Supporting information

Selective mild oxidation of methane to methanol or formic acid on Fe-MOR catalysts

*Zhihao Fang,[1]† Haruno Murayama,[2]† Qi Zhao,[1]† Bing Liu,[1] Feng Jiang,[1] Yuebing Xu,[1] Makoto Tokunaga,[2] Xiaohao Liu[1]**

[1]*Department of Chemical Engineering, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, P. R. China*

[2]*Department of Chemistry, Graduate School of Science, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan*

† These authors contributed equally to this work

* Corresponding author:

Email address: liuxh@jiangnan.edu.cn (X.L.)

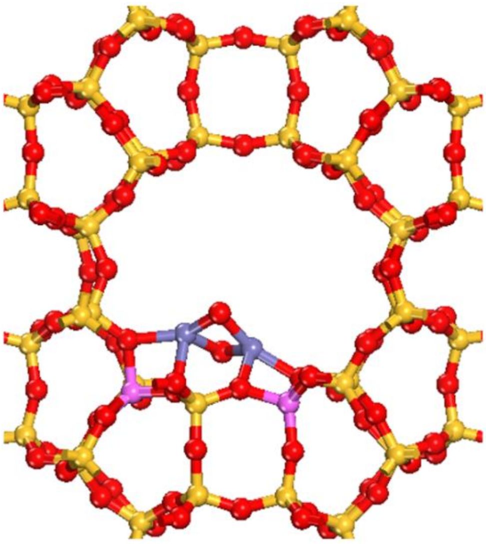

Figure S1. Calculated structure model of MOR-supported $[Fe_2(\mu\text{-}O)_2]^{2+}$ dimer species. Red, yellow, purple, grey blue and white balls represent O, Si, Al, Fe and H atoms, respectively.

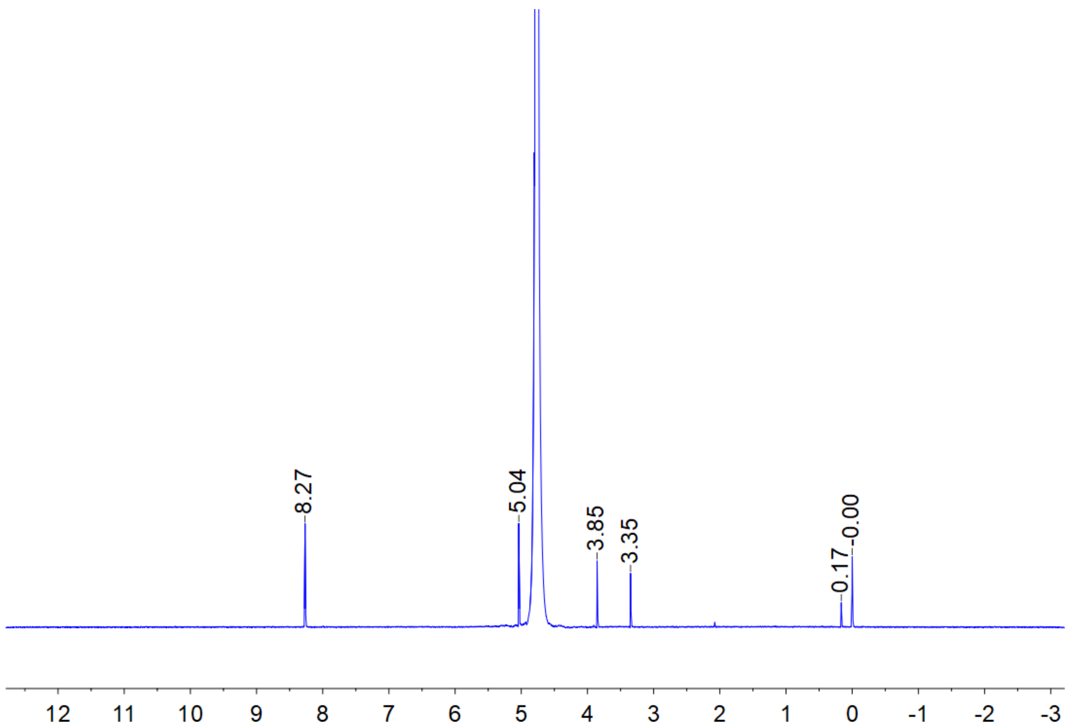

Figure S2. A typical ^{1}H-NMR spectrum obtained from the direct partial oxidation of methane with H_2O_2 on 0.5 wt% Fe/MOR-air. The oxygenated products were identified as methanol (δ = 3.35 ppm), methyl hydroperoxide (δ = 3.85 ppm), methane diol (δ = 5.04 ppm), and formic acid (δ = 8.27 ppm). Resonances at δ = 0.17 and 4.78 ppm arise from the methane and water, respectively.

