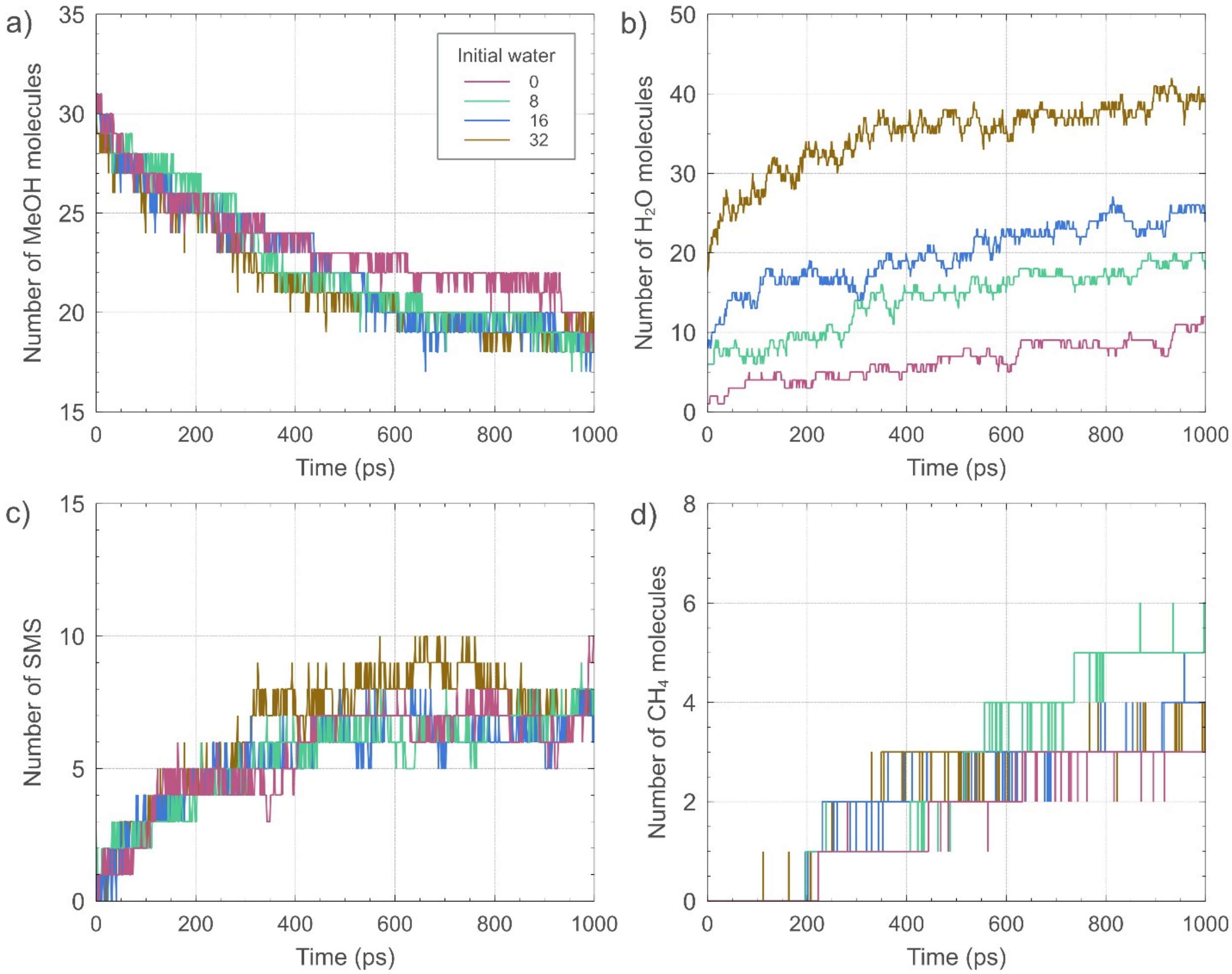

Figure S3. Number profiles of (a) methanol, (b) water, (c) surface methoxy species (SMS), and (d) methane as a function of time of simulations conducted at 1000 K and the initial water loads of 0, 8, 16, and 32.

