

Supporting Information

Roles of Zeolite Confinement and Cu–O–Cu Angle on the Direct Conversion of Methane to Methanol by $[\text{Cu}_2(\mu\text{-O})]^{2+}$ -exchanged AEI, CHA, AFX, and MFI Zeolites

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Table S1. Relative energies and geometrical parameters for $\text{Cu}_2(\mu\text{-O})$ in AEI, CHA, AFX, and MFI zeolites with different numbers of Si atom separating the Al pair, calculated in the triplet ground state.

	#Si separating Al pair	ΔE (kcal/mol)	$d_{\text{Al-Al}}$ (Å)	$d_{\text{Cu-Cu}}$ (Å)	$\angle_{\text{Cu-O-Cu}}$ (deg)	$d_{\text{Cu1-O}}$ (Å)	$d_{\text{Cu2-O}}$ (Å)
$[\text{Cu}_2(\mu\text{-O})]^{2+}\text{-AEI}$	2	0.0	7.616	2.508	90.3	1.769	1.769
	3	0.5	8.020	2.804	106.1	1.761	1.748
$[\text{Cu}_2(\mu\text{-O})]^{2+}\text{-CHA}$	2	0.0	7.679	2.579	93.6	1.768	1.768
	3	1.1	8.354	2.914	112.3	1.755	1.753
$[\text{Cu}_2(\mu\text{-O})]^{2+}\text{-AFX}$	2	0.0	7.702	2.584	93.9	1.768	1.768
	3	0.4	8.340	2.907	112.0	1.755	1.752
$[\text{Cu}_2(\mu\text{-O})]^{2+}\text{-MFI}$	1	11.3	6.198	2.408	84.5	1.790	1.791
	2	0.0	7.788	3.306	143.4	1.741	1.740
	3	7.9	8.948	3.374	152.3	1.741	1.733

