Mechanistic Insights into the Activity of Mo-Carbide Clusters for Methane Dehydrogenation and Carbon-Carbon Coupling Reactions to Form Ethylene in Methane Dehydroaromatization

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Table SI-1. Activation energies calculated for C-H bond activation and C-C coupling steps using two different exchange-correlation functional (PW91 and RPBE)

Mo_4C_2		
Reaction Step	Activation Energy (kJ/mol)	
	PW91	RPBE
$CH_4 \rightarrow CH_3^* + H^*$	116	121
$CH_3^* + CH_3^* \rightarrow C_2H_6$	151	161
Mo_2C_6		
$CH_4 \rightarrow CH_3^* + H$	119	129
$CH_3^* + CH_3^* \rightarrow C_2H_6$	34	35

* Adsorbed CH_3 and H at Mo and C^{Mo} atoms, respectively.

Table SI-2. Binding energy* of CH_3 in kJ/mol over the Mo site as a function of charge in the respective clusters

Charge	**Mo_4C_2**	**Mo_2C_6**
0	-274.6	-218.4
1	-221.8	-206.3
2	-180.4	-178.4

*Binding energies are relative to CH_3(g). Formation energy for CH_3(g) relative to CH_4(g) and H_2(g) is 248.5 kJ/mol.

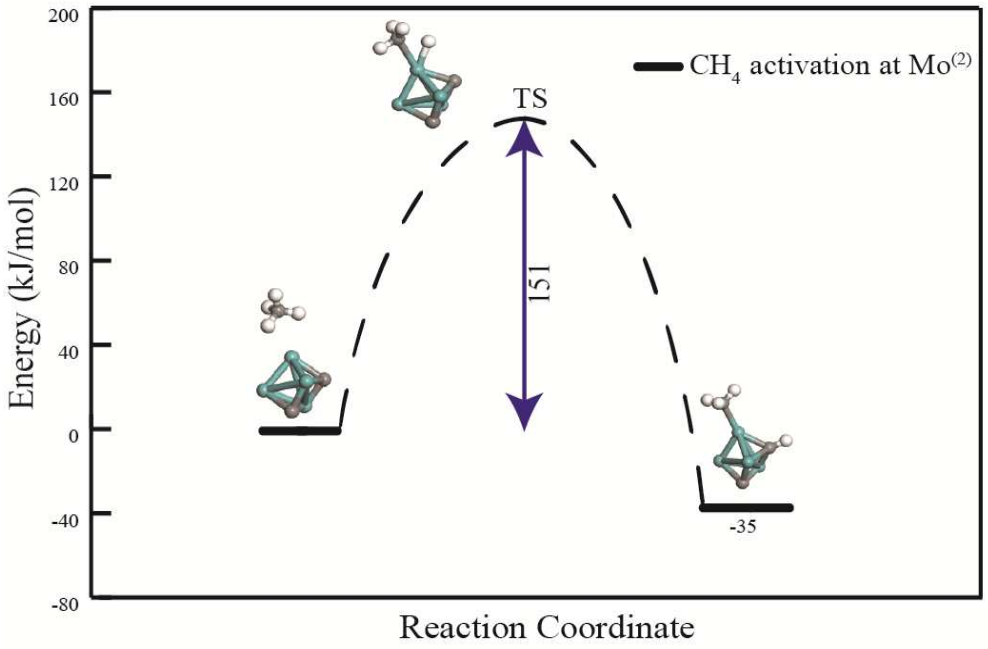

Figure SI-1. Reaction diagram for methane activation over $Mo^{(2)}$ site at Mo_4C_2 cluster.

