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Supporting Information for

Formation Mechanism of the Initial C-C Chain in the Ethanol Synthesis on γ-AlOOH (100)

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Table S1 Adsorption energy (kJ mol^{-1}) and key geometrical parameters (Å) of possible species involved in ethanol synthesis from mixed methanol and syngas.

Species	E_{ads}	Configuration	Key parameters
H	417.4	O_{2b}	O_{2b} – H: 0.980
O	559.6	Al_{IVa} and O_{2a}	Al_{IVa} – O: 1.815 O_{2a} – O: 1.497
OH	428.4	Al_{IVa} via O	Al_{IVa} – O: 1.709
CO	272.4	Al_{IVa} via O and O_{2a} via C	Al_{IVa} – O: 1.796 O_{2a} – C: 1.303 C – O: 1.306
CH_3	293.2	O_{2b} via C	O_{2b} – C: 1.351
CH_3O	345.6	Al_{IVa} via O	Al_{IVa} – O: 1.740
CH_3CO	504.7	Al_{IVa} via O and O_{2a} via C	Al_{IVa} – O: 1.819 O_{2a} – C: 1.273 C – O: 1.279
CH_3OCH_3	158.3	Al_{IVa} via O	Al_{IVa} – O: 1.905
CH_3CHO	325.8	Al_{IVa} via O and O_{2a} via C	Al_{IVa} – O: 1.697 O_{2a} – C: 1.410 C – O: 1.403
CH_3CH_2O	362.2	Al_{IVa} via O	Al_{IVa} – O: 1.719
CH_3CHOH	462.7	Al_{IVa} via O and O_{2a} via C	Al_{IVa} – O: 1.831 O_{2a} – C: 1.332 C – O: 1.678
C_2H_5OH	210.2	Al_{IVa} via O	Al_{IVa} – O: 1.865
H_2	19.0	upon Al_{IVa}	Al_{IVa} – H_1: 2.127 Al_{IVa} – H_2: 1.125
CH_4	33.3	upon Al_{IVa}	Al_{IVa} – C: 2.442
C_2H_6	36.4	upon Al_{IVa}	Al_{IVa} – C_1: 2.772 Al_{IVa} – C_2: 3.370

Figure S1. The unit cell of γ-AlOOH bulk. Gold spheres represent Al atoms, pink spheres represent O atoms and pale blue spheres represent H atoms.

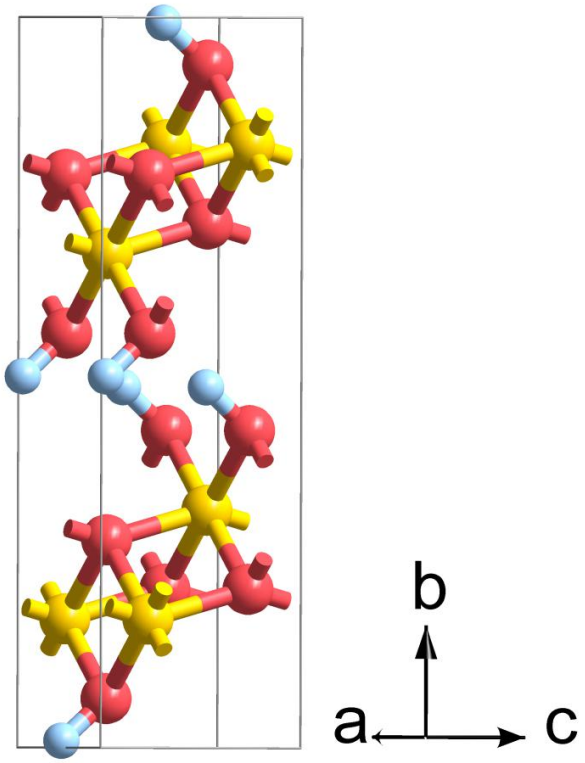

Figure S2. The most stable adsorption configurations of all possible species involved in the pathways of ethanol synthesis over γ-AlOOH (100) surface. Gray spheres represent C atoms, light blue spheres represent H atoms from H_2 or CH_3OH and brown spheres represent O atoms from CH_3OH or CO.

