Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Catalytic cycle of the partial oxidation of methane to methanol over Cu-ZSM-5 revealed by DFT calculations

Xi Yu,[a,b] Liangshu Zhong[a,b,c,*] and Shenggang Li[a,b,c,*]

[a]CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institue, Chinese Academy of Sciences, 100 Haike Road, Shanghai 201210, China. E-mail: lisg@sari.ac.cn; Tel: +86 21 20350994.

[b]University of Chinese Academy of Sciences, 19 Yuquan Road, Shijingshan District, Beijing 100049, China

[c]School of Physical Science and Technology, ShanghaiTech University, 100 Haike Road, Shanghai 201210, China

Emails: zhongls@sari.ac.cn, lisg@sari.ac.cn

Table S1 The relative energies of $Z[O_x]$ (x=1,2) calculated in the high-spin and low-spin states

active sites	spin multiplicity	relative energies (kJ/mol)
$[Cu_2(\mu\text{-}O)]^{2+}$	singlet	0
	triplet	-71.0
$[Cu_2(O_2)]^{2+}$	singlet	0
	triplet	-123.0

Table S2 The atomic charge and key geometric parameters of $Z[O_x]$ (x=1,2) in the ground state

active sites	spin multiplicity	atomic charge (*e*)				$d_{Cux–Oy}$ (Å) (x,y=1,2)	$d_{Cux–Oy}$ (Å) (x,y=1,2)	$d_{O–O}$ (Å)	∠CuOCu (°)
		Cu1	Cu2	O1	O2				
$[Cu_2(\mu\text{-}O)]^{2+}$	triplet	0.59	0.60	-0.52	—	1.77	1.77	—	139.2
$[Cu_2(O_2)]^{2+}$	triplet	0.58	0.61	-0.24	-0.22	1.91	1.92	1.44	—

Table S3 The relative energies of $Z_{L2}[O_x]$ (x=1,2) and key geometric parameters of the active sites in the $Z_{L2}[O_x]$ (x=1,2) in the triplet state and the singlet state

active sites	spin multiplicity	relative energies (kJ/mol)	$d_{Cux–Oy}$ (Å) (x,y=1,2)	$d_{Cux–Oy}$ (Å) (x,y=1,2)	$d_{O–O}$ (Å)	∠CuOCu (°)
$[Cu_2(\mu\text{-}O)]^{2+}$	singlet	0	1.75	1.76	—	101.5
	triplet	-87.8	1.77	1.78	—	102.5
$[Cu_2(O_2)]^{2+}$	singlet	0	1.79	1.80	2.16	—
	triplet	-35.2	1.88	2.00	2.26	—

Table S4 Free energy barriers of the methane activation step and the methanol desorption step for the partial oxidation of methane to methanol over the Z[O] and Z_L[O] models at 0 K, 298.15 K and 473.15 K.

Temperature (K)	Models	Free energy barriers (kJ/mol)	
0	Z[O]	methane activation step	92.7
		methanol desorption step	93.0
	Z_L[O]	methane activation step	91.5
		methanol desorption step	153.2
298.15	Z[O]	methane activation step	110.1
		methanol desorption step	45.3
	Z_L[O]	methane activation step	99.6
		methanol desorption step	101.7
473.15	Z[O]	methane activation step	124.0
		methanol desorption step	16.1
	Z_L[O]	methane activation step	107.3
		methanol desorption step	70.9