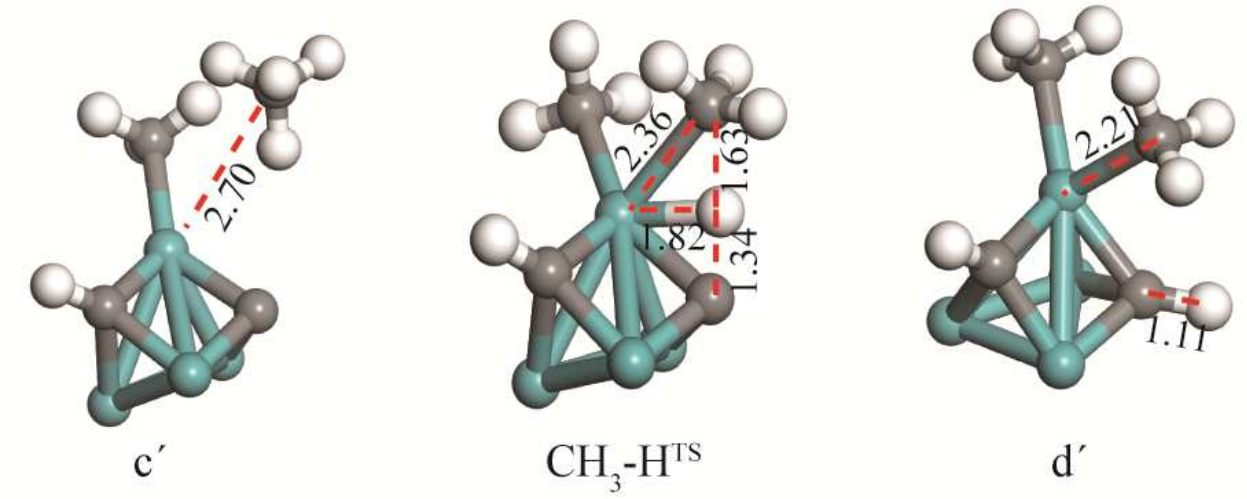

Figure SI-2. Geometry of reactant, transition and product states for second methane activation over the $Mo^{(1)}$ site of the Mo_4C_2 cluster. (bond lengths in Å)

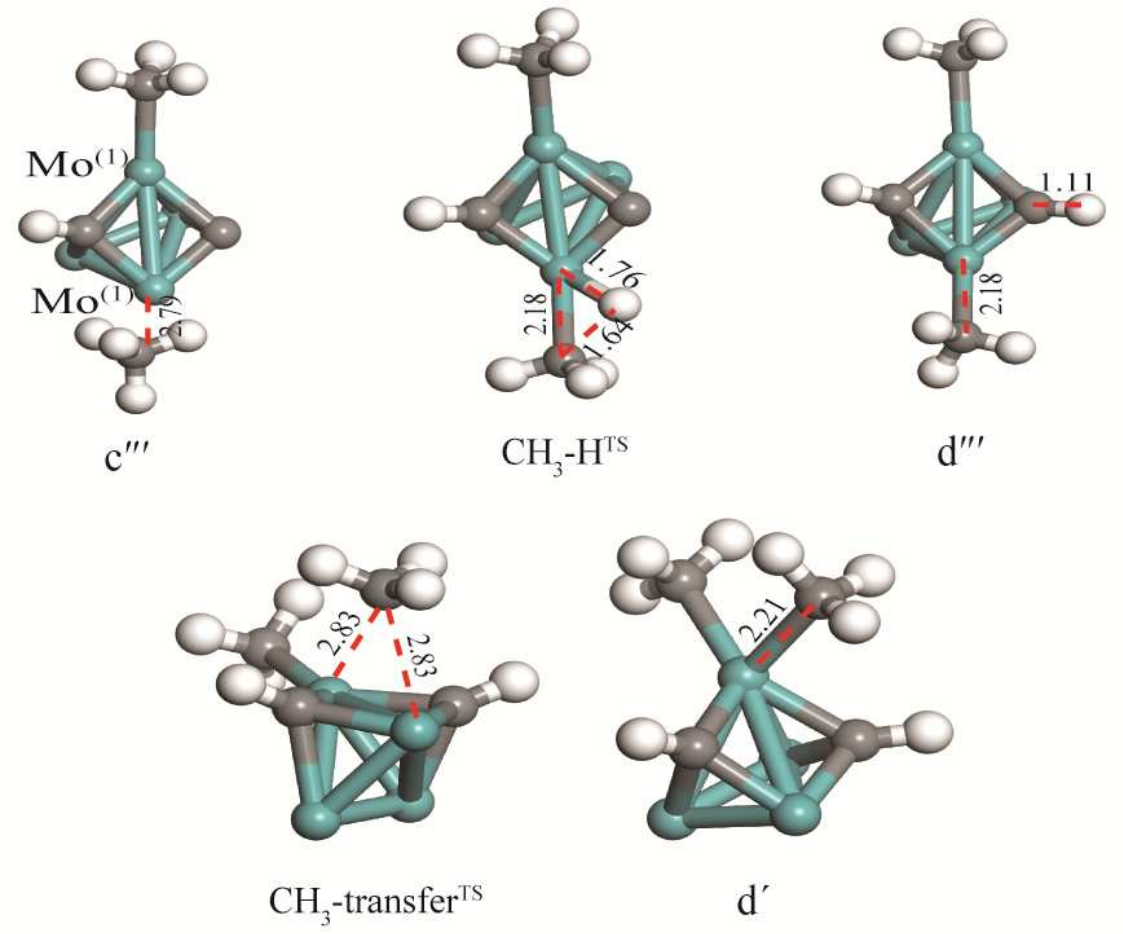

Figure SI-3. Geometry of reactant, transition and product states showing the activation of second methane molecule at the free $Mo^{(1)}$ site of the Mo_4C_2 cluster. (bond lengths in Å)

