Electronic Supporting Information

Conditions to meet for the $[CuOH]^+$ site to be favorable and reactive toward the conversion of methane to methanol over Cu-MOR zeolite

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Table S1. Geometrical parameters and atomic spin densities (ρ) along the CH_4 oxidation to CH_3OH on the 8-MR side pocket of MOR with the assistance of H_2O.

Reaction step	Ground state	d(Cu–O) (Å)	d(Cu–C) (Å)	d(C–H_{Me}) (Å)	d(O–H_{Me}) (Å)	ρ(Cu)	ρ(O)	ρ(C)
AS	doublet	1.81	3.23	1.10	2.52	0.54	0.30	0.00
TS_{He}	doublet	1.93	2.17	1.36	1.29	0.46	0.26	0.20
INT-1_{He}	doublet	2.04	1.94	2.99	0.98	0.53	0.08	0.30
INT-2	doublet	2.09	1.97	2.88	0.98	0.52	0.07	0.29
TS_{Ho}	doublet	1.87	3.56	1.41	1.17	0.18	0.24	0.50
INT-1_{Ho}	doublet	1.91	3.92	2.00	0.99	0.01	0.06	0.87

Table S2. Geometrical parameters and atomic spin densities (ρ) along the CH_4 oxidation to CH_3OH on the 12-MR opening of MOR (Al_{141} arrangement).

Reaction step	Ground state	d(Cu–O) (Å)	d(Cu–C) (Å)	d(C–H_{Me}) (Å)	d(O–H_{Me}) (Å)	ρ(Cu)	ρ(Cu_{spec})	ρ(O)	ρ(C)
AS	triplet	1.77	3.29	1.10	2.73	0.58	0.48	0.41	0.00
TS-1_{He}	triplet	1.91	2.30	1.36	1.29	0.52	0.44	0.26	0.32
INT-1_{He}	triplet	2.05	2.00	3.70	0.97	0.66	0.41	0.03	0.46
TS-2	singlet	1.80	2.07	3.75	4.65	0.00	0.00	0.00	0.00
FS	singlet	1.46	2.89	4.41	4.55	0.00	0.00	0.00	0.00

Table S3. Geometrical parameters and atomic spin densities (ρ) along the CH_4 oxidation to CH_3OH on the 12-MR opening of MOR (Al_{241} arrangement).

Reaction step	Ground state	d(Cu–O) (Å)	d(Cu–C) (Å)	d(C–H_{Me}) (Å)	d(O–H_{Me}) (Å)	ρ(Cu)	ρ(Cu_{spec})	ρ(O)	ρ(C)
AS	triplet	1.77	4.54	1.10	2.64	0.59	0.47	0.39	0.00
TS-1$_{Ho}$	triplet	1.86	3.77	1.32	1.26	0.44	0.38	0.31	0.47
INT-1$_{Ho}$	triplet	1.92	4.02	1.98	1.00	0.37	0.34	0.06	0.87
INT-2	singlet	1.78	1.95	2.30	4.13	0.00	0.00	0.00	0.00
TS-2	singlet	1.79	2.04	3.70	5.13	0.00	0.00	0.00	0.00
FS	singlet	1.88	2.93	4.60	4.65	0.00	0.00	0.00	0.00

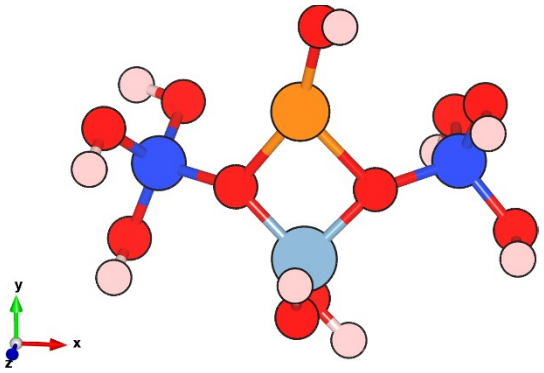

Fig. S1 Small cluster model of CuOH-MOR for molecular orbital calculations.

