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


**Supporting information**

# A Periodic Density Functional Theory Analysis of Direct Methane Conversion into Ethylene and Aromatic Hydrocarbons Catalyzed by $Mo_4C_2$/ZSM-5

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**$CH_4 \rightarrow CH_3(C)+H(Mo)$**

The methane adsorption position is also on the Mo atom site with the adsorption energy is -0.42 eV. The methane dissociated on the Mo atom site as $CH_3$ and H species, and which the $CH_3$ species bond with C atom and H species bond with Mo atom. The activation energy is 1.35 eV and the dissociated energy is 0.64 eV. The C-H bond length of TS is 2.25 Å. The distance between $CH_3$ species and Mo atom is 2.22 Å and between H species and Mo atom is 1.75 Å.

**$2CH_3 \rightarrow C_2H_6$**

Moreover, we also studied the case of $CH_3(C)+CH_3(Mo)$. There are two configurations of $CH_3(C)+CH_3(Mo)$. The first configuration is that there are only two $CH_3$ species respectively bond on Mo atom and C atom. The second configuration is that there are two $CH_3$ species and two H atom with the structure of $CH_3(Mo)+CH_3(Mo)+H(Mo)+H(C)$. The first configuration converted to $C_2H_6$with the energy barrier of 1.37 eV and reaction energy of -0.08 eV. The transition state of this process is that the $CH_3(C)$ species migrated from the C atom to the Mo atom site. The distances of this $CH_3$ species with Mo atom is 2.24 Å and with other $CH_3$ species is 2.64 Å. The distance between two $CH_3$ species is 2.10 Å. The adsorption position of the $C_2H_6$ is different from the previous calculated $C_2H_6$ adsorption position, which the position is on the other Mo atom site. We don't calculate this $C_2H_6$ converted to $C_2H_4$+2H for the $C_2H_6$ can easy migrate between two Mo atoms. For the second configuration converted to ethane, we also ignored the influence of H-atom. The energy barrier of $CH_3(Mo)+CH_3(C)$ converted to $C_2H_6(Mo)$ is 1.73 eV and the reaction energy is 0.32 eV. There have some different between the two configurations converted, which is for the different position of the $CH_3$ species. The adsorption position of the $C_2H_6$ produced by the second $CH_3(Mo)+CH_3(C)$ configuration is same as the previous $C_2H_6$ which produced by the configuration of $CH_3(Mo)+CH_3(Mo)$. So the next step of $C_2H_6$ converted to $C_2H_4$+2H is same as the previous calculated results.