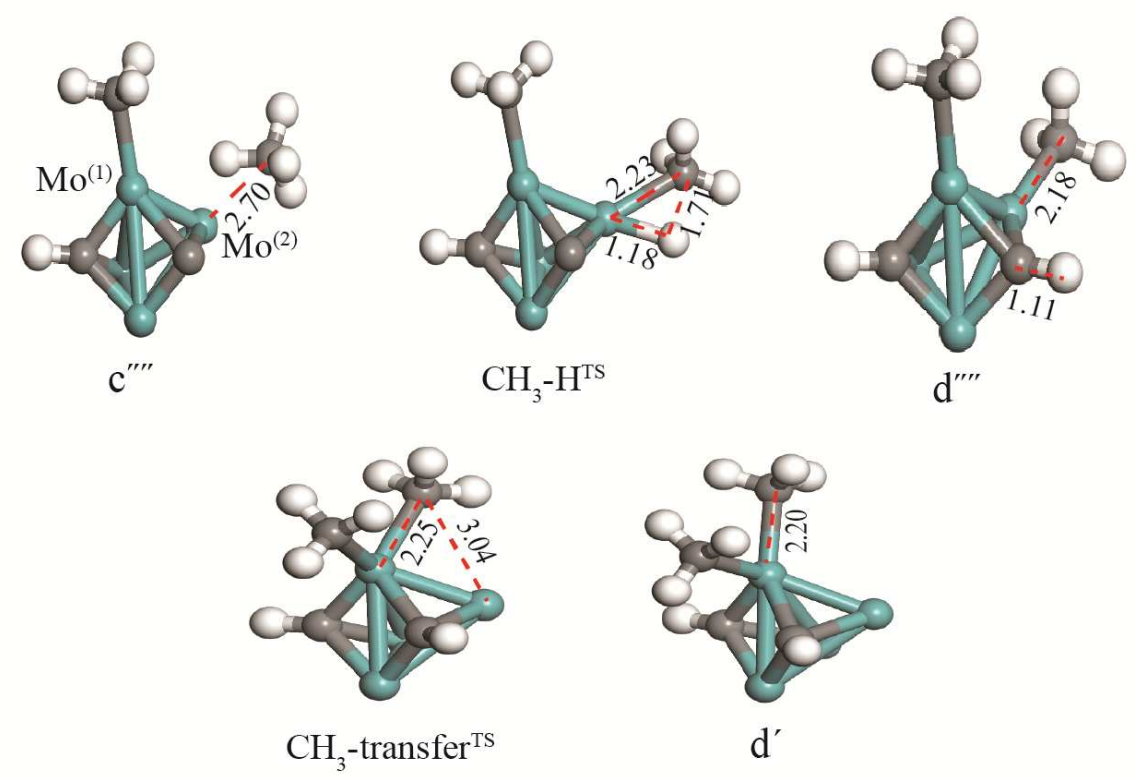

Figure SI-4. Geometry of reactant, transition and product states showing the activation of the second methane molecule at the free $Mo^{(2)}$ atom of Mo_4C_2 cluster. (bond lengths in Å)