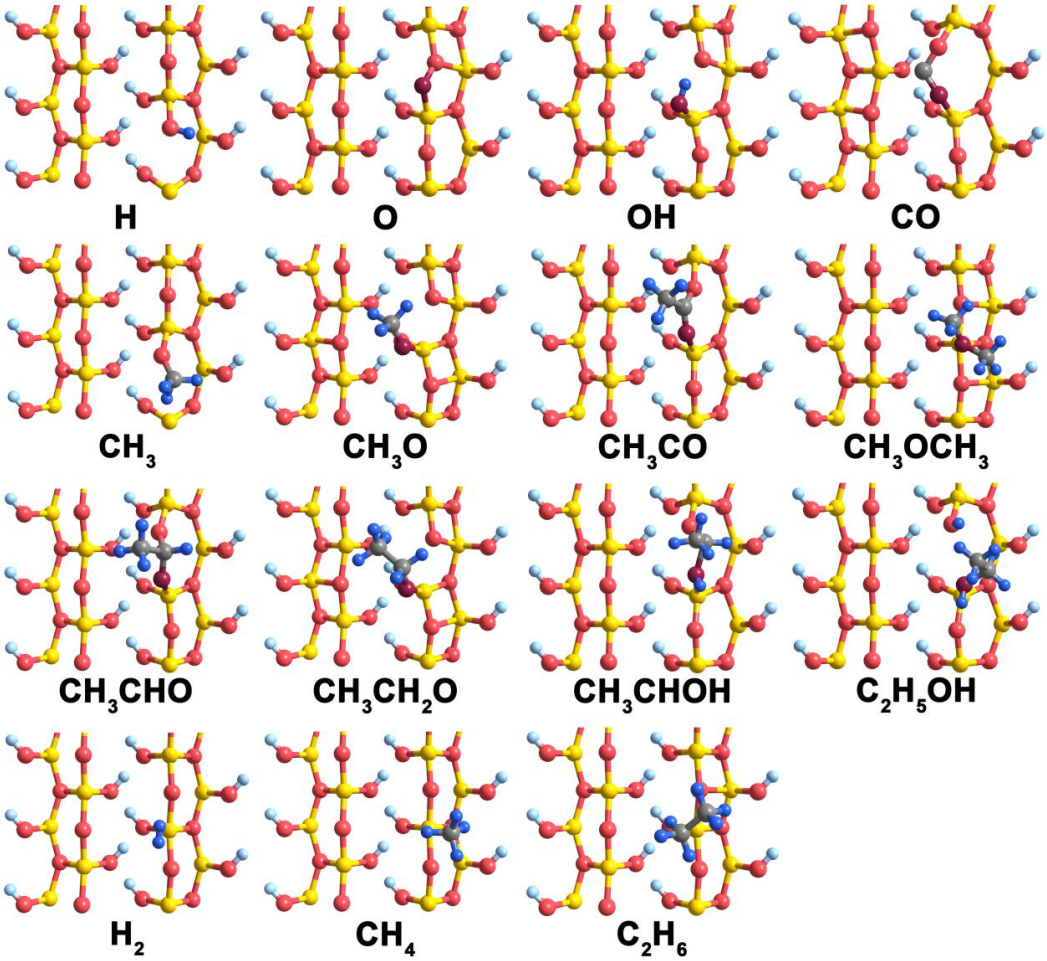
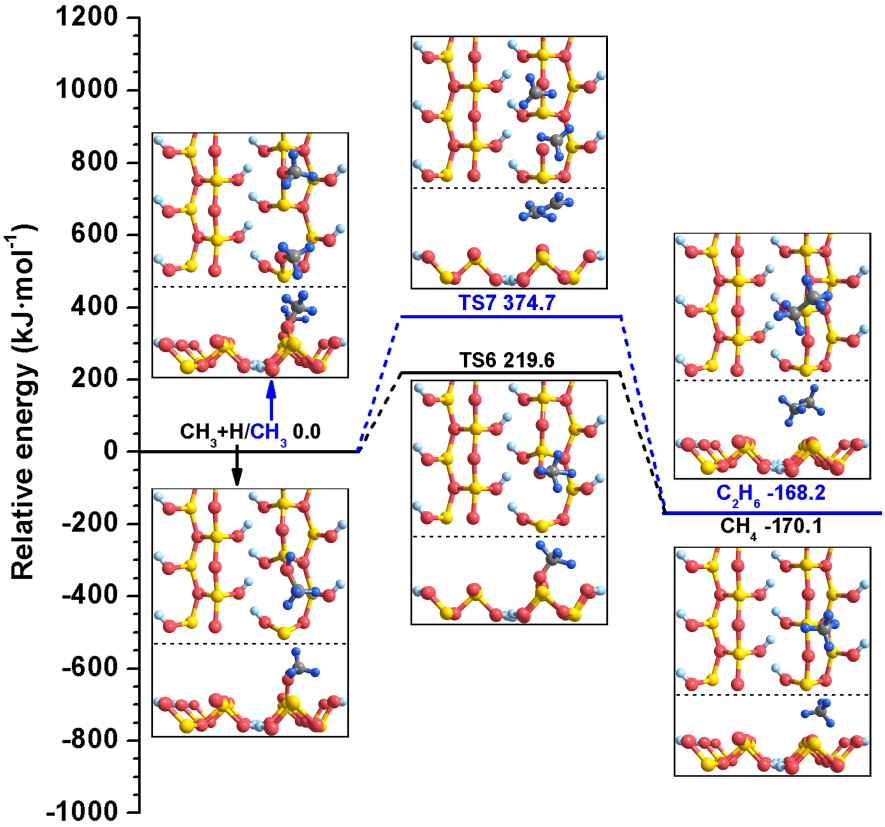
Figure S3. The potential energy profile of CH_3 hydrogenation and coupling with the structures of initial states (ISs), transition states (TSs), and final states (FSs).