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-O-Zn]$^{2+}$.

Figure S2. The reaction pathway and barriers of hydrogenation of 1i [Zn-OCH$_2$-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)\textsubscript{18} cluster) and (b) [Zn-Zn]\textsuperscript{2+} using B3LYP-D3/6-31G(d, p)/LanL2DZ method, and the interaction energy between ketene and (ZnO)\textsubscript{18} (or [Zn-Zn]\textsuperscript{2+}) with consideration of basis set superposition error (BSSE) by counterpoise correction using B3LYP-D3/def2-TZVP method. The (ZnO)\textsubscript{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\textsuperscript{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.