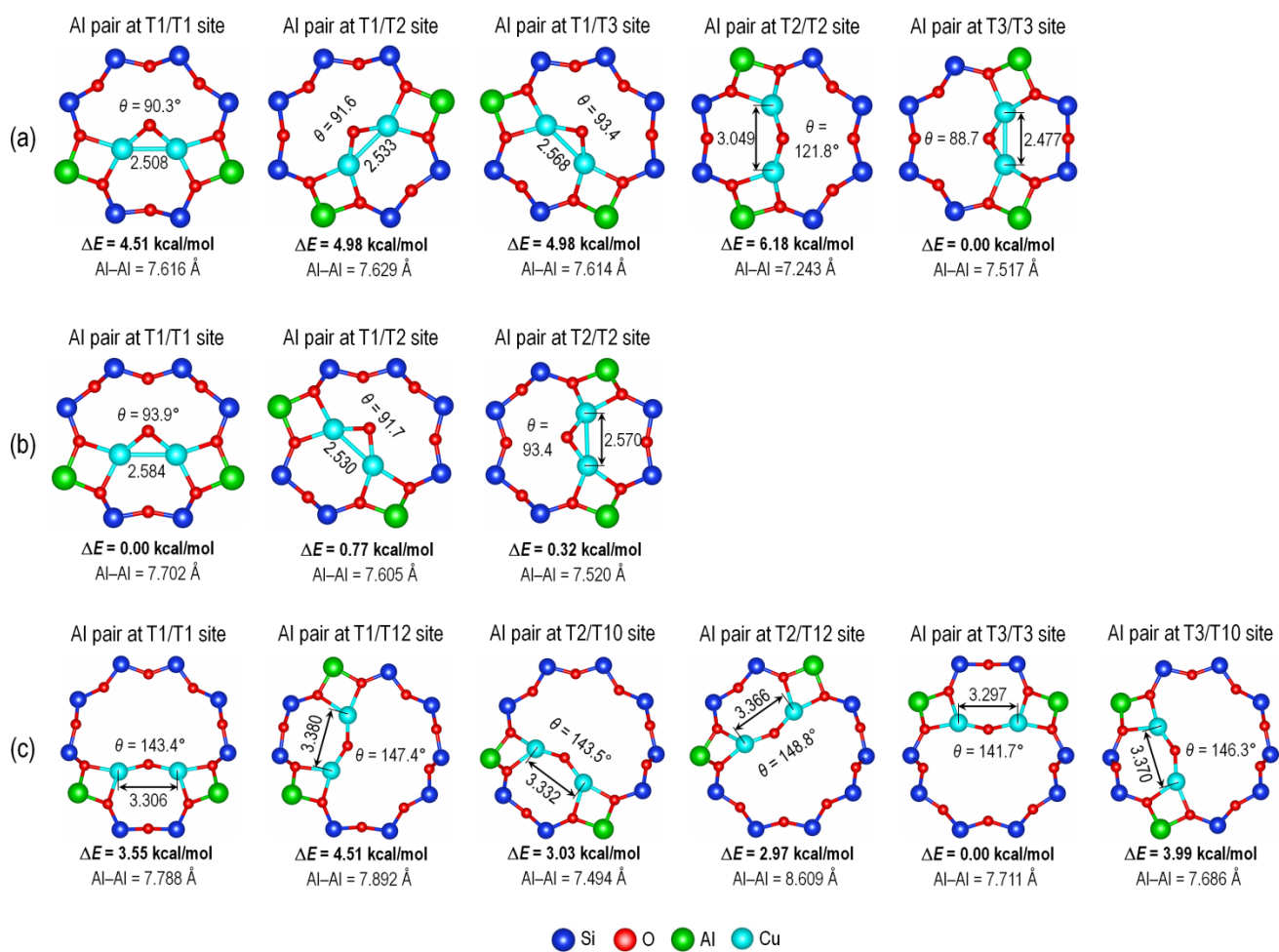


Figure S1. Relative energies and geometrical parameters of (a) [Cu₂(μ-O)]²⁺-AEI, (b) -AFX, and (c) -MFI zeolites with two Si atoms separating the Al pair located at different T sites. Cu-Cu bond length is given in Å.

Table S2. Relative energies and geometrical parameters of intermediates and transition states in the **triplet** state for the reaction over $[\text{Cu}_2(\mu\text{-O})]^{2+}$ -AEI, CHA, -AFX, and -MFI.