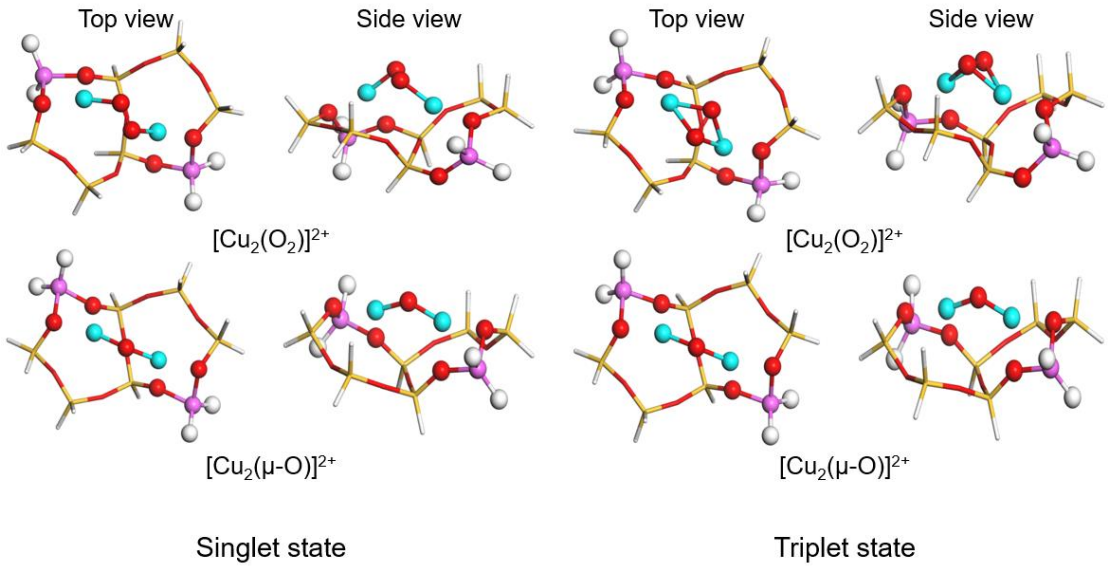

Fig. S1 The optimized Z[O_x] (x=1,2) double-5T-rings cluster models for singlet and triplet states. Cyan, yellow, purple, red and white represent copper, silicon, aluminum, oxygen and hydrogen atoms respectively.

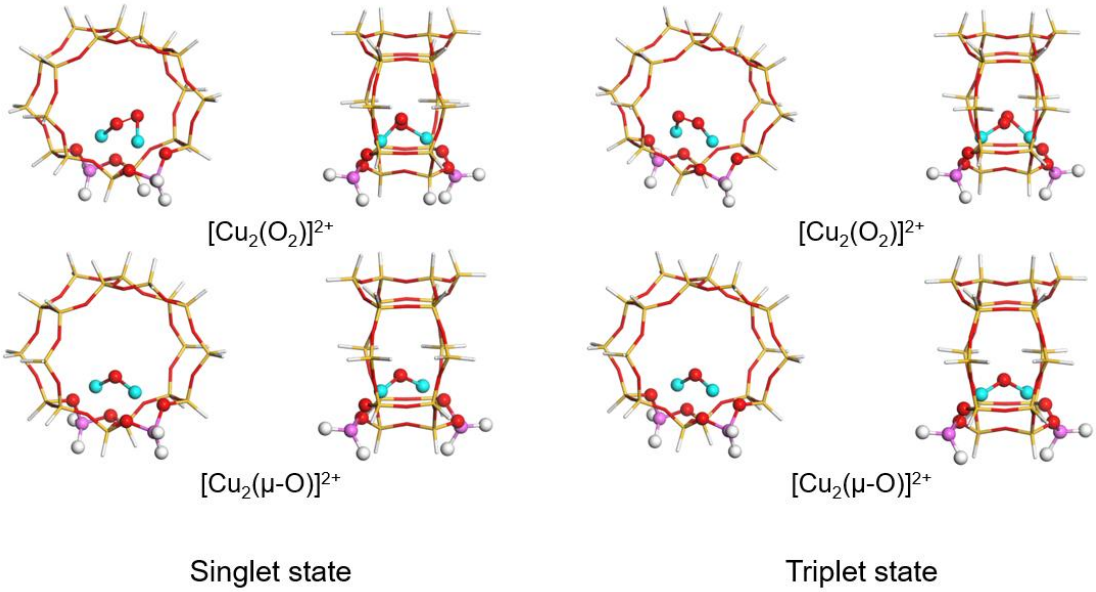

Fig. S2 The optimized $Z_L[O_x]$ (x=1,2) models for singlet and triplet states. Cyan, yellow, purple, red and white represent copper, silicon, aluminum, oxygen and hydrogen atoms respectively.