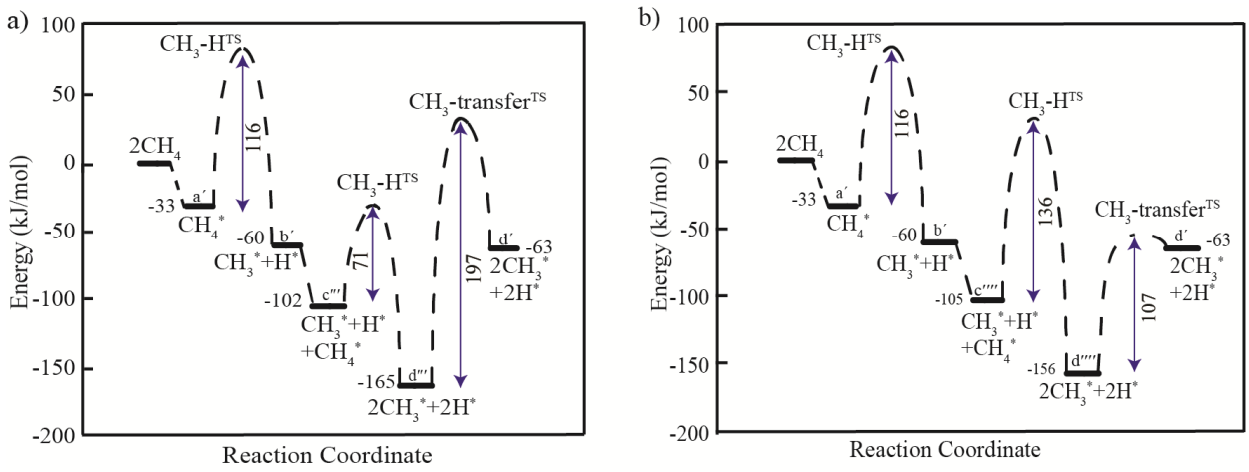

Figure SI-5. Reaction diagram showing the activation of second methane molecule, depending on the choice of active sites: second methane dissociates at, (a) free $Mo^{(1)}$ atom and (b) free $Mo^{(2)}$ atom of Mo_4C_2 cluster.

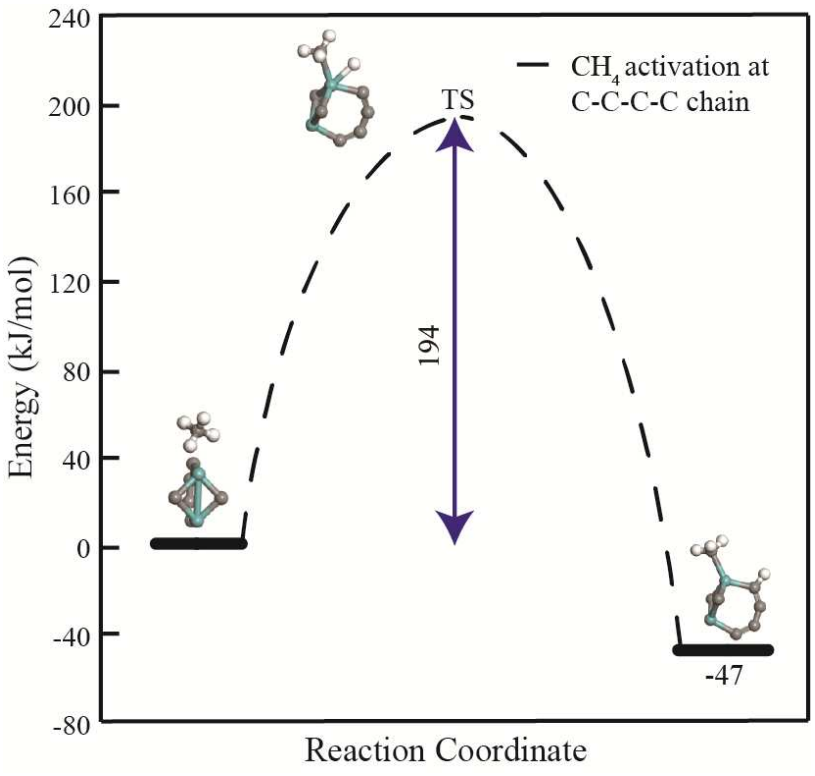

Figure SI-6. Reaction diagram for methane activation over C-C-C-C chain site at Mo_2C_6 cluster.

