Supporting Information

Rationally Designing the Mixed Cu-(μ-O)-M (M=Cu, Ag, Zn, Au) Centers over Zeolite Materials with High Catalytic Activity towards Methane Activation

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The Supporting Information provides:

1. The relative energies and configurations of [Cu(μ-O)M]$^{2+}$-ZSM-5 (M=Cu, Ag, Zn, Au, Ni, Co, Fe)

Table S1. The Relative energies of [Cu(μ-O)M]$^{2+}$-ZSM-5 (M=Cu, Ag, Zn, Au, Ni, Co, Fe) calculated in the high-spin and low-spin states.

Figure S1. The configurations of [Cu(μ-O)M]$^{2+}$-ZSM-5 (M=Cu, Ag, Zn, Au, Ni, Co, Fe) in low and high-spin states.

2. Methane conversion to methanol on [Cu(μ-O)Cu]$^{2+}$-ZSM-5 (singlet)

Figure S2. Reaction energy diagram and optimized structures of intermediates and transition states for the methane conversion to methanol on [Cu(μ-O)Cu]$^{2+}$-ZSM-5 (singlet)

3. The key geometric parameter of reactants, intermediates, transition states for methane conversion on [Cu(μ-O)M]$^{2+}$-ZSM-5 (M=Cu, Ag, Zn, Au)

Table S2. The key geometrical parameters of intermediates and transition states for the reaction over [Cu(μ-O)M]-ZSM-5 (M=Cu, Ag, Zn, Au).

4. The Relative energies of CH_3•-OCuM and M-OH-Cu-CH_3 (M=Cu, Ag, Au) calculated in the high-spin and low-spin states.

Table S3. The Relative energies of CH_3•-OCuM and M-OH-Cu-CH_3 (M=Cu, Ag, Au) calculated in the high-spin and low-spin states.

5. C-H activation of methane on CuOM(M=Cu, Ag, Zn, Au)-ZSM-5 cluster

Table S4. The activation barrier for C-H activation of methane over 10T-[Cu(μ-O)M]$^{2+}$-ZSM-5 cluster and periodic [Cu(μ-O)M]$^{2+}$-ZSM-5 system (M=Cu, Ag, Zn, Au).

Figure S3. The configurations of reactants, transition states, and products on 10T-[Cu(μ-O)M]$^{2+}$-ZSM-5 (M=Cu, Ag, Zn, Au) cluster.

1. Details of relative energies and configurations of $[Cu(\mu\text{-}O)M]^{2+}$-ZSM-5 (M=Cu, Ag, Zn, Au, Ni, Co, Fe)

Table S1. The Relative energies of $[Cu(\mu\text{-}O)M]^{2+}$-ZSM-5 (M=Cu, Ag, Zn, Au, Ni, Co, Fe) calculated in the high-spin and low-spin states.

CuOM	Spin multiplicity	Relative energies (eV)
CuOCu	singlet	0.1
	triplet	0
CuOZn	doublet	0
	quartet	2.90
CuOAg	singlet	0.14
	triplet	0
CuOAu	singlet	0.16
	triplet	0
CuONi	doublet	0.12
	quartet	0
CuOCo	triplet	0.26
	quintuplet	0
CuOFe	quartet	0.04
	sextet	0