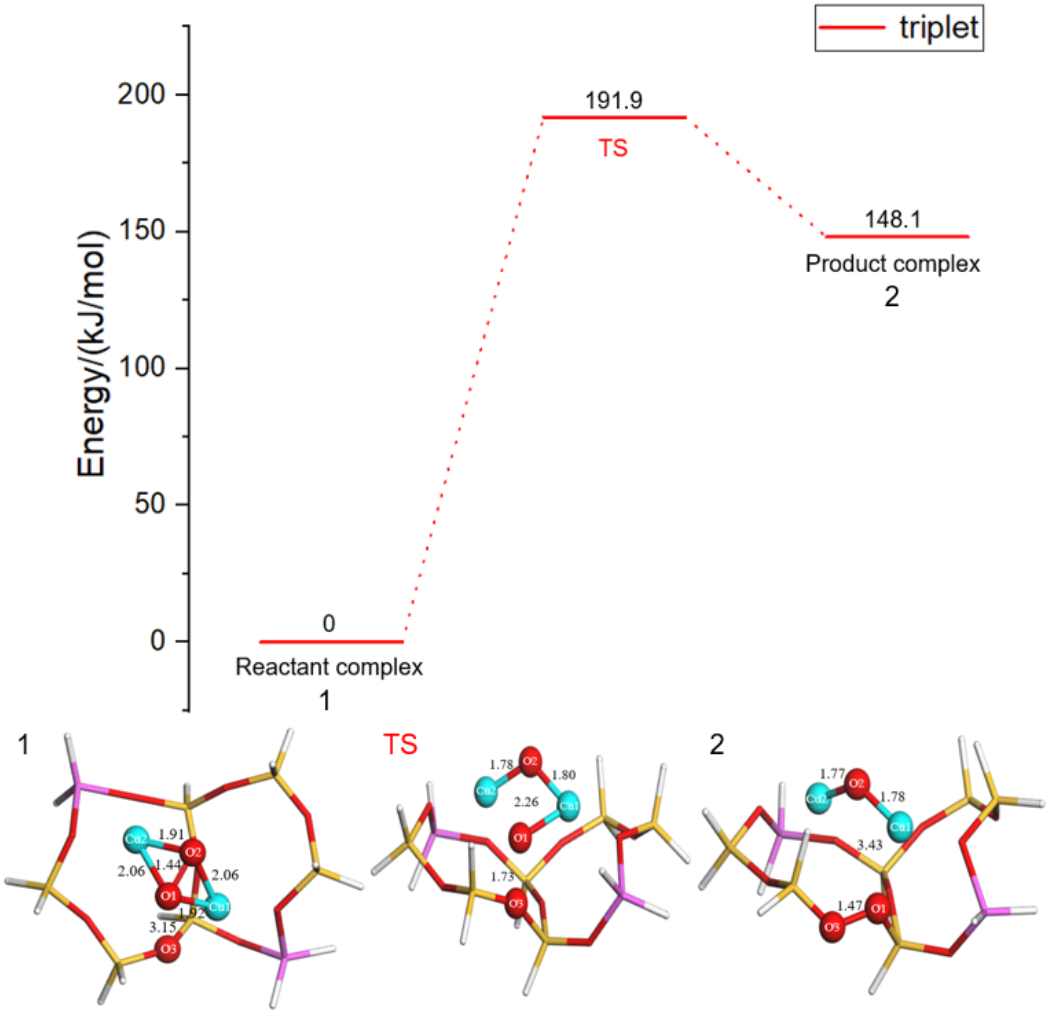

Fig. S3 Potential energy diagram and optimized structures of reactant complex, product complex and transition state of the optimal path for O-O bond cleavage in $[Cu_2(O_2)]^{2+}$-ZSM-5. Cyan, yellow, purple, red and white represent copper, silicon, aluminum, oxygen and hydrogen atoms respectively.