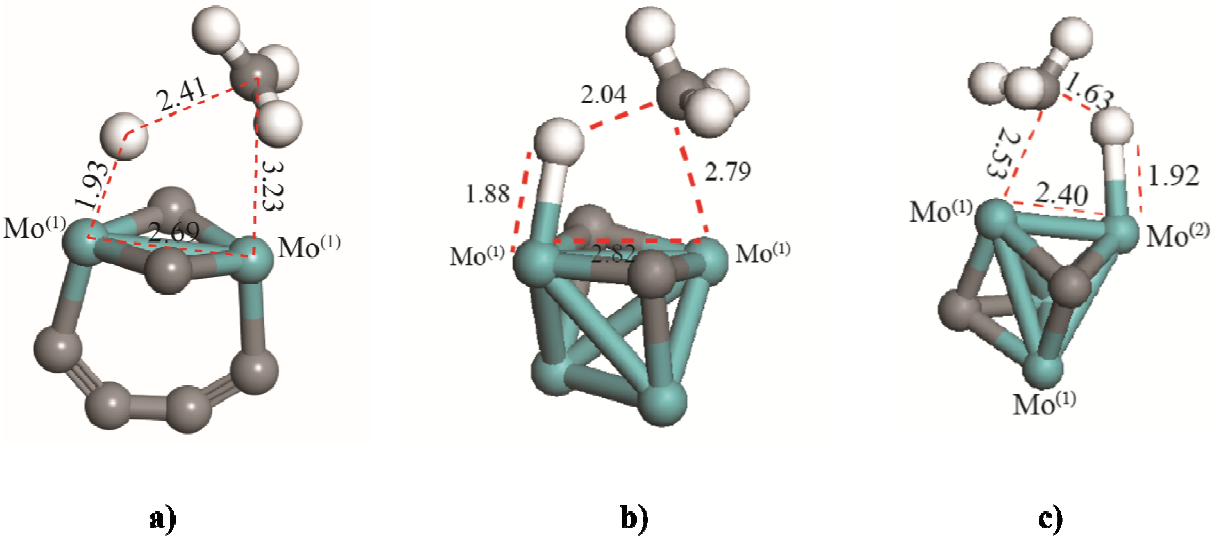

Figure SI-7. Structure of the TS for methane C-H bond activation on neighboring Mo-Mo site for (a) Mo_2C_6,(b) $Mo^{(1)}$-$Mo^{(1)}$ site of Mo_4C_2 and c) and $Mo^{(1)}$-$Mo^{(2)}$ site of Mo_4C_2 (c). (bond lengths in Å)

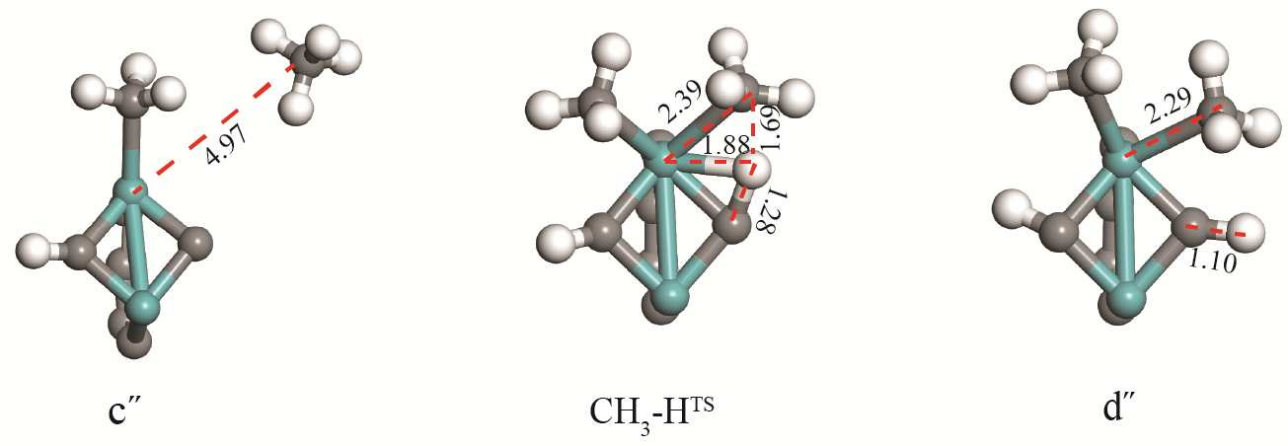

Figure SI-8. Geometry of reactant, transition and product states for second methane activation over the $Mo^{(1)}$ site of the Mo_2C_6 cluster. (bond lengths in Å)

