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# Mechanistic insight into catalytic conversion of methane on $Sr_2Fe_{1.5}Mo_{0.5}O_6$ perovskite anode: A combined EIS-DRT, DFT and TPSR investigation

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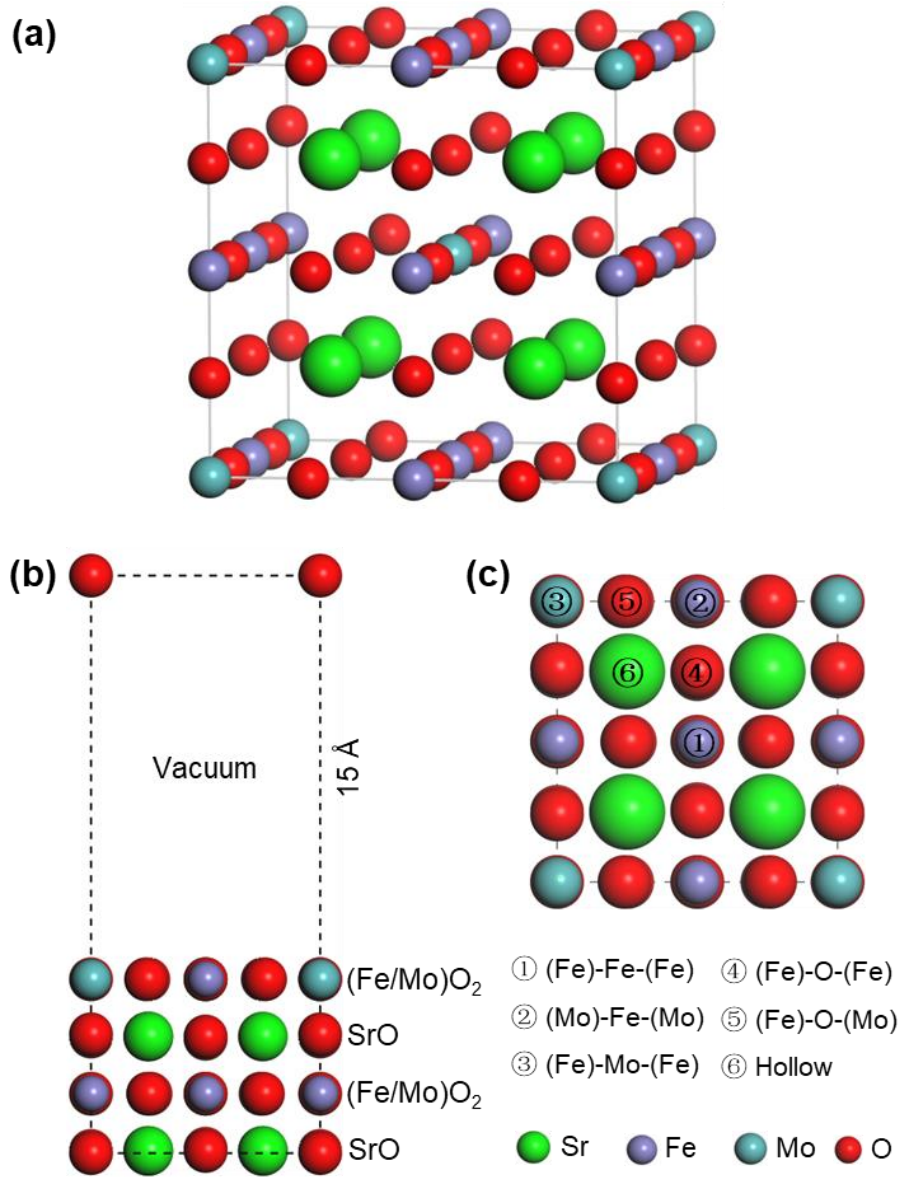


