Supporting Information

An alternative catalytic cycle for selective methane oxidation to methanol with Cu clusters in zeolites

*Mario Gallego, Avelino Corma and Mercedes Boronat**

Instituto de Tecnología Química (UPV-CSIC), Universitat Politècnica de València – Consejo Superior de Investigaciones Científicas, Avda. de los Naranjos s/n, 46022 Valencia, Spain.

*E-mail: boronat@itq.upv.es

Table S1. Calculated adsorption, activation and reaction energies in kJ/mol for the dissociation of molecular O_2 on different catalyst models. The optimized structures are depicted in Figures S1-S2.

	Structure	E_{ads} (kJ/mol)	E_{act} (kJ/mol)	E_{reac} (kJ/mol)
Cu_5[a]		-264	93	-235
Cu_5O_2	1	-69	-	-
Cu_5O	5	-144	13	-70
Cu_5O_3	24	33 / -24[b]	157	58
Cu_5-OH-OCH_3	38	-141	16	-58

[a]Data from reference *Phys. Chem. Chem. Phys.* 2022, 24, 30044.
[a]Quadruplet spin state.

Table S2. Relative energies (E_{rel}) and Gibbs energies (G_{rel}) in kJ/mol for all the structures involved in methane oxidation on Cu_5O_2 clusters. Optimized structures depicted in Figure 1 and Figure S3.

Structure	E_{rel} (kJ/mol)	G_{rel} (kJ/mol)
1 + CH_4	0	0
2	-43	-33
TS(2→3)	74	69
3	67	57
TS(3→4)	106	103
4	-15	-6
5 + CH_3OH	74	78
TS(2→6)	59	93
6	-6	9
TS(2→7)	107	114
7	-47	-36
TS(7→8)	136	167
8	14	34
9 + CH_3OH	132	139
TS(2→10)	32	63
10	-24	-9
TS(10→11)	195	204
11	45	61
24 + CH_4	0	0
25	-23	-19
TS(25→26)	49	37
26	-26	-21
TS(26→27)	95	101
27	-41	-31
28 + CH_3OH	72	77

Table S3. Relative energies (E_{rel}) and Gibbs energies (G_{rel}) in kJ/mol for all the structures involved in methane oxidation on Cu_5O clusters. Optimized structures depicted in Figure 2.

Structure	E_{rel} (kJ/mol)	G_{rel} (kJ/mol)
5 + CH_4	0	0
12	-28	-31
TS(12→13)	79	82
13	67	71
TS(13→14)	121	146
14	-5	20
15 + CH_3OH	132	144
9 + CH_4	58	61
16	7	15
TS(16→17)	128	139
17	50	63
TS(17→18)	227	252
18	91	120
19 + CH_3OH	169	196

Table S4 Relative energies (E_{rel}) and Gibbs energies (G_{rel}) in kJ/mol for all the structures involved in methane oxidation on Cu_5O_3 clusters, both in doublet (D) and quadruplet (Q) spin states. Optimized structures depicted in Figure 2.

Structure	E_{rel} (kJ/mol)		G_{rel} (kJ/mol)	
	D	Q	D	Q
20 + CH_4	0	4	0	10
21	-23	-24	-8	-26
TS(21→22)		48		64
22	37	35	38	29
TS(22→23)	85	96	95	123
23	-163	-7	-110	13
24 + CH_3OH	-69	78	-45	77

Table S5. Relative energies (E_{rel}) and Gibbs energies (G_{rel}) in kJ/mol for all the structures involved in competitive processes on Cu_5O_2 clusters. Optimized structures depicted in Figure 4.

Structure	E_{rel} (kJ/mol)	G_{rel} (kJ/mol)
8	14	34
TS(8→29)	183	201
29	77	88
6	-6	9
TS(6→30)	101	113
30	-16	-4
TS(6→33)	192	208
33	57	75
7	-47	-36
TS(7→31)	129	140
31	-20	-9
TS(7→34)	83	98
34	27	63
10	-24	-9
TS(10→32)	120	139
32	87	88
TS(10→34)	94	100
34	27	63

Table S6. Relative energies (E_{rel}) and Gibbs energies (G_{rel}) in kJ/mol for all the structures involved in competitive processes on Cu_5O_3 clusters and in pathway *I* for methane oxidation on Cu_5-OH-OCH_3 catalytic system. Optimized structures depicted in Figure 5.