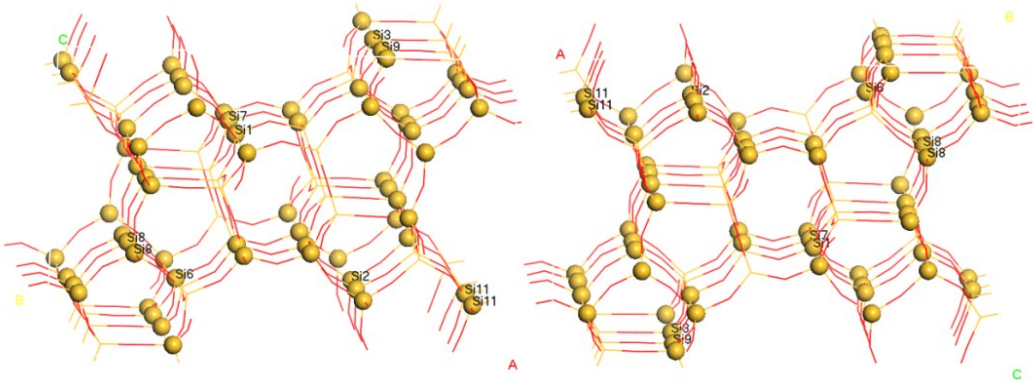


**Figure S1.The anchoring site of Mo oxide and Mo carbide.**

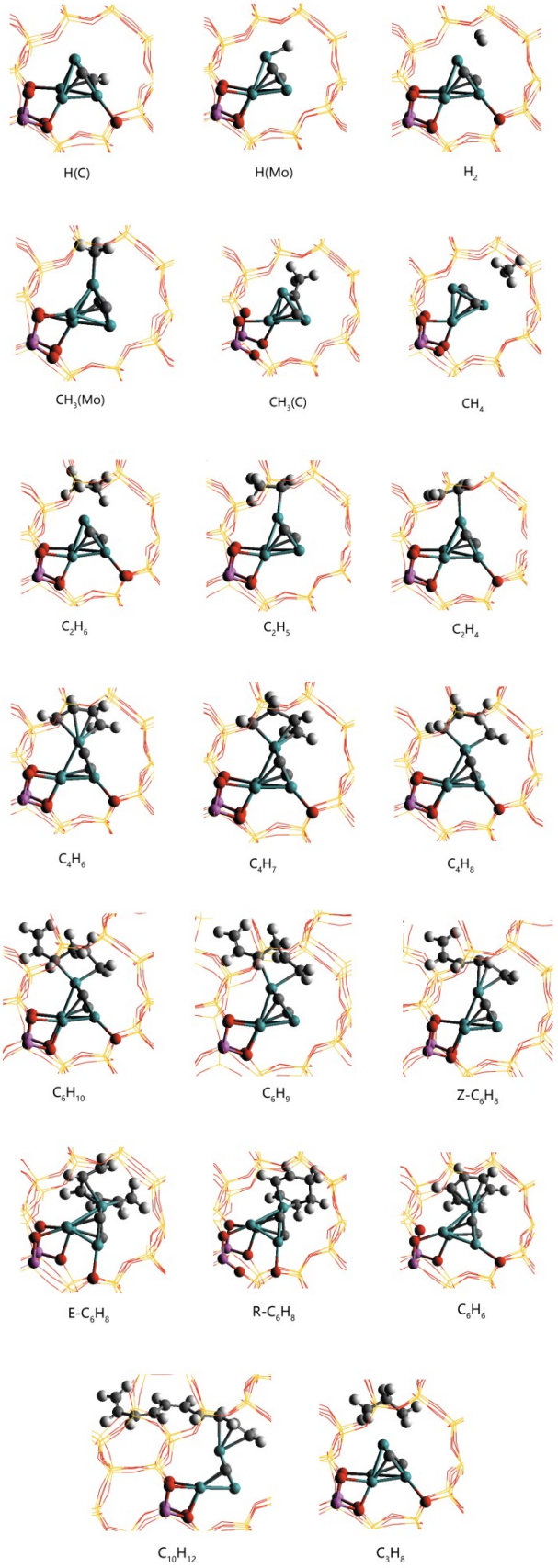


**Figure S2 Most stable adsorption configuration of possible species during the processes of methane cyclization**

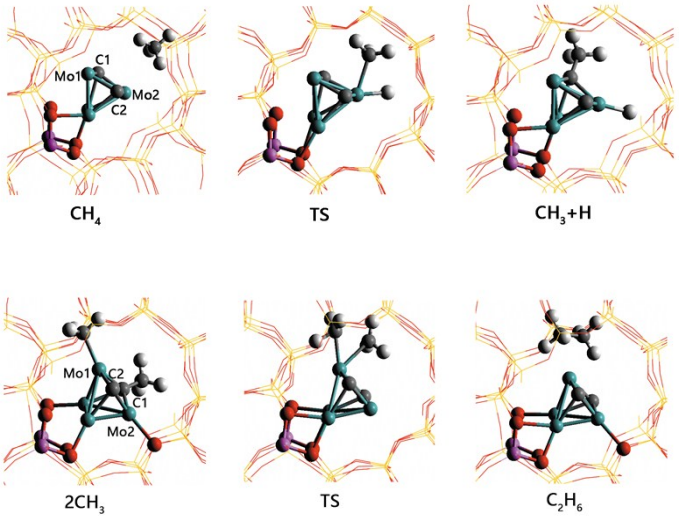


**Figure S3. DFT optimized IS, TS and FS for ethane formation**

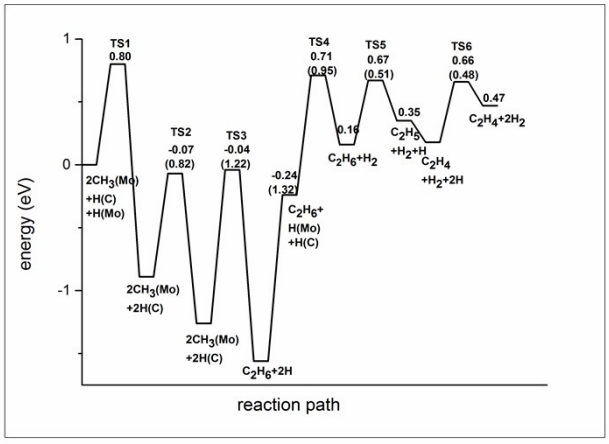


**Figure S4. The Potential Energy Surface of $2CH_3$ to $C_2H_4$ in the presence of H species**

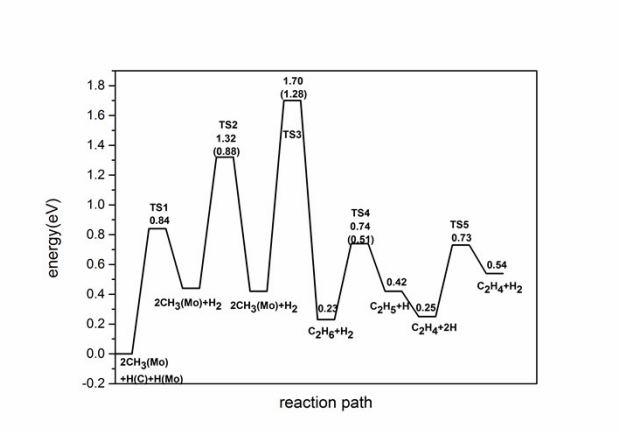


