Electronic Supplementary Information

Methane Selective Oxidation to Methanol by Metal-Exchanged Zeolites: A Review of Active Sites and Their Reactivity

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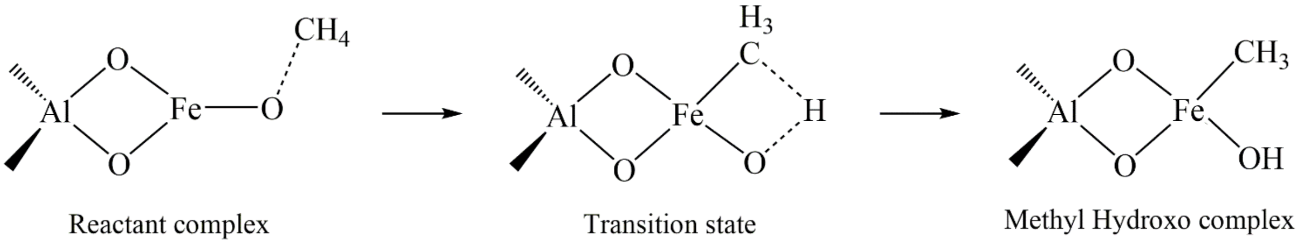

Scheme S1 Heterolytic C–H bond cleavage of methane by $[FeO]^+$-zeolites via a four-center transition state.

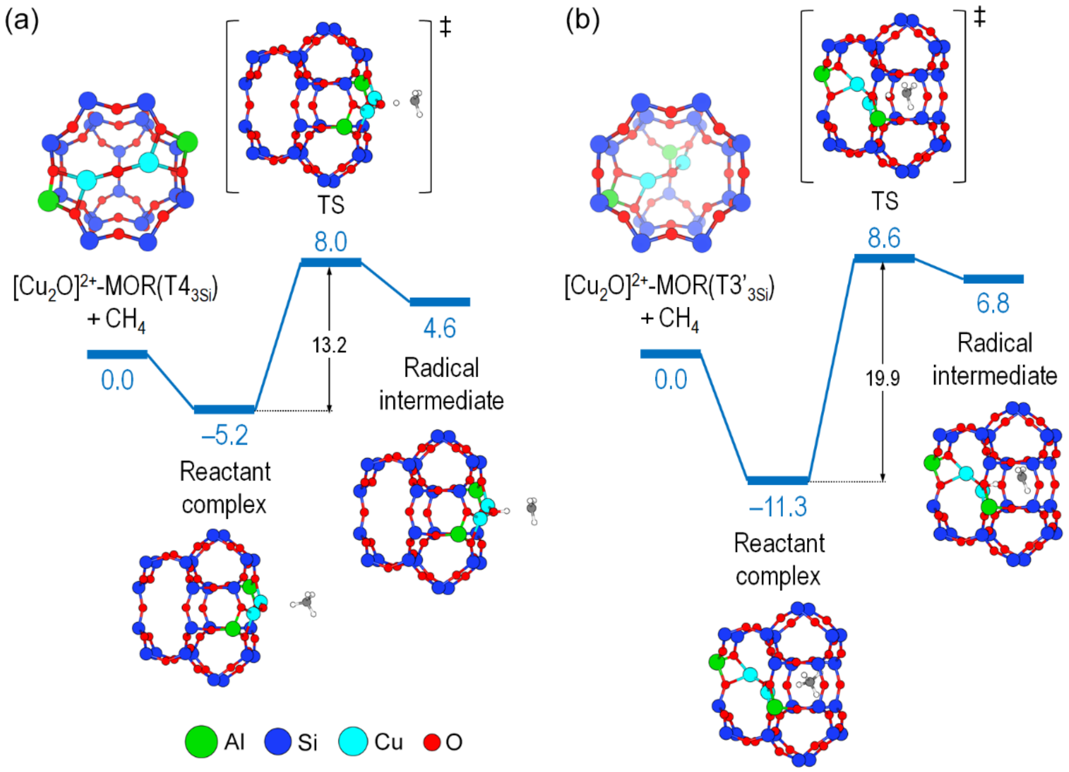

Fig. S1 Triplet-state energy diagrams and optimized structures of methane hydroxylation over $[Cu_2(\mu\text{-}O)]^{2+}$ hosted on the (a) $T4_{3Si}$ and (b) T3'$_{3Si}$ Al pair sites of MOR zeolite framework. All energies are given in kcal/mol and include the vdW-D2 correction. See Table S1 for detailed geometrical parameters.