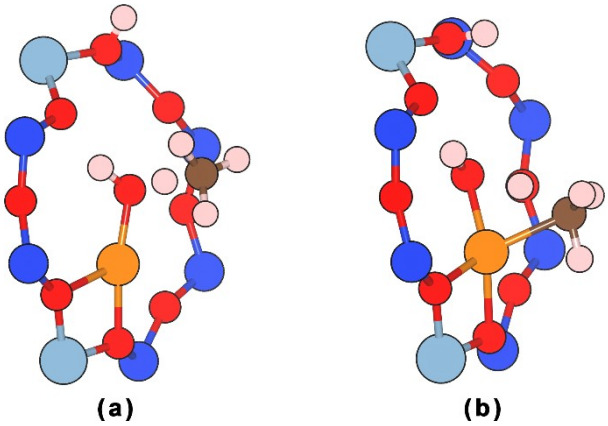

Fig. S2 Structures of (a) $\mathbf{TS_{Ho}}$ and (b) $\mathbf{TS_{He}}$ on CuOH@Al_{44}.

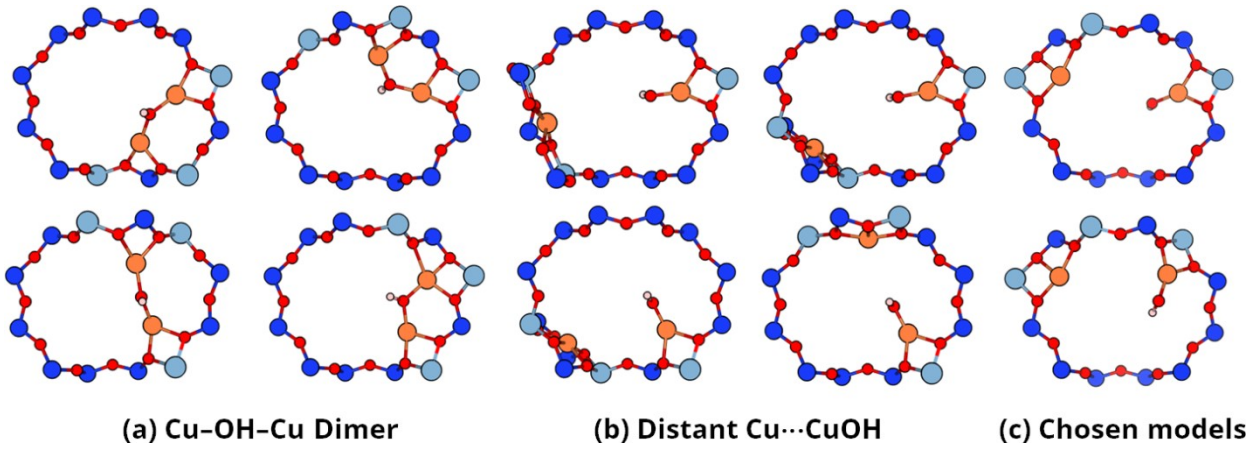

Fig. S3 Considered CuOH-MOR models with the presence of a Cu^{2+} spectator site.

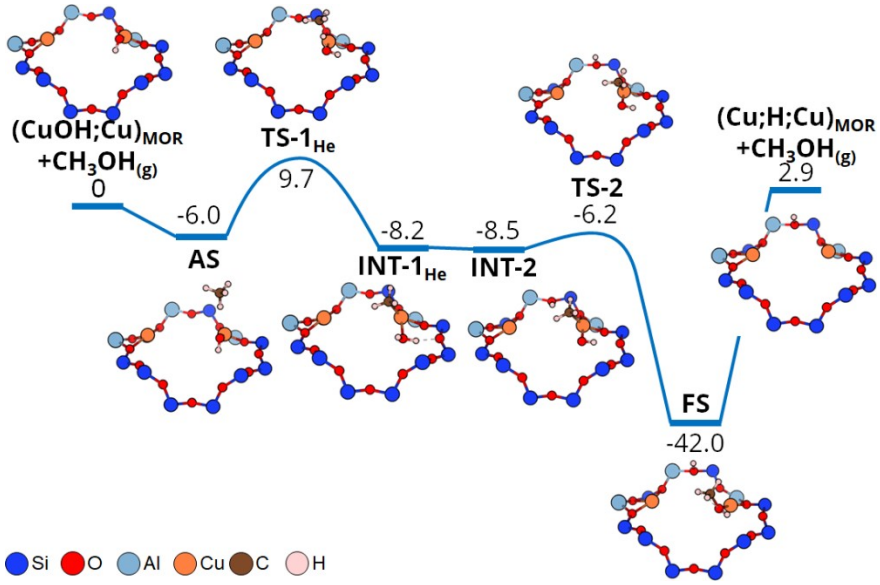

Fig. S4 Energy diagram of the heterolytic C–H bond activation on CuOH@Al_{241}.