**Figure S5: The Potential Energy Surface of $2CH_3$ to $C_2H_4$ without H species**

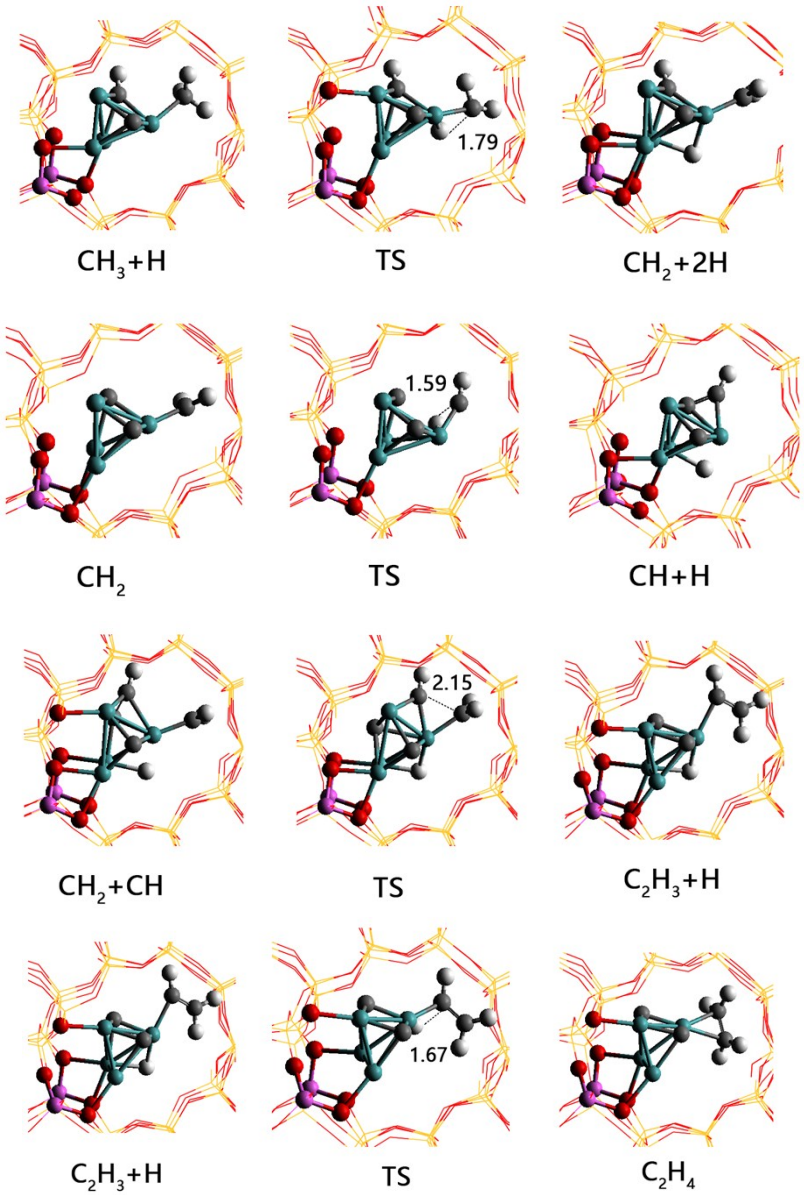


**Figure S6. DFT optimized IS, TS and FS for ethylene formation**

**Table S1.**Calculated total energy of bond length of Al-Al for the various double Al models

| | T1-T3 | T2-T6 | T3-T7 | T1-T9 | T11-T11 | T8-T8 |
|---|---|---|---|---|---|---|
| $E_{tot}$(au) | -2270.868 | -2270.751 | -2270.806 | -2270.768 | -2270.907 | -2270.933 |
| Al-Al(nm) | 0.789 | 0.771 | 0.772 | 0.792 | 0.478 | 0.455 |

