Supporting Information

A Computational Study of K Promotion of CO Dissociation on Hägg carbide

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Figure S27. DOS and COHP of C-O bond of CO in gas phase, CO absorbate on (010*) surface; and K_2O-promoted (010*) surfaces of χ-Fe_5C_2.

Figure S28. (a) K_2O promoted (010) surface of χ-Fe_5C_2. (b) Charge difference of surface Fe atoms on the (010) surface upon K_2O adsorption (Negative values indicate increased electron density upon adsorption). (c) Charge of surface Fe atoms on the pristine (010) and (d) K_2O-promoted (010) surfaces of χ-Fe_5C_2.

Figure S29. Charge density difference upon CO adsorption on the (010) and K_2O-promoted (010) surfaces.

Figure S30. DOS and COHP of C-O bond of HCO^- in gas phase, HCO absorbate on the (510) and K_2O-promoted (510) surfaces of χ-Fe_5C_2.

Figure S31. DOS and COHP of C-O bond of HCO^- in gas phase, HCO absorbate on the (111) and K_2O-promoted (111) surfaces of χ-Fe_5C_2.

Figure S32. DOS and COHP of C-O bond of HCO^- in gas phase, HCO absorbate on the (010) and K_2O-promoted (010) surfaces of χ-Fe_5C_2.

Figure S33. DOS and COHP of C-O bond of HCO^- in gas phase, HCO absorbate on the (010*) and K_2O-promoted (010*) surfacse of χ-Fe_5C_2.

Figure S34. DOS and COHP of C-O bond of COH^- in gas phase, COH absorbate on the (510) and K_2O-promoted (510) surfaces of χ-Fe_5C_2.

Figure S35. DOS and COHP of C-O bond of COH^- in gas phase, COH absorbate on the (111) and K_2O-promoted (111) surfaces of χ-Fe_5C_2.

Figure S36. DOS and COHP of C-O bond of COH^- in gas phase, COH absorbate on the (010) and K_2O-promoted (010) surfaces of χ-Fe_5C_2.

Figure S37. DOS and COHP of C-O bond of COH^- in gas phase, COH absorbate on the (010*) and K_2O-promoted (010*) surfaces of χ-Fe_5C_2.

Figure S38. DOS and COHP of C-O bond of CH_2O in gas phase, CH_2O absorbate on the (010) and K_2O-promoted (010) surfaces of χ-Fe_5C_2.

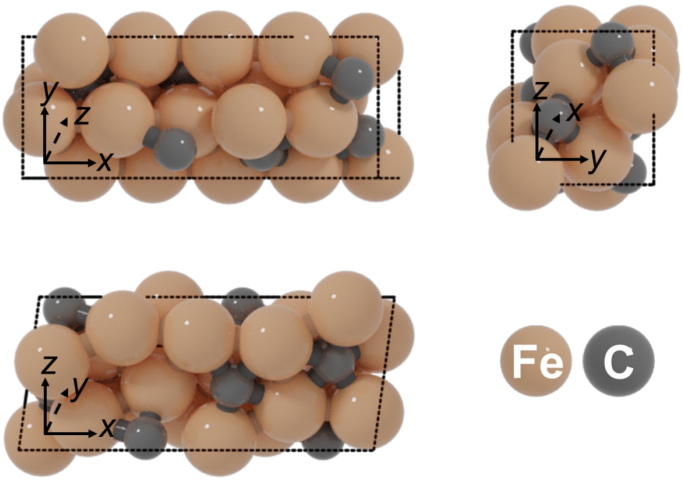

Figure S1. The configurations of optimized bulk of Fe_5C_2.

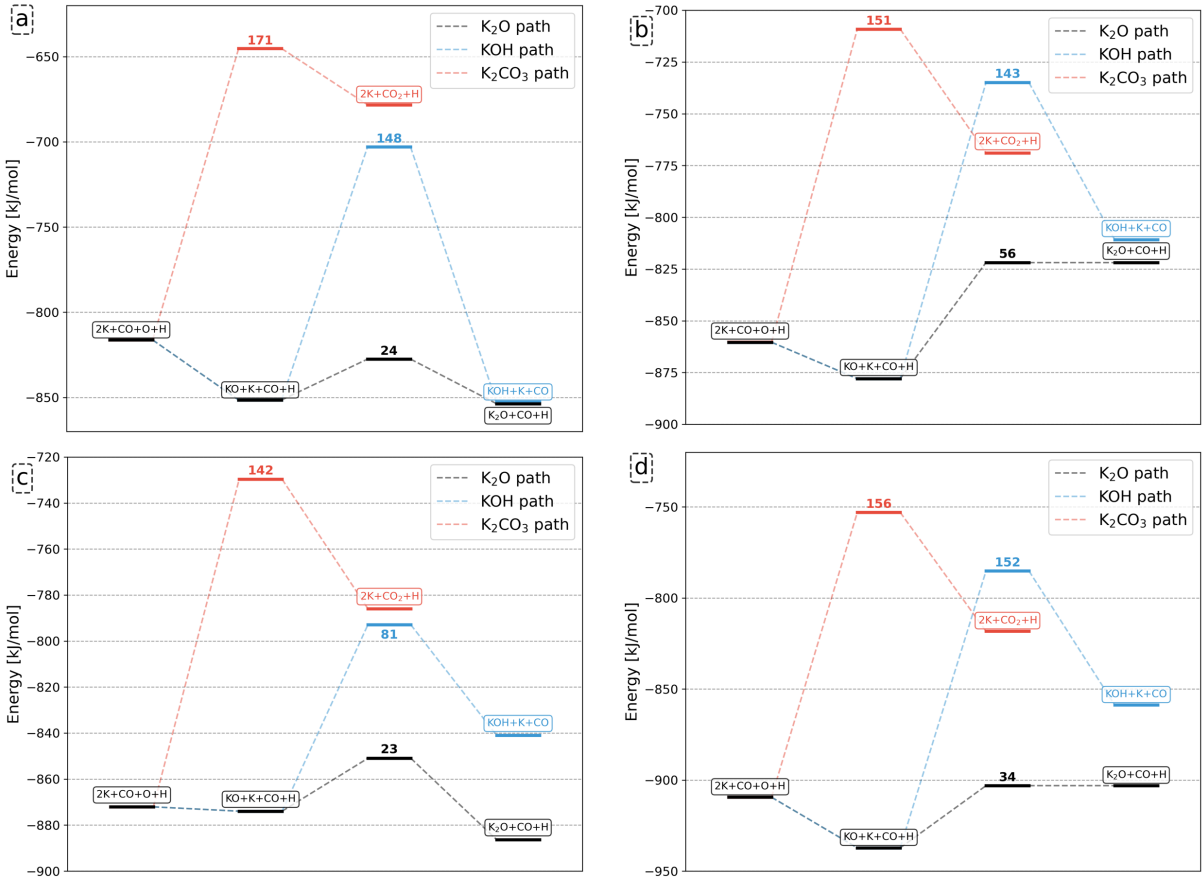

Figure S2. Reaction energy diagrams of the formation of K_2O, KOH, and K_2CO_3 on the (a) (510), (b) (111), (c) (010) and (d) (010*) surfaces of χ-Fe_5C_2. In practice, the high oxygen content makes K_2O the most stable form of the K promoter, with the lowest overall barrier on these surfaces, while the significantly difficult CO_2 formation results in the formation of K_2CO_3 unfavored on all surfaces.

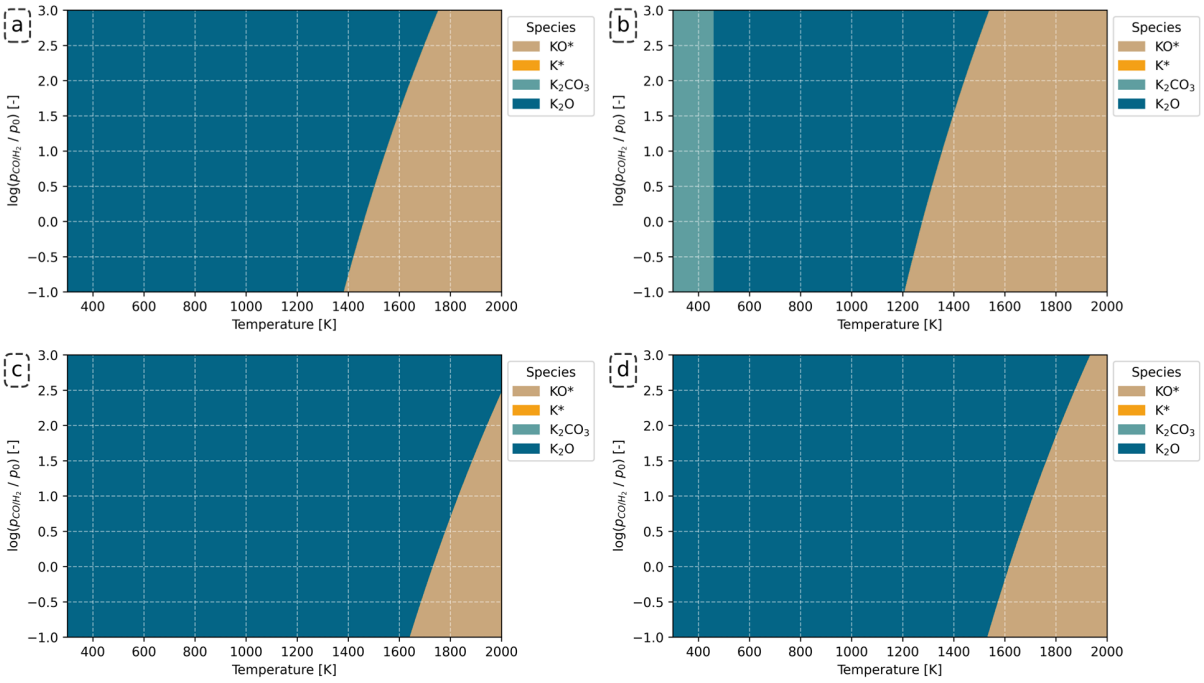

Figure S3. Phase diagrams illustrating the stability of K, KO, K_2O and K_2CO_3 as a function of CO and H_2 partial pressures and temperature on the (a) (510), (b) (111), (c) (010) and (d) (010*) surfaces of χ-Fe_5C_2. (P_{CO/H_2} is the partial pressure of CO and H_2).

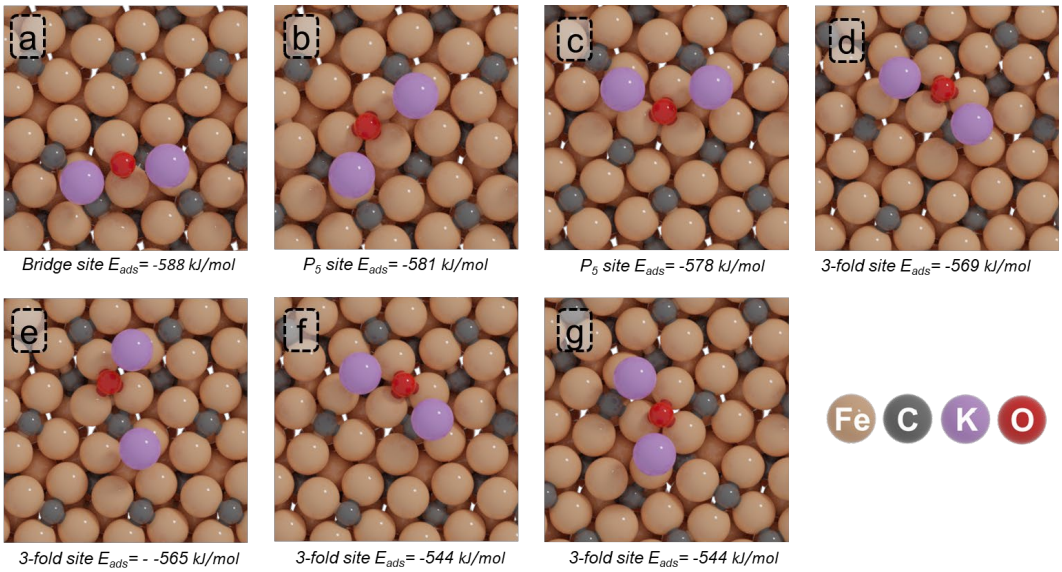

Figure S4. The adsorption structures and energy values of K_2O promoter in the possible sites on the (510) surface of χ-Fe_5C_2.

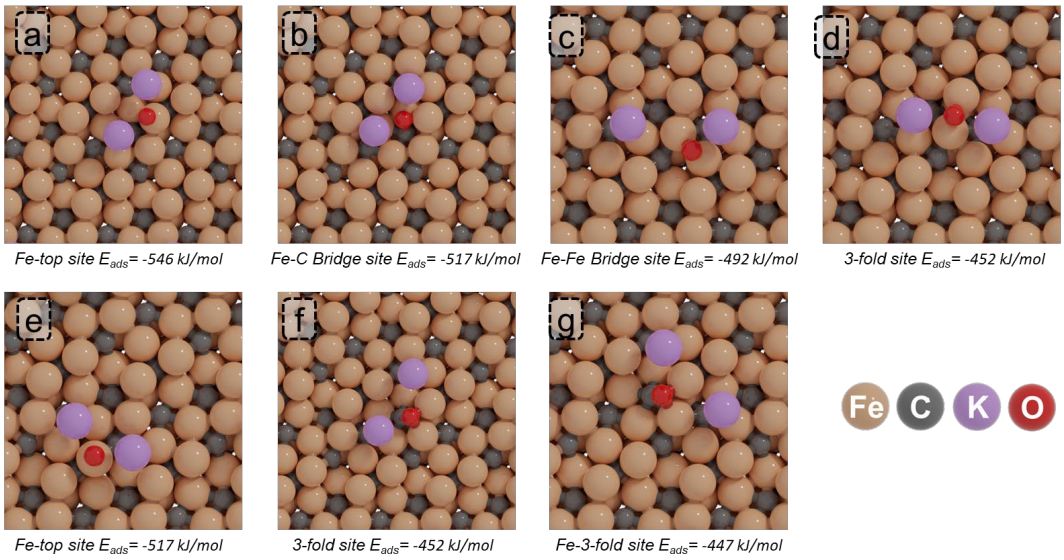

Figure S5. The adsorption structures and energy values of K_2O promoter in the possible sites on the (111) surface of χ-Fe_5C_2.

