Supporting Information of

Selective Conversion of Syngas over Zn sites Grafted on ZSM-5 Zeolite: Mechanistic Insights from DFT Modeling

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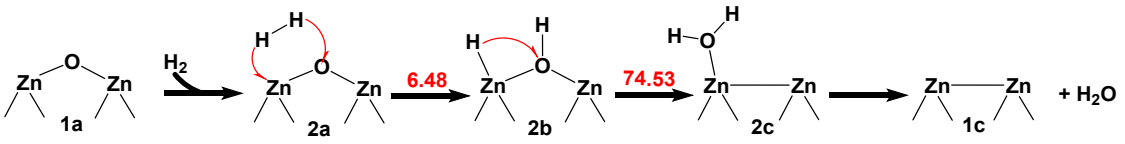

Figure S1. The reaction pathway and barriers of hydrogen reduction of $[Zn\text{-}O\text{-}Zn]^{2+}$.

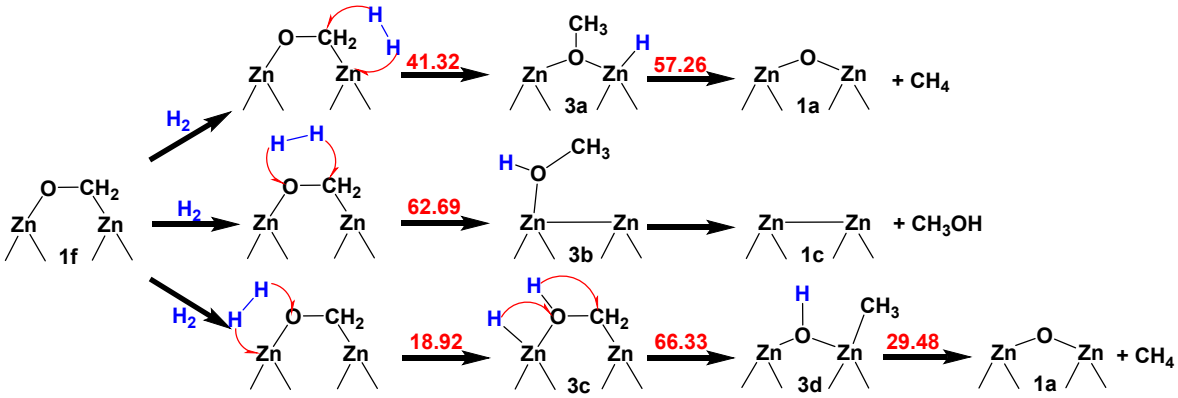

Figure S2. The reaction pathway and barriers of hydrogenation of 1i $[Zn\text{-}OCH_2\text{-}Zn]^{2+}$

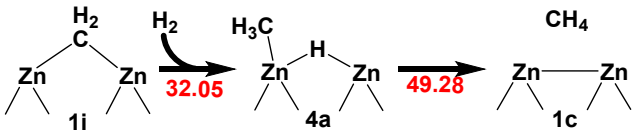

Figure S3. The reaction pathway and barriers of CH_4 formation based on 1i.

