Ethylene Formation by Methane Dehydrogenation and C-C Coupling Reaction on Stoichiometric IrO2 (110) Surface -A Density Functional Theory Investigation

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1. Adsorption of Methane on IrO_2(110) surface

Benchmark calculations were carried out to justify the van der Waals corrected functional used in this work. We studied the adsorption of CH_4 on IrO_2(110) surface with different vdW functionals including optPBE-vdW, optB88-vdW and optB86b-vdW, and the results are summarized in the table S1. From the table, it should be noted that the results calculated by three vdW functionals are comparable. We actually do not have experiment data on the adsorption of CH_4 on IrO_2(110) surface to evaluate which one is the best van der Waal inclusive functional in this case. Therefore, in our work, we choose optB88-vdW functional since the results calculated by this functional is the closest to the average result of three functionals.

Table S1. Binding energies, activated C-H bond lengths and Ir_{cus}-C bond distances of CH_4 on IrO_2 (110) calculated by different van der Waals-corrected functionals

vdW Functional	E_b (eV)	d(C-H)(Å)	d(Ir_{cus}-C) (Å)
optPBE-vdW	0.69	1.15	2.54
optB88-vdW	0.76	1.15	2.51
optB86b-vdW	0.82	1.15	2.50

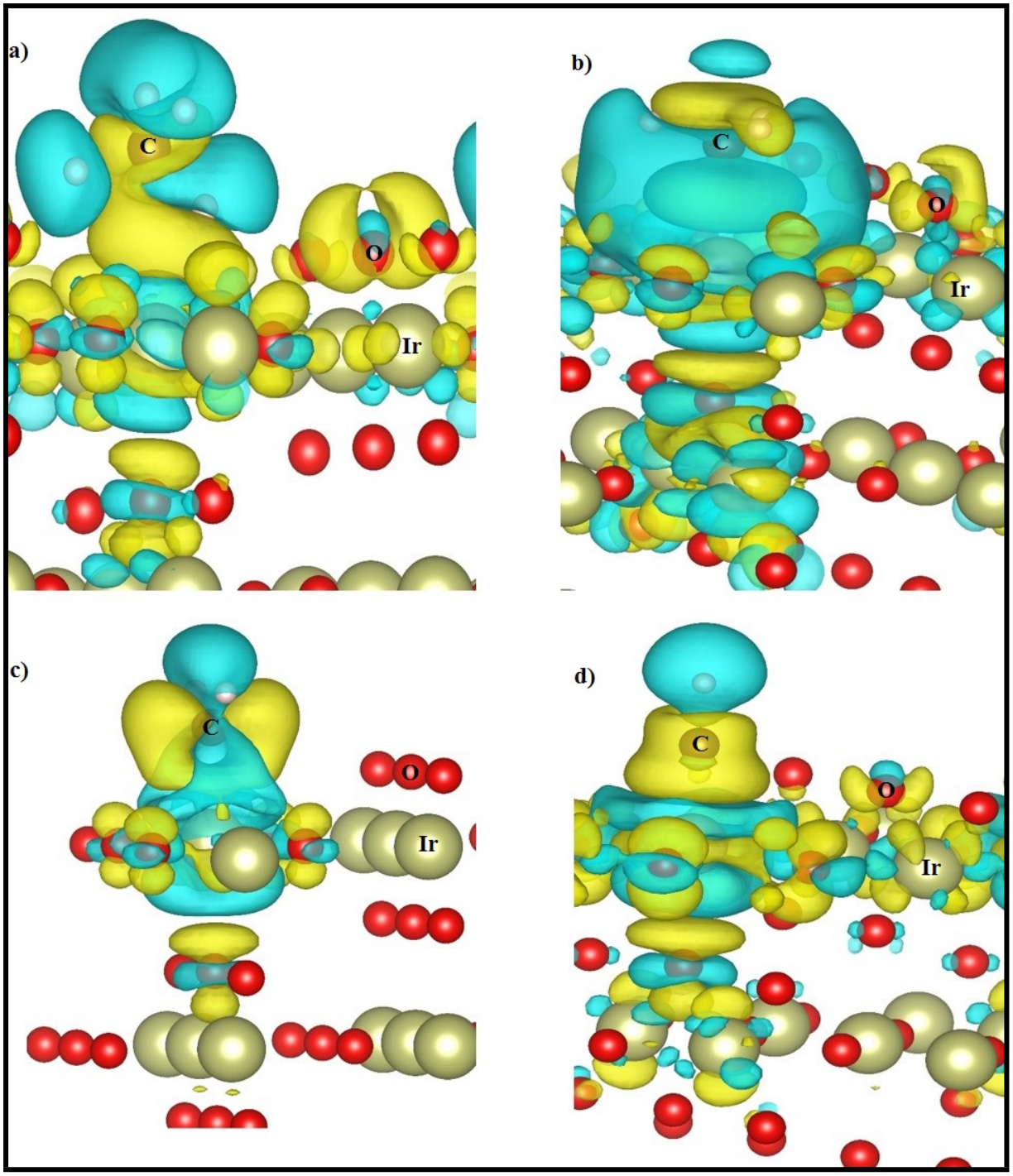

Figure S1. Electron Density Difference (EDD) of CH_x species on $IrO_2(110)$: a) CH_4; b) CH_3; c)CH_2; d) CH. The green color represents electron depletion and the yellow color represents electron accumulation.

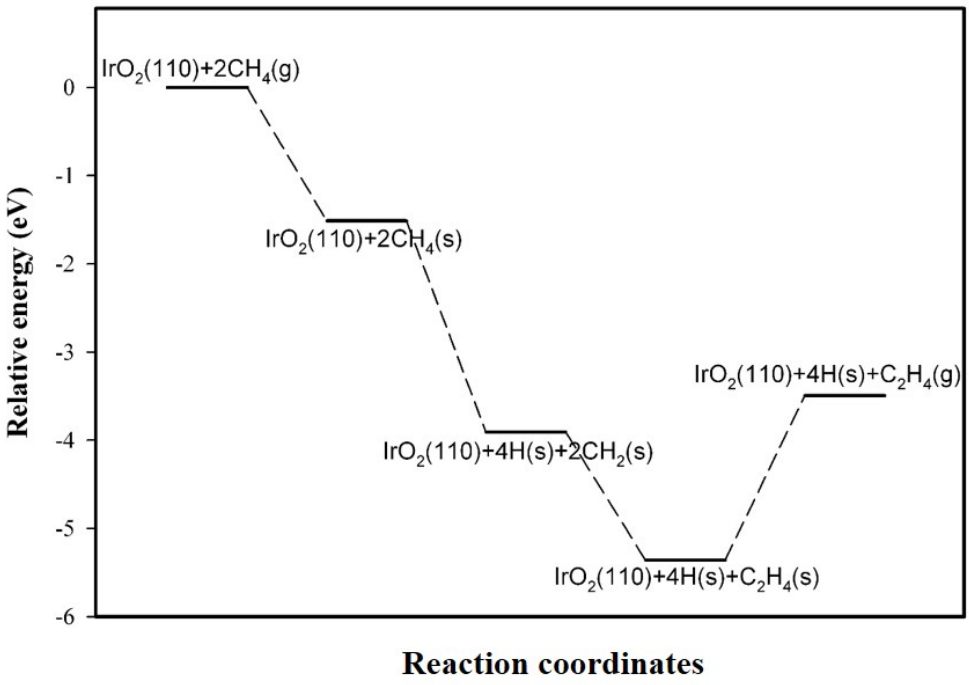

Figure S2. Energy profile for CH_4 conversion to C_2H_4 on $IrO_2(110)$. The values are relative energies in eV.