Supplementary Material: CH_4 Activation and C-C coupling on Ti_2C(100) Surface in presence of intrinsic C-vacancies: Is excess good?

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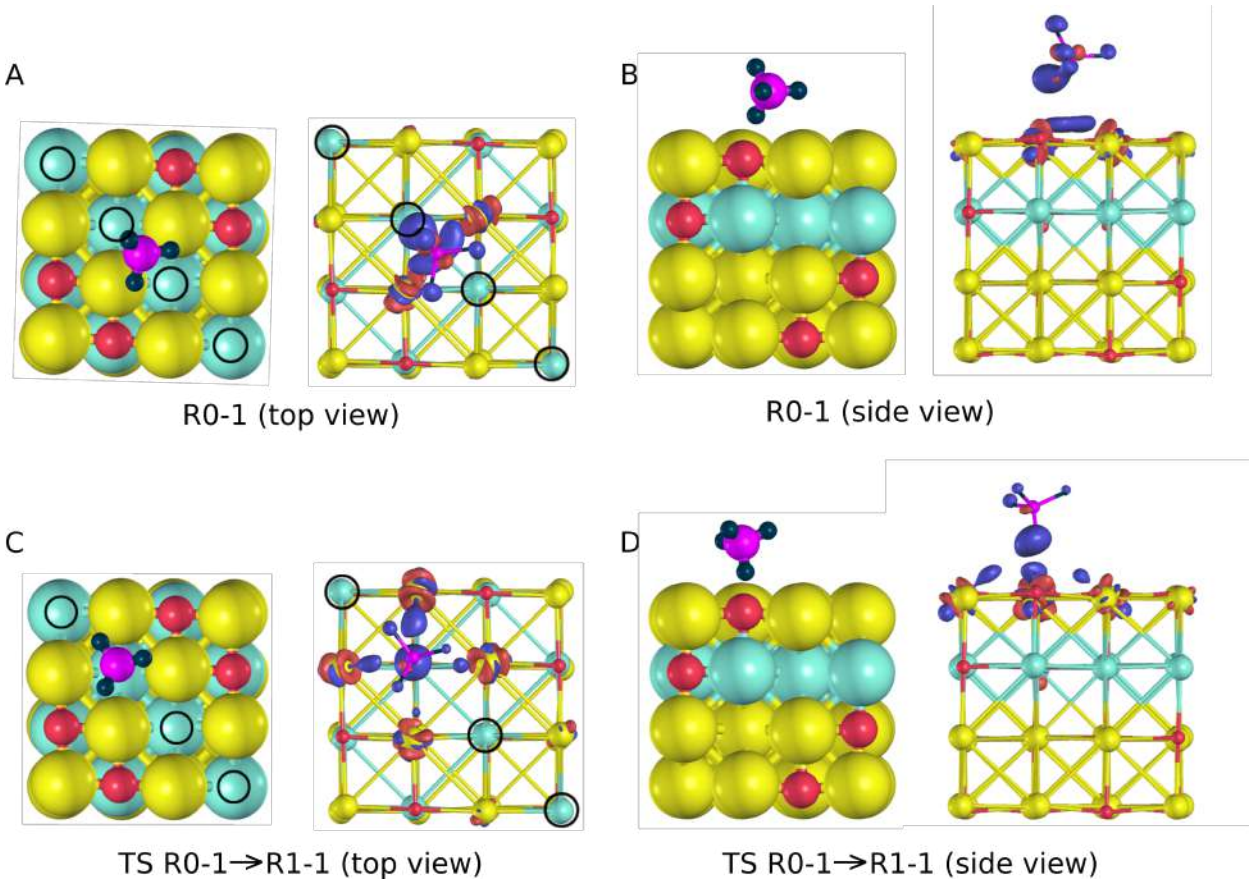

FIG. S1. Top and side views of the initial state (R0-1; upper panel) and transition state R0-1 → R1-1 (lower panel) of the first CH bond activation of CH_4. Also shown are the charge density isosurfaces (blue denotes charge depletion and red denotes charge accumulation). While in the initial state, methane interacts with two Ti atoms on the surface, in the transition state it interacts with four Ti atoms surrounding the vacancy.