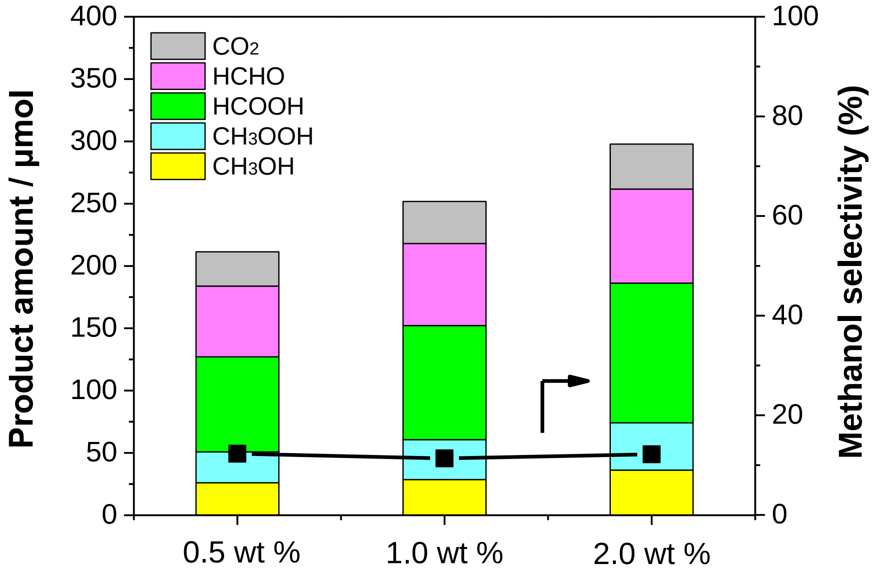

Figure S3. Comparison of the activity and selectivity on H-MOR supported Fe catalysts with different Fe loading in weight % for methane partial oxidation. Reaction condition: autoclave reactor, H_2O_2 solution 20 mL, [H_2O_2] = 0.5M, 30 bar of 95% CH_4/N_2, 80 ℃, 1 h, 30 mg catalyst.

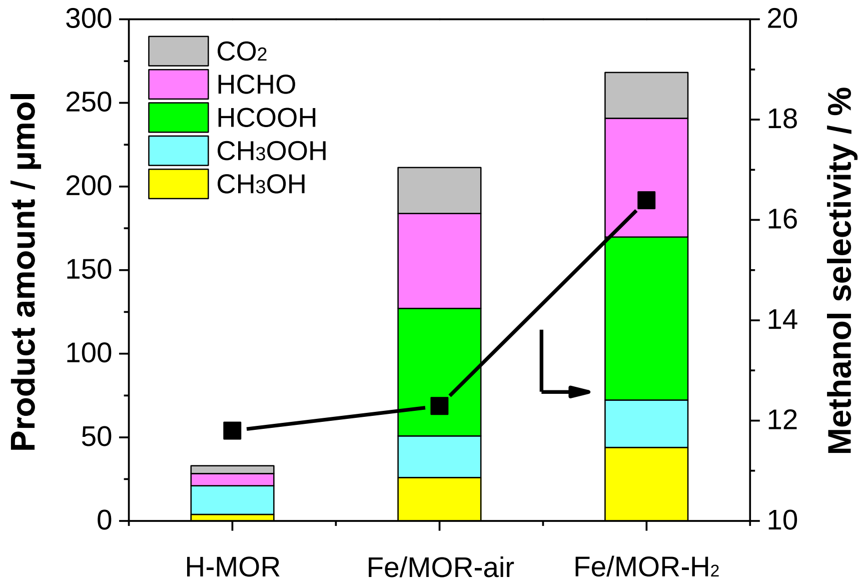

Figure S4. Comparison of the activity and selectivity for methane partial oxidation with H_2O_2 over H-MOR, 0.5 wt % Fe/MOR-air and 0.5 wt% Fe/MOR-H_2 catalysts. Reaction condition: H_2O_2 solution 20 mL, [H_2O_2] = 0.5M, 30 bar of 95% CH_4/N_2, 80 ℃, 30 mg catalyst.