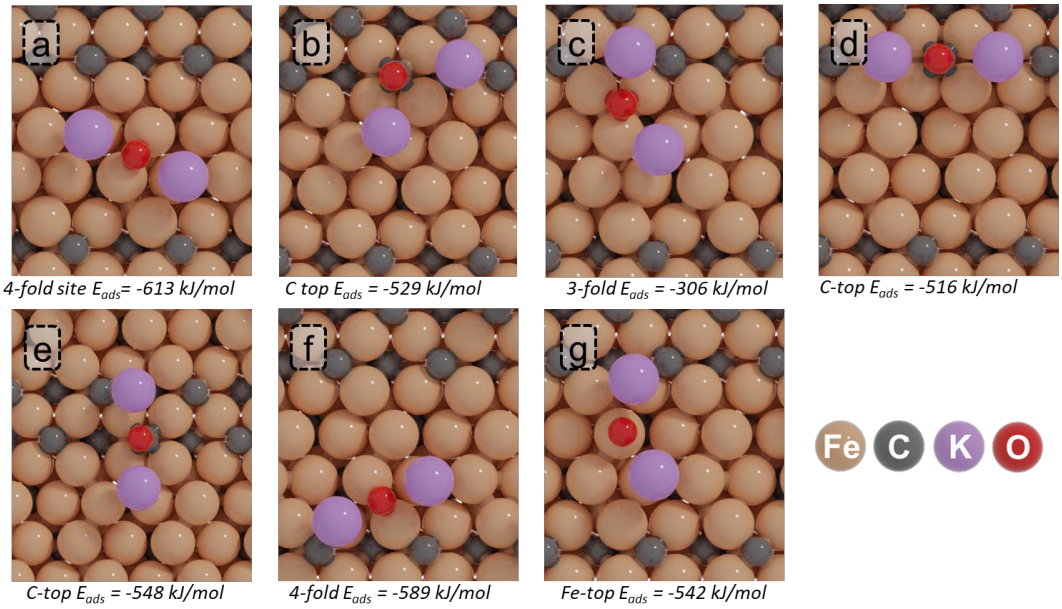

Figure S6. The adsorption structures and energy values of K_2O promoter in the possible sites on the (010) surface of χ-Fe_5C_2.

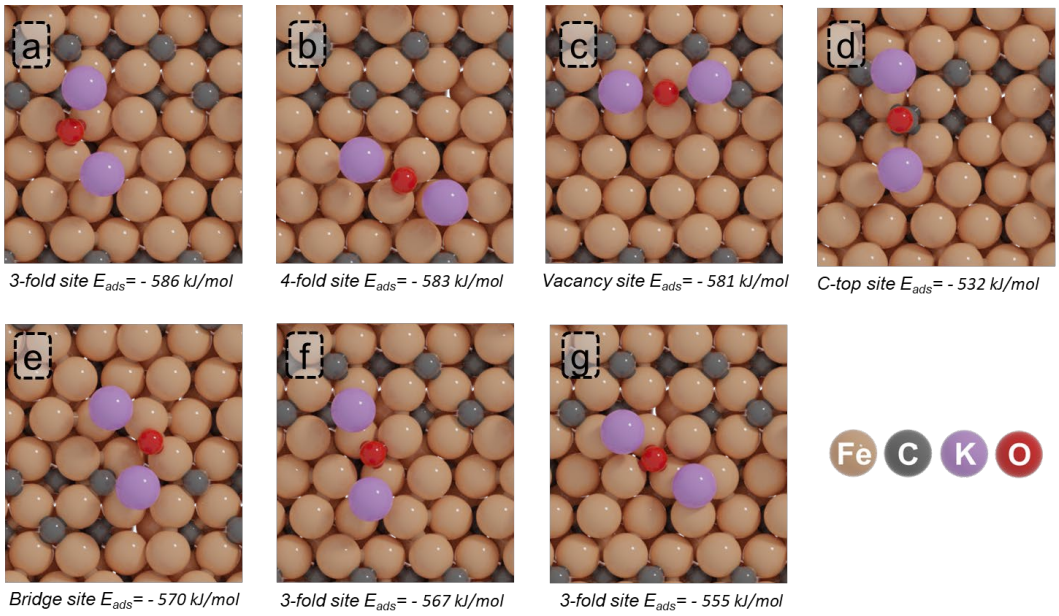

Figure S7. The adsorption structures and energy values of K_2O promoter in the possible sites on the (010*) surface of χ-Fe_5C_2.

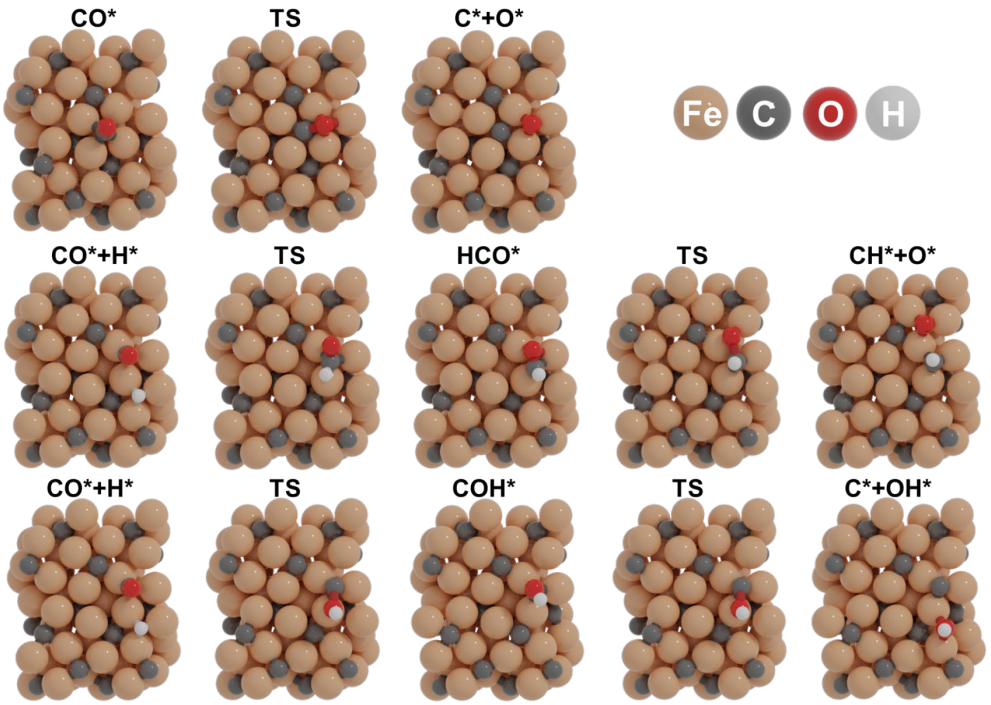

Figure S8. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the (510) surface of χ-Fe_5C_2.

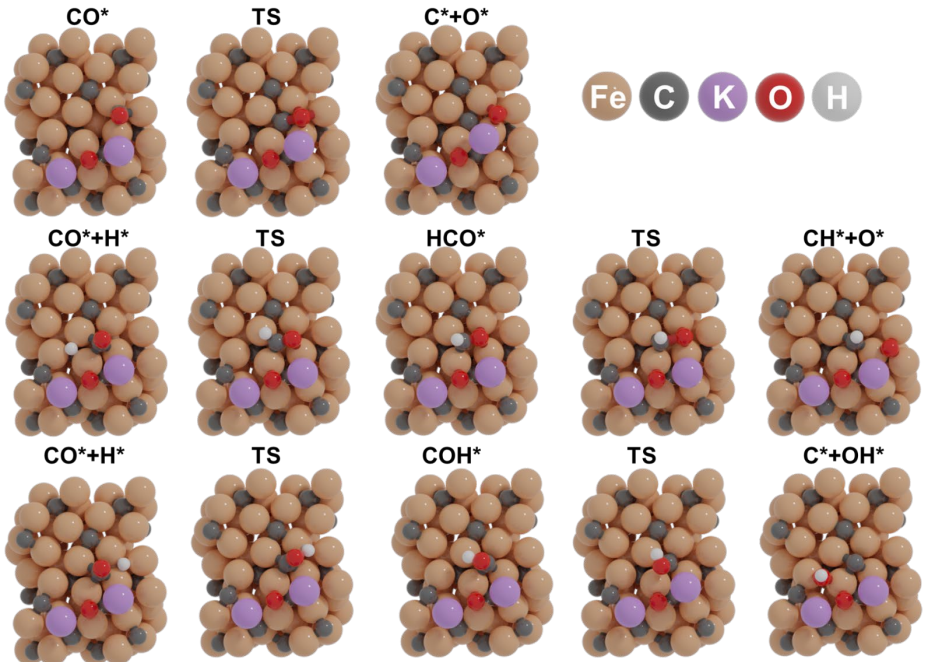

Figure S9. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the K_2O-promoted (510) surface of χ-Fe_5C_2.

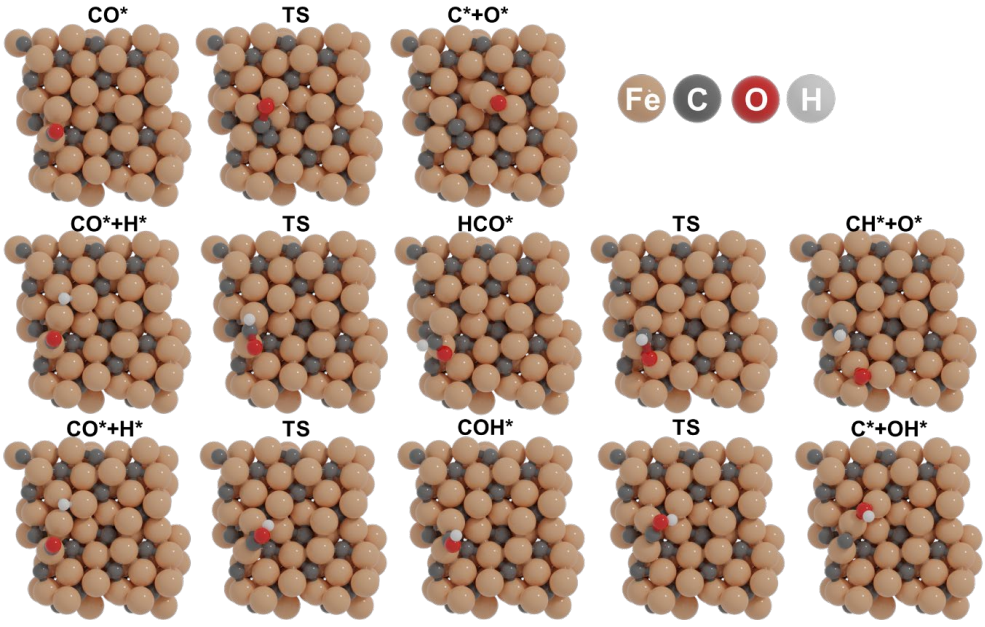

Figure S10. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the (111) surface of χ-Fe_5C_2.

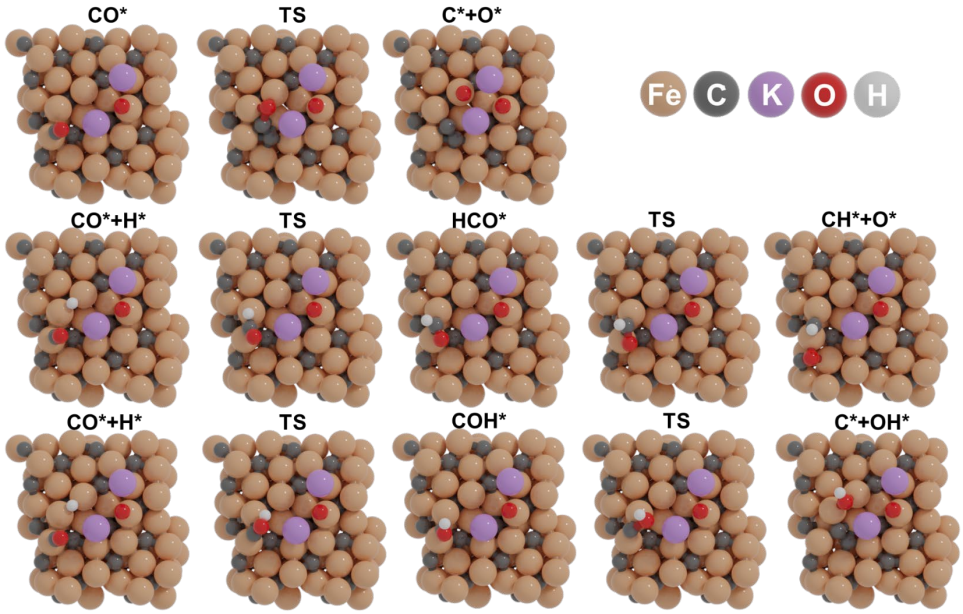

Figure S11. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the K_2O-promoted (111) surface of χ-Fe_5C_2.