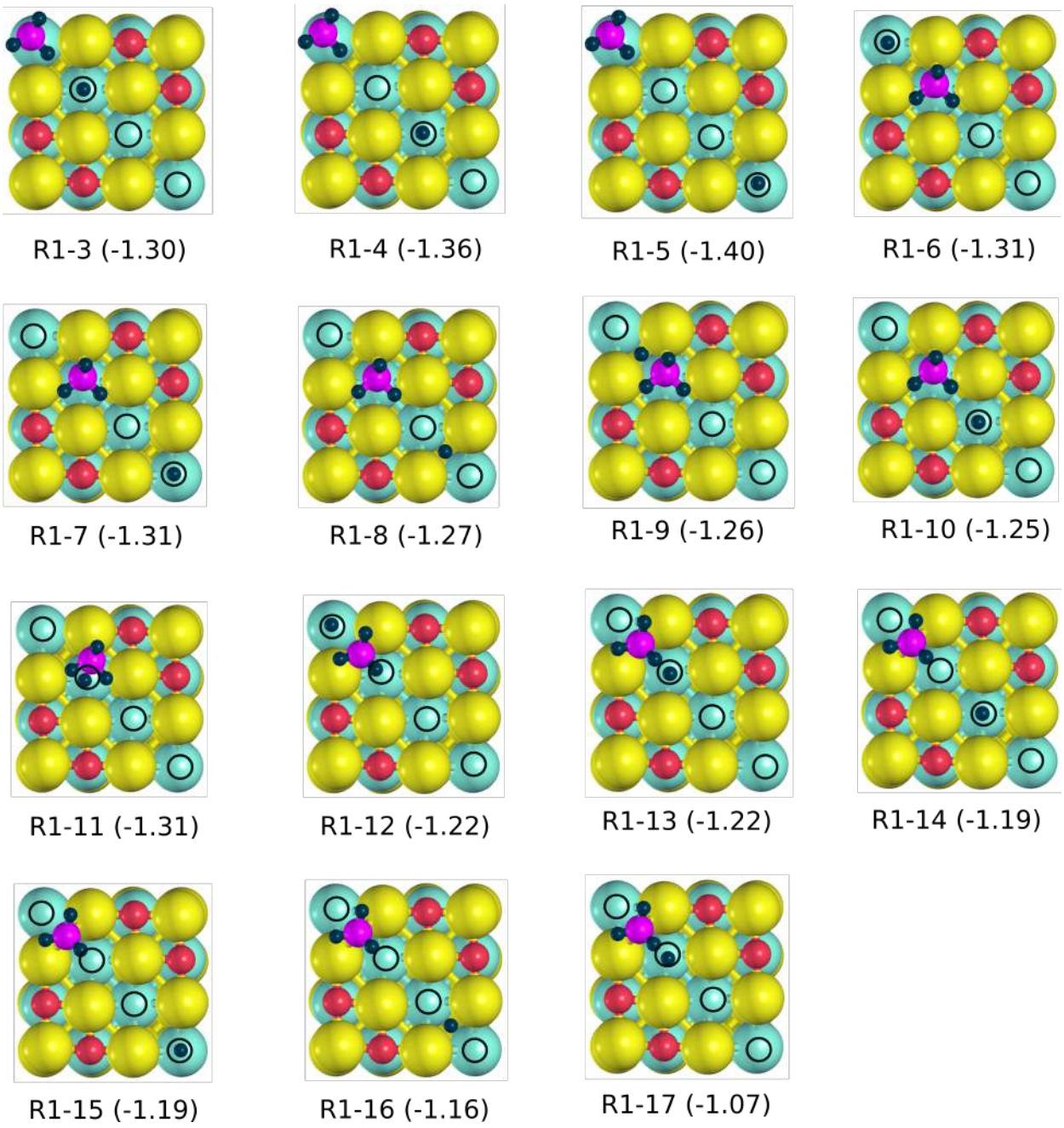

FIG. S2. Relaxed configurations of $Ti_2C(100)$ surface with CH_3 and H. The energies in parenthesis are the co-adsorption energies of the species adsorbed on the surface with respect to the clean surface and methane in gas phase. The energies are given in eV.