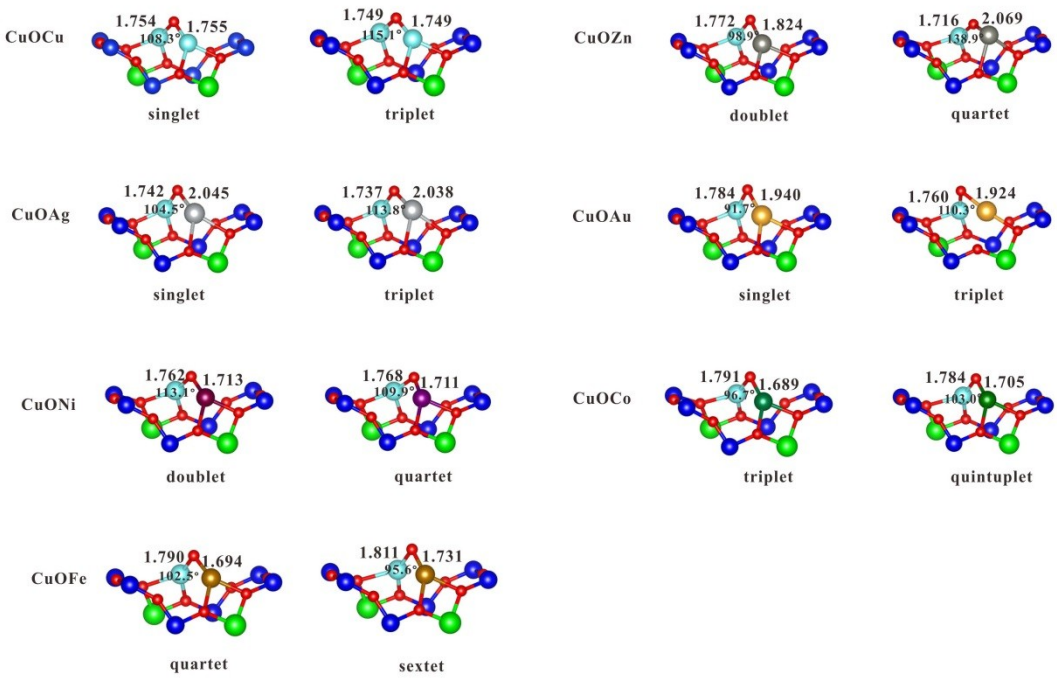

Figure S1. The configurations of $[Cu(\mu\text{-}O)M]^{2+}$-ZSM-5 (M=Cu, Ag, Zn, Au, Ni, Co, Fe) in low and high-spin states.

2. Methane conversion to methanol on $[Cu(\mu\text{-}O)Cu]^{2+}$-ZSM-5 (singlet)

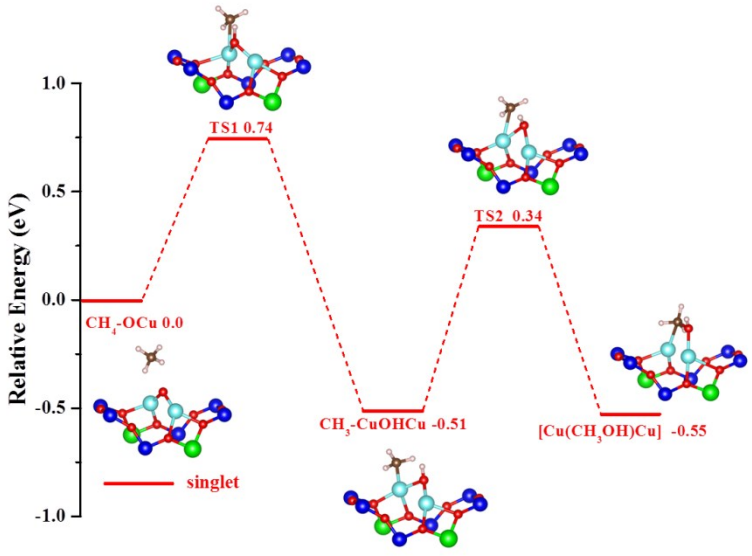

Figure S2. Reaction energy diagram and optimized structures of intermediates and transition states for the methane conversion to methanol on $[Cu(\mu\text{-}O)Cu]^{2+}$-ZSM-5 (singlet).

3. The key geometric parameter of reactants, intermediates, transition states for methane conversion on $[Cu(\mu\text{-}O)M]^{2+}$-ZSM-5 (M=Cu, Ag, Zn, Au)

Table S2. The key geometrical parameters of intermediates and transition states for the reaction over [Cu(μ-O)M]-ZSM-5 (M=Cu, Ag, Zn, Au).