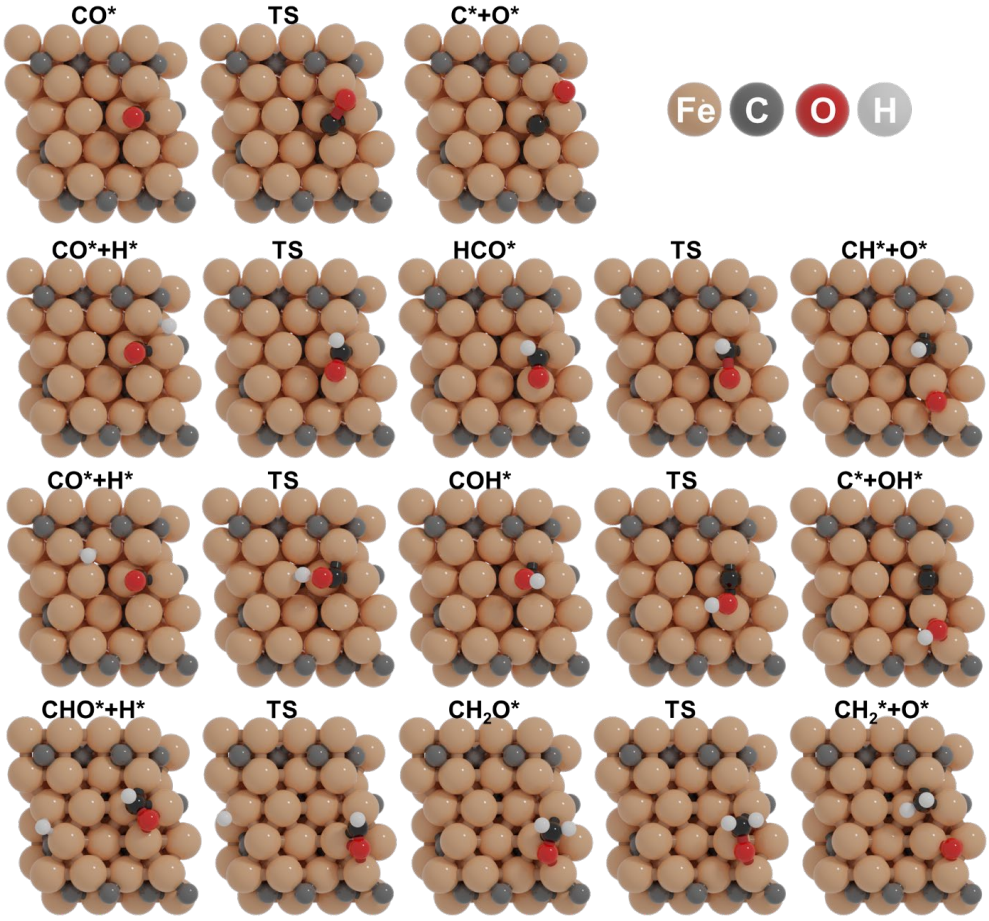

Figure S12. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the (010) surface of χ-Fe_5C_2.

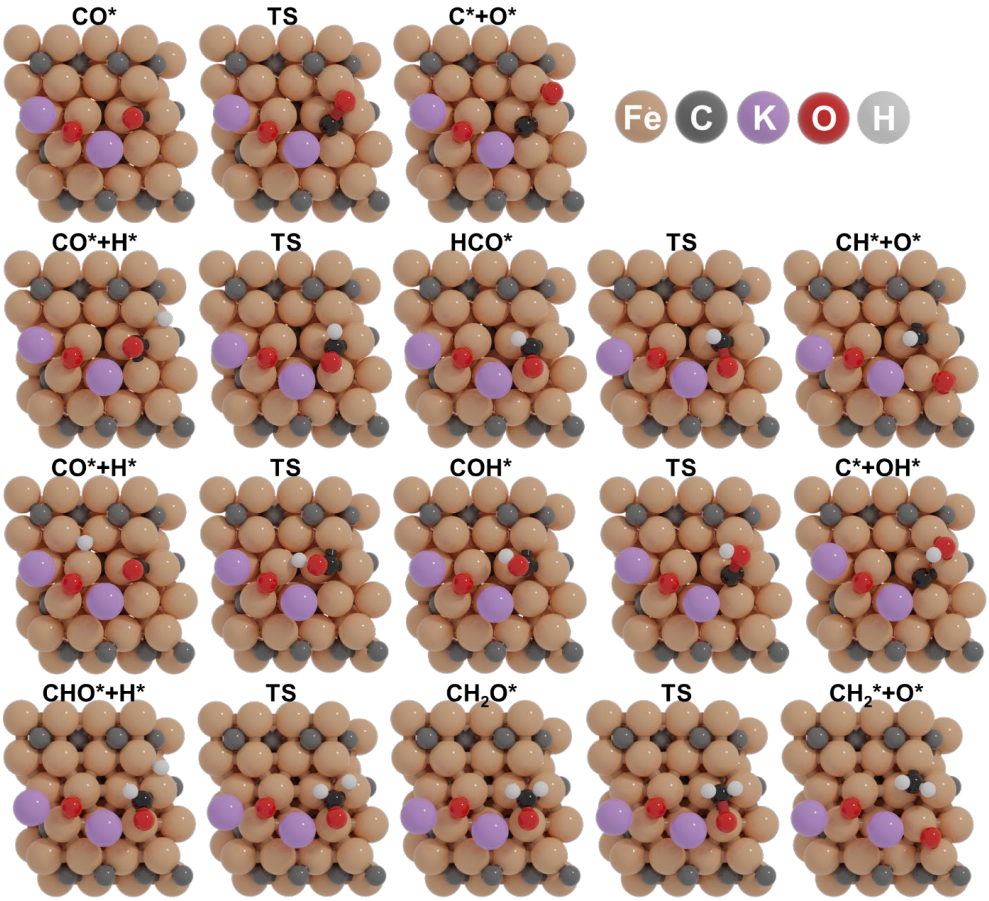

Figure S13. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the K_2O-promoted (010) surface of χ-Fe_5C_2.

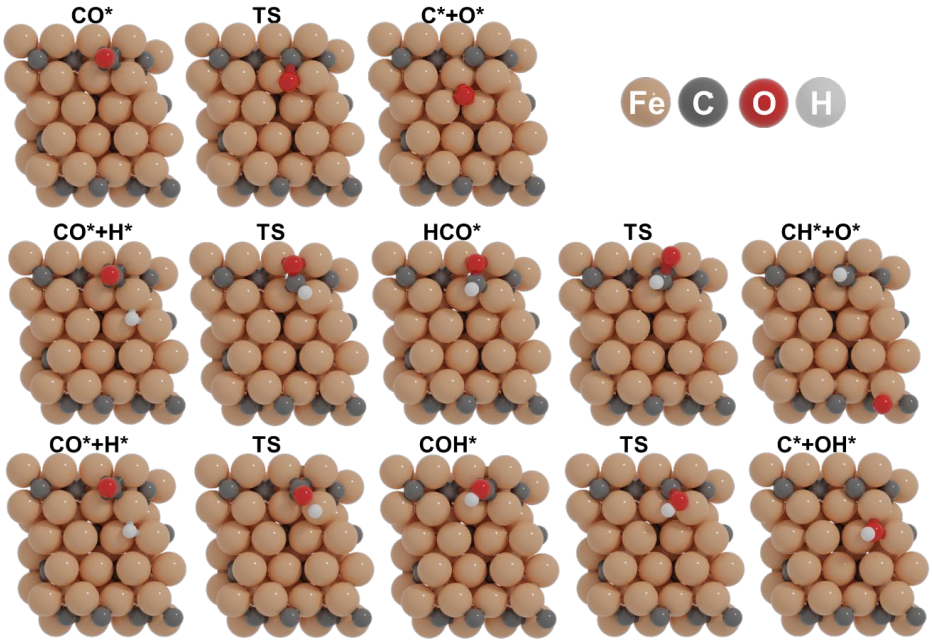

Figure S14. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the (010*) surface of χ-Fe_5C_2.

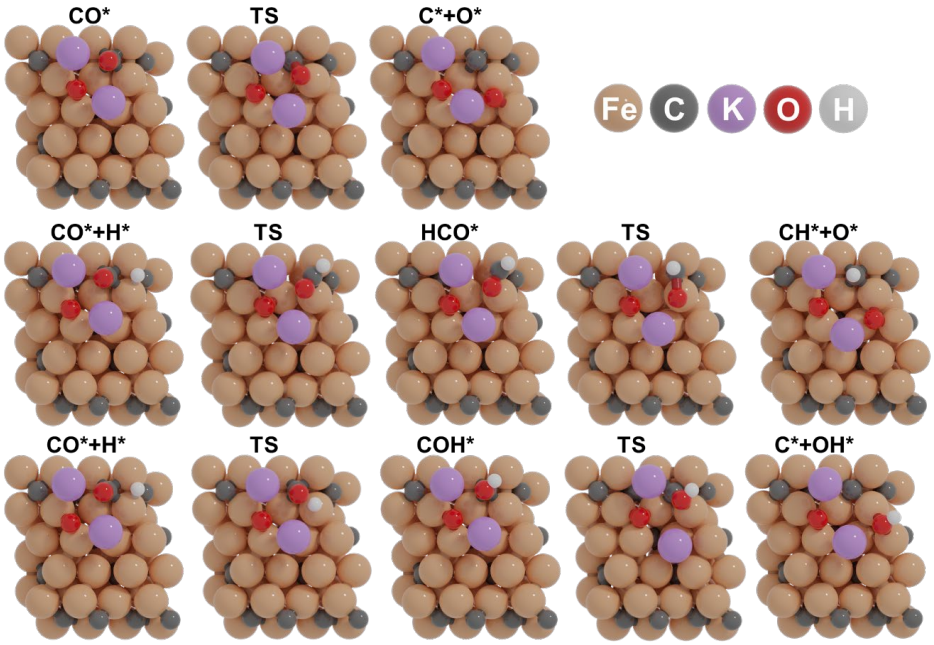

Figure S15. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the K_2O-promoted (010*) surface of χ-Fe_5C_2.

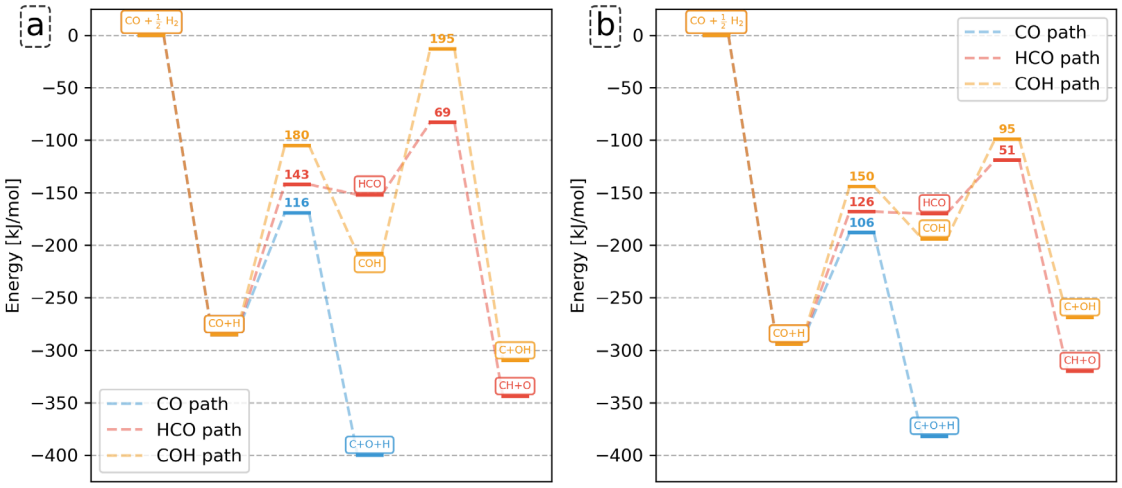

Figure S16. Energy profiles for the direct or H-assisted dissociation of CO from co-adsorbed H and CO on the (a) (510) and (b) K_2O-promoted (510) surfaces of χ-Fe_5C_2. The value upon the TS corresponds to the activation barrier of each elementary step.