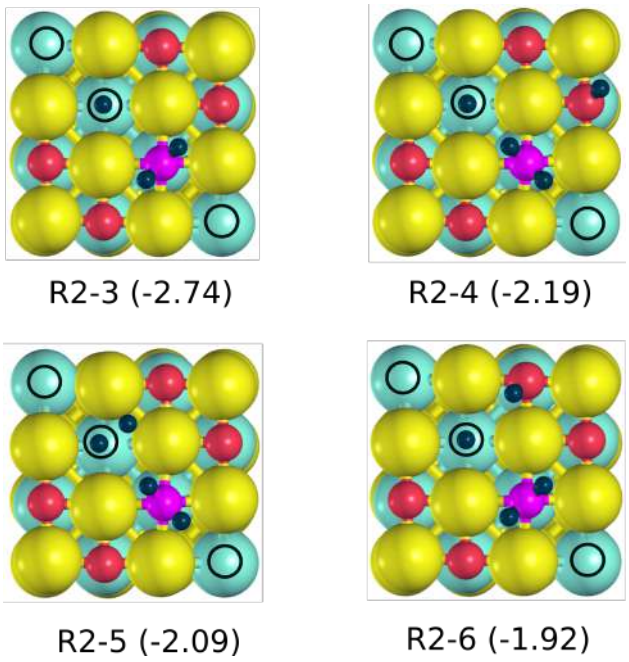

FIG. S3. Relaxed configurations of $Ti_2C(100)$ surface with CH_2 and 2H. The energies in parenthesis are the co-adsorption energies of the species adsorbed on the surface with respect to the clean surface and methane in gas phase. The energies are given in eV.

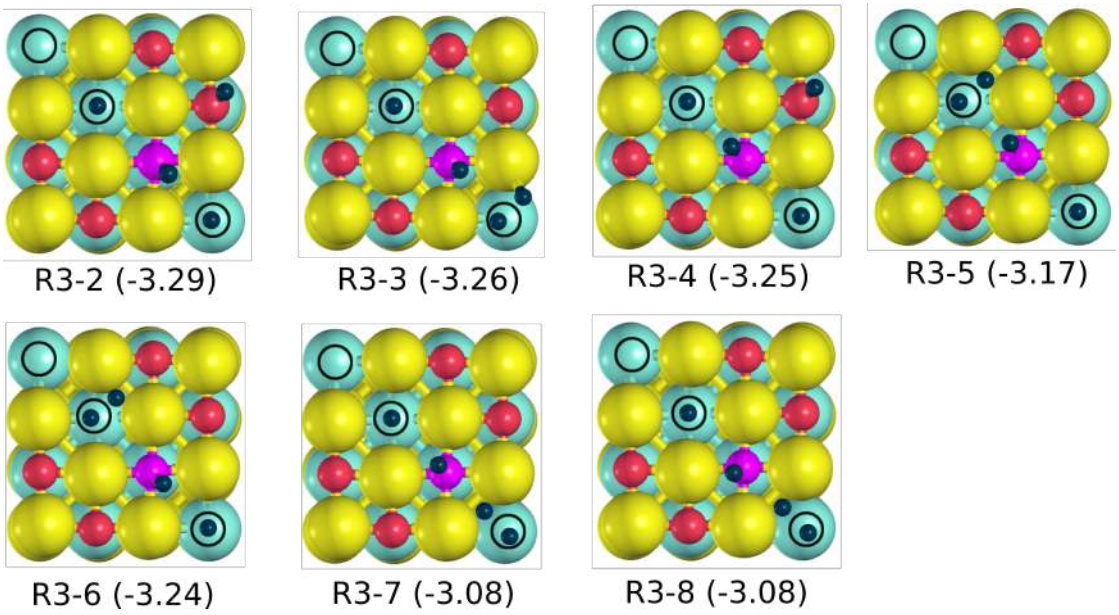

FIG. S4. The relaxed geometries of the final state corresponding to CH formation (reaction R3). The numbers given in parenthesis are the co-adsorption energies of the species adsorbed on the surface with respect to the clean surface and methane in gas phase. The energies are given in eV.

