



First principles study of propane dehydrogenation on Pt-based catalysts

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Abstract

Alloying Pt with a secondary metal is an extensively used strategy to get enhanced catalytic performances, stabilities and reduce usage of precious Pt as compared to that of pure Pt. For reactions including oxygen reduction reaction, CO oxidation, most promoters lie in transition metals like Ni, Co, Fe. While for propane dehydrogenation (PDH), only Sn has received massive attentions. Previous studies have mainly focused on the role of Sn. It's still not clear why Sn is helpful in this reaction but other transition metals are not. Density functional theory calculations were performed to address this issue. Sn was found to distribute normally on Pt surface, isolating Pt atoms efficiently, and have weak interactions with propylene. Transition metals suffer from the accumulation on Pt surfaces or strong affinity to propylene which is likely to result in deep dehydrogenations.

Results and Discussion

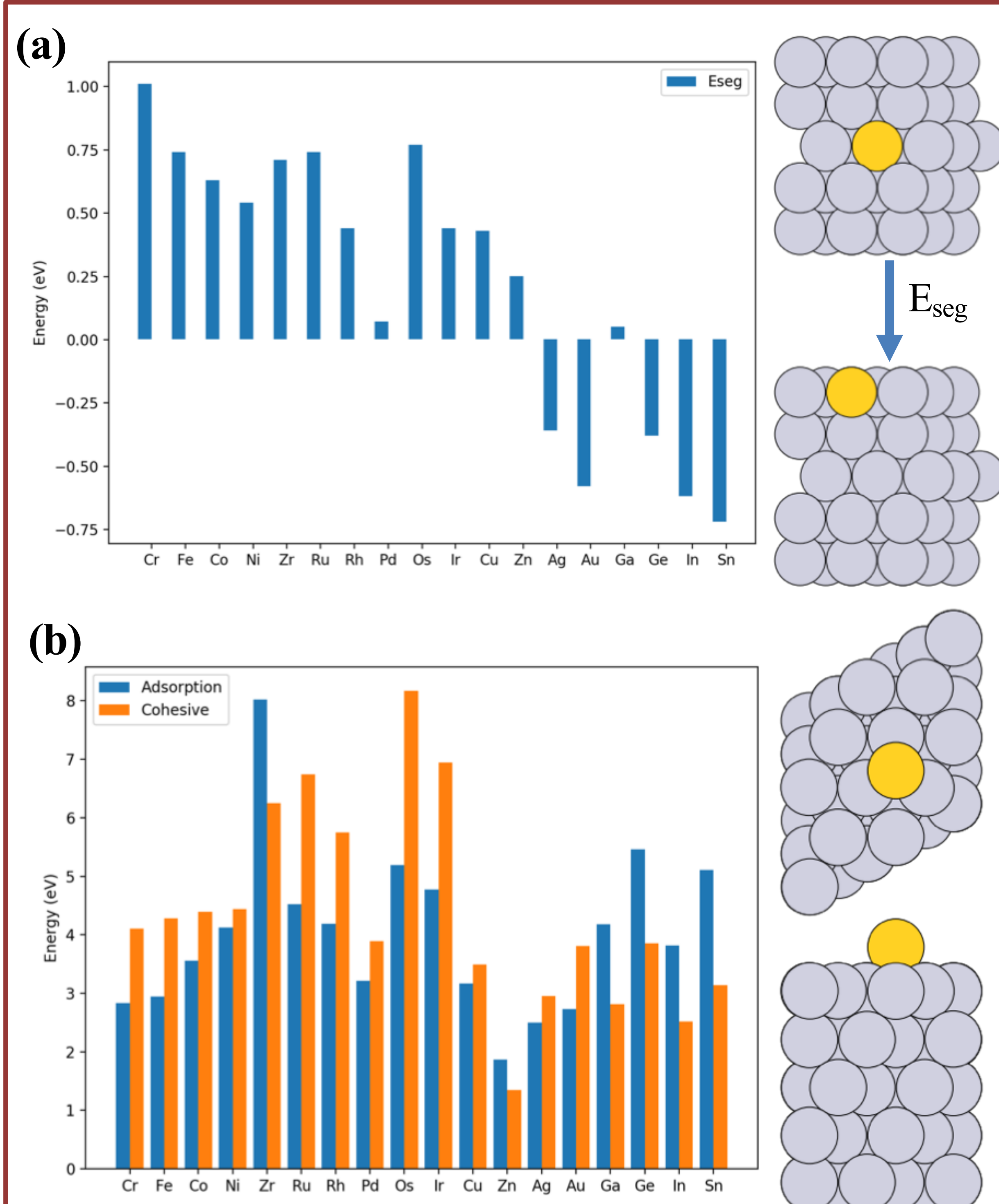


Figure 1. (a) The segregation energy for Pt-based alloys, (b) the dispersion of second metal on Pt(111)