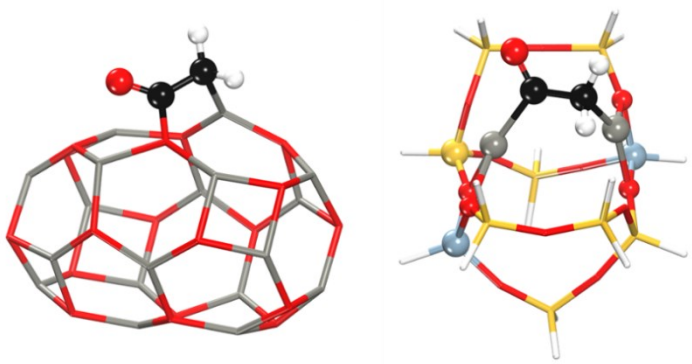

Figure S4. The optimized structures of ketene adsorbed on (a) bulk ZnO (modeled by $(ZnO)_{18}$ cluster) and (b) $[Zn\text{-}Zn]^{2+}$ using B3LYP-D3/6-31G(d, p)/LanL2DZ method, and the interaction energy between ketene and $(ZnO)_{18}$ (or $[Zn\text{-}Zn]^{2+}$) with consideration of basis set superposition error (BSSE) by counterpoise correction using B3LYP-D3/def2-TZVP method. The $(ZnO)_{18}$ cluster was constructed based on the Reference. [M. Chen, T. P. Straatsma, Z. Fang, D. A. Dixon, *J Phys Chem C* **2016**, *120*, 20400-20418.]

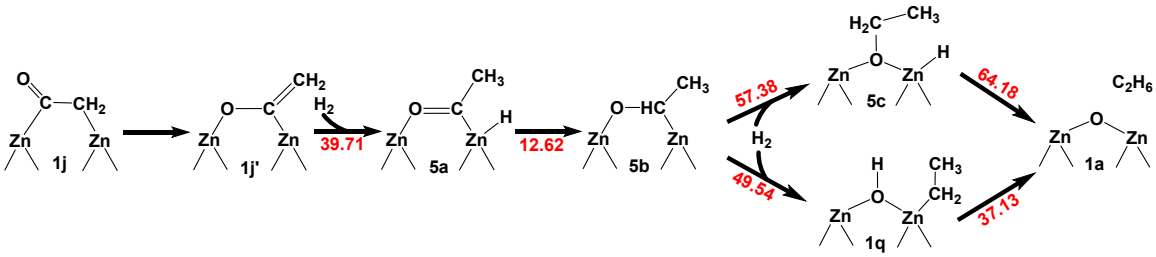

Figure S5. The other reaction pathways and barriers of 1j hydrogenation *via* 1j' (the isomer of 1j).

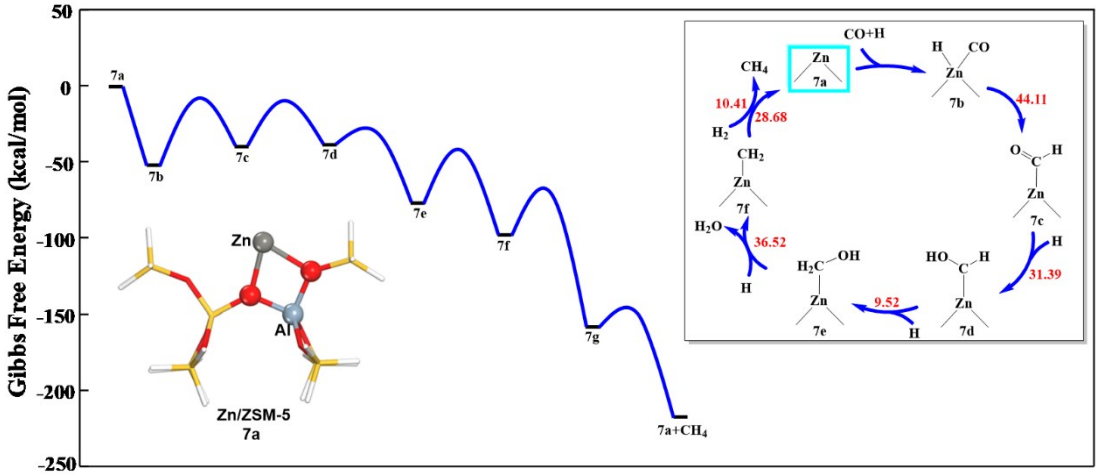

Figure S6. The single Zn^{2+} site graft on 8T ZSM-5 cluster model (Zn/ZSM-5), the Gibbs free energy and reaction cycle of CO hydrogenation to methane over Zn/ZSM-5. Values in red are the free energy barrier of each step.