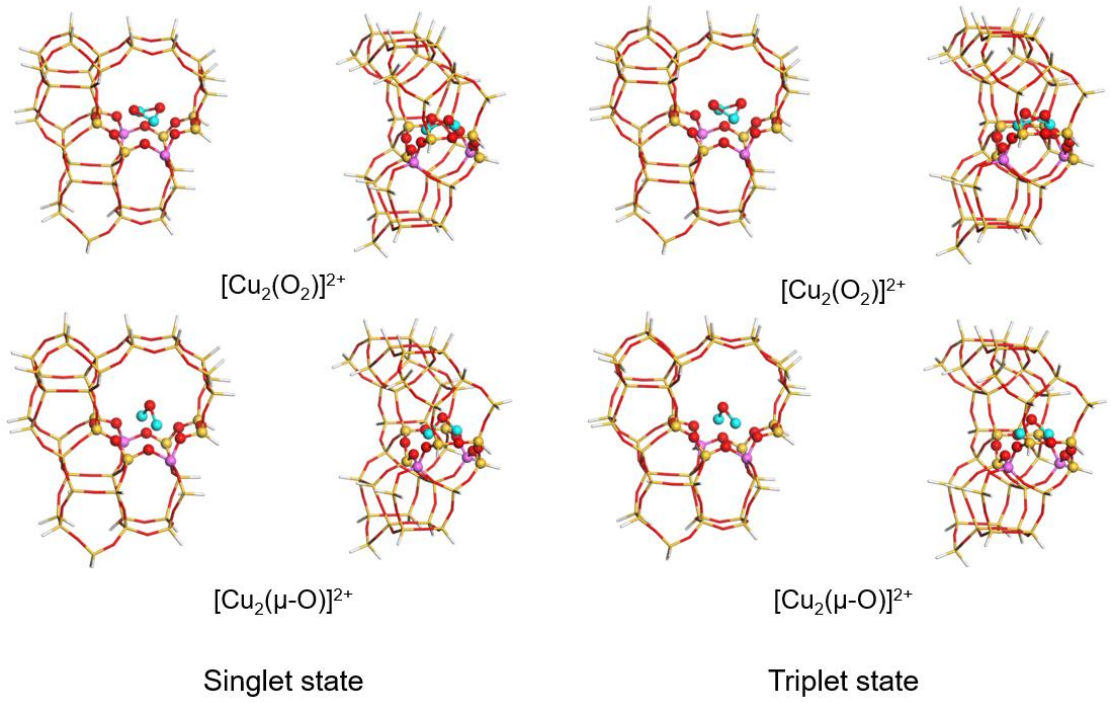

Fig. S4 The optimized $Z_{L2}[O_x]$ (x=1,2) models for singlet and triplet states. Cyan, yellow, purple, red and white represent copper, silicon, aluminum, oxygen and hydrogen atoms respectively.