Structure	E_{rel} (kJ/mol)	G_{rel} (kJ/mol)
35	-50	-33
TS(35→36)	109	126
36	-30	-10
TS(35→37)	-4	17
37	-160	-136
TS(37→38)	-133	-111
38	-154	-136
39 + CH_2=O	-120	-129
TS(38→40)	-43	-40
40	-177	-156
37 + CH_4	-160	-136
41	-192	-157
TS(41→42)	-104	-72
42	-116	-83
TS(42→43)	-56	-16
43	-155	-115
44 + CH_3OH	-78	-49
45	-202	-145
TS(45→43)	-57	3

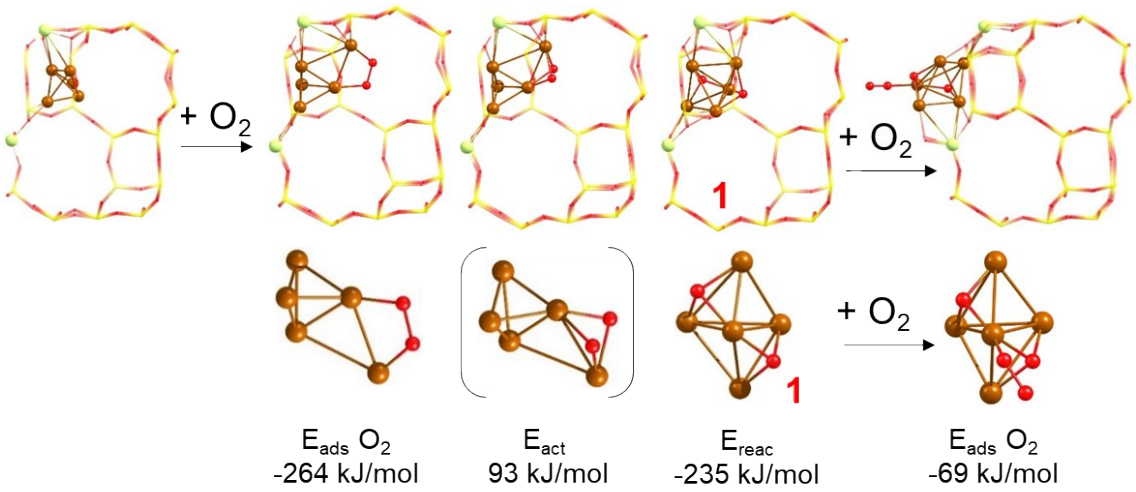

Figure S1. Optimized structures and calculated adsorption (E_{ads}), activation (E_{act}) and reaction (E_{reac}) energies involved in the oxidation of Cu_5 to Cu_5O_2 (data from *Phys. Chem. Chem. Phys.*2022, 24, 30044), and subsequent adsorption of an additional O_2 molecule that remains mono-coordinated, in a non-activating adsorption mode that doesn´t favor its dissociation. Si and O atoms in the framework depicted as yellow and red wires, Al, Cu and reactant O depicted as light green, brown and red balls, respectively.

