Electronic Supplementary Information

Molecular Insight into the Role of Zeolite Lattice Constraints on Methane Activation over Cu–O–Cu Active Site

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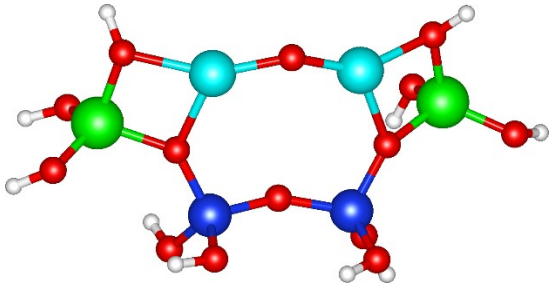

Fig. S1 Small cluster model of $[Cu_2(\mu\text{-}O)]^{2+}$-MOR for the molecular orbital calculations. Color legend: Si (blue), Al (green), Cu (cyan), O (red), H (white).

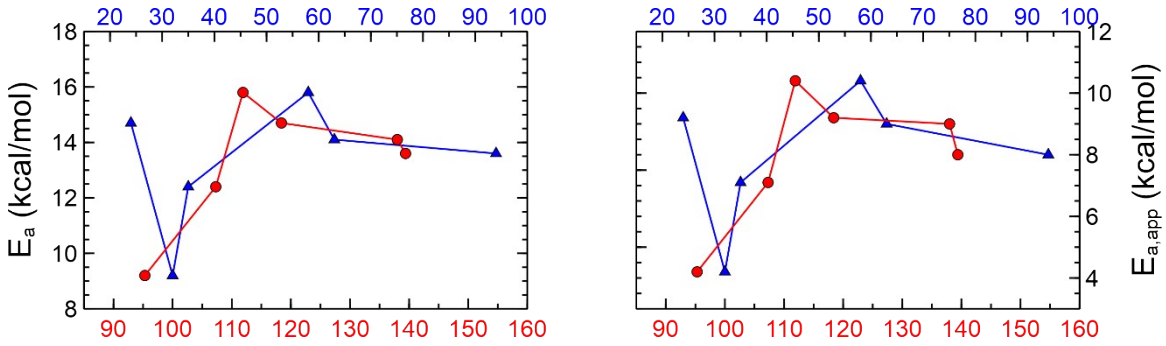

Fig. S2 Plots of H–CH_3 (a) activation barrier and (b) apparent activation barrier against the ∠CuOCu and φ angles.

Table S1. Geometrical parameters, imaginary frequency (*iν*), and atomic spin densities (ρ) along the H_3C–H activation in the 12-MR opening. All reaction steps are in the triplet state.

Al-pair arr.	React. step	*i*(ν) (cm^{-1})	d(Al···Al) (Å)	d(Cu···Cu) (Å)	d(Cu–O) (Å)	∠CuOCu (°)	φ (°)	d(C–H) (Å)	*d*(O–H) (Å)	ρ(Cu1, Cu2)	ρ(O, C)	ρ(H)
$T2/T4_{1Si}$	AS		6.07	3.04	1.75, 1.77	119.7	19/23	1.10	2.48	0.64, 0.57	0.50, 0.00	0.001
	TS	1296.7	6.02	2.97	1.81, 1.82	110.2	25/28	1.32	1.24	045, 0.35	0.52, 0.46	0.033
	FS		6.03	3.00	1.84, 1.84	109.6	26/28	1.95	1.00	0.42, 0.32	0.19, 087	0.036
$T2_{2Si}$	AS		7.68	2.61	1.76, 1.76	96.0	30/30	1.10	2.34	0.56, 0.56	0.62, 0.00	0.001
	TS	1117.7	7.56	2.45	1.82, 1.82	84.5	27/27	1.30	1.26	0.39, 0.39	0.54, 0.45	0.030
	FS		7.57	2.46	1.84, 1.84	83.9	25/25	2.01	1.00	0.37, 0.37	0.17, 0.86	0.037
$T4_{2Si}$	AS		7.75	3.30	1.77, 1.75	139.8	49/63	1.10	2.42	0.58, 0.63	0.52, 0.00	0.001
	TS	1410.1	7.64	3.28	1.82, 1.82	128.1	51/66	1.33	1.23	0.39, 0.40	0.53, 0.48	0.029
	FS		7.69	3.32	1.85, 1.85	128.0	52/64	2.01	1.00	0.36, 0.36	0.20, 0.87	0.034
$T2/T4_{2Si}$	AS		7.68	2.85	1.76, 1.76	108.5	27/35	1.10	2.36	0.62, 0.60	0.53, 0.00	0.000
	TS	1187.2	7.55	2.56	1.82, 1.83	88.7	25/31	1.30	1.26	042, 0.38	0.53, 0.44	0.032
	FS		7.58	2.57	1.84, 1.85	88.3	22/28	1.96	1.00	0.39, 0.36	018, 0.86	0.035
$T2_{3Si}$	AS		8.23	2.92	1.75, 1.75	113.6	53/58	1.10	2.34	0.61, 0.58	0.54, 0.00	0.000
	TS	1398.9	8.08	2.77	1.80, 1.81	100.1	43/43	1.33	1.23	0.42, 0.40	0.46, 0.47	0.035
	FS		8.12	2.82	1.82, 1.83	101.2	41/42	1.96	1.00	0.38, 0.37	0.16, 0.86	0.036
$T4_{3Si}$	AS		8.34	3.30	1.77, 1.76	138.5	88/94	1.10	2.51	0.57, 0.61	0.57, 0.00	0.001
	TS	1495.2	8.29	3.35	1.83, 1.83	133.1	85/92	1.34	1.23	0.40, 0.40	0.51, 0.48	0.032
	FS		8.35	3.42	1.85, 1.85	134.9	86/91	2.01	1.00	0.36, 0.36	0.21, 0.87	0.033