		ΔE (kcal/mol)	$d_{\text{Cu-Cu}}$ (Å)	$\angle_{\text{Cu-O-Cu}}$ (deg)	$d_{\text{Cu1-O}}$ (Å)	$d_{\text{Cu2-O}}$ (Å)	$d_{\text{Cu1-C}}$ (Å)	$d_{\text{Cu2-C}}$ (Å)	$d_{\text{C-H}}$ (Å)	$d_{\text{O-H}}$ (Å)	$d_{\text{C-O}}$ (Å)
$[\text{Cu}_2(\mu\text{-O})]^{2+}$ -AEI	RC	0.0	2.491	89.5	1.769	1.770	4.543	4.300	1.096	2.801	3.438
	TS1	10.8	2.453	84.1	1.832	1.833	3.749	3.608	1.367	1.197	2.564
	RI	7.4	2.469	83.7	1.848	1.852	4.069	3.862	1.954	1.003	2.952
	TS2 (d)	14.2	2.594	92.0	1.802	1.805	3.984	3.762	2.943	0.966	3.077
	MC	1.3	2.515	84.9	1.833	1.893	3.358	2.127	-	0.985	2.935
	TS2 (i)	29.4	2.405	74.2	1.994	1.993	3.528	3.343	-	0.988	1.870
	PC	15.7	2.334	52.7	2.866	2.232	3.908	3.326	-	0.977	1.455
	FC	25.5	2.350	-	-	-	-	-	-	-	-
$[\text{Cu}_2(\mu\text{-O})]^{2+}$ -CHA	RC	0.0	2.582	93.8	1.767	1.767	4.686	4.527	1.096	2.590	3.479
	TS1	12.0	2.502	86.0	1.834	1.834	3.723	3.622	1.378	1.190	2.568
	RI	8.9	2.515	85.5	1.852	1.852	4.085	3.965	2.029	0.999	3.025
	TS2 (d)	13.6	2.643	93.9	1.808	1.808	4.066	3.971	2.879	0.970	3.194
	MC	1.4	2.668	91.7	1.822	1.895	3.705	2.104	-	0.989	2.889
	TS2 (i)	24.1	2.413	75.3	1.977	1.973	3.480	3.446	-	1.000	1.854
	PC	14.0	2.329	61.9	2.263	2.265	3.427	3.429	-	0.994	1.460
	FC	26.5	2.339	-	-	-	-	-	-	-	-
$[\text{Cu}_2(\mu\text{-O})]^{2+}$ -AFX	RC	0.0	2.567	93.1	1.767	1.768	4.786	4.526	1.096	2.631	3.538
	TS1	12.6	2.508	86.3	1.835	1.834	3.730	3.596	1.381	1.189	2.570
	RI	9.2	2.523	86.1	1.848	1.847	3.951	3.841	2.040	0.998	3.020
	TS2 (d)	13.8	2.635	93.6	1.806	1.807	3.900	3.804	2.824	0.967	3.073
	MC	-1.0	2.617	89.6	1.826	1.886	3.337	2.054	-	0.990	3.226
	TS2 (i)	24.3	2.414	75.5	1.971	1.969	3.466	3.444	-	1.000	1.858
	PC	14.2	2.334	61.8	2.266	2.281	3.430	3.444	-	0.993	1.461
	FC	26.6	2.337	-	-	-	-	-	-	-	-
$[\text{Cu}_2(\mu\text{-O})]^{2+}$ -MFI	RC	0.0	3.300	142.7	1.740	1.743	4.432	3.282	1.098	2.766	3.614
	TS1	16.3	3.346	134.2	1.815	1.817	3.573	3.437	1.391	1.187	2.575
	RI	13.1	3.392	134.0	1.843	1.842	3.863	3.797	1.962	1.003	2.954
	MC	3.9	3.332	124.2	1.833	1.937	3.835	2.033	-	0.978	3.054
	TS2 (i)	34.8	2.547	79.3	2.019	1.971	3.496	3.234	-	0.989	1.880
	PC	22.1	2.463	57.9	2.806	2.137	3.797	3.176	-	0.976	1.464
	FC	37.1	2.483	-	-	-	-	-	-	-	-

RC: Reactant complex, TS: Transition state, RI: Radical intermediate, MC: Methyl complex, PC: Product complex, FC: Final complex, (d): direct and (i): indirect rebound mechanisms, O: Oxo atom, H: Abstracted H atom.

Table S3. Relative energies and geometrical parameters of intermediates and transition states in the **open-shell** and **closed-shell SINGLET** states for the reaction over $[\text{Cu}_2(\mu\text{-O})]^{2+}$ -AEI, CHA, -AFX, -MFI with two Si atoms separating the Al pair located at T1/T1 site.