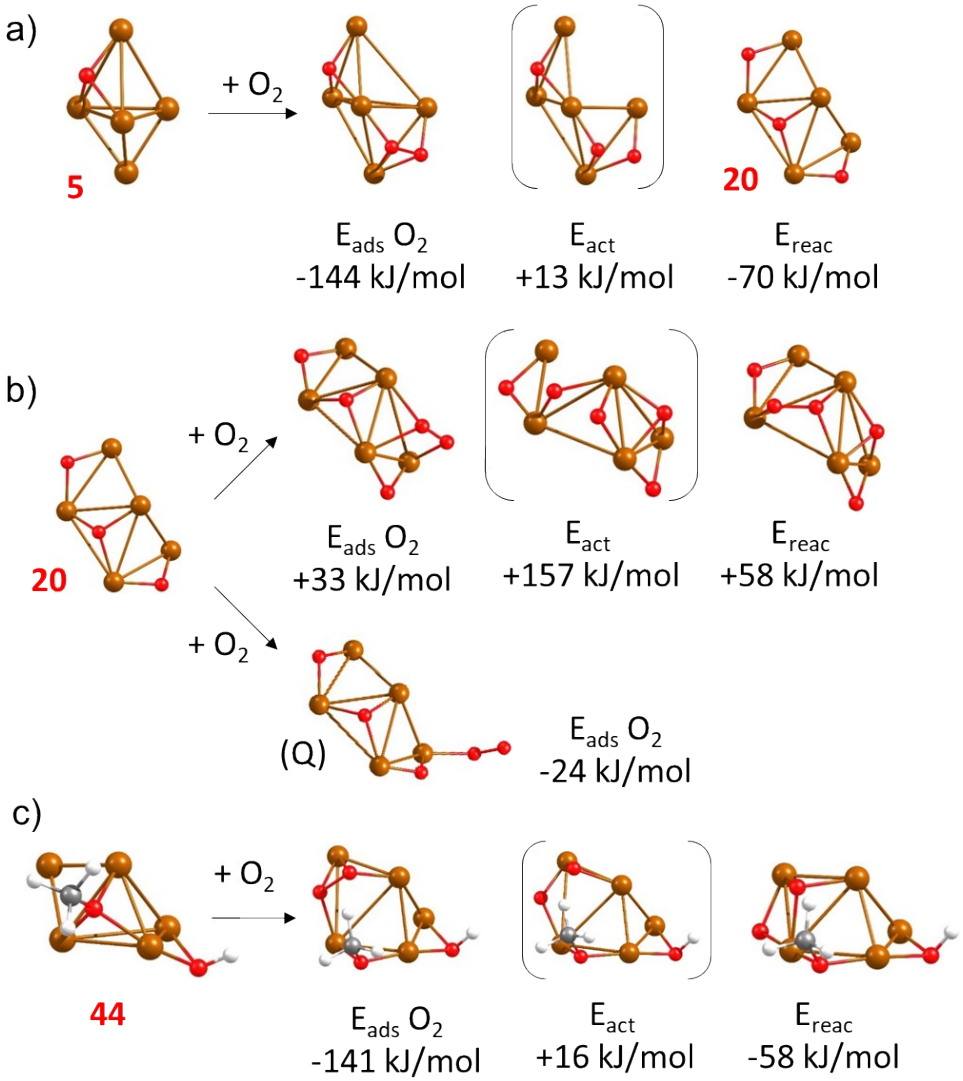

Figure S2. Optimized structures and calculated adsorption (E_{ads}), activation (E_{act}) and reaction (E_{reac}) energies involved in the dissociation of molecular O_2 on a) Cu_5O, b) Cu_5O_3 and c) Cu_5OCH_3OH clusters. The spin state of all structures is doublet (D), with the only exception of the structure labeled (Q) which is a quadruplet. Cu, O, C and H atoms depicted as brown, red, gray and white balls. Transition states are in brackets.

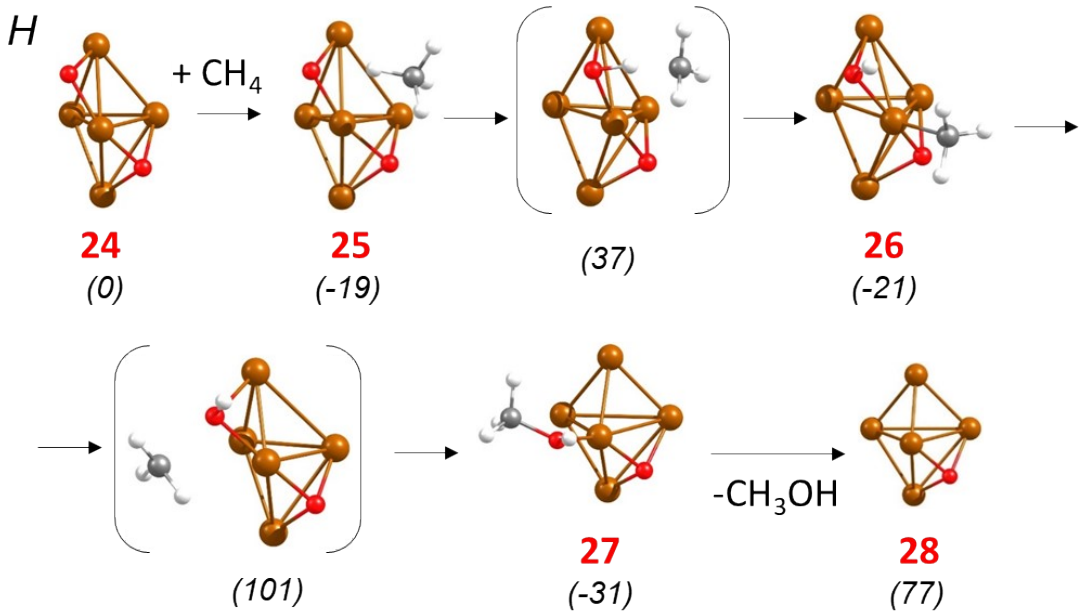

Figure S3. Optimized geometries of minima and transition state structures involved in the oxidation of methane to methanol following pathway *H* on a Cu_5O_2 cluster supported on CHA zeolite. Cu, O, C and H depicted as brown, red, gray and white balls, respectively. Relative Gibbs energies at 478.15 given in brackets in kJ/mol.