Table S1. Geometrical properties and atomic spin densities (ρ) along the methane hydroxylation over $[Cu_2(\mu\text{-}O)]^{2+}$-MOR($T4_{3Si}$) and -MOR(T3'$_{3Si}$) in the triplet ground state.

	∠CuOCu (°)	$d_{C–H}$ (Å)	$d_{O–H}$ (Å)	$d_{O–C}$ (Å)	$d_{Cu–O}$ (Å)	ϱ(Cu1, Cu2)	ϱ(O, C)
				MOR($T4_{3Si}$)			
Cu_2O-MOR	148.5	-	-	-	1.744, 1.744	0.53, 0.53	0.74
RC	148.6	1.100	2.375	3.473	1.744, 1.744	0.53, 0.53	0.73, 0.00
TS	132.5	1.398	1.182	2.581	1.826, 1.826	0.40, 0.40	0.46, 0.53
RI	133.6	1.870	1.005	2.874	1.841, 1.842	0.36, 0.36	0.23, 0.84
				MOR(T3'$_{3Si}$)			
Cu_2O-MOR	133.0	-	-	-	1.743, 1.758	0.51, 0.55	0.71
RC	135.2	1.097	2.385	3.271	1.746, 1.759	0.51, 0.55	0.70, 0.00
TS	122.2	1.448	1.162	2.576	1.825, 1.852	0.40, 0.42	0.42, 0.53
RI	126.9	2.191	0.985	3.026	1.850, 1.860	0.38, 0.38	0.16, 0.87

RC, TS, and RI stand for reactant complex, transition state, and radical intermediate, respectively.

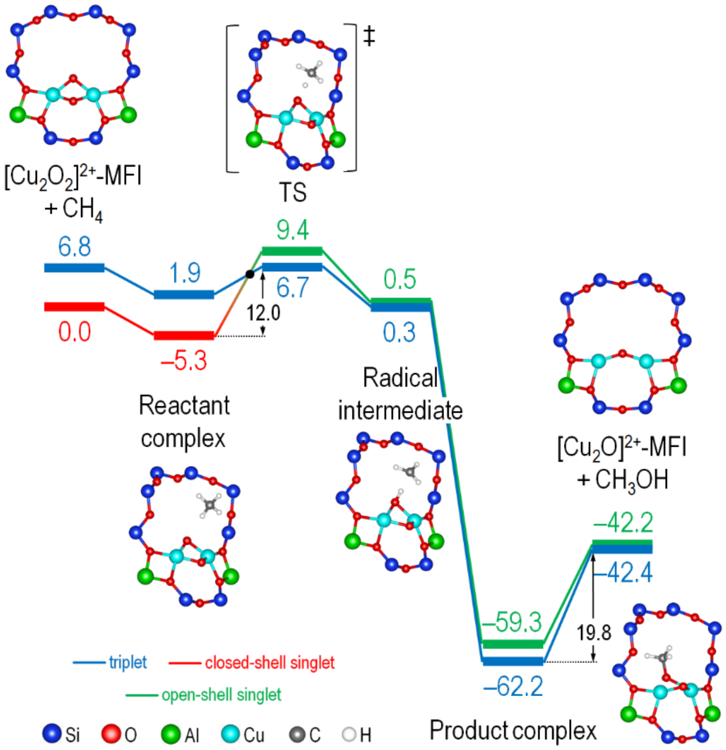

Fig. S2 Reaction energy diagrams of methane hydroxylation over [Cu$_2$(μ-O)$_2$]$^{2+}$ (O···O = 2.152 Å) hosted on the T3/T3 Al pair site of MFI zeolite framework. All energies are given in kcal/mol and include the vdW-D2 correction. While the two Cu centers are initially Cu^{III}, those in TS are better described as a combination of Cu^{II} and Cu^{III}. The TS and radical intermediate can be formed only in the triplet and open-shell singlet states, but not in the closed-shell singlet state, showing the importance of spin inversion in this reaction. See Table S2 for detailed geometrical parameters and atomic spin densities.