		ΔE (kcal/mol) ^a	$d_{\text{Cu-Cu}}$ (Å)	$\angle_{\text{Cu-O-Cu}}$ (deg)	$d_{\text{Cu1-O}}$ (Å)	$d_{\text{Cu2-O}}$ (Å)	$d_{\text{Cu1-C}}$ (Å)	$d_{\text{Cu2-C}}$ (Å)	$d_{\text{C-H}}$ (Å)	$d_{\text{O-H}}$ (Å)	$d_{\text{C-O}}$ (Å)
$[\text{Cu}_2(\mu\text{-O})]^{2+}$ -AEI	RC	1.0	2.418	86.6	1.761	1.764	4.561	4.323	1.096	2.980	3.636
	TS1	12.6	2.454	84.3	1.829	1.830	3.739	3.597	1.324	1.237	2.562
	RI	7.6	2.469	83.7	1.848	1.852	4.077	3.868	1.962	1.001	2.959
	MC	-9.2	2.562	88.1	1.869	1.814	3.852	1.991	-	0.990	2.730
	TS2 (i)	2.8	2.421	79.1	1.955	1.843	3.526	2.253	-	0.999	1.963
	PC	-22.0	2.413	74.5	1.986	1.998	3.016	3.018	-	0.997	1.478
	FC	13.2	2.629	-	-	-	-	-	-	-	-
$[\text{Cu}_2(\mu\text{-O})]^{2+}$ -CHA	RC	0.8	2.426	87.4	1.756	1.756	4.801	4.648	1.096	2.995	3.950
	TS1	13.5	2.503	86.2	1.831	1.833	3.714	3.609	1.337	1.226	2.563
	RI	9.1	2.515	85.5	1.852	1.852	4.087	3.967	2.032	0.998	3.026
	MC	-6.4	2.762	97.8	1.840	1.823	3.905	1.990	-	0.991	2.637
	TS2 (i)	3.9	2.529	84.8	1.900	1.848	3.541	2.275	-	0.998	1.998
	PC	-23.9	2.455	76.4	1.985	1.985	2.982	2.982	-	1.016	1.473
	FC	23.1	2.460	-	-	-	-	-	-	-	-
$[\text{Cu}_2(\mu\text{-O})]^{2+}$ -AFX	RC	0.9	2.424	87.2	1.757	1.757	4.864	4.622	1.096	3.017	3.958
	TS1	14.0	2.505	86.3	1.830	1.833	3.714	3.576	1.338	1.227	2.564
	RI	9.4	2.523	86.1	1.848	1.848	3.954	3.842	2.044	0.997	3.023
	MC	-6.0	2.773	98.5	1.838	1.822	3.917	1.990	-	0.991	2.639
	TS2 (i)	4.2	2.523	84.6	1.900	1.846	3.535	2.276	-	0.997	2.008
	PC	-23.8	2.444	75.9	1.985	1.989	2.987	2.990	-	1.015	1.474
	FC	22.9	2.454	-	-	-	-	-	-	-	-
$[\text{Cu}_2(\mu\text{-O})]^{2+}$ -MFI	RC	0.1	3.272	140.8	1.735	1.737	4.450	3.351	1.097	2.824	3.662
	TS1	18.1	3.345	134.6	1.812	1.813	3.559	3.425	1.346	1.226	2.571
	RI	13.2	3.393	133.8	1.843	1.845	3.875	3.809	1.992	0.999	2.979
	TS2(d)	19.6	3.015	108.4	1.858	1.858	3.633	3.556	2.542	0.969	2.672
	MC	-9.0	3.460	136.6	1.861	1.862	3.786	1.957	-	0.977	2.730
	TS2(i)	10.8	3.232	117.9	1.898	1.875	3.364	2.262	-	0.976	1.920
	PC	-14.2	2.534	77.6	2.040	2.004	3.077	2.910	-	0.979	1.493
	FC	30.3	2.702	-	-	-	-	-	-	-	-

^aRelative energies are measured from the corresponding RC in the triplet state. RC: Reactant complex, TS: Transition state, RI: Radical intermediate, MC: Methyl complex, PC: Product complex, FC: Final complex, (d): direct and (i): indirect rebound mechanisms, O: Oxo atom, H: Abstracted H atom.

Table S4. Atomic spin density (SD) for the Cu and O_{oxo} atoms of initial complex, reactant complex, **TS1**, radical intermediate, methyl complex, **TS2**, and product complex in the triplet state.