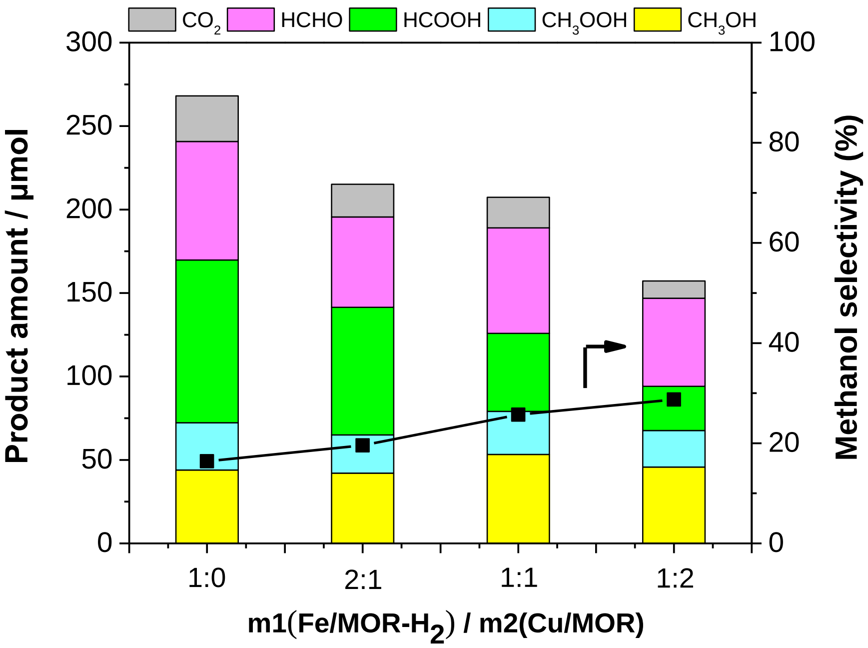

Figure S5. Effect of heterogeneous Cu on the methanol selectivity for methane partial oxidation with H_2O_2 using 0.5 wt % Fe/MOR-H_2 catalyst. Reaction condition: H_2O_2 solution 20 mL, [H_2O_2] = 0.5M, 30 bar of 95% CH_4/N_2, 80 ℃, 30 mg catalyst.

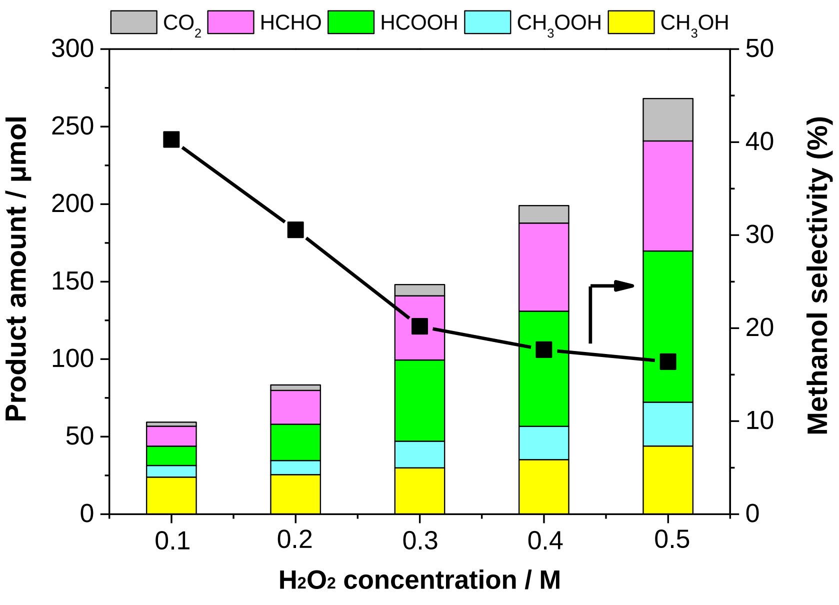

Figure S6. Effect of H_2O_2 concentration on the methanol selectivity for methane partial oxidation with H_2O_2 using 0.5 wt % Fe/MOR-H_2 catalyst. Reaction condition: H_2O_2 solution 20 mL, [H_2O_2] = 0.5M, 30 bar of 95% CH_4/N_2, 80 ℃, 30 mg catalyst.