Table S2. Geometrical properties and atomic spin densities (ρ) along the methane hydroxylation over bis(μ-oxo)dicopper [Cu$_2$(μ-O)$_2$]$^{2+}$-MFI (T3/T3 Al pair site).

	Ground state	∠CuOCu (°)	$d_{\mathrm{C–H}}$ (Å)	$d_{\mathrm{O–H}}$ (Å)	$d_{\mathrm{O–C}}$ (Å)	$d_{\mathrm{Cu–O}}$ (Å)	ρ(Cu1, Cu2)	ρ(O, C)
Cu$_2$O$_2$-MFI	CSS	97.8	-	-	-	1.858, 1.858	0.00, 0.00	0.00
RC	CSS	98.6	1.096	2.369	3.464	1.858, 1.859	0.00, 0.00	0.00, 0.00
TS	T	91.0	1.212	1.393	2.602	2.064, 1.858	0.52, –0.01	0.74, 0.33
RI	T	87.8	1.927	1.002	2.918	2.133, 1.883	0.55, 0.04	0.14, 0.81
PC	T	68.4	-	0.976	1.459	3.254, 2.054	0.48, 0.59	0.06, 0.00
Cu$_2$O-MFI	T	141.5	-	-	-	1.745, 1.745	0.53, 0.53	0.72

T and CSS stand for triplet and closed-shell singlet states, respectively. O is the abstracting O atom.

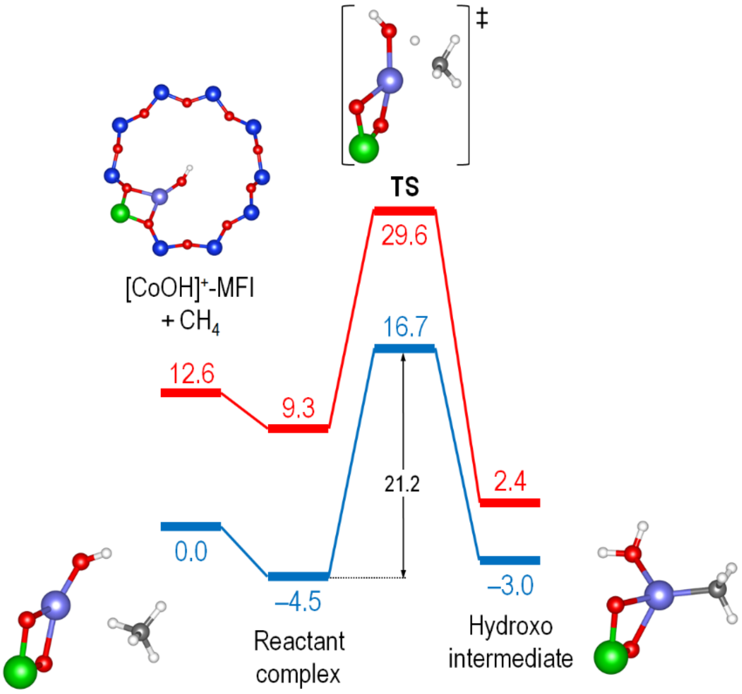

Fig. S3 Reaction energy diagrams of methane hydroxylation over $[CoOH]^+$-MFI in the quartet (blue lines) and doublet (red lines) states. All energies are given in kcal/mol and include the vdW-D2 correction. See Table S3 for detailed geometrical parameters.

Table S3. Geometrical properties and atomic spin densities (ρ) along the methane hydroxylation over $[CoOH]^+$-MFI (T1 Al site).