**Fig. S1** SFMO bulk model (s), SFMO (001) surface model (b) and potential adsorption sites (c) on SFMO (001) surface.

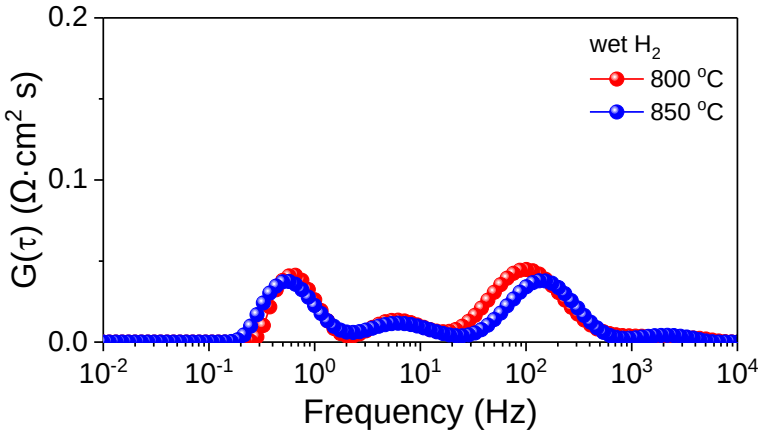


**Fig. S2** DRT curves of the SFM/LSGM/LSCF cell in wet hydrogen fuel.

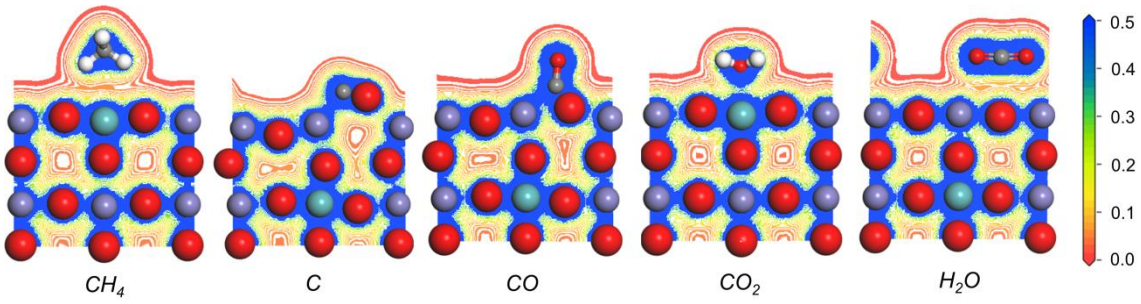


**Fig. S3** Electron density distribution in the most stable adsorption configurations of the key species on SFMO (001) surface. Electron density is given in units of electrons per $Å^3$.

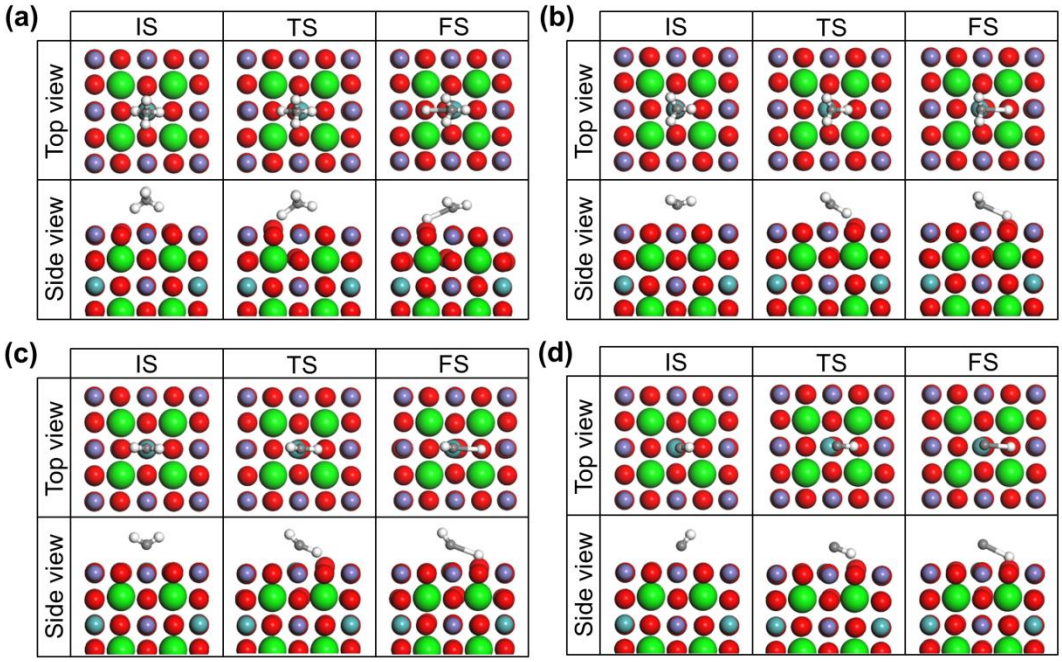


**Fig. S4** Geometry of the IS, TS and FS of methane cracking on the (Fe)-Mo-(Fe) site over SFMO surface. (a) $CH_4 = CH_3 + H$; (b) $CH_3 = CH_2 + H$; (c) $CH_2 = CH + H$; (d) $CH = C + H$.