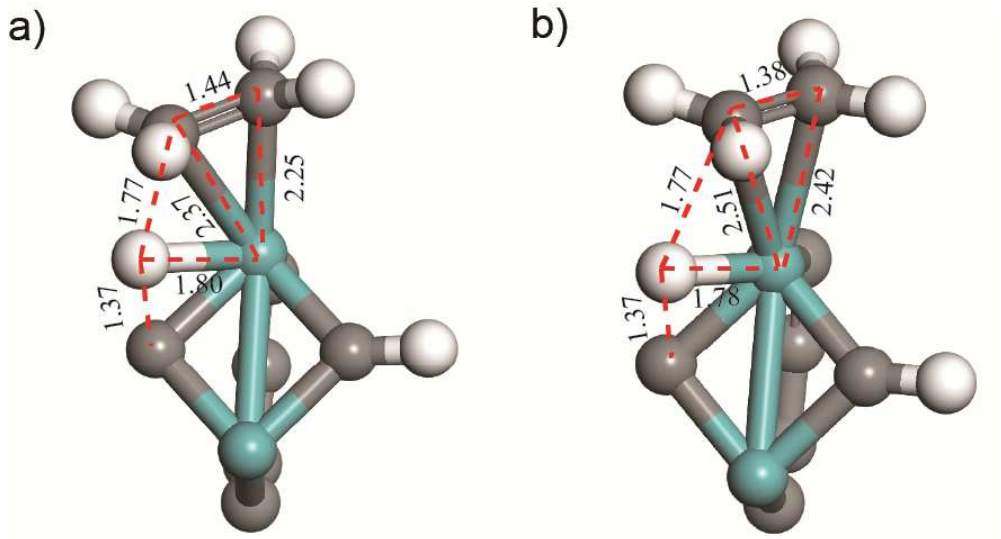

Figure SI-9. Transition state geometry of C_2H_6-H^{TS} on (a) neutral and (b) +1 charged Mo_2C_6 cluster. (bond lengths in Å)

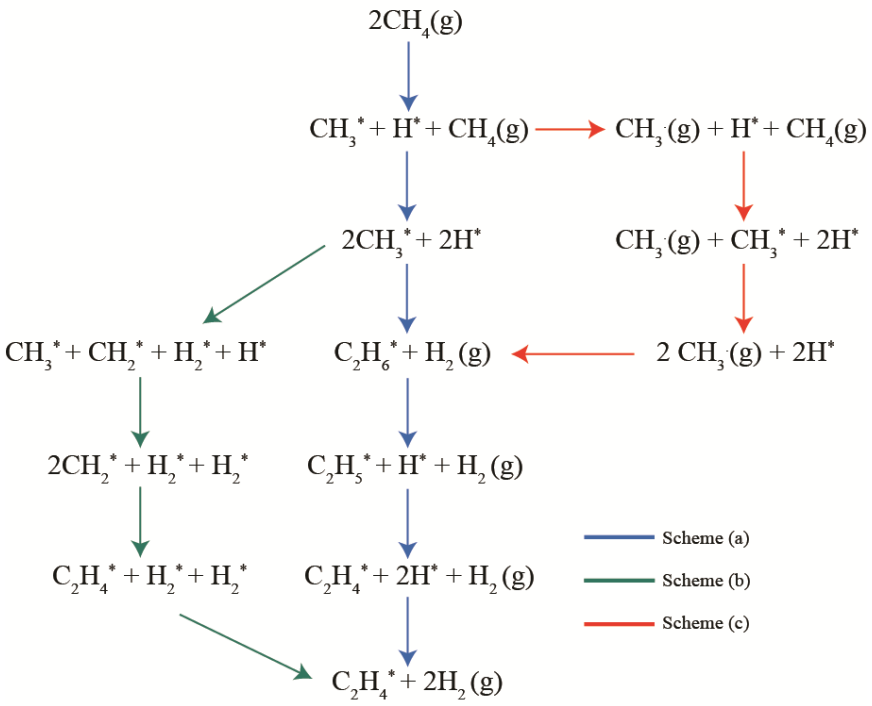

Figure SI-10. Formation of ethylene through methane activation following three different schemes.