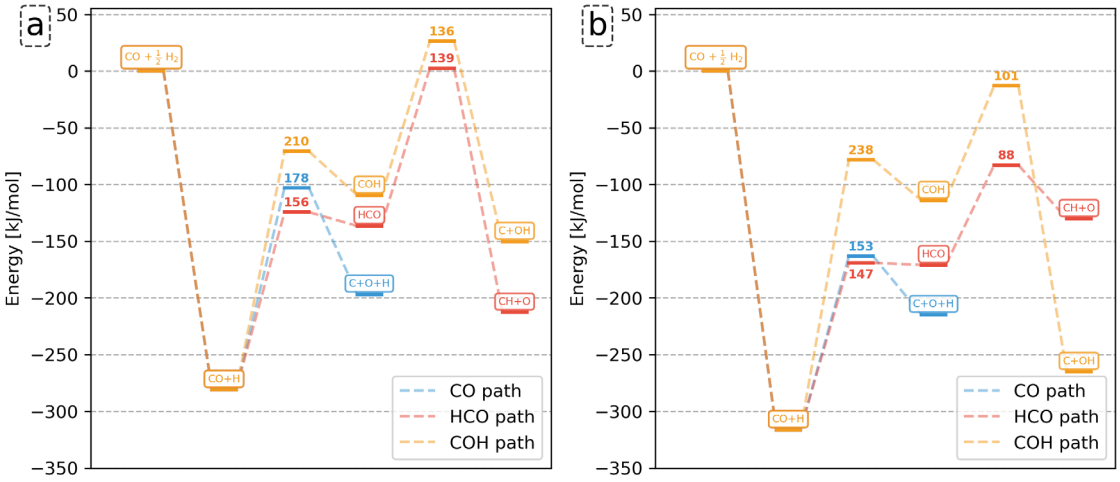

Figure S17. Energy profiles for the direct or H-assisted dissociation of CO from co-adsorbed H and CO on the (a) (111) and (b) K_2O-promoted (111) surfaces of χ-Fe_5C_2.

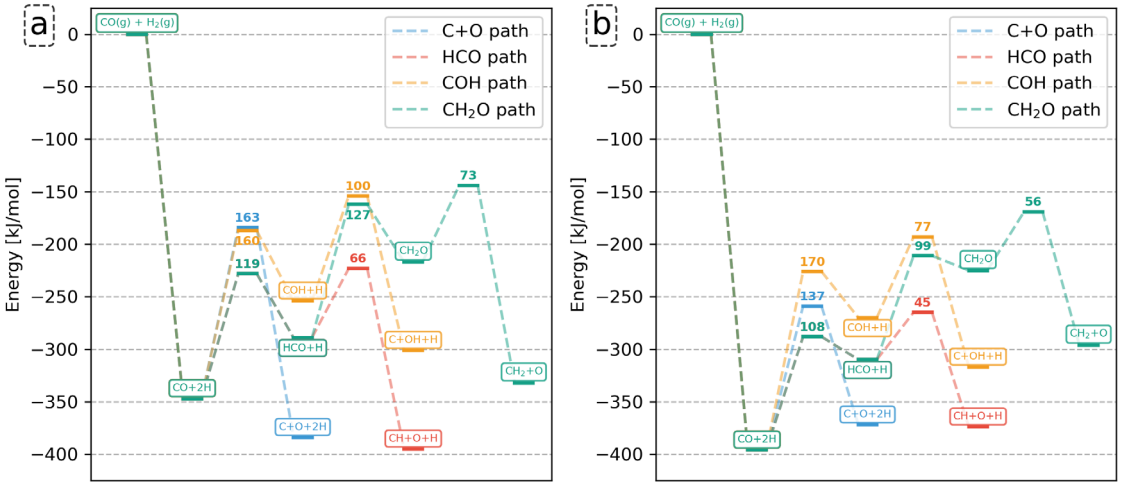

Figure S18. Energy profiles for the direct or H-assisted dissociation of CO from co-adsorbed H and CO on the (a) (010) and (b) K_2O-promoted (010) surfaces of χ-Fe_5C_2.

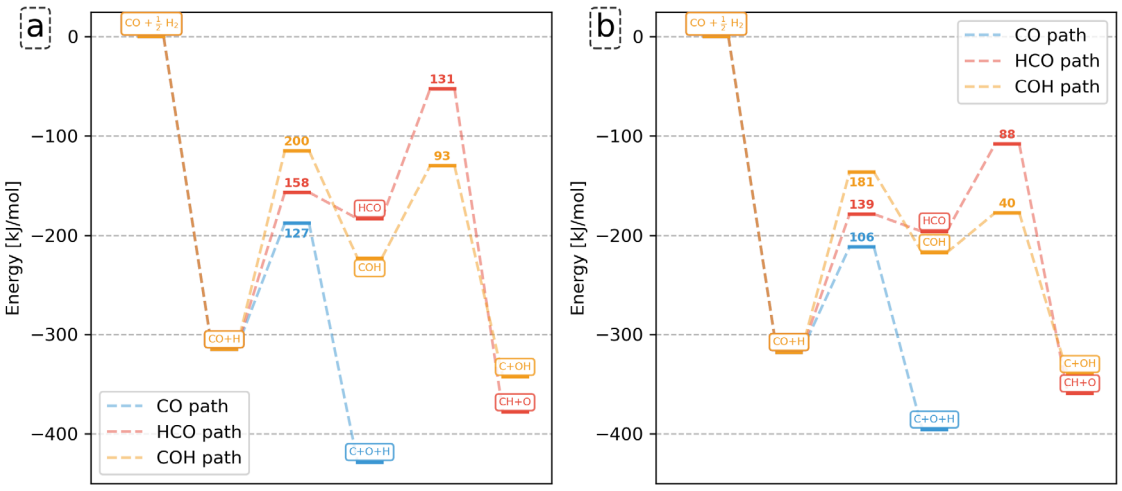

Figure S19. Energy profiles for the direct or H-assisted dissociation of CO from co-adsorbed H and CO on the (a) (010*) and (b) K_2O-promoted (010*) surfaces of χ-Fe_5C_2.

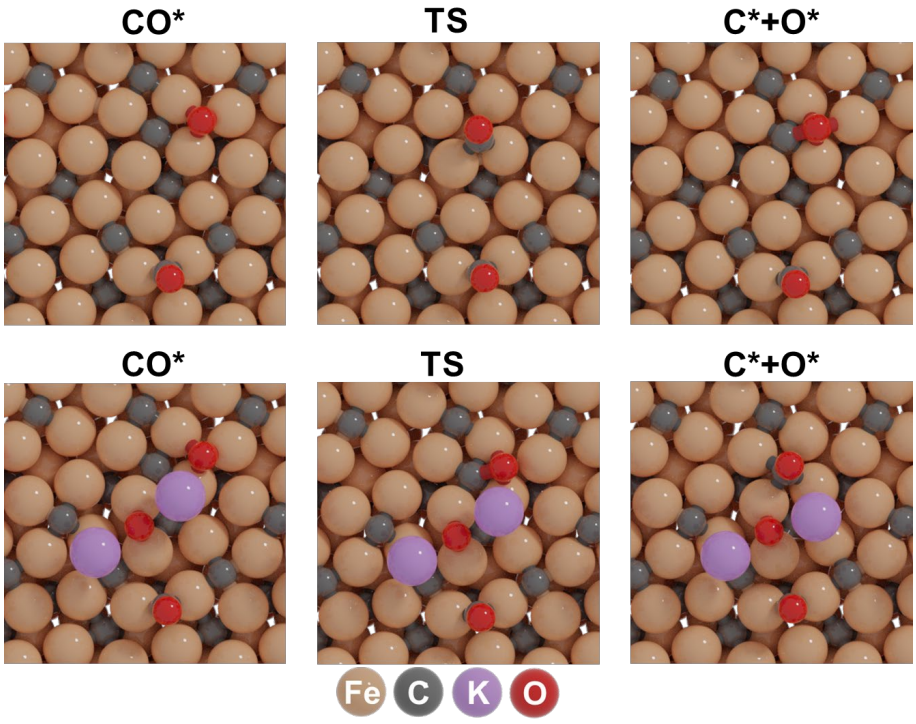

Figure S20. Configurations of IS, TS and FS for the direct dissociation of CO with the presence of a pre-adsorbed CO on the (510) and K_2O-promoted (510) surfaces of χ-Fe_5C_2.

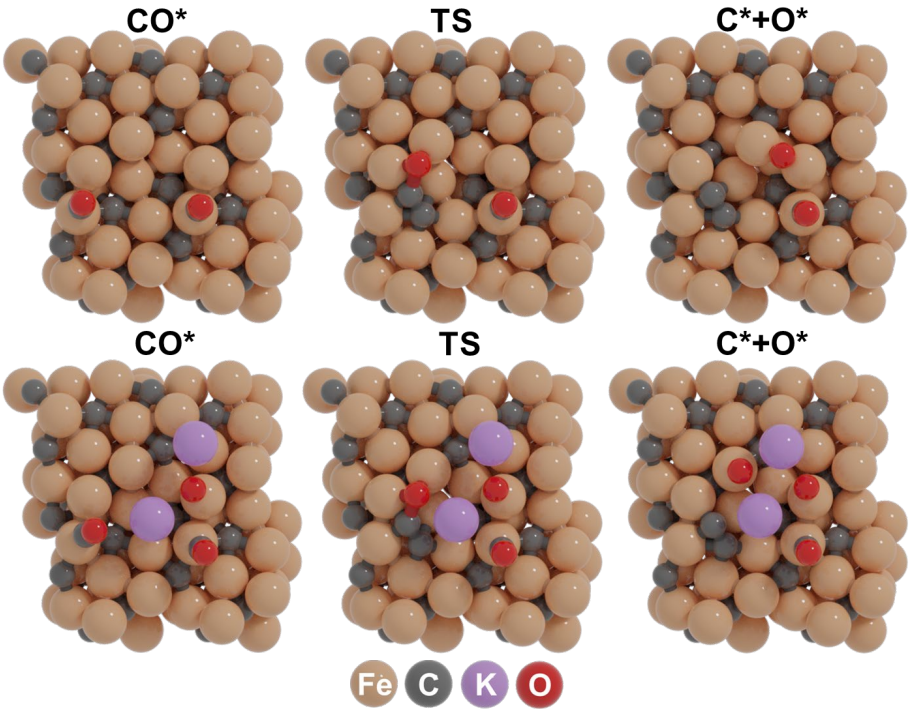

Figure S21. Configurations of IS, TS and FS for the direct dissociation of CO with the presence of a pre-adsorbed CO on the (111) and K_2O-promoted (111) surfaces of χ-Fe_5C_2.

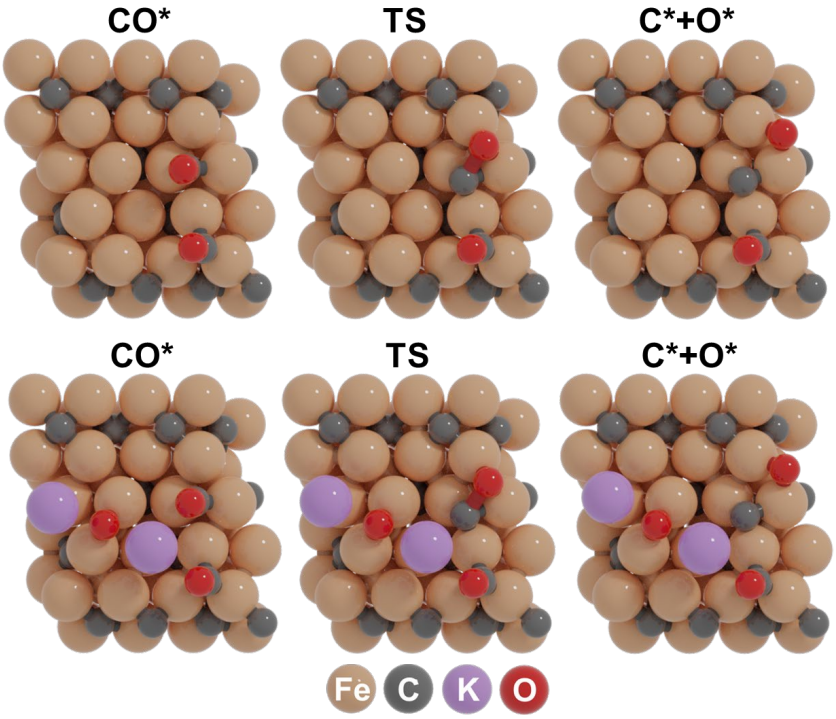

Figure S22. Configurations of IS, TS and FS for the direct dissociation of CO with the presence of a pre-adsorbed CO on the (010) and K_2O-promoted (010) surfaces of χ-Fe_5C_2.

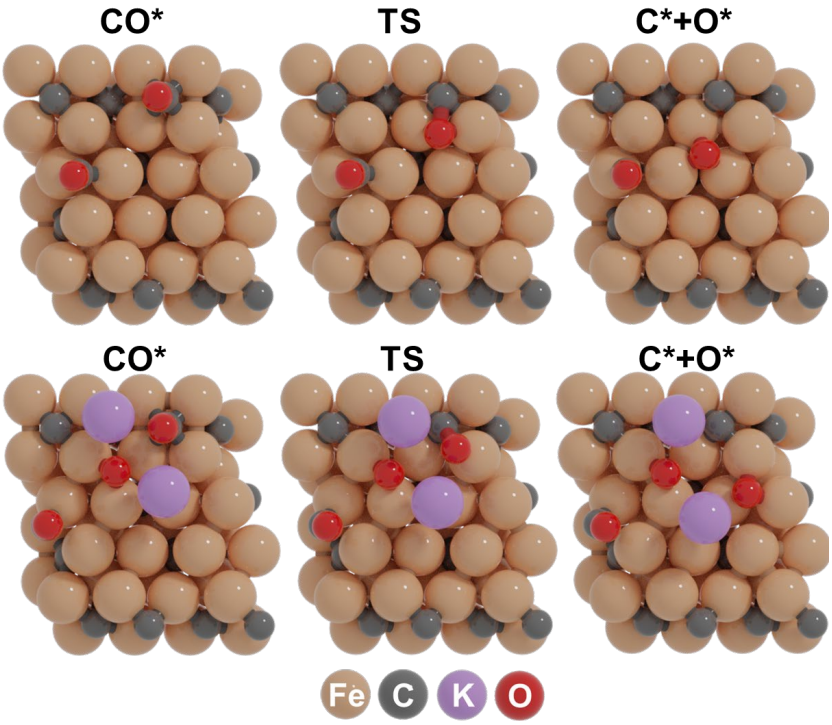

Figure S23. Configurations of IS, TS and FS for the direct dissociation of CO with the presence of a pre-adsorbed CO on the (010*) and K_2O-promoted (010*) surfaces of χ-Fe_5C_2.