	Ground state	$d_{C\text{–}H}$ (Å)	$d_{O\text{–}H}$ (Å)	$d_{O\text{–}C}$ (Å)	$d_{Co\text{–}O}$ (Å)	ϱ(Co)	ϱ(O, C)
CoO-MFI	Qa	-	-	-	1.752	2.53	0.31
RC	Qa	1.103	2.816	3.741	1.759	2.54	0.30, 0.00
TS	Qa	1.468	1.243	2.665	1.963	2.53	0.16, 0.12
HI	Qa	3.614	0.972	3.447	2.080	2.62	0.05, 0.11

RC, TS, HI, and Qa stand for reactant complex, transition state, hydroxo intermediate, and quartet state, respectively. O is the abstracting O atom.

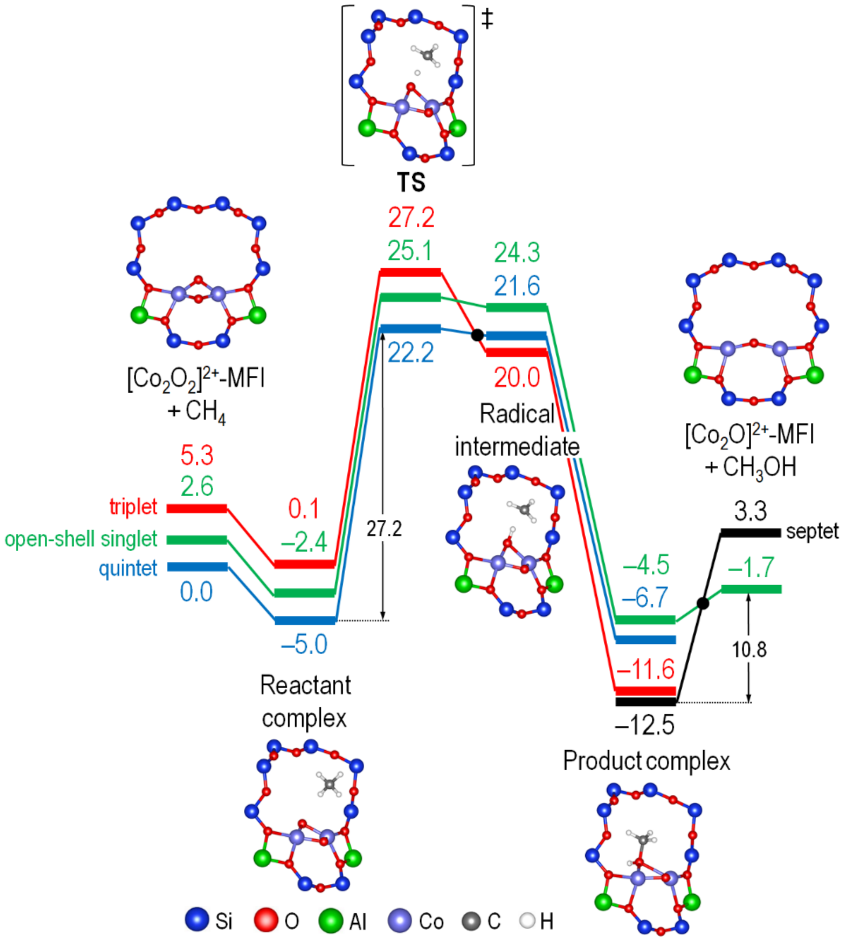

Fig. S4 Reaction energy diagrams of methane hydroxylation over $[Co_2(\mu\text{-}O)_2]^{2+}$ hosted on the T3/T3 Al pair site of MFI zeolite framework. All energies are given in kcal/mol and include the vdW-D2 correction. See Table S4 for detailed geometrical parameters.

Table S4. Geometrical properties and atomic spin densities (ρ) along the methane hydroxylation over bis(μ-oxo)dicobalt $[Co_2(\mu\text{-}O)_2]^{2+}$-MFI (T3/T3 Al pair site).