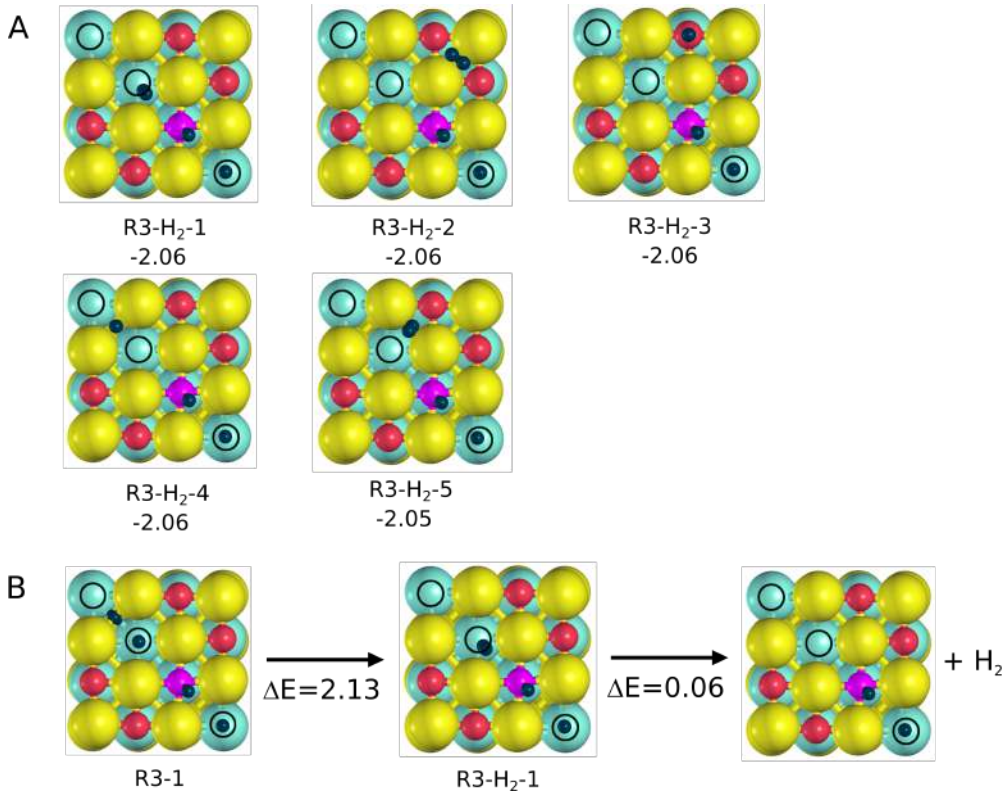

FIG. S5. (A) The different configurations for adsorption of molecular H2 in presence of CH and H on Ti2C(100) surface. (B) The reaction energies for the formation of molecular H2 from R3-1. The energies are given in eV.

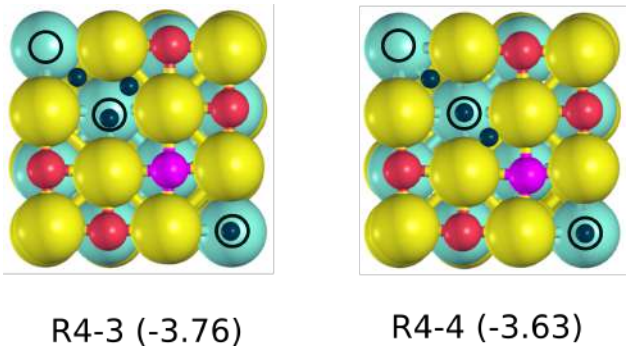

FIG. S6. Relaxed configurations of $Ti_2C(100)$ surface with C and 4H . The energies in parenthesis are the co-adsorption energies of the species adsorbed on the surface with respect to the clean surface and methane in gas phase. The energies are given in eV.

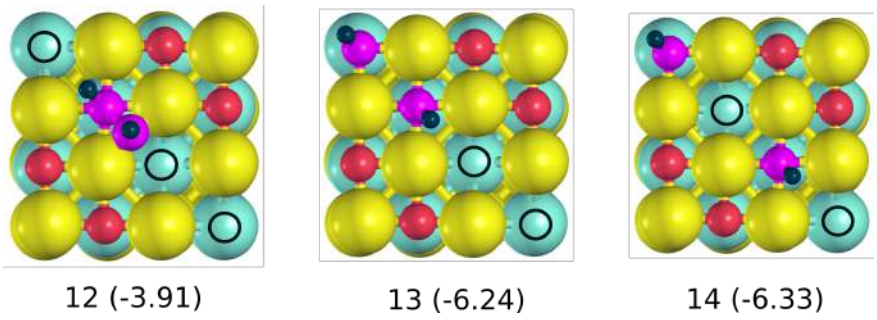

FIG. S7. Relaxed configurations of $Ti_2C(100)$ surface with two CH fragments and C_2H_2. The energies in parenthesis are the co-adsorption energies of the species adsorbed on the surface with respect to the clean surface and acetylene in gas phase. The energies are given in eV.