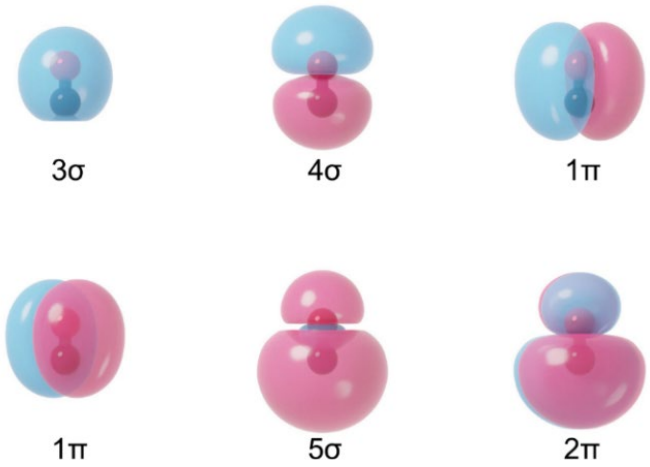

Figure S24. The canonical molecular orbital solutions of CO in the gas phase. This figure is generated by Quantumsculpt suite.

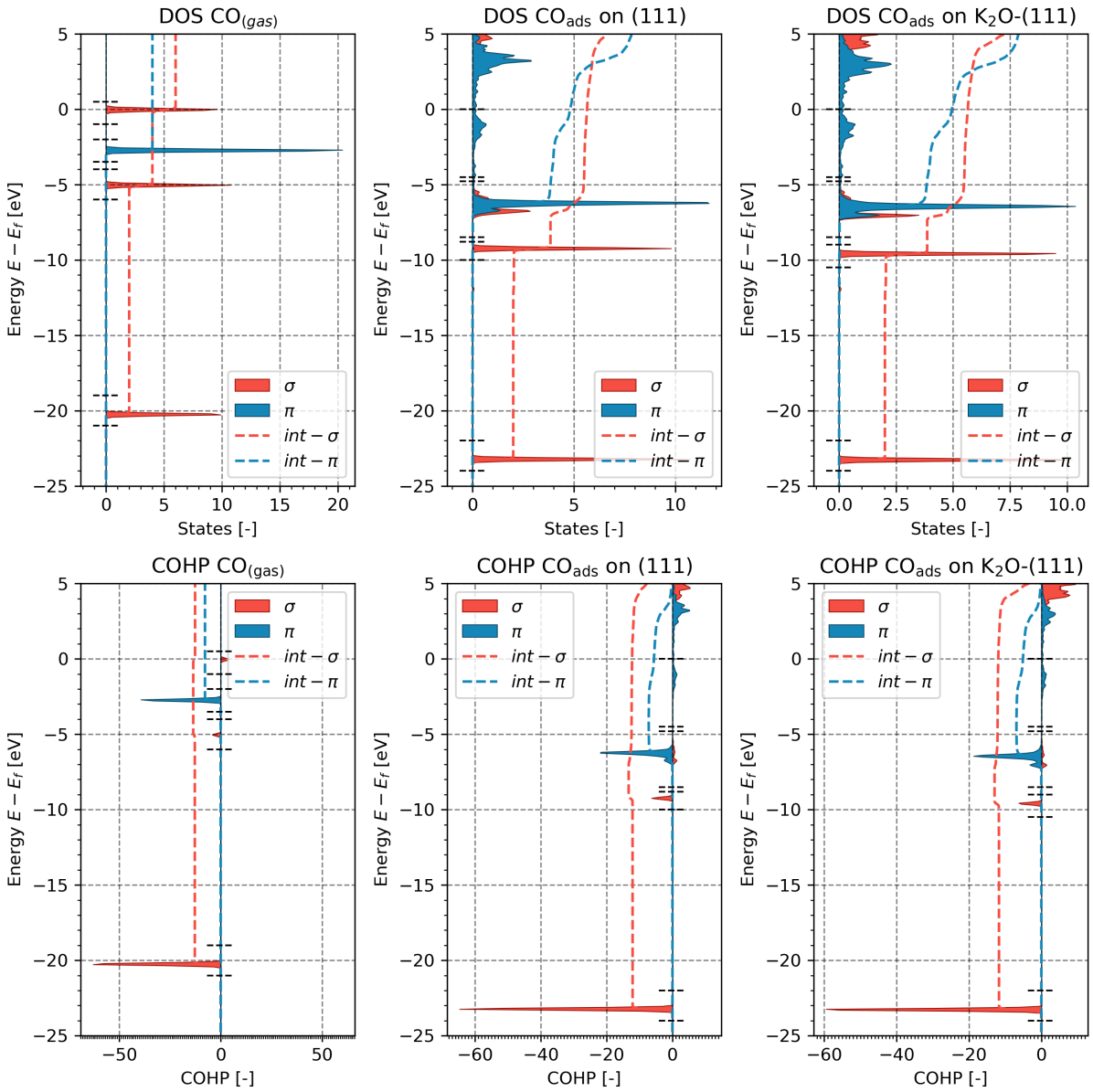

Figure S25. DOS and COHP of C-O bond of CO in the gas phase, CO absorbate on the (111) and K_2O-promoted (111) surfaces of χ-Fe_5C_2.

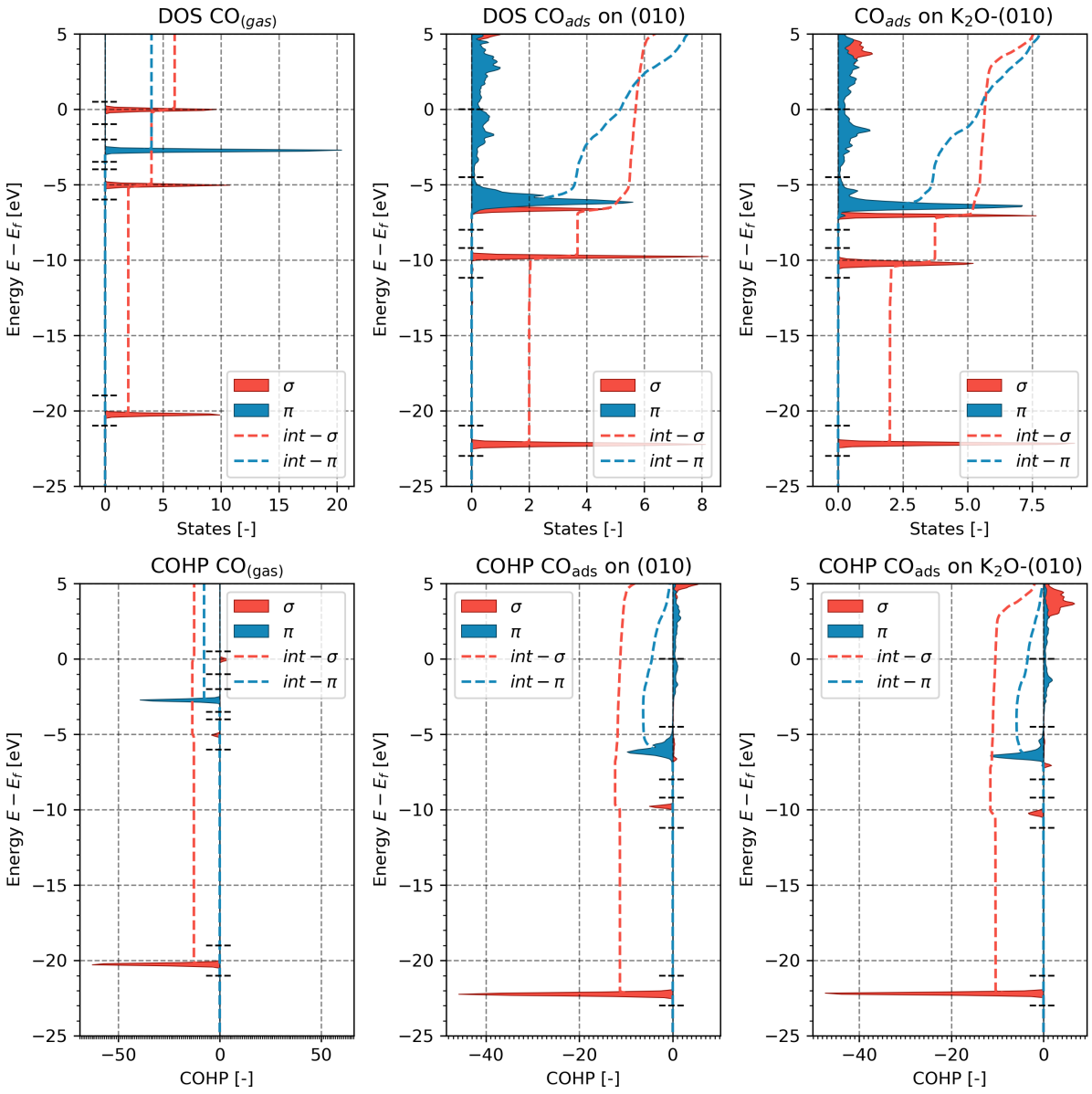

Figure S26. DOS and COHP of C-O bond of CO in the gas phase, CO absorbate on the (010) and K_2O-promoted (010) surfaces of χ-Fe_5C_2.

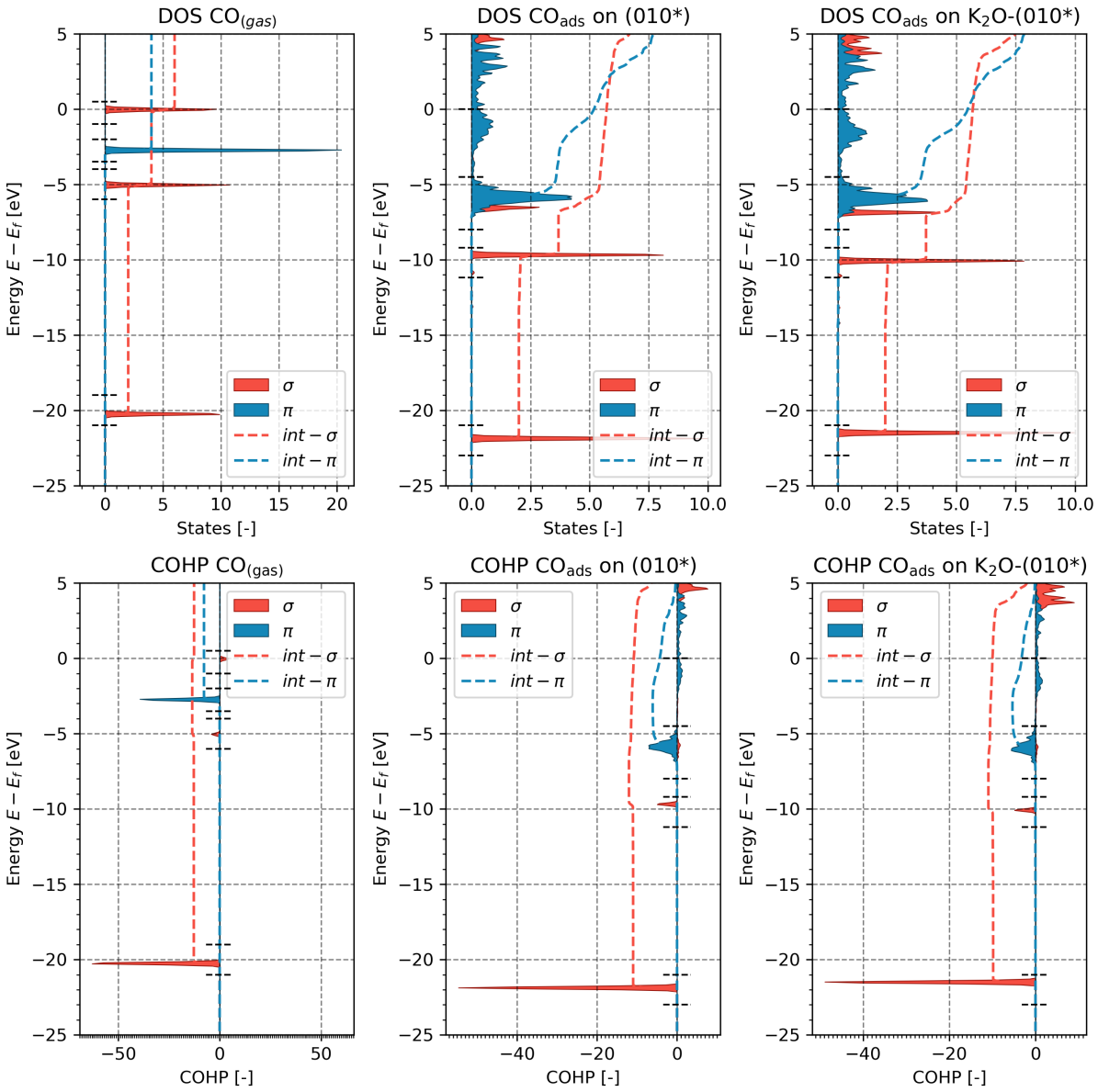

Figure S27. DOS and COHP of C-O bond of CO in the gas phase, CO absorbate on the (010*) and K_2O-promoted (010*) surfaces of χ-Fe_5C_2.