		Spin Multiplicity	∠Cu–O-Cu (deg)	$d_{Cu1–Cu2}$ (Å)	$d_{Cu1–C}$ (Å)	$d_{Cu1–O}$ (Å)	$d_{Cu2–O}$ (Å)	$d_{C–H}$ (Å)	$d_{O–H}$ (Å)	$d_{C–Ooxo}$ (Å)
CuOCu-ZSM-5	**RC**	triplet	117.0	2.981	3.215	1.754	1.741	1.096	2.424	3.259
	TS1	triplet	88.8	2.551	3.155	1.827	1.819	1.399	1.187	1.399
	RI	triplet	100.5	2.820	3.331	1.842	1.826	2.185	0.981	2.937
	AI	singlet	95.7	2.741	1.976	1.832	1.864	2.761	0.978	2.761
	MC	singlet	95.3	2.724	1.978	1.978	1.857	2.750	0.979	2.750
	MC'	triplet	118.8	3.237	1.998	1.939	1.821	2.908	0.976	2.969
	TS2	singlet	78.2	2.448	2.301	1.988	1.891	2.180	0.981	1.895
	PC	singlet	68.1	2.849	2.221	2.936	1.930	2.009	0.978	1.895
	FC	-	-	2.482	-	-	-	-	-	1.429
		Spin Multiplicity	∠Cu–O-Ag (deg)	$d_{Cu–Ag}$ (Å)	$d_{Cu–C}$ (Å)	$d_{Cu–O}$ (Å)	$d_{Ag–O}$ (Å)	$d_{C–H}$ (Å)	$d_{O–H}$ (Å)	$d_{C–O}$ (Å)
CuOAg-ZSM-5	**RC**	triplet	118.4	3.246	3.255	1.740	2.035	1.098	2.312	3.192
	TS1	triplet	103.5	2.424	3.353	1.782	2.132	1.316	1.227	2.525
	RI	triplet	109.1	3.244	3.458	1.810	2.164	1.965	0.995	2.864
	AI	singlet	87.8	2.783	1.965	1.810	2.184	2.747	0.978	2.698
	MC	singlet	87.4	2.776	1.964	1.809	2.189	2.792	0.978	2.718
	MC'	triplet	106.9	3.204	2.055	1.883	2.102	3.114	0.975	3.080
	TS2#	singlet	74.4	2.628	2.137	1.833	2.474	2.280	0.981	1.980
	PC	singlet	-	2.585	3.176	1.994	3.261	2.027	0.983	1.455
	FC	-	-	2.307	-	-	-	-	-	-
CuOZn-ZSM-5		Spin Multiplicity	∠Cu–O-Zn (deg)	$d_{Cu–Zn}$ (Å)	$d_{Cu–C}$ (Å)	$d_{Cu–O}$ (Å)	$d_{Zn–O}$ (Å)	$d_{C–H}$ (Å)	$d_{O–H}$ (Å)	$d_{C–O}$ (Å)