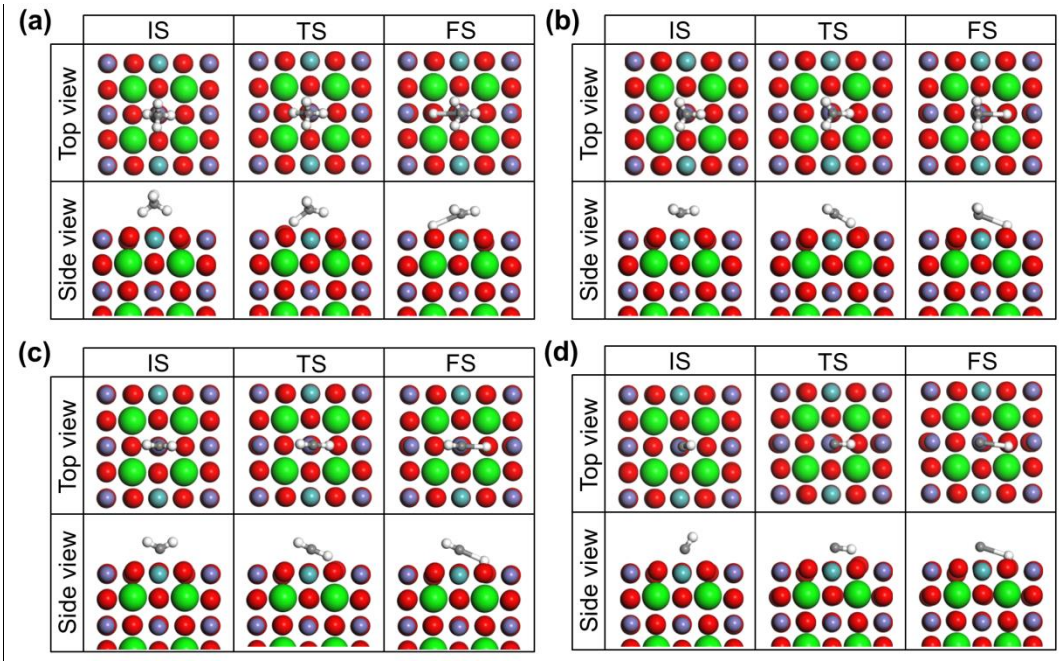


**Fig. S5** Geometry of the IS, TS and FS of methane cracking on the (Mo)-Fe-(Mo) site over SFMO surface. (a) $CH_4 = CH_3 + H$; (b) $CH_3 = CH_2 + H$; (c) $CH_2 = CH + H$; (d) $CH = C + H$.