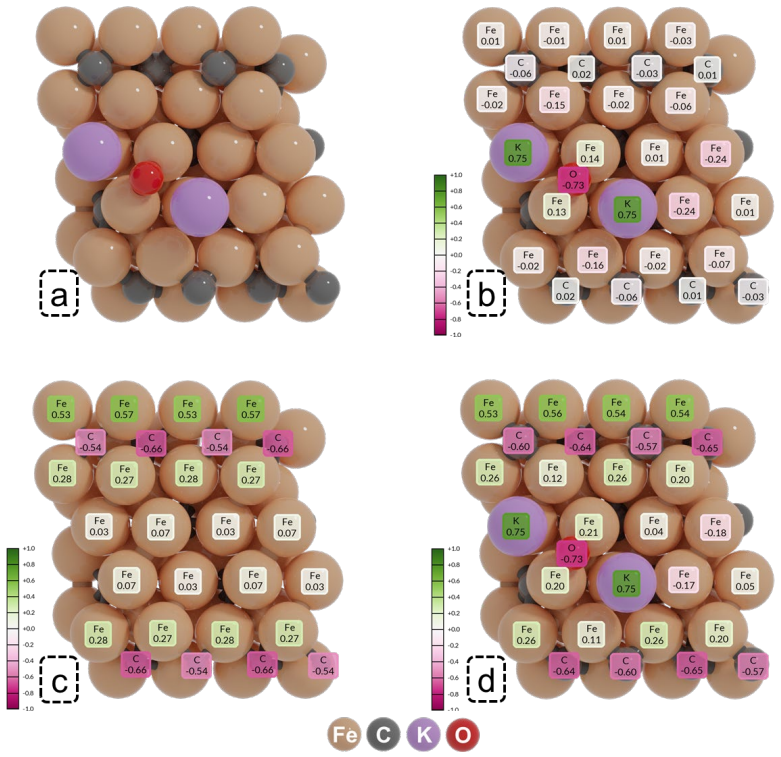

Figure S28. (a) K_2O promoted (010) surface of χ-Fe_5C_2. (b) Charge difference of surface Fe atoms on the (010) surface upon K_2O adsorption (Negative values indicate increased electron density upon adsorption). (c) Charge of surface Fe atoms on the pristine (010) and (d) K_2O-promoted (010) surfaces of χ-Fe_5C_2.

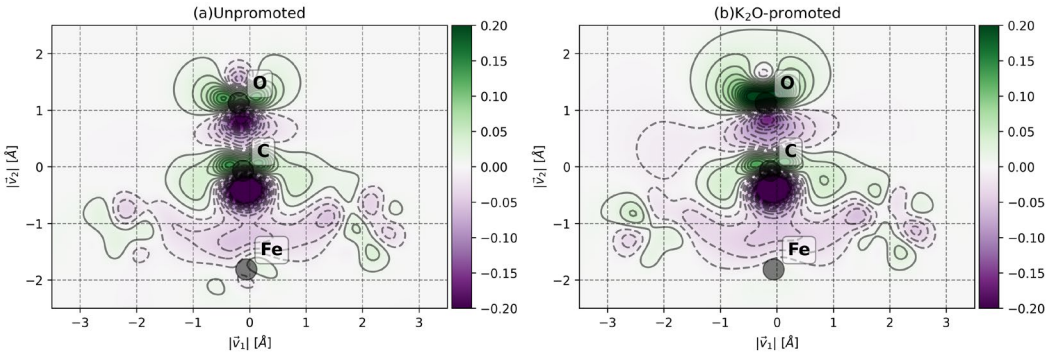

Figure S29. Charge density difference upon CO adsorption on the (010) and K_2O-promoted (010) surfaces of χ-Fe_5C_2.

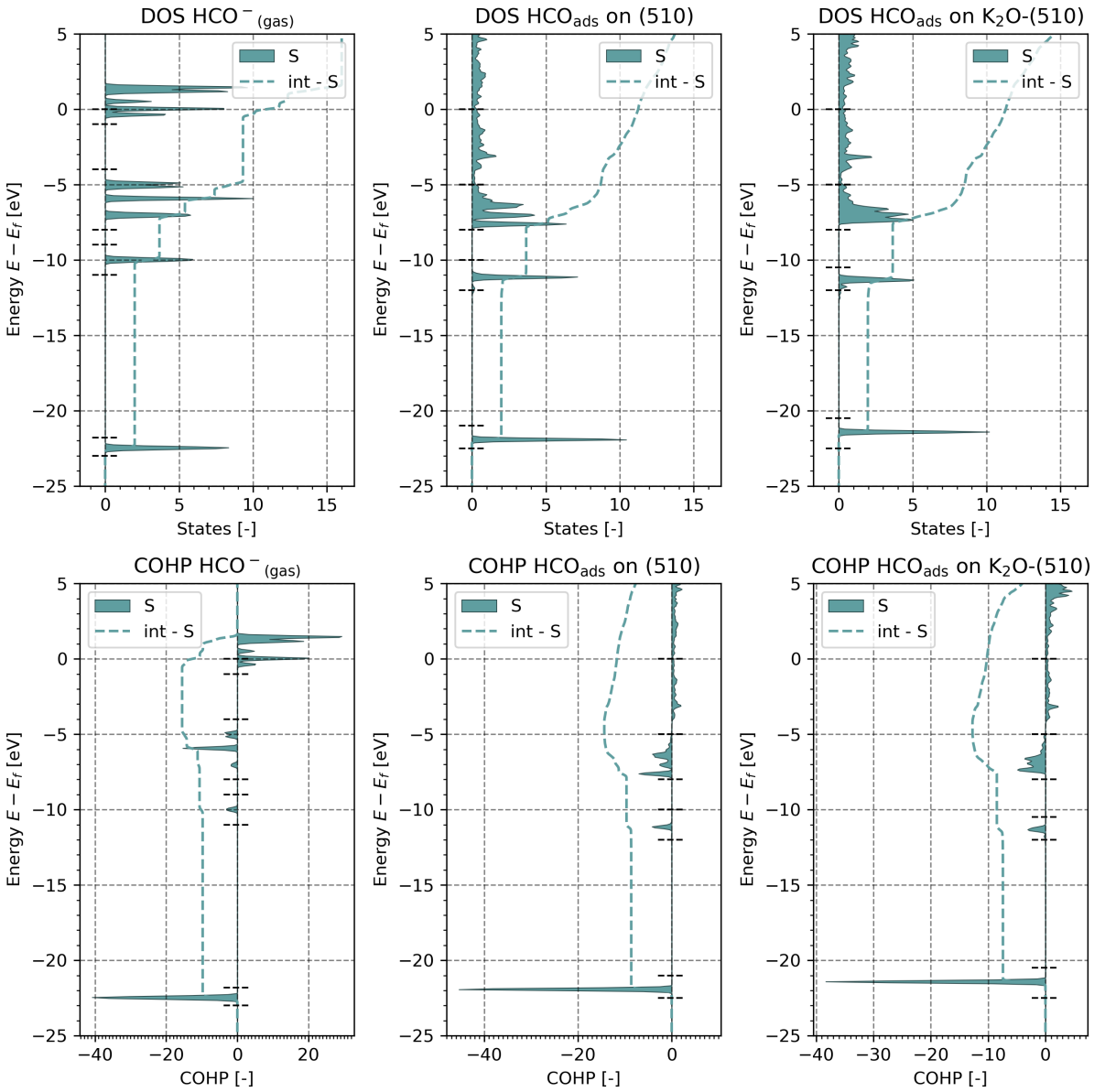

Figure S30. DOS and COHP of C-O bond of HCO^- in the gas phase, HCO absorbate on the (510) and K_2O-promoted (510) surfaces of χ-Fe_5C_2.

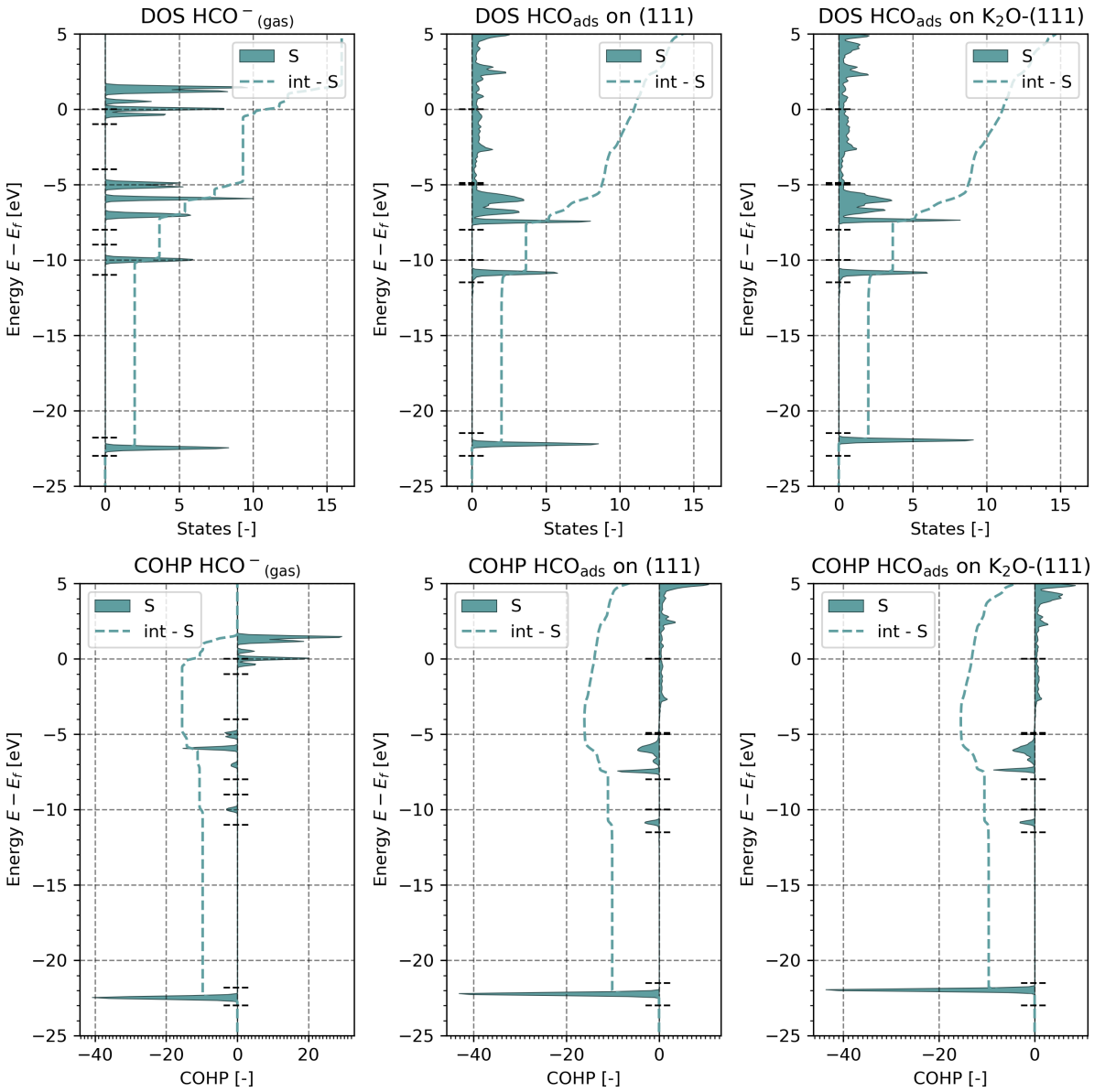

Figure S31. DOS and COHP of C-O bond of HCO^- in the gas phase, HCO absorbate on the (111) and K_2O-promoted (111) surfaces of χ-Fe_5C_2.