		Cu1	Cu2	O _{oxo}
[Cu ₂ (μ-O)] ²⁺ -AEI	IC	0.509	0.514	0.712
	RC	0.504	0.508	0.723
	TS1	0.393	0.385	0.461
	RI	0.359	0.352	0.196
	MC	0.414	0.574	0.183
	TS2	0.563	0.575	0.158
	PC	0.810	0.738	0.081
[Cu ₂ (μ-O)] ²⁺ -CHA	IC	0.521	0.521	0.691
	RC	0.519	0.519	0.693
	TS1	0.391	0.392	0.452
	RI	0.356	0.357	0.183
	MC	0.402	0.607	0.183
	TS2	0.574	0.563	0.167
	PC	0.752	0.740	0.136
[Cu ₂ (μ-O)] ²⁺ -AFX	IC	0.521	0.521	0.692
	RC	0.518	0.518	0.697
	TS1	0.390	0.391	0.454
	RI	0.355	0.356	0.188
	MC	0.419	0.626	0.242
	TS2	0.571	0.567	0.175
	PC	0.752	0.746	0.140
[Cu ₂ (μ-O)] ²⁺ -MFI	IC	0.530	0.530	0.712
	RC	0.527	0.533	0.712
	TS1	0.387	0.385	0.468
	RI	0.355	0.356	0.213
	MC	0.434	0.610	0.206
	TS2	0.576	0.560	0.159
	PC	0.826	0.705	0.089

IC: Initial complex of [Cu₂(μ-O)]²⁺-zeolites with two Si atoms separating the Al pair, RC: Reactant complex, TS: Transition state, RI: Radical intermediate, MC: Methyl complex, PC: Product complex

Table S5. Relative energies and geometrical parameters of N₂O adsorption and **TS3** in the triplet and closed-shell singlet states for the N₂O decomposition by [2Cu]²⁺-AEI zeolite

Spin state		Binding mode	ΔE (kcal/mol)	$d_{\text{N-O}}$ (Å)	$d_{\text{N=N}}$ (Å)	$d_{\text{Cu-Cu}}$ (Å)	$\angle_{\text{Cu-O-Cu}}$ (deg)	$d_{\text{Cu1-O}}$ or $d_{\text{Cu1-N}}$ (Å)	$d_{\text{Cu2-O}}$ or $d_{\text{Cu2-N}}$ (Å)
Triplet	DL	-	12.3	-	-	2.350	-	-	-
	N ₂ O ads	μ -1,1-O	11.2	1.202	1.141	2.350	-	3.279	3.039
		η^1 -N	9.7	1.190	1.149	2.360	-	2.119	3.171
	TS3	μ -1,1-O	19.8	1.275	1.149	2.377	63.0	2.108	2.417
CS-Singlet	DL	-	0.0	-	-	2.629	-	-	-
	N ₂ O ads	μ -1,1-O	-6.0	1.210	1.137	2.695	-	2.847	1.984
		η^1 -N	-34.6	1.190	1.164	2.433	-	1.869	1.878
	TS3	μ -1,1-O	-4.8	1.223	1.138	2.538	70.5	2.355	2.016

DL: dissociation limit [2Cu]²⁺-AEI + N₂O. Geometry optimizations for the μ -1,3-O,N binding mode cannot converge to the minimum required accuracy.