**Table S2.**Calculated total energy of $CH_3$ species and H species co-adsorption configurations.

| | $CH_3$(C)+H(C) | $CH_3$(Mo)+H(C) | $CH_3$(C)+H(Mo) | $CH_3$(Mo)+H(Mo) |
|---|---|---|---|---|
| E(eV) | -2353.22 | -2352.36 | -2351.88 | -2352.25 |

**Table S3** Energetic results and bond length at TSs of each elemental step in methane conversion into aromatic hydrocarbons catalyzed by Mo/ZSM-5

| Elemental step | ΔE(eV) | $E_a$(eV) | Bond length(Å) |
|---|---|---|---|
| $CH_4$→$CH_3$(C1)+H(Mo2) | 0.36 | 1.35 | 2.25 |
| $CH_3$(Mo1)+$CH_3$(Mo2)+H(C1)+H(Mo1)→$CH_3$(Mo1)+$CH_3$(Mo2)+H(C1)+H(C2) | -0.89 | 0.80 | -- |
| $CH_3$(Mo1)+$CH_3$(Mo2)+H(C1)+H(C2)→2$CH_3$(Mo1)+H(C1)+H(C2) | -0.37 | 0.82 | --- |
| 2$CH_3$(Mo1)+H(C1)+H(C2)→$C_2H_6$+H(C1)+H(C2) | -0.30 | 1.22 | 2.02 |
| $C_2H_6$+H(C1)+H(C2)→$C_2H_6$+H(Mo2)+H(C1) | 1.32 | 0.00 | -- |
| $C_2H_6$+H(Mo2)+H(C1)→$C_2H_6$+$H_2$ | 0.40 | 0.95 | 1.17 |

**Table S4.** The activation energy and pre-exponential factor for the Micro-kinetic simulation

| Elementary reaction | $E_a$ | $E_{a\_r}$ | A | A_r |
|---|---|---|---|---|
| $CH_4(g)+* \rightarrow CH_4*$ | 0.00 | 10.38 | 1.72E+03 | 8.29E+17 |
| $CH_4*+*\rightarrow CH_3*+H*$ | 23.29 | 20.98 | 9.01E+12 | 8.82E+12 |
| $CH_4(g)+CH_3*+H*+*\rightarrow CH_4*+CH_3*+H*$ | 0.00 | 12.22 | 1.72E+03 | 8.29E+17 |
| $CH_4*+ CH_3*+ H *+*\rightarrow 2CH_3*+2H *$ | 23.52 | 11.07 | 9.12E+12 | 8.99E+12 |
| $2\ CH_3*+2H *\rightarrow 2CH_3*+ H_2*+*$ | 17.76 | 7.84 | 8.75E+12 | 7.96E+12 |
| $2\ CH_3*+ H_2*\rightarrow 2\ CH_3*+ H_2(g)+*$ | 11.99 | 0.00 | 2.16E+15 | 4.87E+3 |
| $2\ CH_3*\rightarrow C_2H_6*+*$ | 31.13 | 32.05 | 8.44E+12 | 9.04E+12 |
| $C_2H_6*\rightarrow C_2H_6\ (g)+*$ | 20.06 | 0.00 | 4.97E+17 | 1.26E+03 |
| $C_2H_6*+2*\rightarrow C_2H_4*+2H*$ | 8.76 | 6.69 | 9.14E+12 | 8.73E+12 |
| $C_2H_4*+2H *\rightarrow C_2H_4*+ H_2*+*$ | 9.92 | 2.54 | 8.83E+12 | 7.37E12 |
| $C_2H_4*+ H_2*\rightarrow C_2H_4*+ H_2\ (g)+*$ | 11.99 | 0.00 | 4.32E+15 | 4.87E+03 |
| $C_2H_4*\rightarrow C_2H_4(g)+*$ | 32.05 | 10.38 | 7.54E+17 | 1.30E+03 |

Note: $E_{a\_r}$ means the energy barrier of reverse reaction, and A_r means pre-exponential factor for reverse reaction. $E_a$ in kcal/mol, and A in $s^{-1.}\ Pa^{-1}$ for adsorption process and $s^{-1}$ for reaction and desorption process.