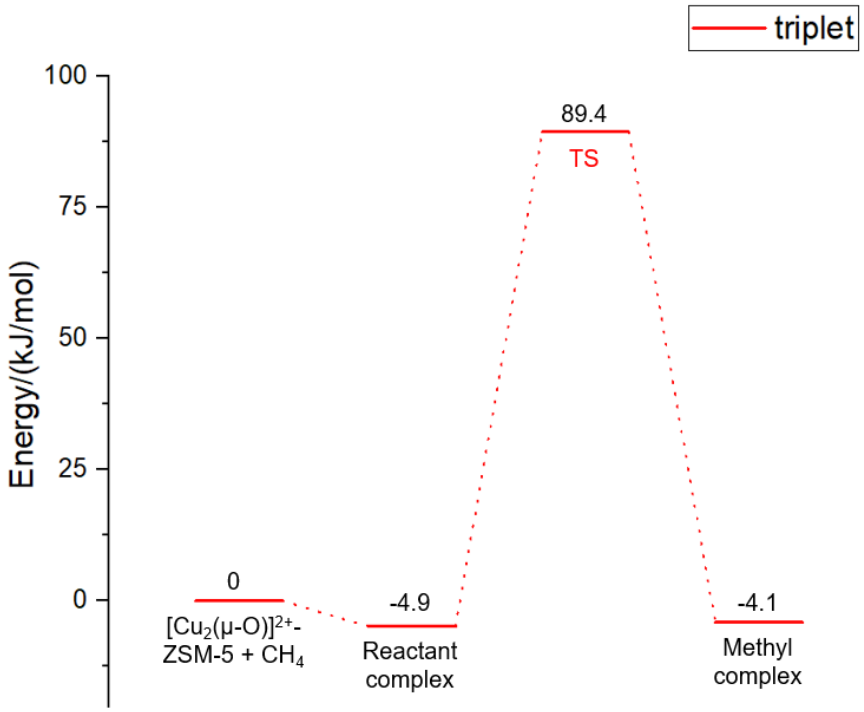

Fig. S5 Potential energy diagram of the optimal pathway of the methane activation step of methane to methanol conversion by $Z_{L2}[O]$ ($Z_{L2}[O_x]$ (x=1,2) model with $[Cu_2(\mu\text{-}O)]^{2+}$).

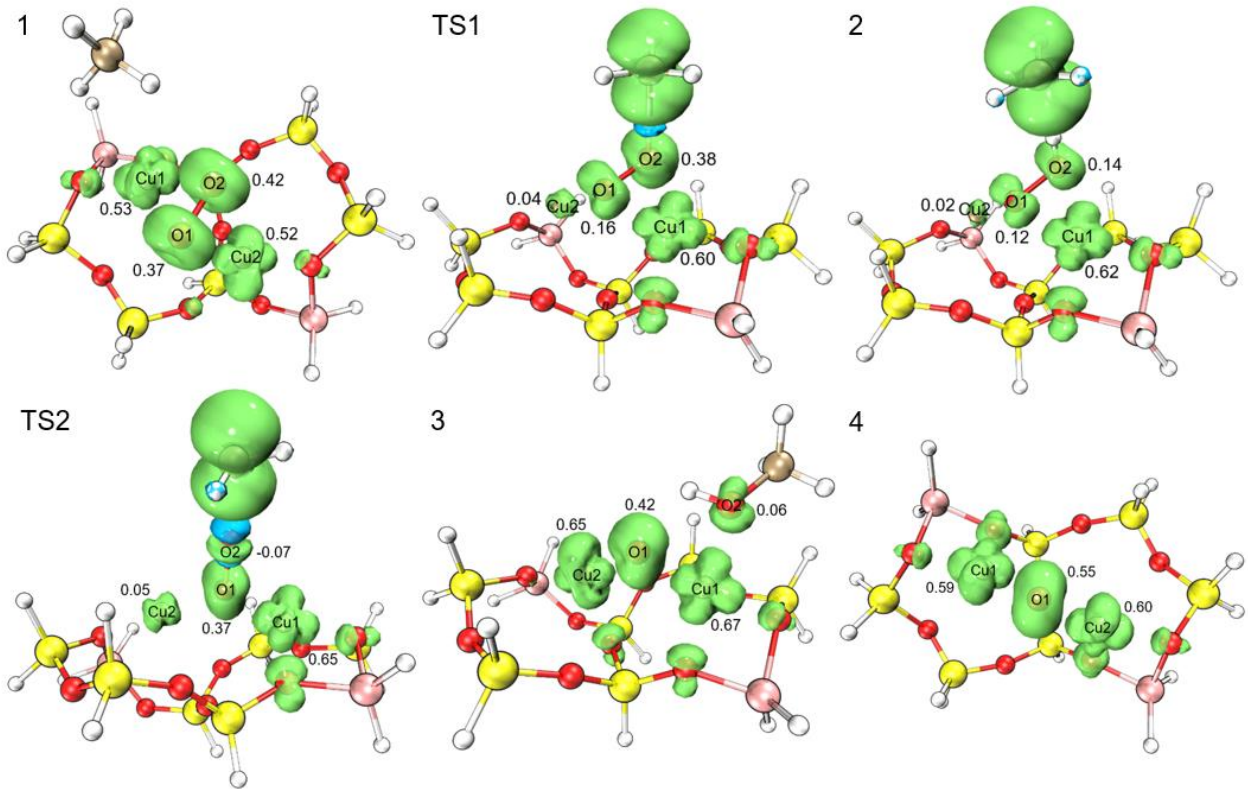

Fig. S6 Atomic spin densities for Cu and O atoms of intermediates and transition states of the optimal path for partial oxidation of methane to methanol on $[Cu_2(O_2)]^{2+}$-ZSM-5. Green and blue correspond to the parts with positive and negative spin density, respectively.