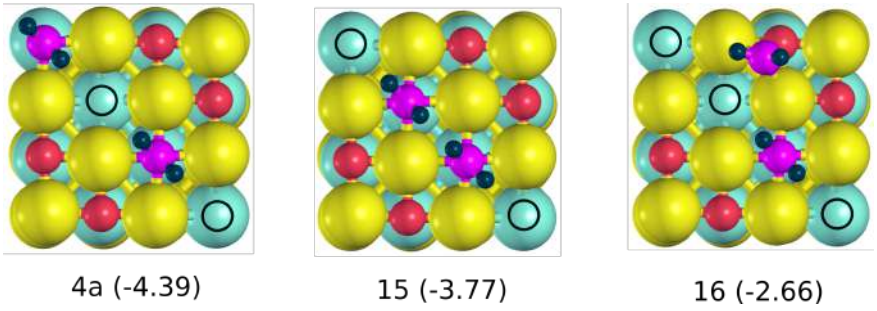

FIG. S8. Relaxed configurations of $Ti_2C(100)$ surface with two C_2H_2 fragments. The energies in parenthesis are the co-adsorption energies of the species adsorbed on the surface with respect to the clean surface and ethylene in gas phase. The energies are given in eV.

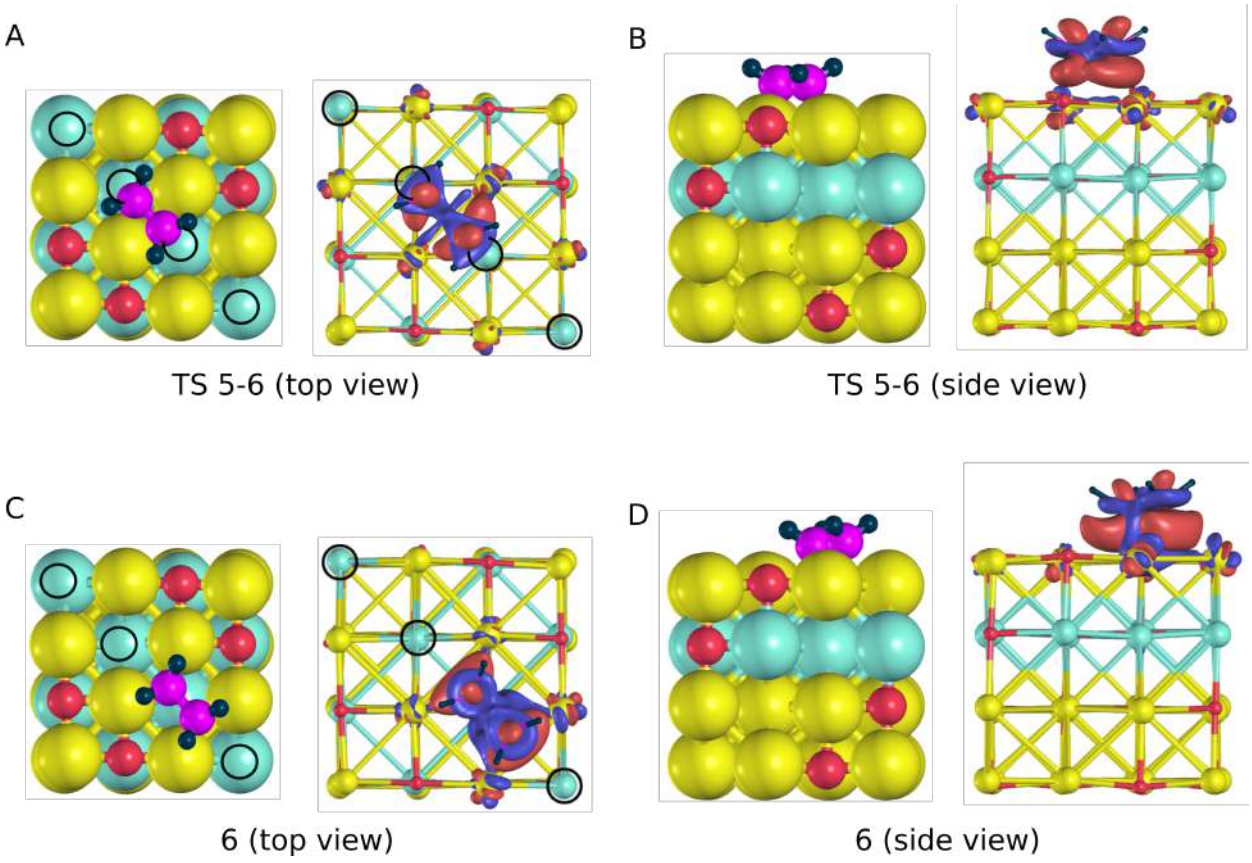

FIG. S9. Top panel: top (A) and side (B) views of the transition state corresponding to the C_2H_4 formation, **TS 5-6**. Bottom panel: top (C) and side (D) views of the final state corresponding to the C_2H_4 formation, **6**. Also shown are the charge transfer isosurfaces. The red (blue) isosurfaces corresponds to charge accumulation (depletion).