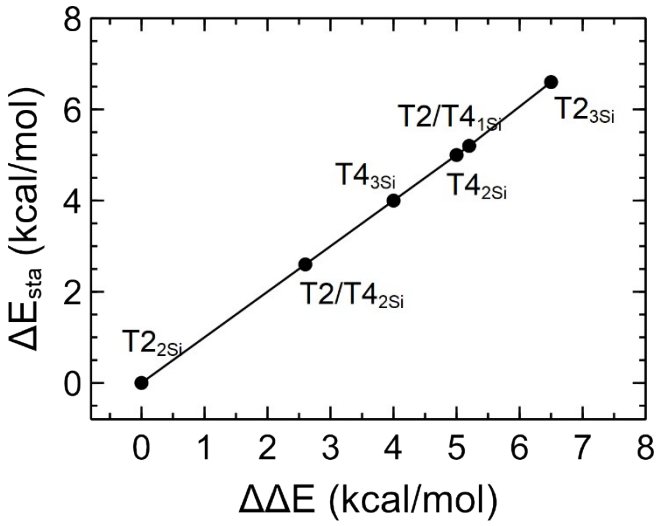

Fig. S3 Plot of E_{sta} relative to that for $T2_{2Si}$ against ΔE relative to that for $T2_{2Si}$.