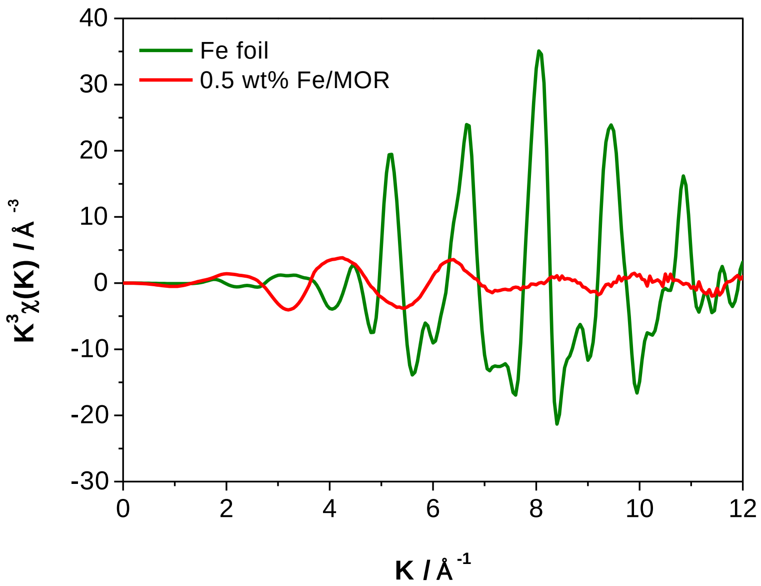

Figure S7. k^3-weighted EXAFS oscillation for 0.5 wt% Fe/MOR-air catalyst and reference Fe foil.

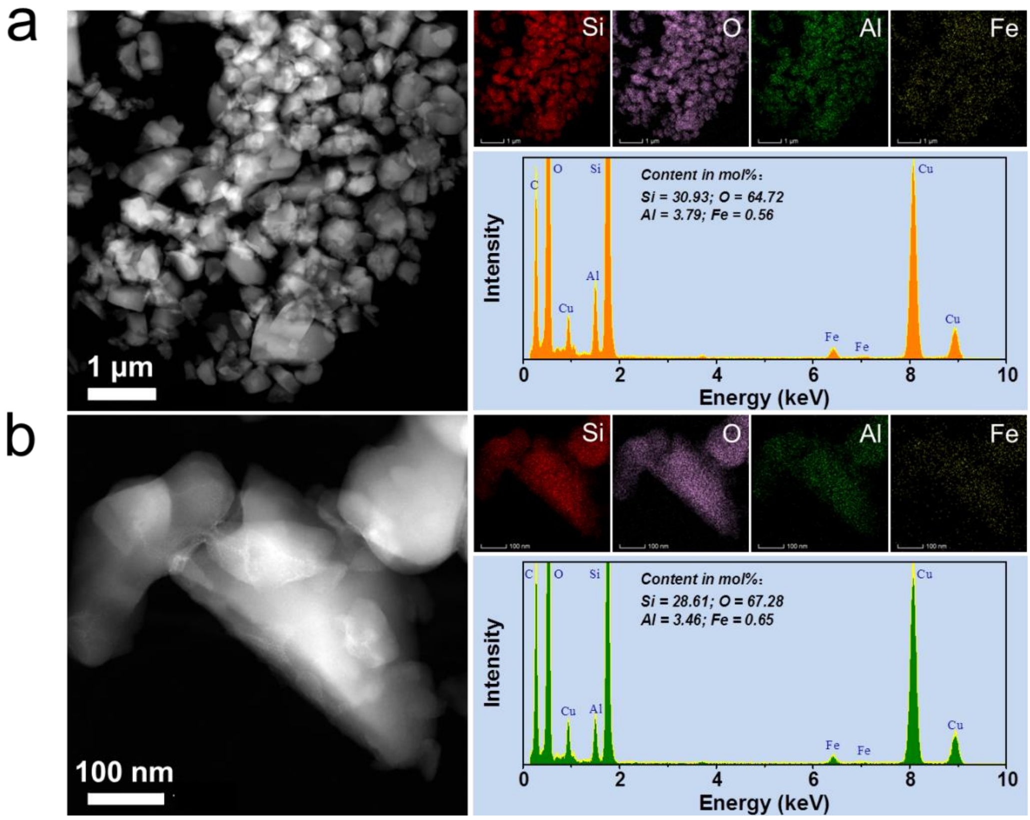

Figure S8. HAADF-STEM images, STEM-EDX elemental mappings and STEM-EDX spectrum of 0.5 wt% Fe/MOR-H_2 catalyst.