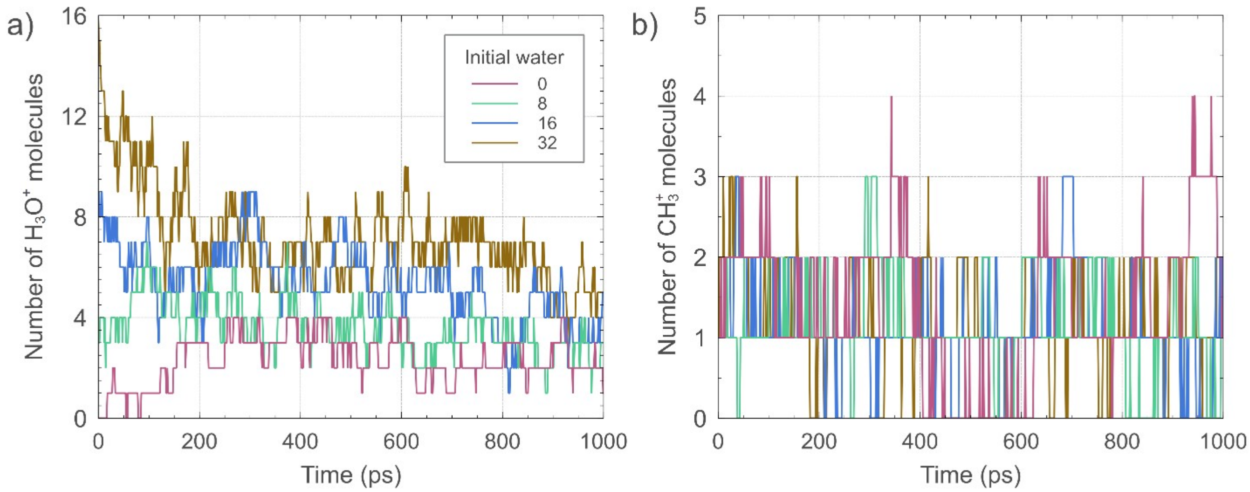

Figure S4. Number profiles of the (a) hydronium ions and (b) methyl cations species as a function of time of simulations conducted at 1000 K and the initial water loads of 0, 8, 16, and 32.

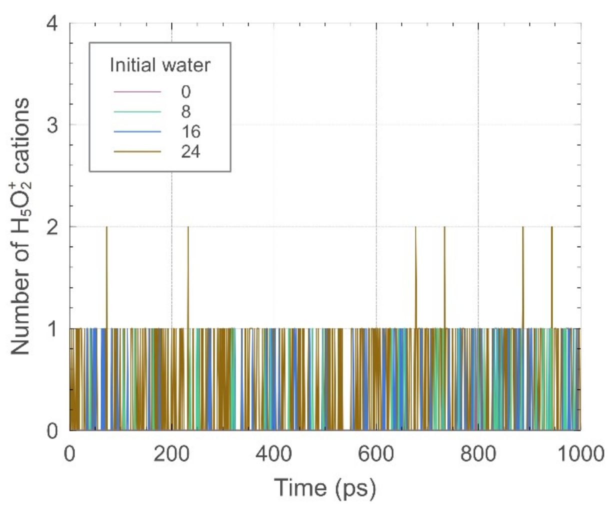

Figure S5. Number profiles of the Zundel cation as a function of time of simulations conducted at 800 K and the initial water loads of 0, 8, 16, and 32.

References

[1] Structure Commission of the International Zeolite Association, Database of Zeolite Structures, 2022.

[2] J.A. Ryder, A.K. Chakraborty, A.T. Bell, Density Functional Theory Study of Proton Mobility in Zeolites: Proton Migration and Hydrogen Exchange in ZSM-5, J. Phys. Chem. B 104 (30) (2000) 6998–7011.

[3] K.L. Joshi, G. Psofogiannakis, A.C.T. van Duin, S. Raman, Reactive molecular simulations of protonation of water clusters and depletion of acidity in H-ZSM-5 zeolite, Phys. Chem. Chem. Phys. 16 (34) (2014) 18433–41.