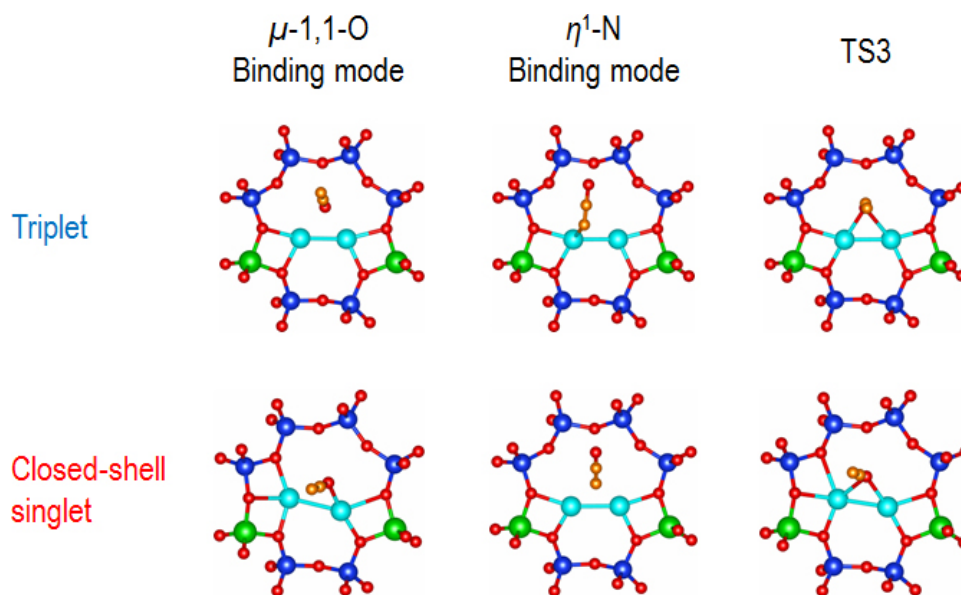


Figure S2. Optimized structures of N₂O adsorption and **TS3** in the triplet and closed-shell singlet states for the N₂O decomposition by [2Cu]²⁺-AEI zeolite.