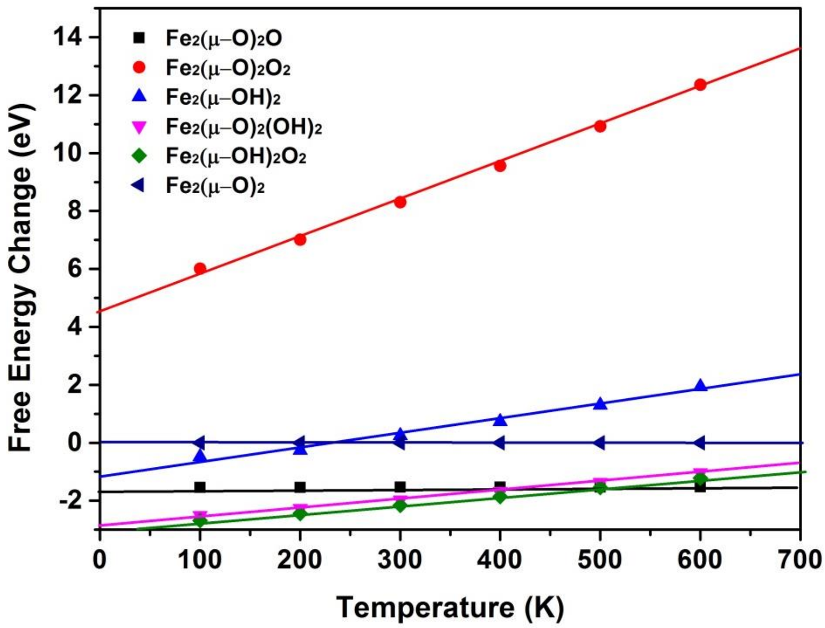

Figure S9. Calculated Gibbs free energy change (ΔG) of the formation of [Fe_2(μ-O)$_2$O], [Fe_2(μ-O)$_2O_2$], [Fe_2(μ-O)$_2$(OH)$_2$], [Fe_2(μ-OH)$_2$] and [Fe_2(μ-OH)$_2O_2$] species.

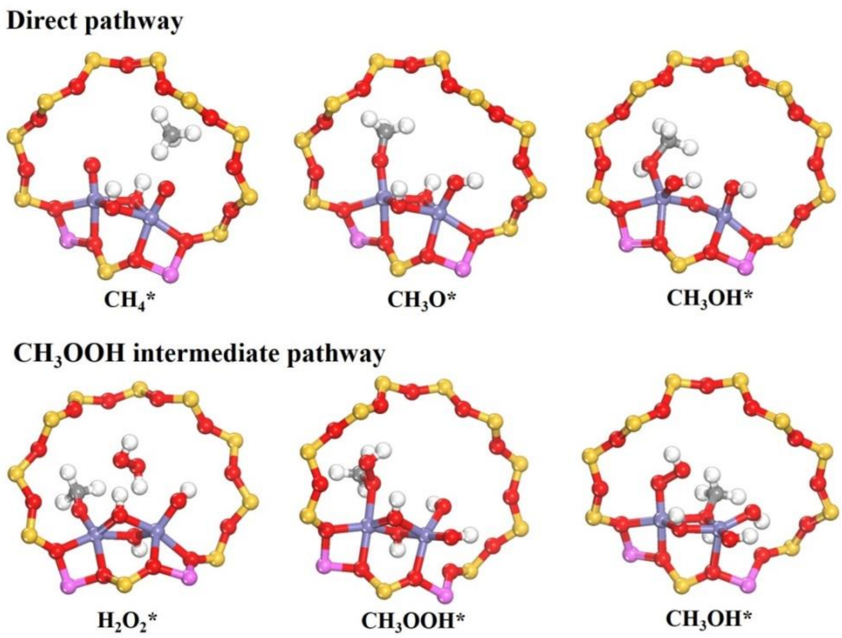

Figure S10. Calculated intermediate structures for CH_3OH formation via direct pathway and CH_3OOH intermediate pathway in Fe/MOR. Red, yellow, purple, grey blue, grey and white balls represent O, Si, Al, Fe, C and H atoms, respectively.