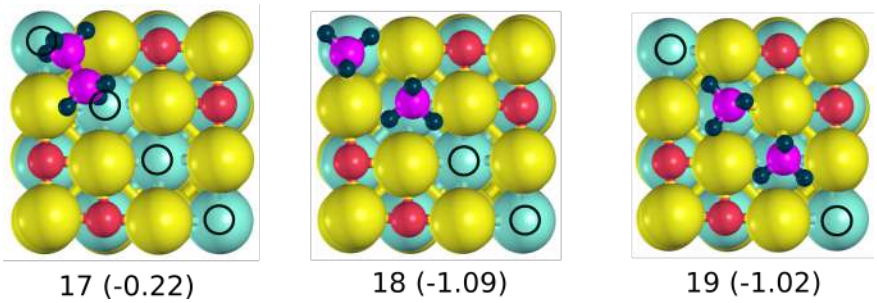

FIG. S10. Relaxed configurations of $Ti_2C(100)$ surface with two CH_3 fragments and C_2H_6. The energies in parenthesis are the co-adsorption energies of the species adsorbed on the surface with respect to the clean surface and ethane in gas phase. The energies are given in eV.

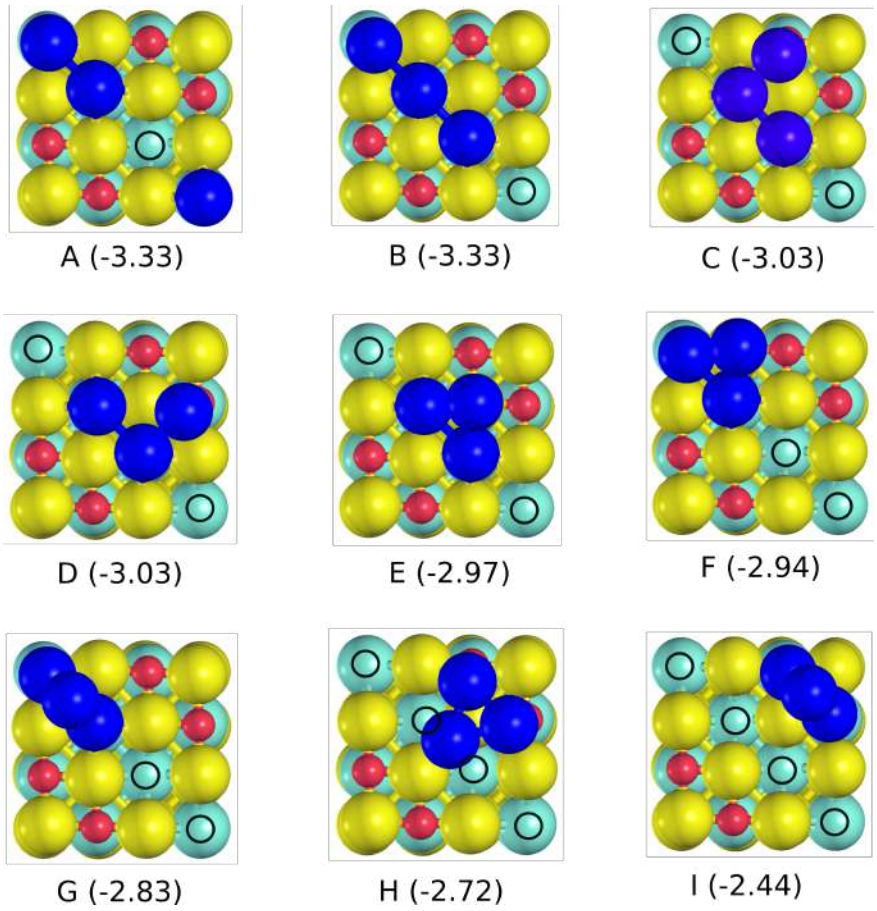

FIG. S11. Relaxed configurations of $Ti_2C(100)$ surface with Cu_3 cluster. The energies in parenthesis are the adsorption energies per Cu atom (blue spheres) of the species adsorbed on the surface with respect to the clean surface and Cu_3 in gas phase. The energies are given in eV.