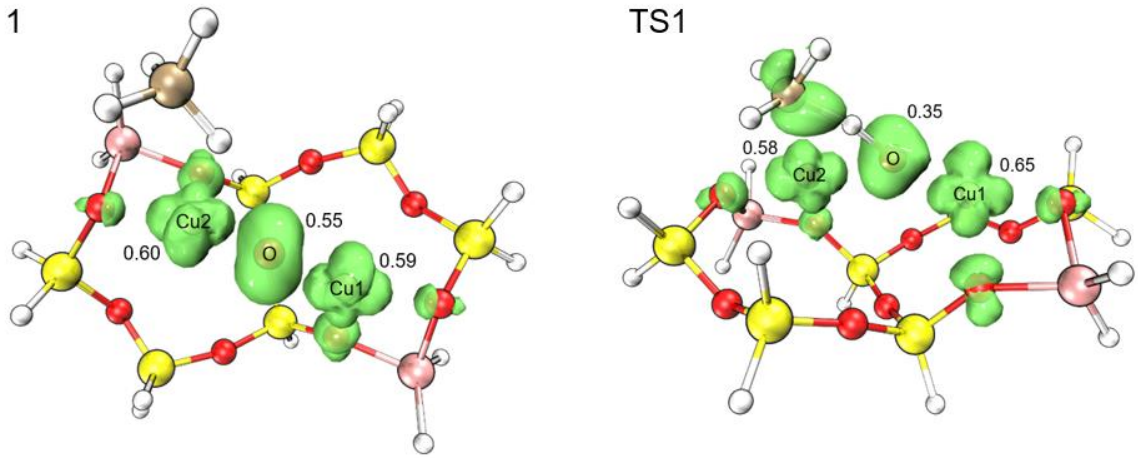

Fig. S7 Atomic spin densities for Cu and O atoms of reactant complex and TS1 of the optimal path for partial oxidation of methane to methanol on $[Cu_2(\mu\text{-}O)]^{2+}$-ZSM-5.