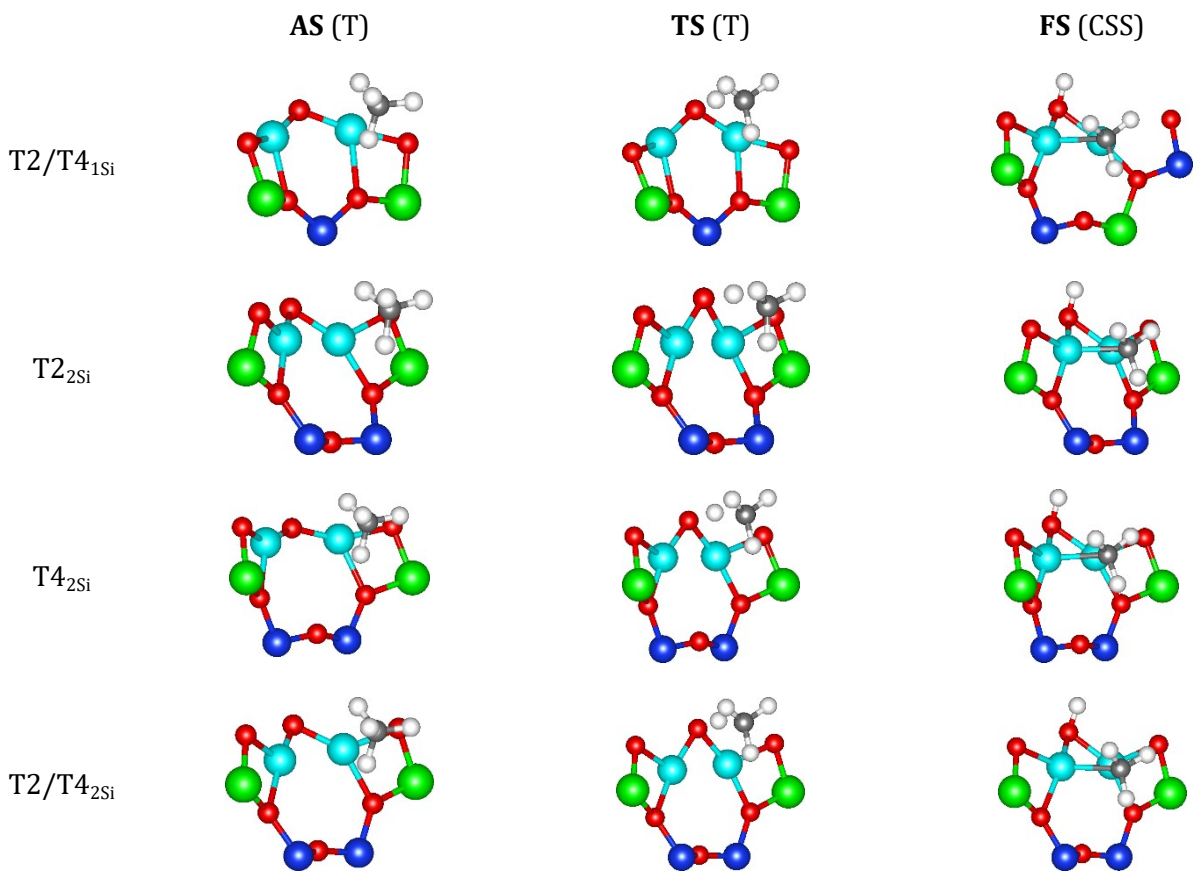

Fig. S4 Optimized structures of **AS**, **TS**, and **FS** for the CH_4 activation inside the 8-MR side pocket. T and CSS stand for the triplet and closed-shell singlet states, respectively.

Table S2. Geometrical parameters, imaginary frequency (*iν*), and atomic spin densities (ρ) along the H_3C–H activation inside the 8-MR side pocket.

Al-pair arr.	Reaction step (spin state) [a]	*i*(ν) (cm^{-1})	d(Al···Al) (Å)	d(Cu···Cu) (Å)	d(Cu–O) (Å)	∠CuOCu (°)	φ (°)	d(C–H) (Å)	*d*(O–H) (Å)	ρ(Cu1, Cu2)	ρ(O, C)	ρ(H)
$T2/T4_{1Si}$	AS (T)		6.07	3.04	1.75, 1.77	119.7	19/23	1.10	2.97	0.64, 0.57	0.50, 0.00	0.001
	TS (T)	1591.6	6.06	3.05	1.80, 1.83	114.4	3/4	1.38	1.22	0.42, 0.37	0.51, 0.49	0.029
	FS (CSS)		5.96	2.40	1.84, 1.86	81.0	68/78	-	0.99	0.00, 0.00	0.00, 0.00	0.000
$T2_{2Si}$	AS (T)		7.68	2.61	1.76, 1.76	96.0	30/30	1.10	2.98	0.56, 0.56	0.62, 0.00	0.001
	TS (T)	1412.7	7.64	2.46	1.82, 1.82	84.9	7/7	1.34	1.25	0.38, 0.38	0.57, 0.46	0.023
	FS (CSS)		7.62	2.36	1.88, 1.88	78.1	84/84	-	0.99	0.00, 0.00	0.00, 0.00	0.000
$T4_{2Si}$	AS (T)		7.75	3.30	1.77, 1.75	139.8	49/63	1.10	2.93	0.58, 0.63	0.52, 0.00	0.001
	TS (T)	1209.5	7.65	2.69	1.81, 1.81	95.7	9/15	1.31	1.26	0.41, 0.40	0.53, 0.44	0.033
	FS (CSS)		7.62	2.42	1.86, 1.86	81.2	75/82	-	0.99	0.00, 0.00	0.00, 0.00	0.000
$T2/T4_{2Si}$	AS (T)		7.68	2.85	1.76, 1.76	108.5	27/35	1.10	3.28	0.62, 0.60	0.53, 0.00	0.000
	TS (T)	1250.0	7.61	2.50	1.80, 1.82	87.0	6/7	1.32	1.24	0.38, 0.38	0.55, 0.46	0.033
	FS (CSS)		7.68	2.40	1.84, 1.90	79.8	82/85	-	0.99	0.00, 0.00	0.00, 0.00	0.000

[a] T and CSS stand for the triplet and closed-shell singlet states, respectively.

Table S3. Energetic results for the CH_4 activation in the 12-MR opening and inside the 8-MR side pocket calculated using GGA-PBE functional.

Al-pair arrangement	E_{rel} (kcal/mol)		E_{ads} (kcal/mol)		E_a (kcal/mol)		$E_{a,app}$ (kcal/mol)		ΔE (kcal/mol)	
	12-MR	**8-MR**	**12-MR**	**8-MR**	**12-MR**	**8-MR**	**12-MR**	**8-MR**	**12-MR**	**8-MR**
$T2/T4_{1Si}$	10.0	10.0	–6.3	–11.6	12.9	25.6	6.6	14.0	4.0	–24.5
$T2_{2Si}$	0.0	0.0	–5.3	–11.2	11.2	19.6	5.8	8.4	2.2	–21.0
$T4_{2Si}$	4.9	4.9	–5.5	–11.4	13.6	24.6	8.0	13.2	4.8	–21.9
$T2/T4_{2Si}$	5.9	5.9	–5.5	–11.2	12.1	21.2	6.6	10.0	3.3	–22.4
$T2_{3Si}$	3.0	3.0	–4.9	-	15.1	-	10.2	-	7.4	-
$T4_{3Si}$	4.9	4.9	–5.5	-	14.1	-	8.6	-	5.5	-

Comparing the results calculated with the PBE functional to the results calculated with the PBE+U method, we found no significant changes in the energetic trend.