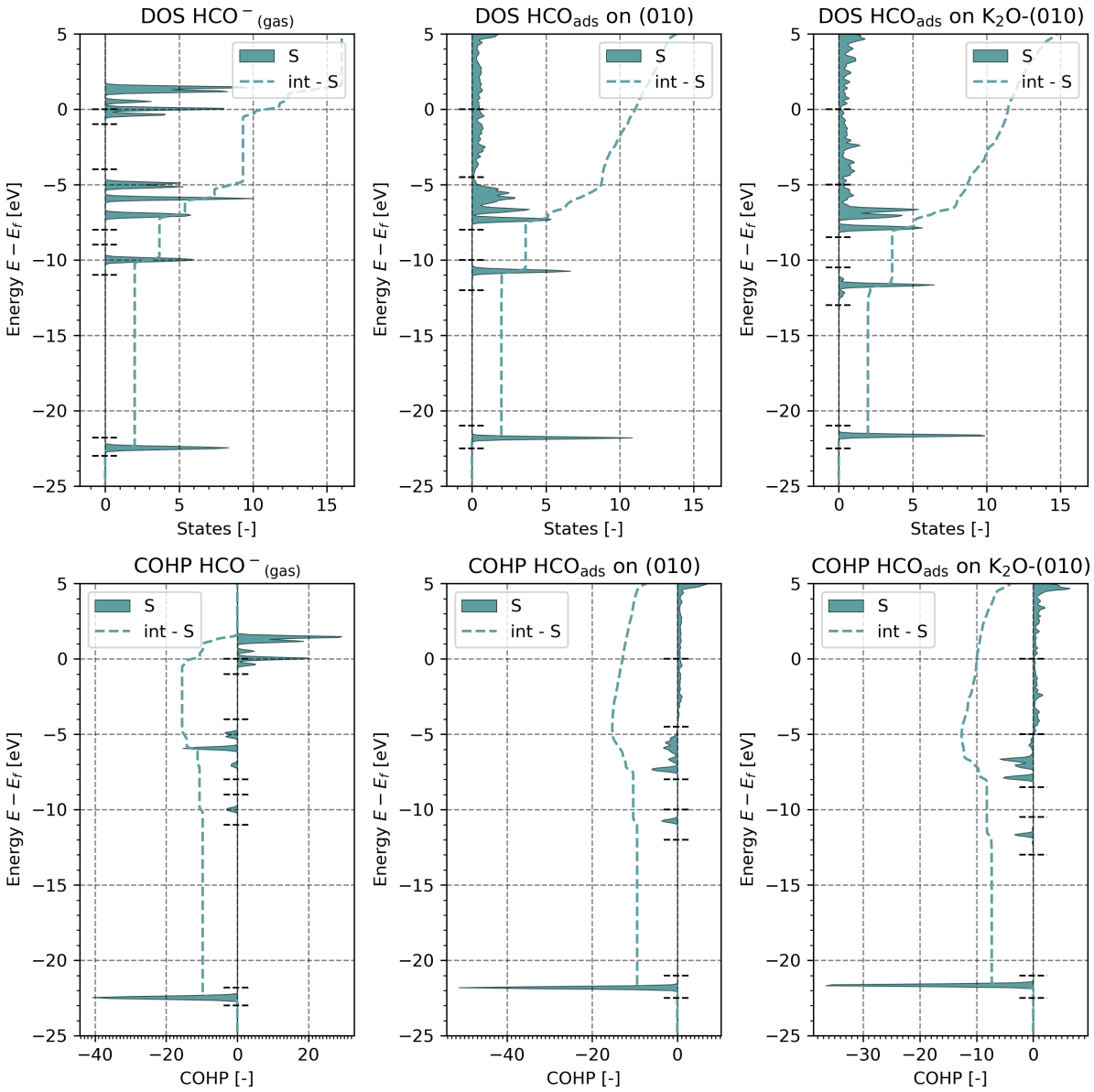

Figure S32. DOS and COHP of C-O bond of HCO^- in the gas phase, HCO absorbate on the (010) and K_2O-promoted (010) surfaces of χ-Fe_5C_2.

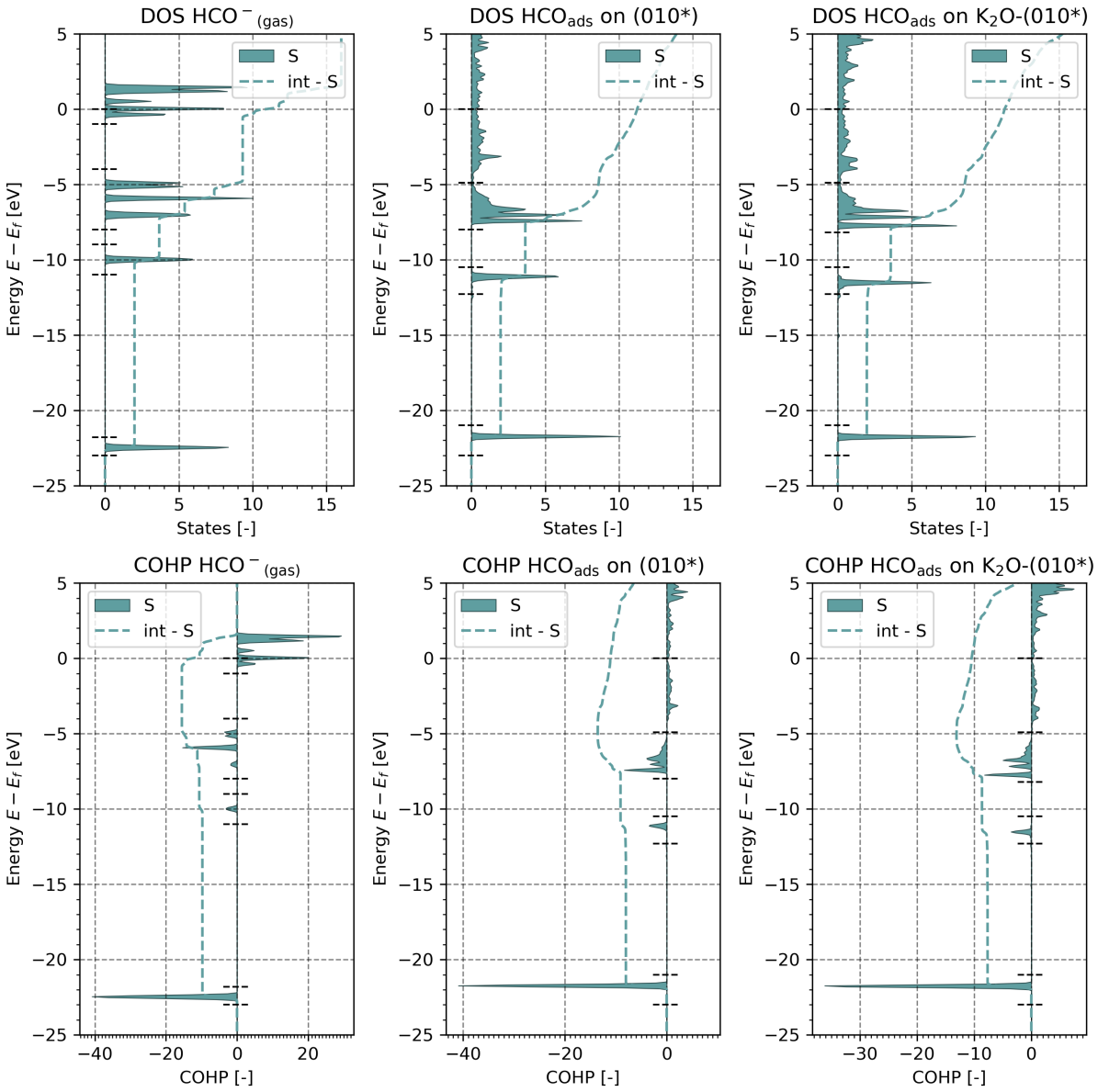

Figure S33. DOS and COHP of C-O bond of HCO^- in the gas phase, HCO absorbate on the (010*) and K_2O-promoted (010*) surfaces of χ-Fe_5C_2.

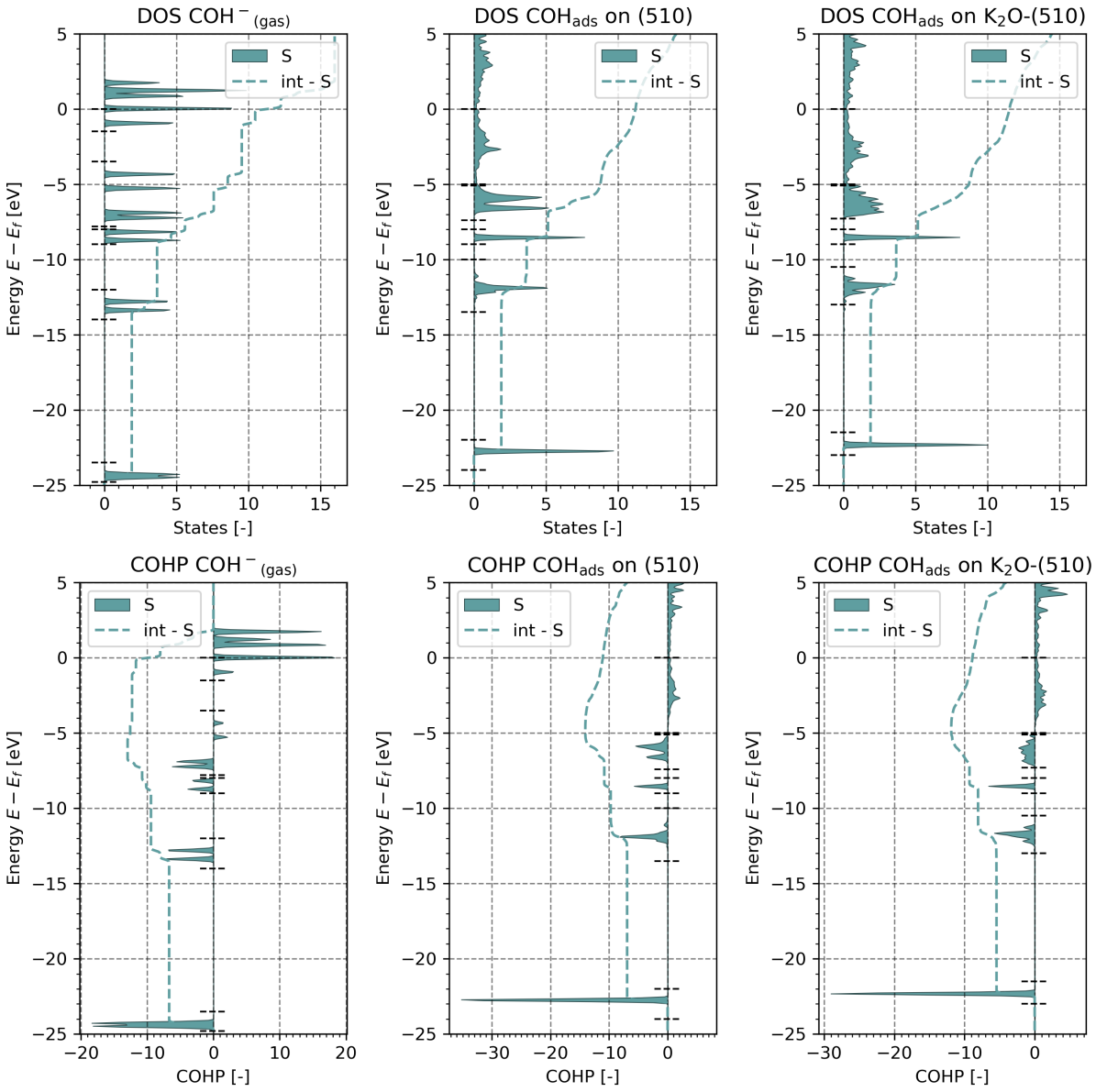

Figure S34. DOS and COHP of C-O bond of COH^- in the gas phase, COH absorbate on the (510) and K_2O-promoted (510) surfaces of χ-Fe_5C_2.

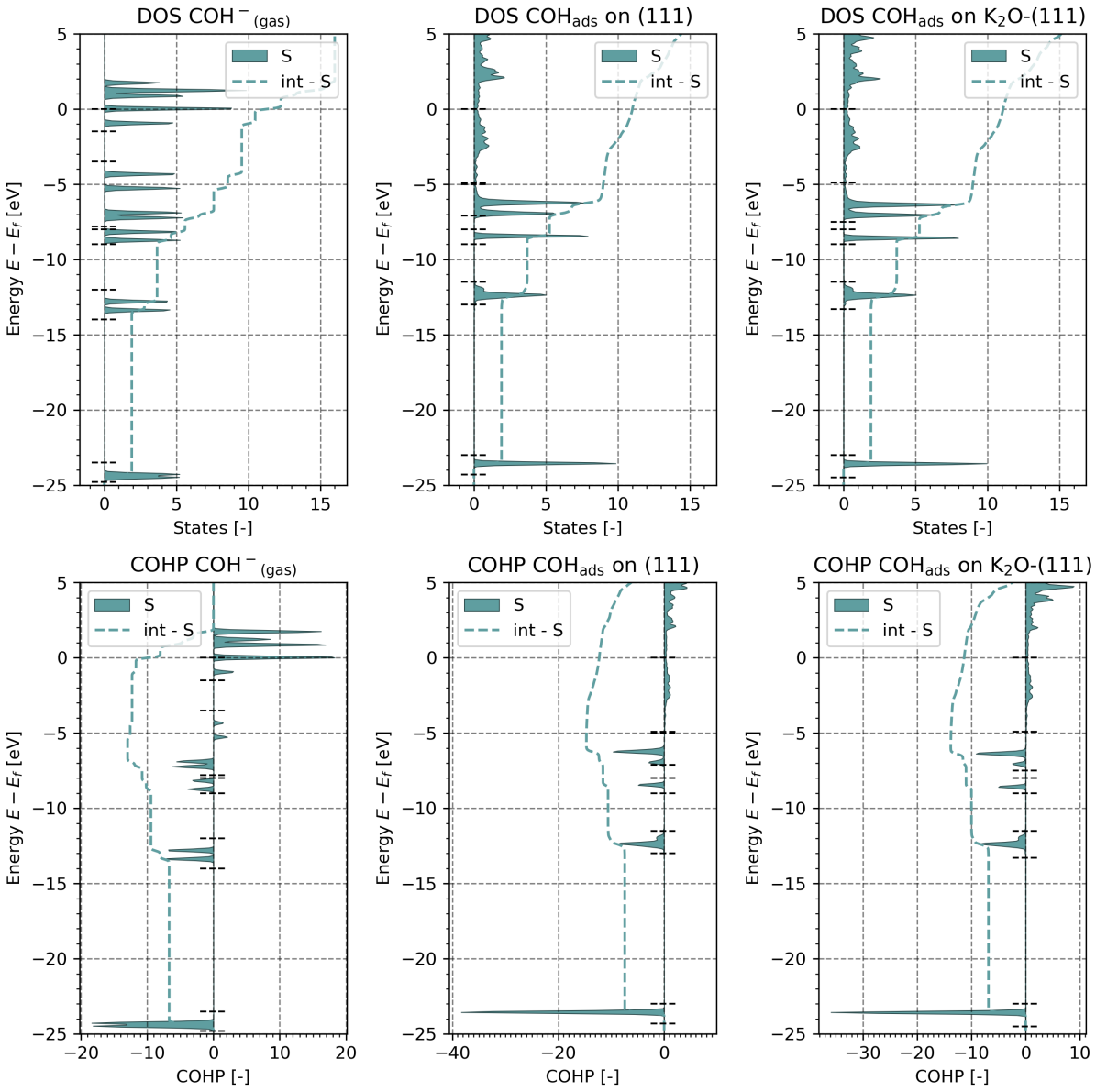

Figure S35. DOS and COHP of C-O bond of COH^- in the gas phase, COH absorbate on the (111) and K_2O-promoted (111) surfaces of χ-Fe_5C_2.