	Ground state	∠CoOCo (°)	$d_{C–H}$ (Å)	$d_{O–H}$ (Å)	$d_{O–C}$ (Å)	$d_{Co–O}$ (Å)	ϱ(Co1, Co2)	ϱ(O, C)
Co_2O_2-MFI	Qi	89.3	-	-	-	1.800, 1.801	1.64, 1.64	0.28
RC	Qi	89.5	1.098	2.610	3.693	1.794, 1.806	1.64, 1.64	0.28, 0.00
TS	Qi	82.6	1.513	1.108	2.617	1.917, 1.914	1.42, 1.42	0.19, 0.61
RI	OST	84.8	1.719	1.030	2.701	1.907, 1.904	1.29, 1.29	–0.07, –0.75
PC	Sp	74.2	-	0.978	1.473	2.304, 2.284	2.54, 2.54	0.08, 0.01
Co_2O-MFI	OSS	149.0	-	-	-	1.709, 1.708	2.28, –2.28	0.00

Qi, OST, OSS, and Sp stand for quintet, open-shell triplet, open-shell singlet states, and septet states, respectively. O is the abstracting O atom.

Table S5. Geometrical properties and atomic spin densities (ρ) along the N_2O decomposition over $[Fe]^{2+}$-MFI methane hydroxylation over $[FeO]^{2+}$-MFI (T11/T11 Al pair site)

	Ground state	$d_{\text{N–O}}$ (Å)	$d_{\text{C–H}}$ (Å)	$d_{\text{O–H}}$ (Å)	$d_{\text{O–C}}$ (Å)	$d_{\text{Fe–O}}$ (Å)	ϱ(Fe)	ϱ(O, C)
Fe-MFI	Qi	-	-	-	-	-	3.61	-
N_2O Ads	Qi	1.214	-	-	-	2.263	3.63	0.03
TS	Qi	1.467	-	-	-	1.819	3.77	0.05
FeO-MFI	Qi	-	-	-	-	1.617	3.10	0.51
RC	Qi	-	1.099	2.550	3.589	1.618	3.10	0.51, 0.00
TS1	Qi	-	1.234	1.319	2.547	1.701	3.65	0.24, –0.28
RI	Qi	-	1.772	1.016	2.785	1.774	3.97	0.37, –0.77
TS2	Qi	-	2.192	0.978	2.725	1.795	3.95	0.36, –0.75
PC	Qi	-	-	0.973	1.463	2.041	3.62	0.07, 0.00

Qi stands for quintet state. RC, TS, RI, and PC stand for reactant complex, transition state, radical intermediate, and respectively.

Table S6. Geometrical properties and atomic spin densities (ρ) along the methane hydroxylation over mono(μ-oxo)dicopper $[Cu_2(\mu\text{-}O)]^{2+}$-MFI (T3/T3 Al pair site).

	Ground state	∠CuOCu (°)	$d_{\text{C–H}}$ (Å)	$d_{\text{O–H}}$ (Å)	$d_{\text{O–C}}$ (Å)	$d_{\text{Cu–O}}$ (Å)	ϱ(Cu1, Cu2)	ϱ(O, C)
Cu_2O-MFI	T	141.5	-	-	-	1.745, 1.745	0.53, 0.53	0.72
RC	T	142.4	1.100	2.413	3.510	1.743, 1.743	0.53, 0.53	0.71, 0.00
TS	T	127.1	1.404	1.182	2.584	1.823, 1.823	0.40, 0.40	0.45, 0.54
RI	T	128.5	1.922	1.003	2.916	1.841, 1.841	0.36, 0.36	0.21, 0.86
PC	CSS	77.1	-	0.978	1.495	2.026, 2.027	0.00, 0.00	0.00, 0.00
2Cu-MFI	CSS	-	-	-	-	-	0.00, 0.00	-

T and CSS stand for triplet and closed-shell singlet states, respectively. RC, TS, RI, and PC stand for reactant complex, transition state, radical intermediate, and product complex, respectively.

Table S7. Geometrical properties and atomic spin densities (ρ) along the methane hydroxylation over $[CoO]^{2+}$-MFI (T11/T11 Al pair site).

	Ground state	$d_{C–H}$ (Å)	$d_{O–H}$ (Å)	$d_{O–C}$ (Å)	$d_{Co–O}$ (Å)	ϱ(Co)	ϱ(O, C)
CoO-MFI	Qa	-	-	-	1.598	2.00	0.69
RC	Qa	1.098	2.483	3.564	1.600	2.00	0.69, 0.00
TS1	Qa	1.213	1.365	2.570	1.660	2.46	0.40, –0.20
RI	Qa	1.697	1.030	2.726	1.738	2.85	0.44, –0.68
TS2	Qa	1.916	0.992	2.540	1.762	2.83	0.41, –0.65
PC	Qa	-	0.974	1.460	1.986	2.63	0.07, 0.00
Co-MFI	Qa	-	-	-	-	2.60	-

Qa stands for quartet state. O is the abstracting O atom.