	RC	doublet	100.6	2.765	3.255	1.781	1.812	1.096	2.353	3.226
	TS1*	doublet	84.7	2.500	3.153	1.841	1.869	1.331	1.235	2.539
	RI	doublet	83.8	2.519	3.265	1.903	1.870	2.136	0.988	2.946
	TS2*	doublet	71.8	2.424	3.101	1.890	2.220	2.301	0.985	2.056
	MC	doublet	114.6	3.261	1.953	2.036	1.836	2.941	0.975	3.068
	TS3*	doublet	71.8	2.424	3.101	1.890	2.220	2.301	0.985	2.056
	PC	doublet	-	2.356	3.011	1.984	3.335	2.008	0.976	1.457
	FC	-	-	2.688	-	-	-	-	-	-
		Spin Multiplicity	∠Cu–O-Au	$d_{Cu–Au}$	$d_{Cu–C}$	$d_{Cu–O}$	$d_{Au–O}$	$d_{C–H}$	$d_{O–H}$	$d_{C–O}$
			(deg)	(Å)	(Å)	(Å)	(Å)	(Å)	(Å)	(Å)
CuOAu-ZSM-5	**RC**	triplet	86.6	2.578	3.144	1.810	1.946	1.098	2.603	3.191
	TS1*	triplet	80.7	2.516	3.276	1.863	2.020	1.346	1.220	2.550
	RI	triplet	80.6	2.540	3.532	1.886	2.040	2.136	1.001	2.930
	AI	singlet	86.1	2.678	1.969	1.843	2.071	2.680	0.979	2.773
	TS2*	singlet	72.4	2.497	2.190	1.857	2.324	2.301	0.982	1.897
	MC	singlet	82.3	2.577	1.967	1.840	2.066	2.941	0.980	2.806
	MC'	triplet	99.2	3.018	2.024	1.944	2.016	3.278	0.977	3.120
	PC	singlet	-	2.865	2.257	2.950	2.121	2.008	0.974	1.453
	FC	-	-	2.582	-	-	-	-	-	-

RC: Reactant complex, TS: transition state, RI: Radical intermediate (triplet), AI: Adsorbed intermediate, MC: Methyl complex (singlet), MC': Methyl complex (triplet), PC: Product complex (adsorbed), FC: Final complex (desorbed).

4. The Relative energies of CH_3•-OCuM and M-OH-Cu-CH_3 (M=Cu, Ag, Au) calculated in the high-spin and low-spin states.

Table S3. The Relative energies of CH_3•-OCuM and M-OH-Cu-CH_3 (M=Cu, Ag, Au) calculated in the high-spin and low-spin states.

species	Singlet (eV)	Triplet (eV)
CH_3•-OCu_2	0 (adsorbed)	0.94 (radical)
CH_3•-OCuAg	0 (adsorbed)	1.38 (radical)
CH_3•-OCuAu	0 (adsorbed)	1.00 (radical)

Cu-OH-Cu-CH_3	0	0.52
Ag-OH-Cu-CH_3	0	0.87
Au-OH-Cu-CH_3	0	0.93

5. C-H activation of methane on CuOM(M=Cu, Ag, Zn, Au)-ZSM-5 cluster

The activation barrier for methane activation on 10T-CuOM-ZSM-5 cluster and $[Cu(\mu\text{-}O)M]^{2+}$-ZSM-5 (M=Cu, Ag, Zn, Au) periodic system are displayed in **Table S4**. The reactants, transition states, products involved in methane activation on cluster model are shown in **Figure S3**.

The activation barriers for methane activation on 10T-$[Cu(\mu\text{-}O)M]^{2+}$-ZSM-5 (M=Cu, Ag, Zn, Au) cluster are 0.80, 0.32, 0.84, and 0.45 eV, respectively, which are in according with those (0.73, 0.33, 0.90 and 0.49 eV) on periodic CuOM-ZSM-5 (M=Cu, Ag, Zn, Au) periodic system. The calculated results indicated that GGA-PBE method in our wok is reliable.

Table S4. The activation barrier for C-H activation of methane over 10T-$[Cu(\mu\text{-}O)M]^{2+}$-ZSM-5 cluster and periodic $[Cu(\mu\text{-}O)M]^{2+}$-ZSM-5 system (M=Cu, Ag, Zn, Au).

Method	Model	*E*a (eV)
B3LYP-D3	10T-$[Cu(\mu\text{-}O)Cu]^{2+}$-ZSM-5	0.80
	10T-$[Cu(\mu\text{-}O)Ag]^{2+}$-ZSM-5	0.32
	10T-$[Cu(\mu\text{-}O)OZn]^{2+}$-ZSM-5	0.84
	10T-$[Cu(\mu\text{-}O)Au]^{2+}$-ZSM-5	0.45
PBE-D3	periodic-$[Cu(\mu\text{-}O)Cu]^{2+}$-ZSM-5	0.73
	periodic-$[Cu(\mu\text{-}O)Ag]^{2+}$-ZSM-5	0.33
	periodic-$[Cu(\mu\text{-}O)OZn]^{2+}$-ZSM-5	0.90
	periodic-$[Cu(\mu\text{-}O)Au]^{2+}$-ZSM-5	0.49