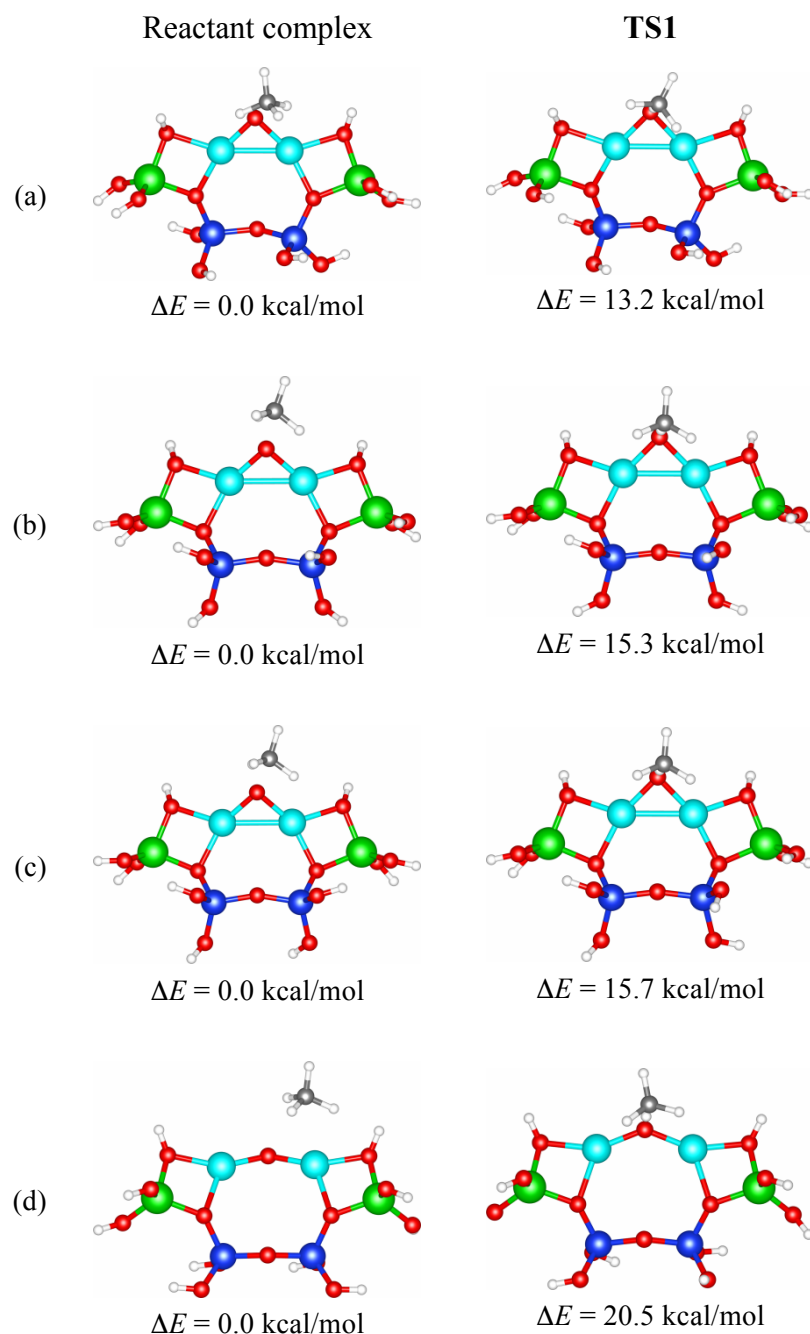


Figure S3. Relative energies and optimized structures for reactant complexes and TS1s of (a) $[\text{Cu}_2(\mu\text{-O})]^{2+}$ -AEI, (b) -CHA, (c) -AFX, and (d) -MFI zeolite clusters calculated in the triplet state. All energies include vdW-D2 dispersion corrections. The clusters are obtained from the optimized periodic-structures and then terminated by H atoms to construct neutral systems. During calculations, only the H-atom terminations are allowed to fully relax, while the others are fixed to their optimized positions.

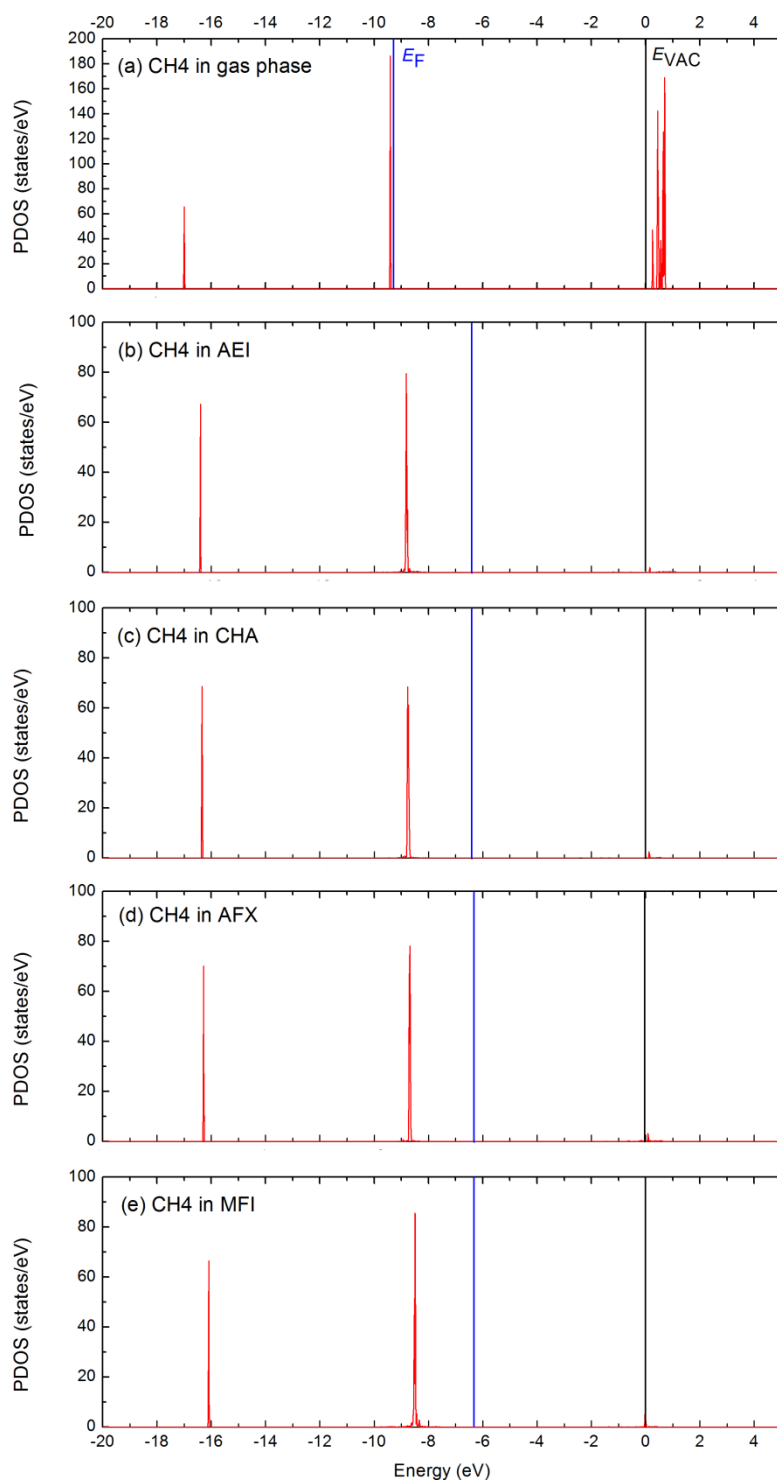
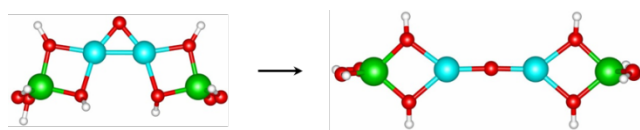