Table S8. Geometrical properties and atomic spin densities (ρ) along dioxygen activation on $[2Ni]^{2+}$-MFI.

	Ground state	$d_{O–O}$ (Å)	$d_{Ni–O}$ (Å)	ϱ(Ni)	ϱ(O)
$[2Ni]^{2+}$-MFI + O_2	Qi	1.207	-	0.94, 0.93	1.00, 1.00
Peroxo-Ni^{II}_2	Qi	1.517	1.930, 1.933, 1.948, 1.946	1.62, 1.62	0.30, 0.25
TS	OSS	1.724	1.851, 1.852, 1.820, 1.820	0.53, –0.53	0.00, 0.00
Bisoxo-Ni^{III}_2	OSS	2.207	1.796, 1.797, 1.783, 1.783	1.02, –1.02	0.00, 0.00

Qi and OSS stand for quintet and open-shell singlet states, respectively.

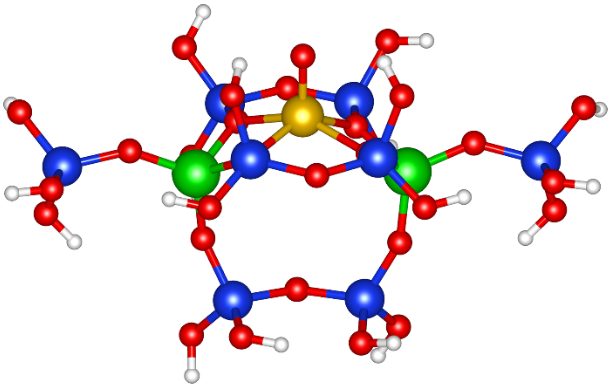

Fig. S5 Hydrogen-terminated large cluster model of $[FeO]^{2+}$-MFI in the quintet ground state. The model was constructed from the optimized periodic structure reported previously by our group (ref. 74). The geometry optimization was performed by fixing the Si atoms while the other atoms were allowed to fully relaxed. Color legend: Fe (gold), Si (blue), Al (green), O (red), H (white).

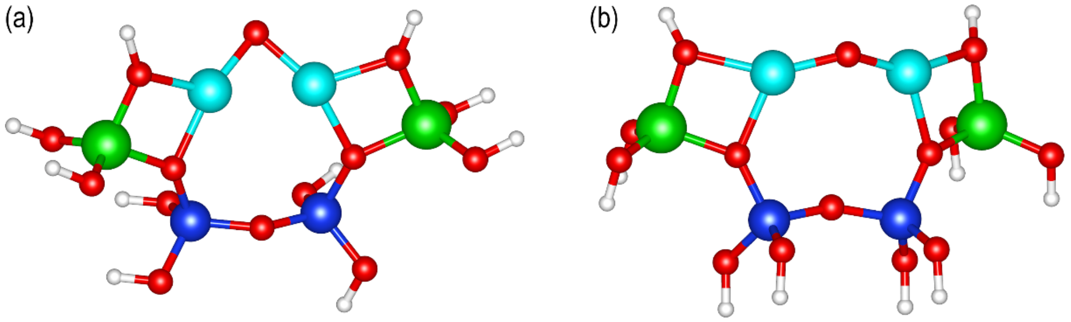

Fig. S6 Hydrogen-terminated large cluster models of $[Cu(\mu\text{-}O)]^{2+}$ hosted on (a) $T2_{2Si}$ and (b) $T4_{2Si}$ Al pair sites of MOR. The models were constructed from the optimized periodic structures reported previously by our group (ref. 100). The MO calculations were performed by fixing all atoms except the terminating H atoms. Color legend: Cu (cyan), Si (blue), Al (green), O (red), C (grey), H (white).