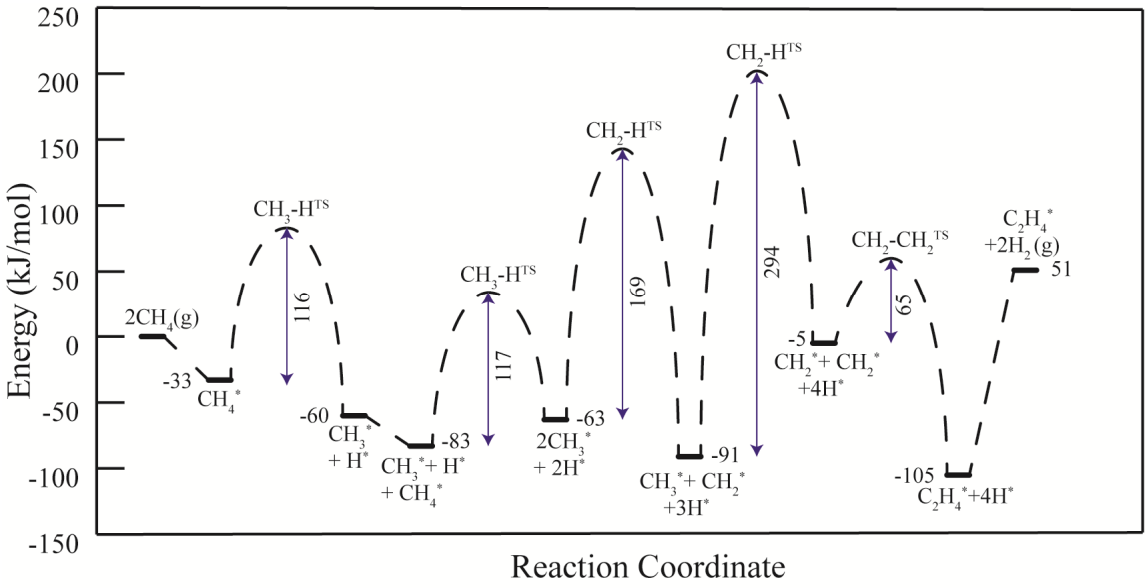

Figure SI-11. Reaction diagram for methane dehydrogenation and the coupling of the two CH_2 species to form ethylene on Mo_4C_2 cluster following Scheme (b) as shown in Figure SI-10.

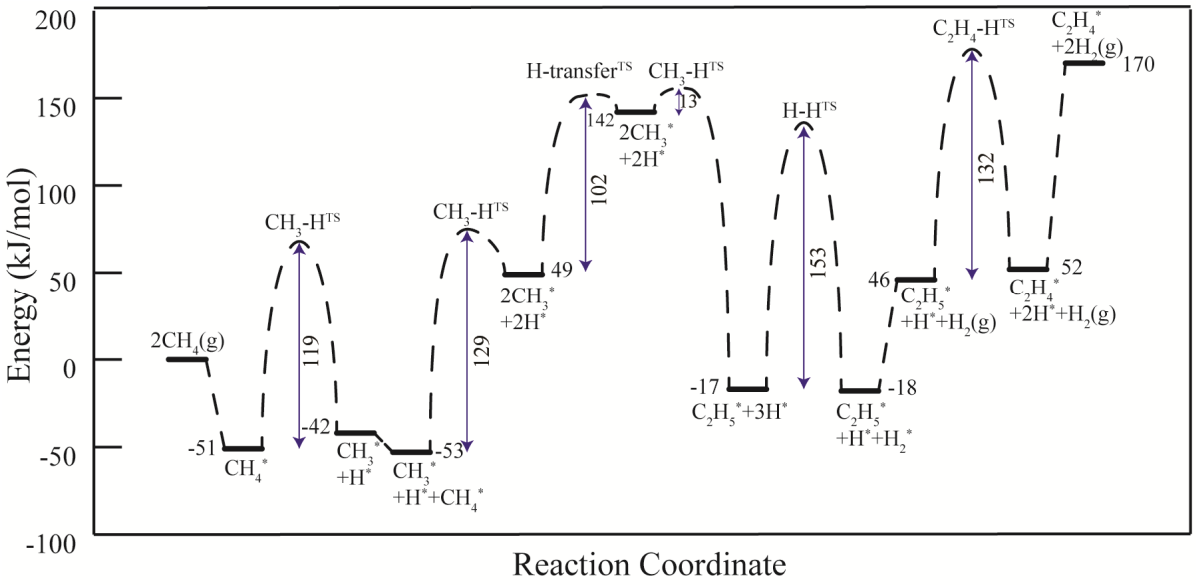

Figure SI-12. Reaction diagram for methane dehydrogenation and the coupling of the two CH_2 species to form ethylene on Mo_2C_6 cluster, following Scheme (b) as shown in Figure SI-10.