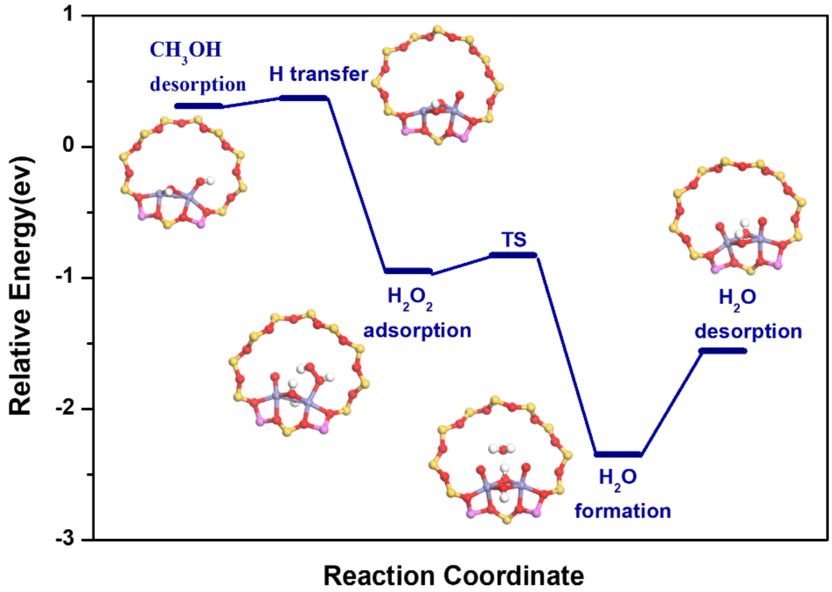

Figure S11. Catalyst regeneration process for direct CH_3OH formation pathway.

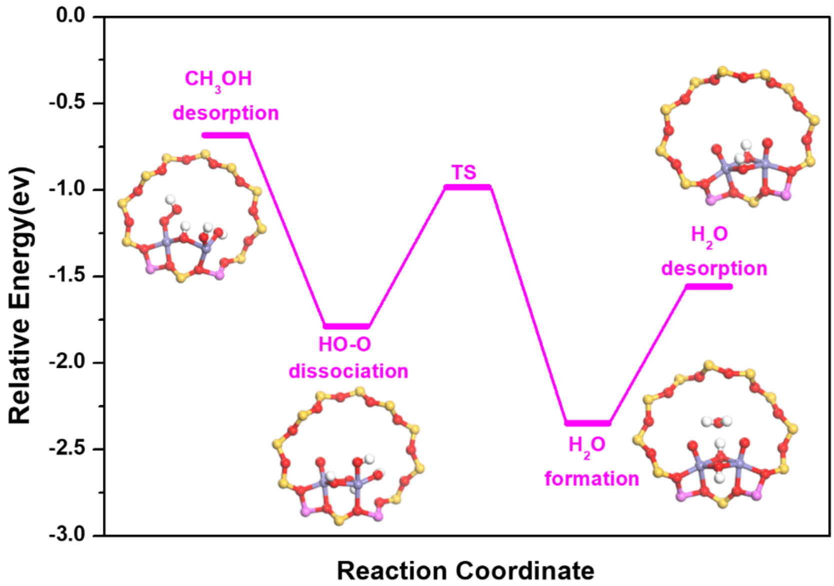

Figure S12. Catalyst regeneration process for CH_3OH formation via CH_3OOH intermediate pathway.