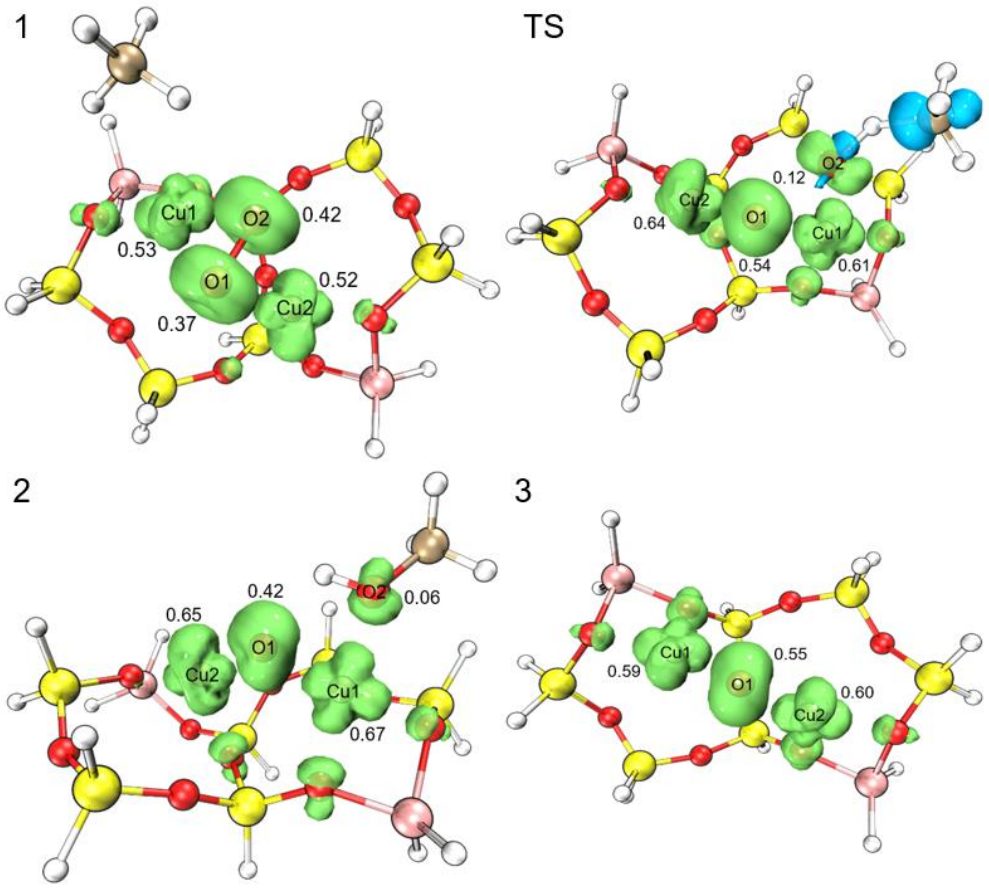

Fig. S8 Atomic spin densities for Cu and O atoms of intermediates and transition state of the optimal path for partial oxidation of methane to methanol in one step on $[Cu_2(O_2)]^{2+}$-ZSM-5. Green and blue correspond to the parts with positive and negative spin density, respectively.

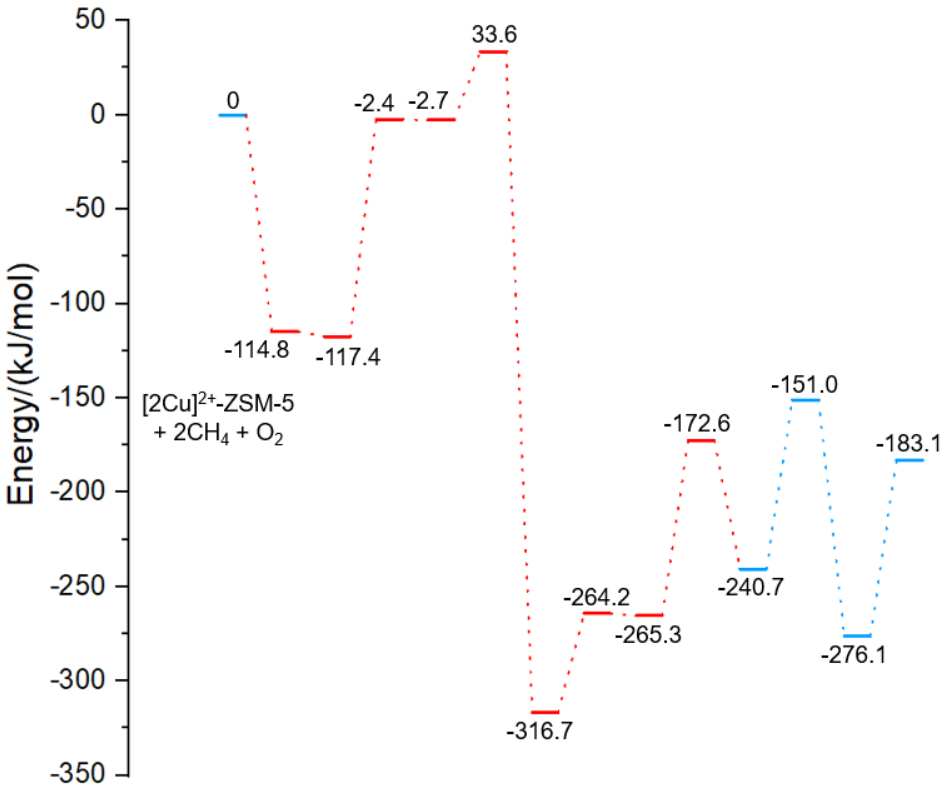

Fig. S9 Potential energy diagram for the catalytic cycle reaction of partial oxidation of methane to methanol on Cu-ZSM-5. The red lines and blue lines represent the triplet state and the singlet state, respectively.