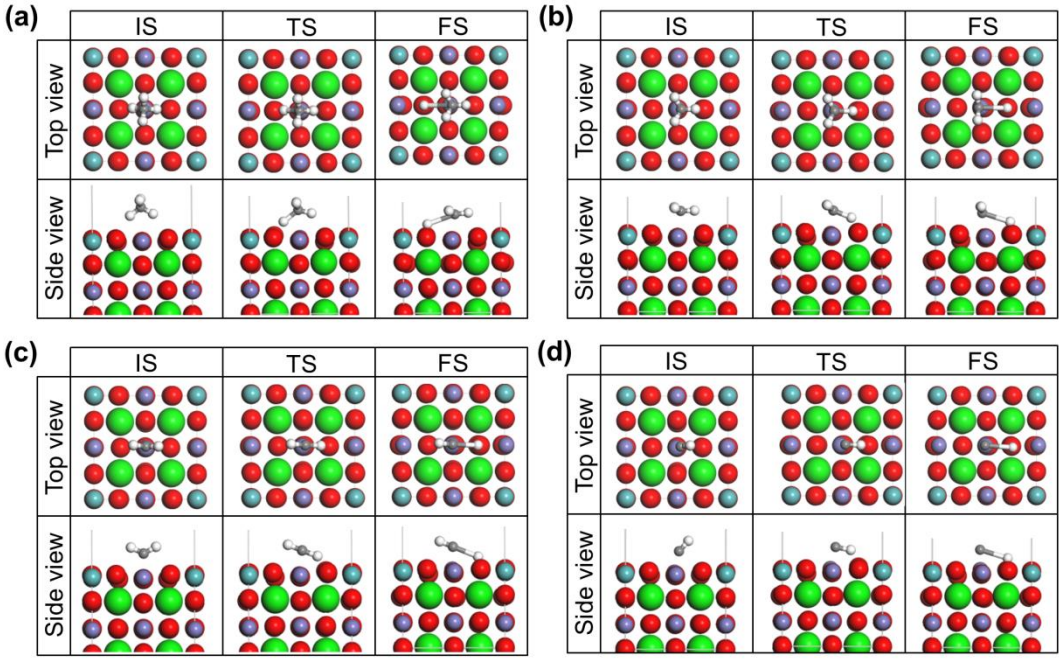


**Fig. S6** Geometry of the IS, TS and FS of methane cracking on the (Fe)-Fe-(Fe) site over SFMO surface. (a) $CH_4 = CH_3 + H$; (b) $CH_3 = CH_2 + H$; (c) $CH_2 = CH + H$; (d) $CH = C + H$.