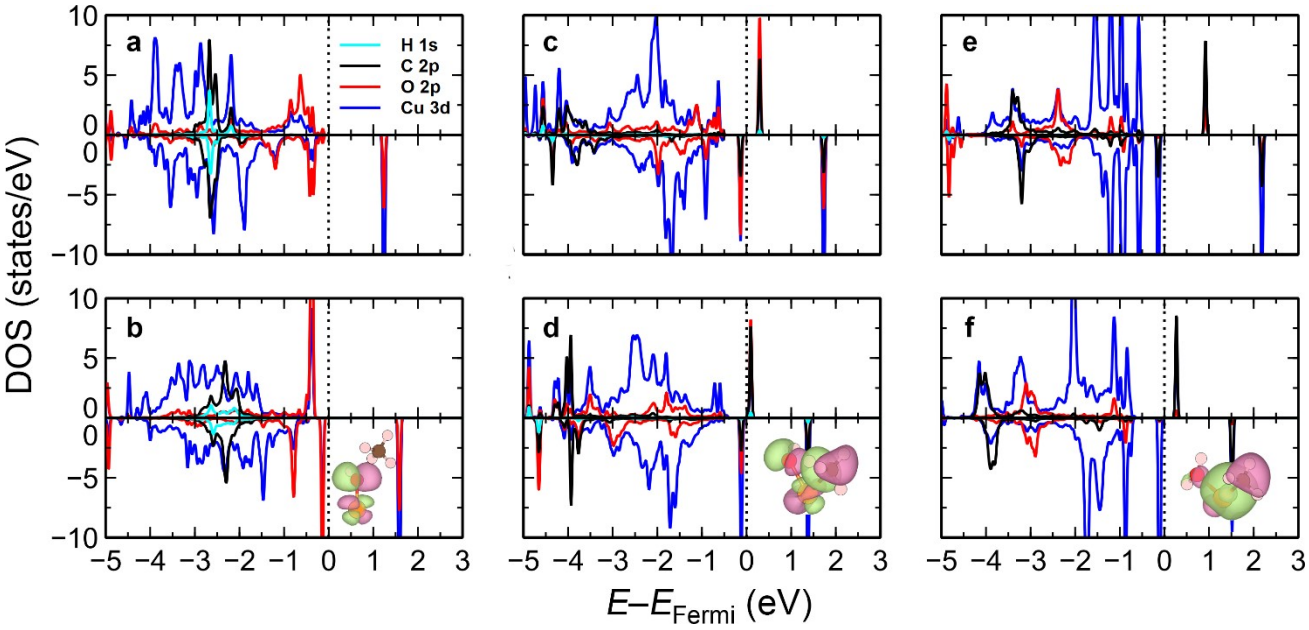

Fig. S5 PDOS of (a,b) **AS**, (c,d) **TS-1$_{He}$**, and (e,f) **INT-1$_{He}$** in the respective ground state for the heterolytic CH_4 activation on the (top) CuOH@Al_{44} and (below) CuOH@Al_{241} sites.

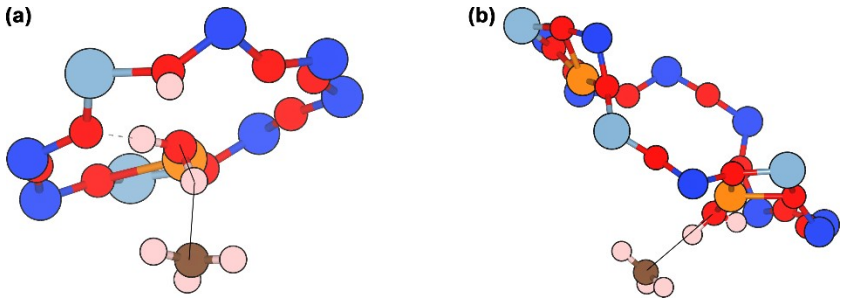

Fig. S6 HOH···CH_3 interaction in **INT-1$_{Ho}$** for the (a) CuOH@Al_{44} and (b) CuOH@Al_{241} sites.