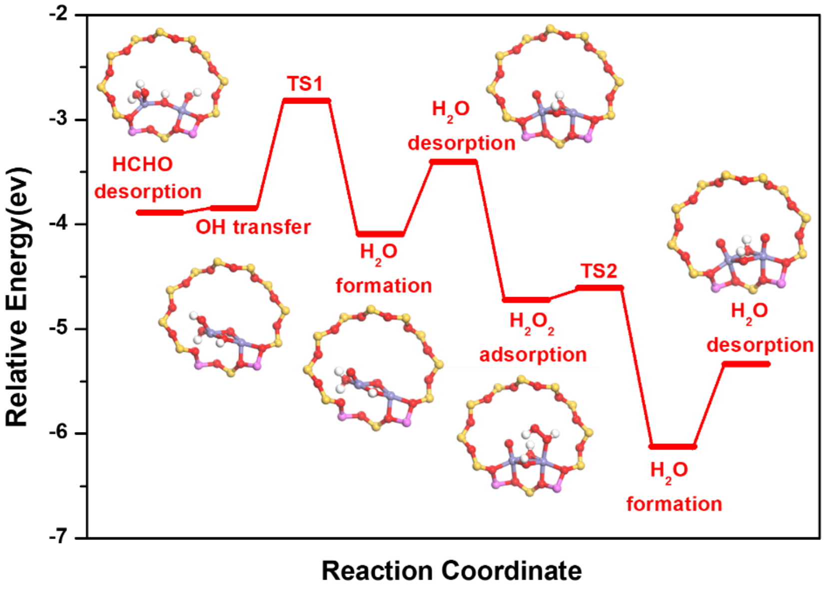

Figure S13. Catalyst regeneration process for HCHO formation pathway.

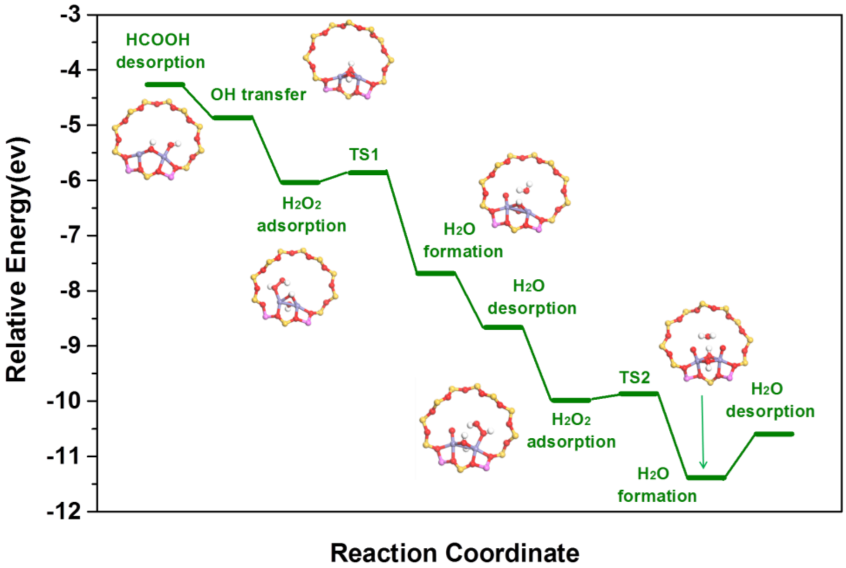

Figure S14. Catalyst regeneration process for HCOOH formation pathway.