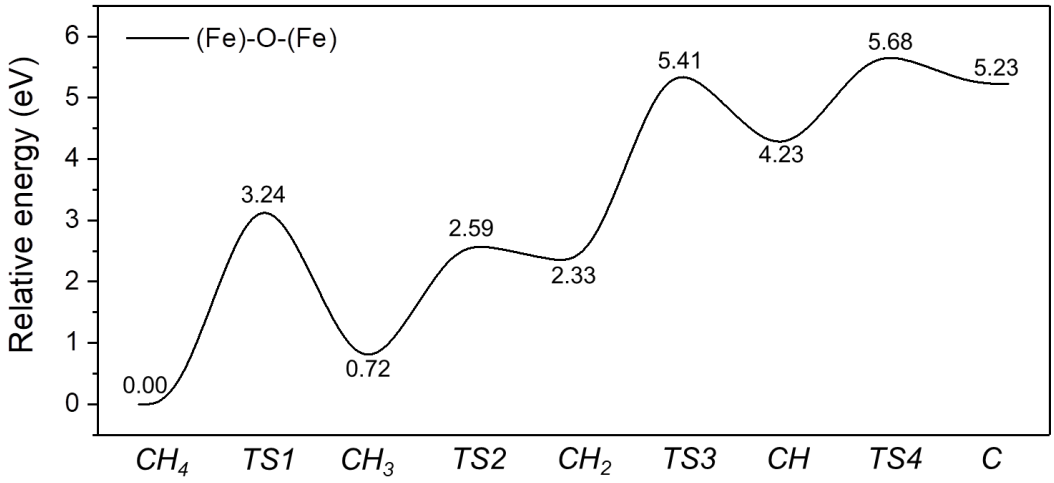


**Fig. S7** Energy profile of methane cracking on surface oxygen site of SFMO (001) surface.

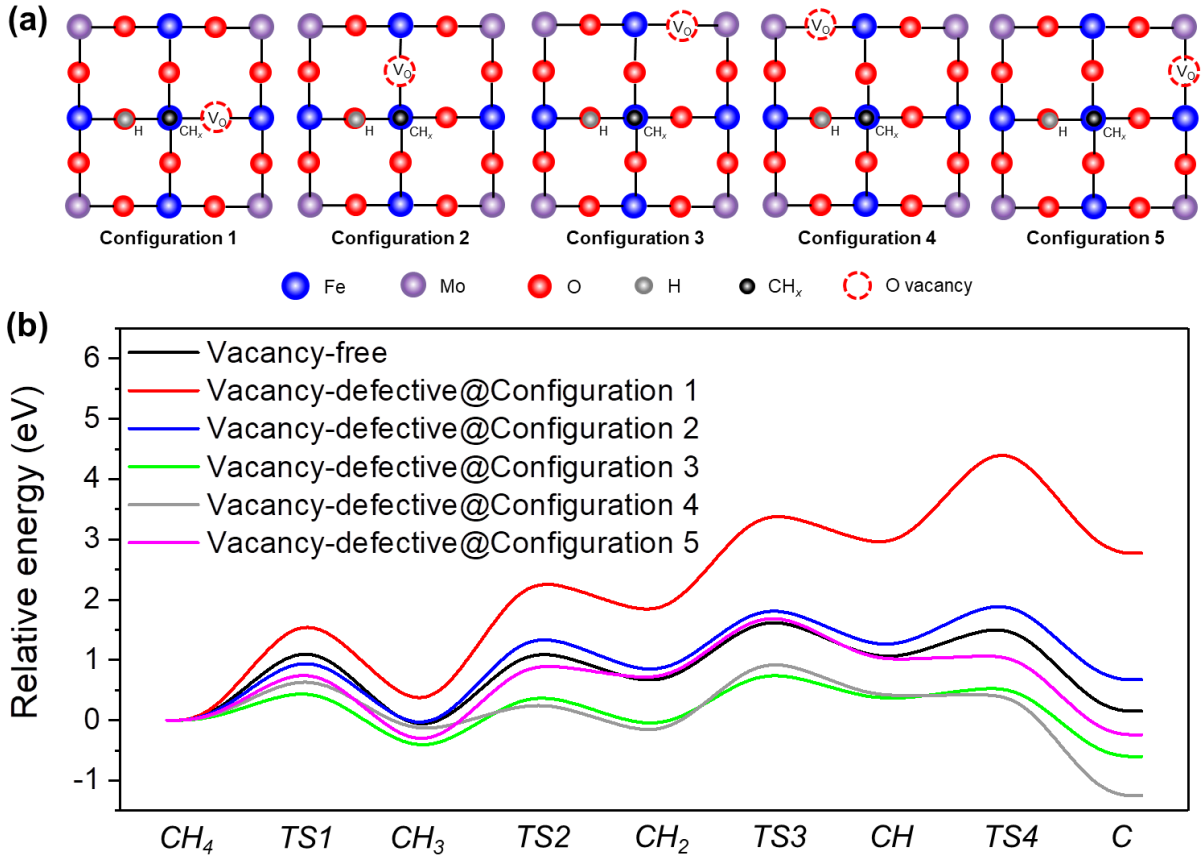


**Fig. S8** (a) Schematic diagram of five type of methane cracking configurations on the preferred surface (Fe)-Fe-(Fe) site of oxygen vacancy-defective SFMO surface; (b) Comparison of the energy profiles of methane cracking on the preferred surface (Fe)-Fe-(Fe) site (Fe)-Fe-(Fe) site with and without oxygen vacancy.