Figure S4. Partial density of states (PDOS) projected to C and H atoms of methane (a) in the gas phase, confined in (b) AEI, (c) CHA, (d) AFX, and (e) MFI zeolites. E_F and E_{VAC} stand for Fermi energy and vacuum energy, respectively. For methane in the gas phase, the first high-intensity peak below E_F (at -9.41 eV) corresponds to the threefold degenerate orbital of tetrahedral methane. After confinement in AEI, CHA, AFX, and MFI zeolites, this threefold degenerate orbital is split into two orbitals: one twofold degenerate orbital and one non-degenerate orbital, resulting in two lower-intensity peaks that are neighboring to each other.

Table S6. Relative energies and geometrical parameters of the optimized $[\text{Cu}_2(\mu\text{-O})]^{2+}$ -zeolite cluster with different Cu–O–Cu angles



$\angle_{\text{Cu-O-Cu}}$ (deg)	ΔE (kcal/mol)	$d_{\text{Cu-Cu}}$ (Å)	$d_{\text{Cu1-O}}$ (Å)	$d_{\text{Cu2-O}}$ (Å)
80	2.49	2.349	1.835	1.818
90	1.33	2.542	1.792	1.802
100	1.42	2.733	1.781	1.787
110	1.24	2.910	1.774	1.779
120	1.35	3.061	1.769	1.771
130	1.70	3.194	1.764	1.760
140	1.22	3.308	1.761	1.759
150	0.70	3.393	1.757	1.756
160	0.29	3.457	1.755	1.755
170	0.04	3.495	1.754	1.754
180	0.00	3.505	1.753	1.754

Calculation Details:

To optimize the above $[\text{Cu}_2(\mu\text{-O})]^{2+}$ -zeolite clusters and obtain their MOs, we employed Gaussian09 program code with B3LYP method. This method consists of the Slater exchange, the Hartree-Fock exchange, the exchange functional of Becke,¹ the correlation functional of Lee, Yang, Parr (LYP),² and the correlation functional of Vosko, Wilk, and Nusair.³ The 6-311+G** basis set is used for Cu atom, while the D95** basis set is used for Al, O, C, and H atoms. During calculations, the Cu–O–Cu angle is fixed, while the other geometrical parameters are fully relaxed.

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- (3) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200–1211.