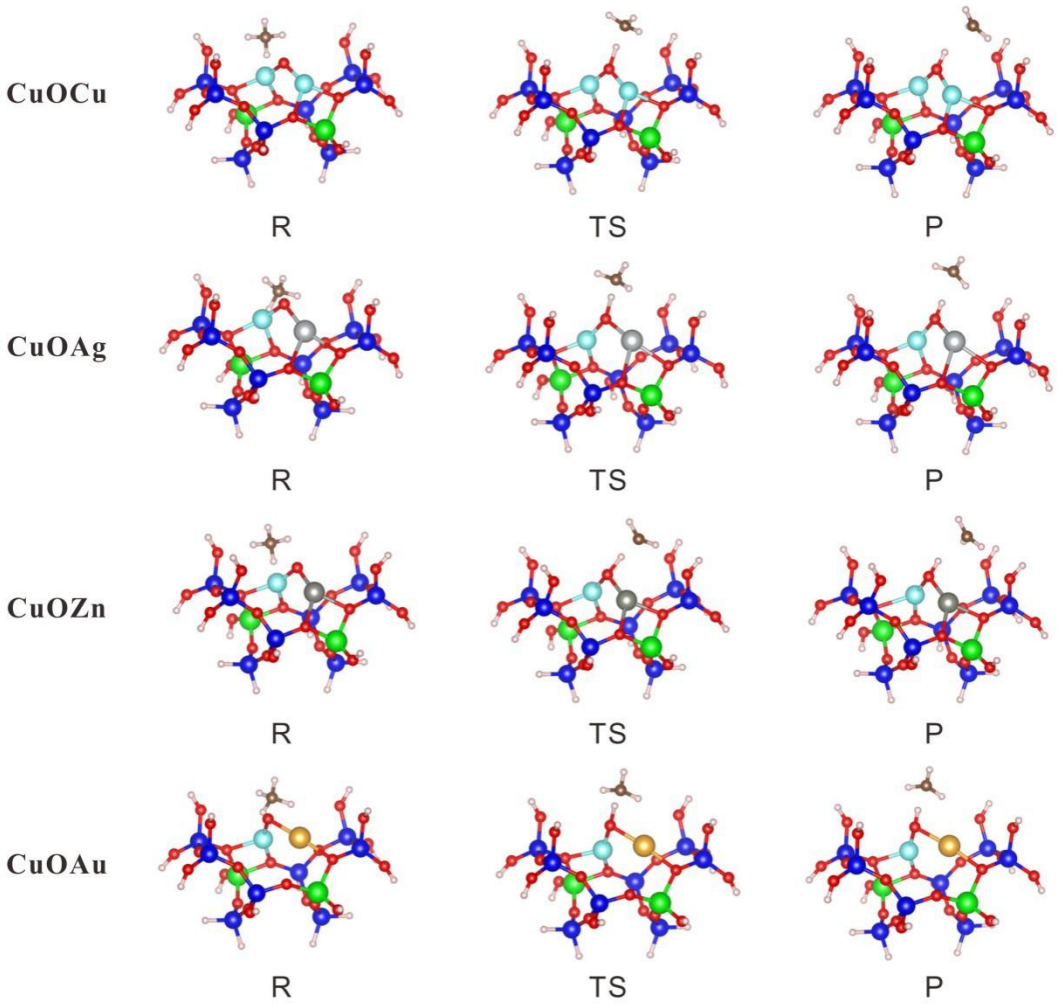

Figure S3. The configurations of reactants, transition states, and products on 10T-[Cu(μ-O)M]$^{2+}$-ZSM-5 (M=Cu, Ag, Zn, Au) cluster.

References

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