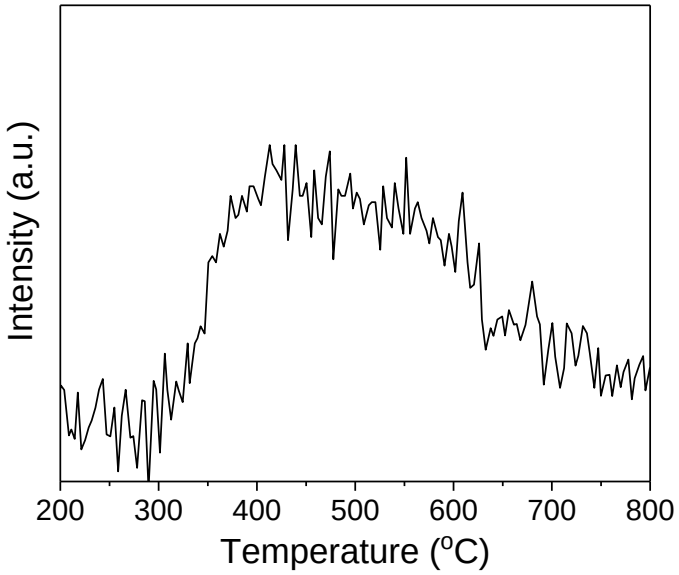


**Fig. S9** The $CH_4$ desorption profile over the as-synthesized SFMO perovskite.

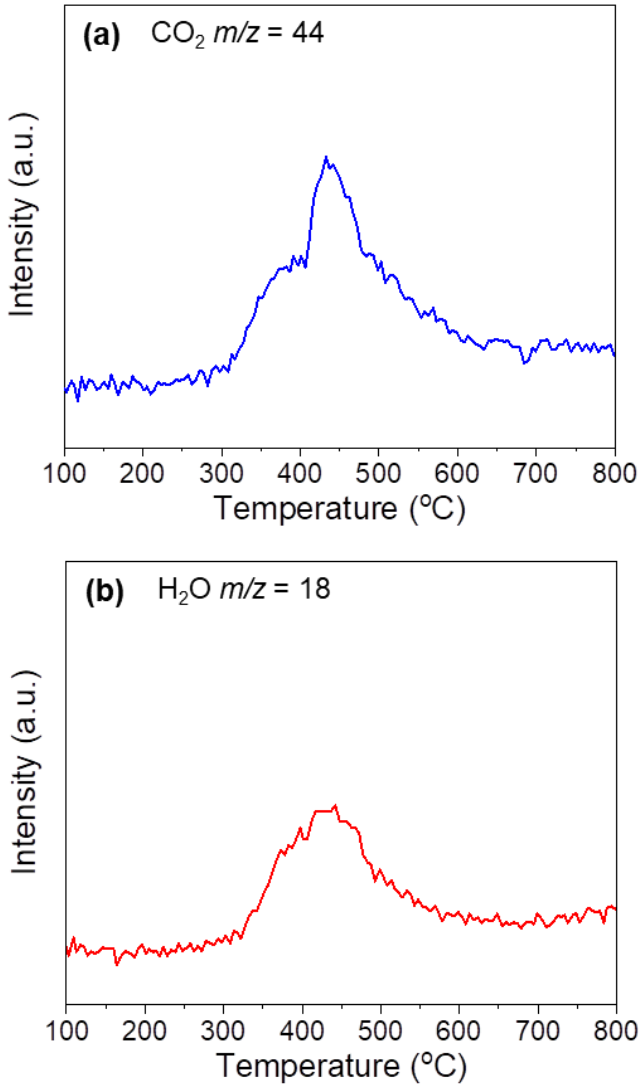


**Fig. S10** $CH_4$-TPSR profiles corresponding to the reaction of $CH_4$ and lattice oxygen over Ni-YSZ as function of temperature.

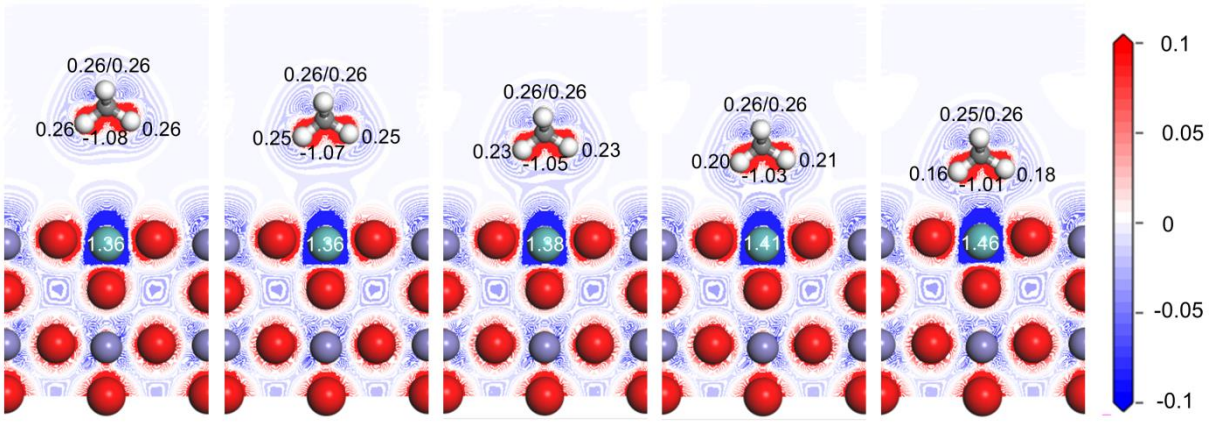


**Fig. S11** Electron density differences as the methane molecule approaches the surface given in units of electrons per $Å^3$. In this plot a loss of electrons is indicated in blue, while electron enrichment is indicated in red. Inserted values represent the Mulliken charge of H and C atoms in $CH_4$ molecule and the beneath Mo atom on the surface.