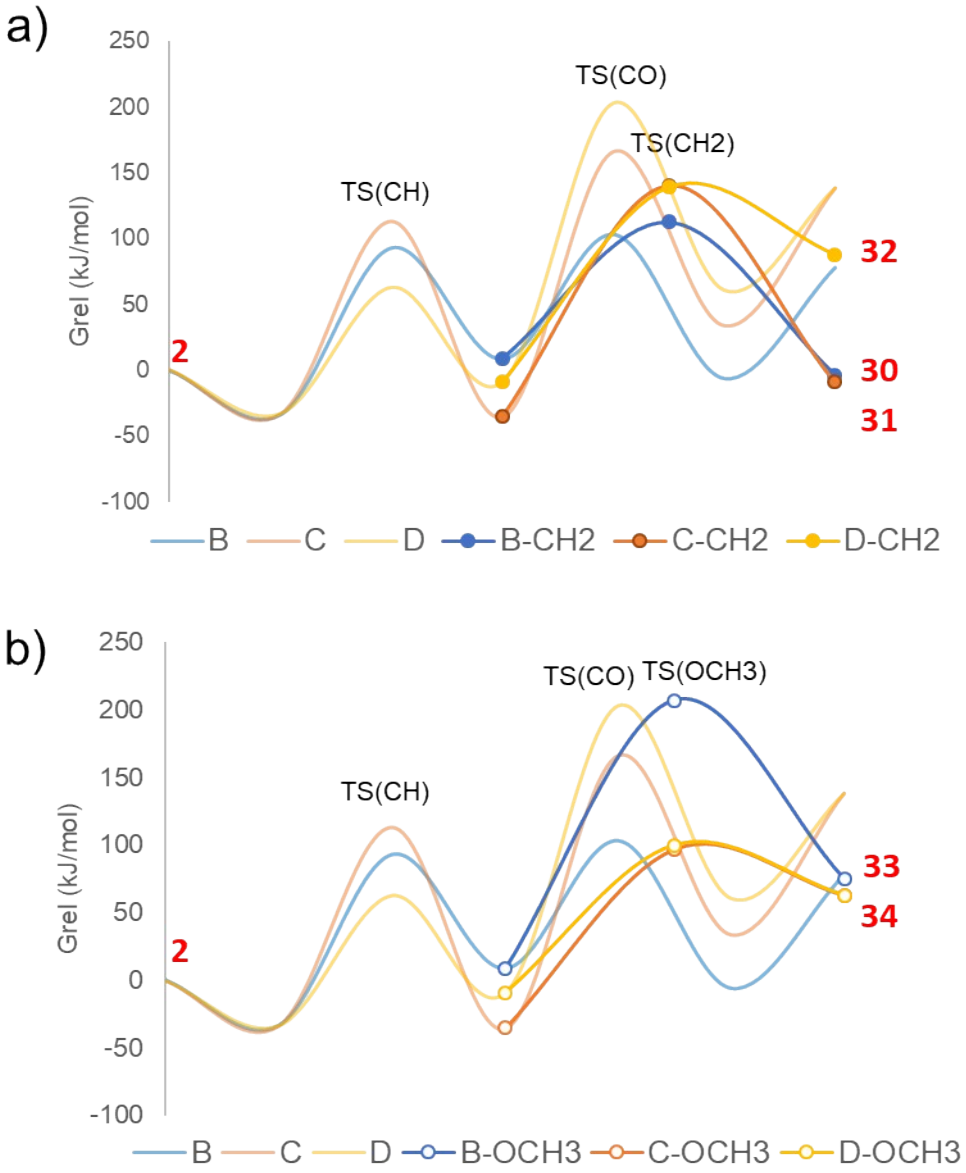

Figure S4. Calculated Gibbs energy profiles at 478.15 K for competing (a) C-H bond breaking in adsorbed methyl and (b) formation of methoxy on Cu_5O_2 clusters supported on CHA zeolite. The transition states for methane C-H bond dissociation (TS(CH)), C-O bond formation (TS(CO)), C-H bond breaking in methyl (TS(CH2)) and formation of methoxy (TS(OCH3)) are indicated on the plots.