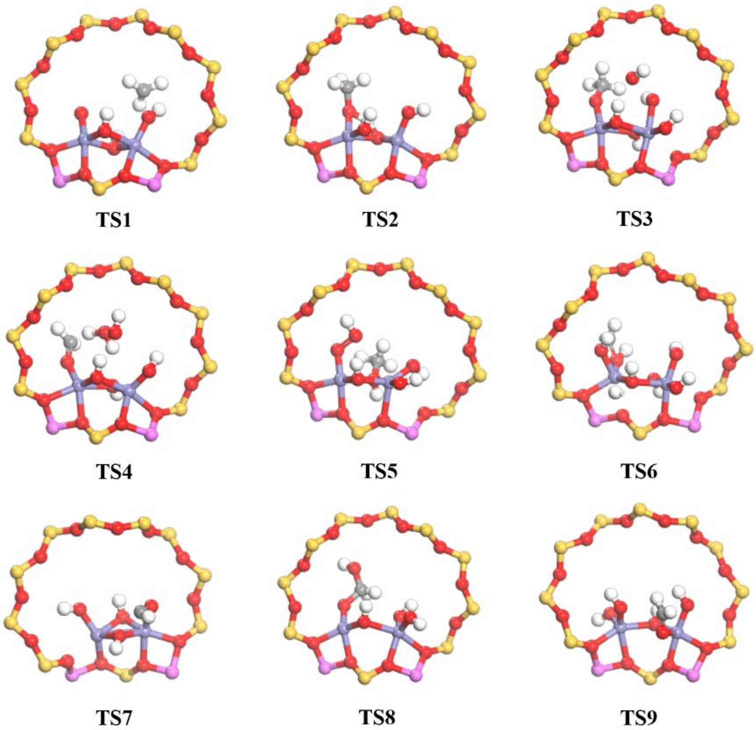

Figure S15. Structures of transition states for each elementary reaction step in CH_3OH formation, HCOOH formation, and HCHO formation.

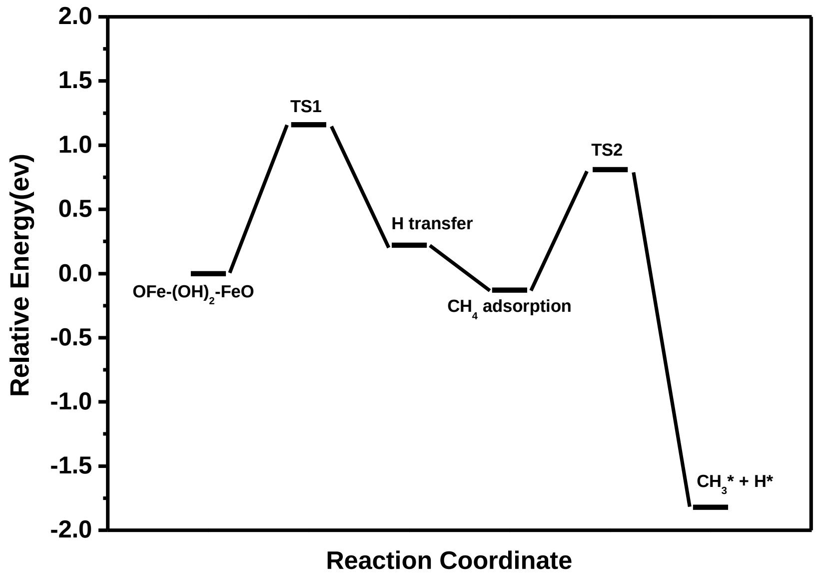

Figure S16. Energy profile for H transfer from bridge OH to one bare O and CH_4 dissociation.

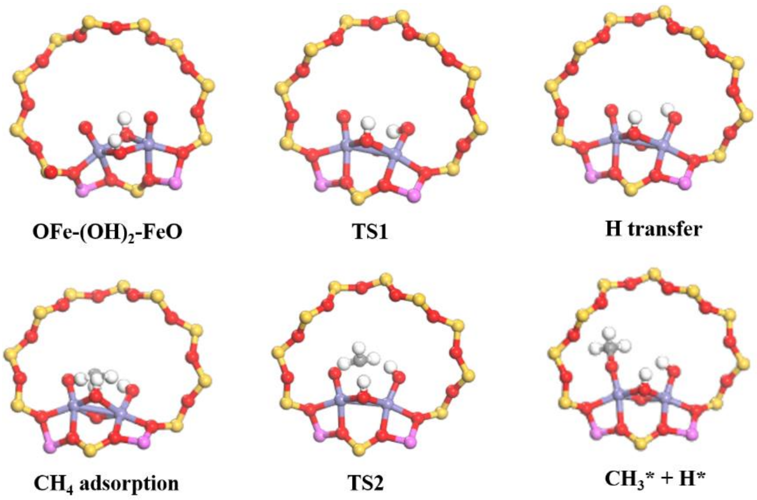

Figure S17. Calculated structures in H transfer from bridge OH to one bare O and subsequent CH_4 dissociation.

Table S1. R-space fitting and coordination parameters obtained from EXAFS analysis.

Sample	N (Fe-Fe)[a]	N (Fe-O)[a]	R(Fe-Fe)[b] / Å	R(Fe-O)[b] / Å
γ-Fe_2O_3	13.5	5.25	3.345	1.920
0.5% Fe–MOR-air	1.155±0.368	5.758±1.748	3.328±0.021	1.910±0.025

[a] Coordination number; [b] Coordination distance.