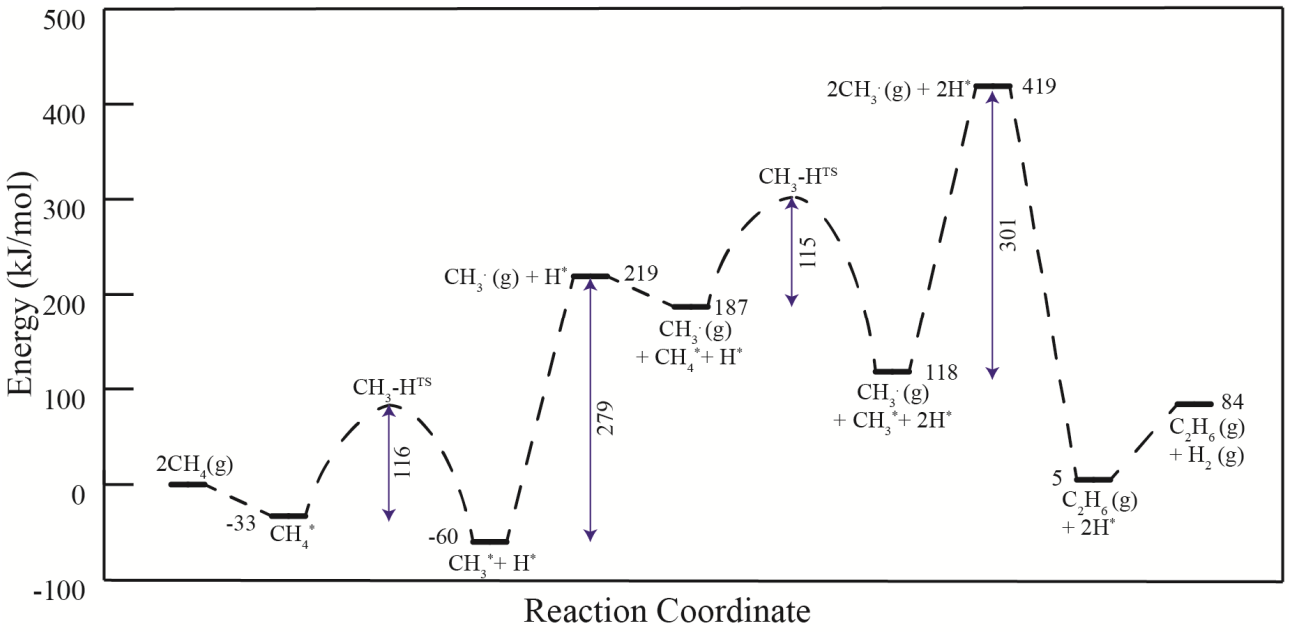

Figure SI-13. Reaction diagram for methane dehydrogenation and coupling of two CH_3* radicals to form ethylene on Mo_4C_2 cluster, following Scheme (c) as shown in Figure SI-10.

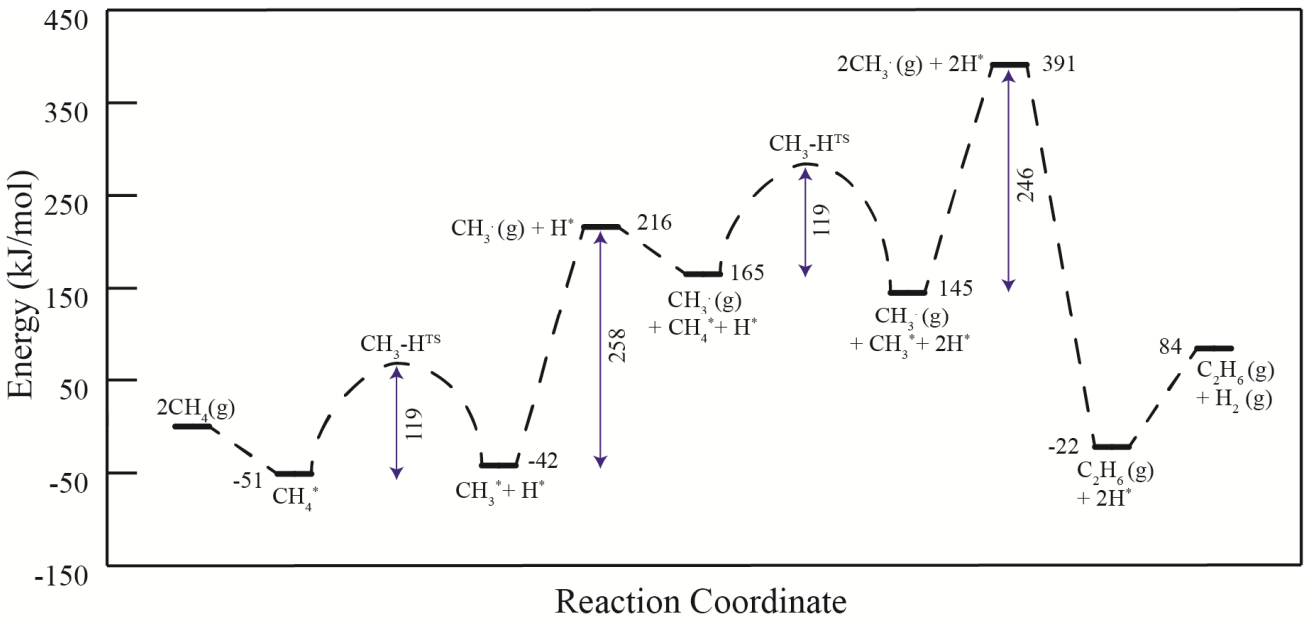

Figure SI-14. Reaction diagram for methane dehydrogenation and coupling of two CH_3* radicals to form ethylene on Mo_2C_6 cluster, following Scheme (c) as shown in Figure SI-10.