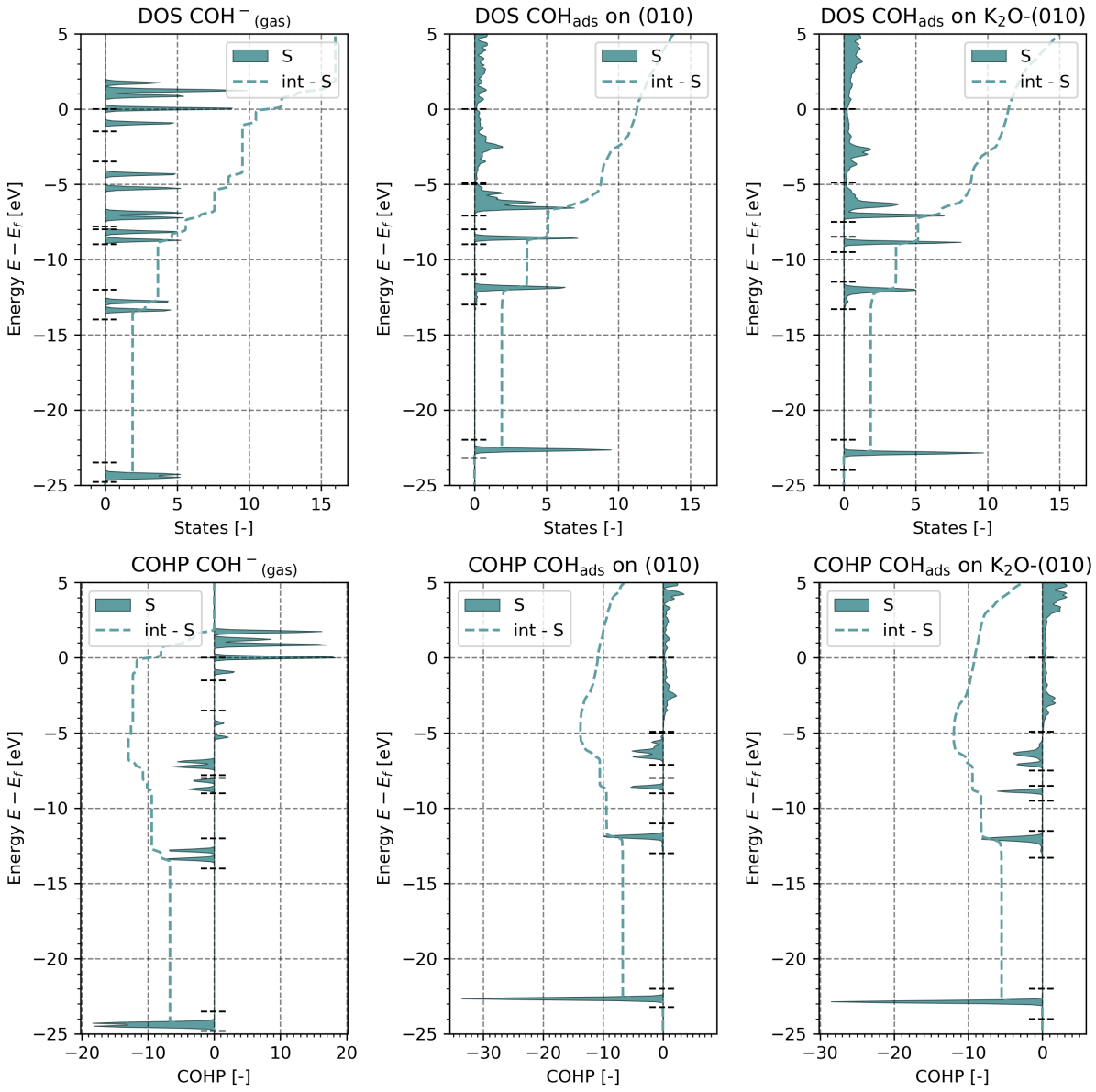

Figure S36. DOS and COHP of C-O bond of COH^- in the gas phase, COH absorbate on the (010) and K_2O-promoted (010) surfaces of χ-Fe_5C_2.

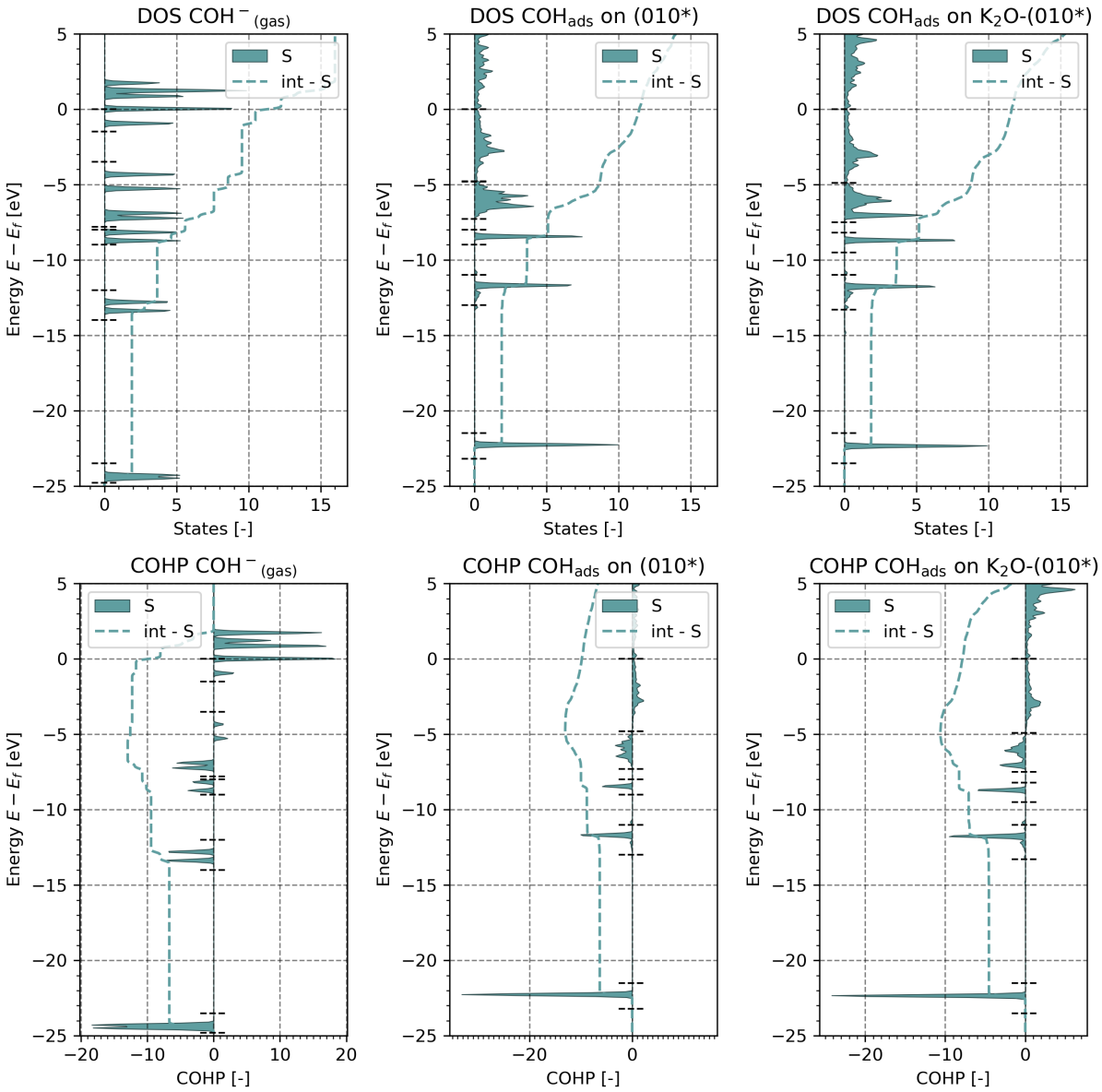

Figure S37. DOS and COHP of C-O bond of COH^- in the gas phase, COH absorbate on the (010*) and K_2O-promoted (010*) surfaces of χ-Fe_5C_2.

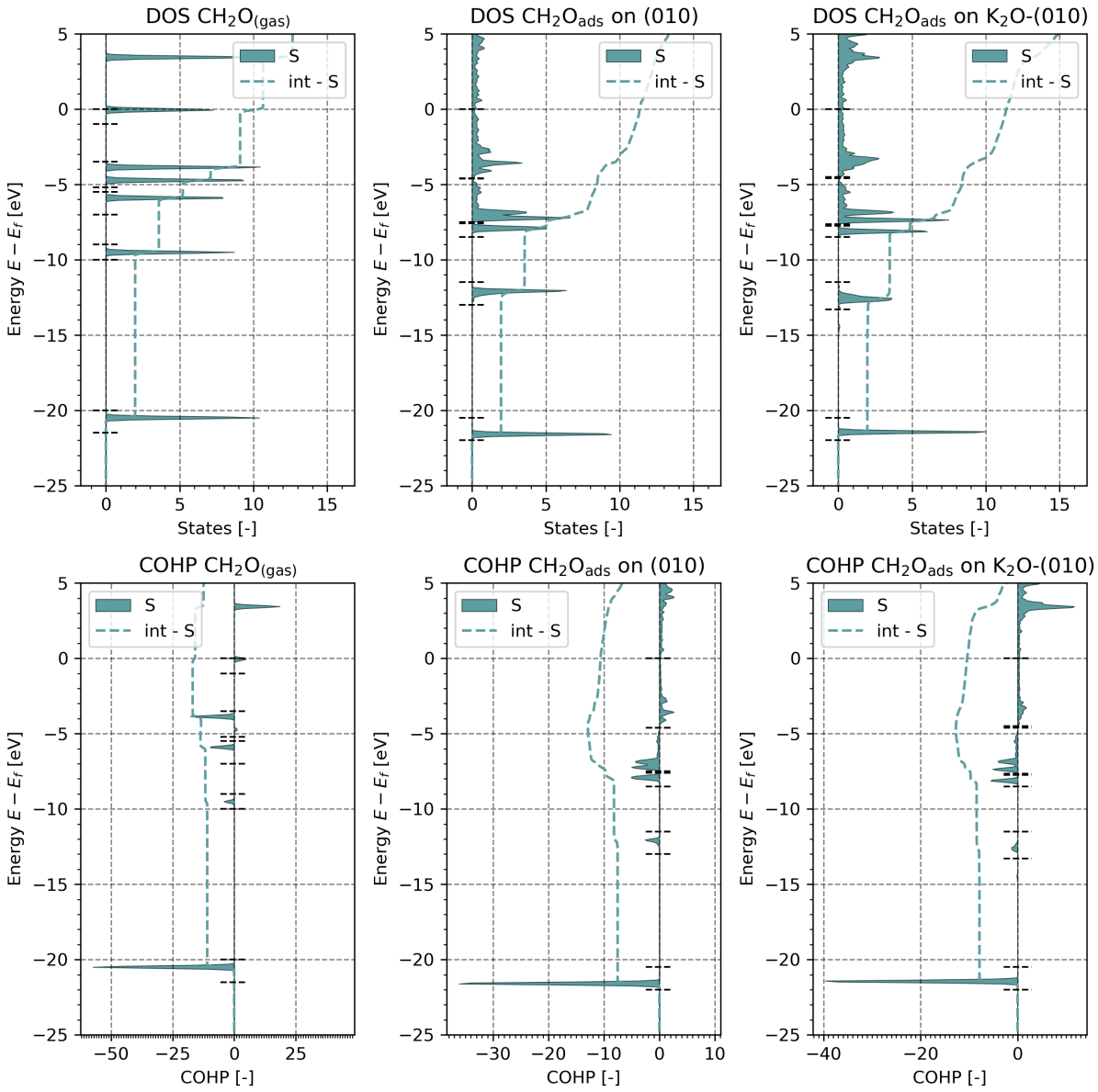

Figure S38. DOS and COHP of C-O bond of CH_2O in the gas phase, CH_2O absorbate on the (010) and K_2O-promoted (010) surfaces of χ-Fe_5C_2.