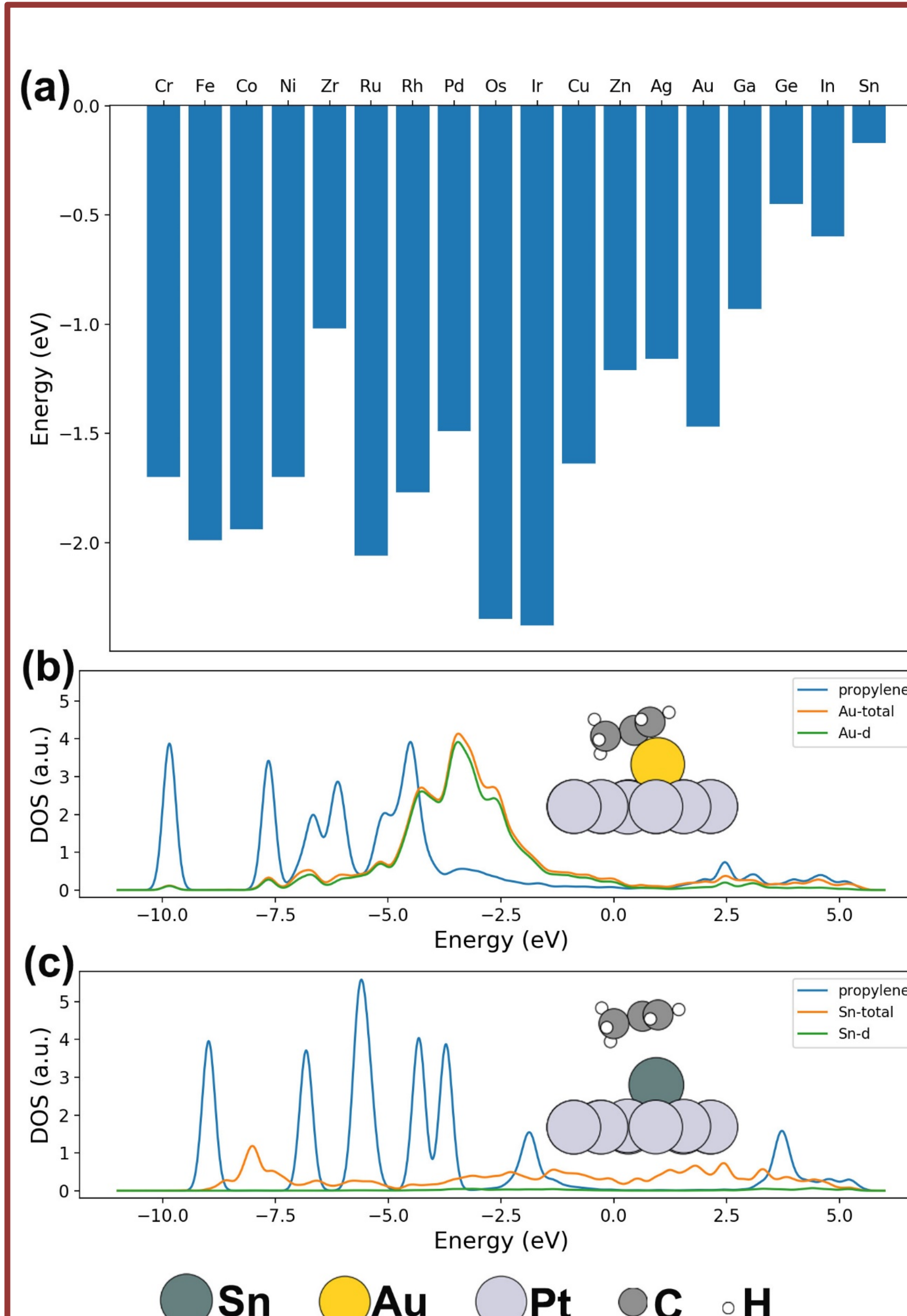


Figure 2. (a) Propylene adsorption energy at the atop site of second metal (b) propylene adsorption configuration on Pt(111)-Au and density of states (DOS) (c) propylene adsorption configuration on Pt(111)-Sn and density of states (DOS)

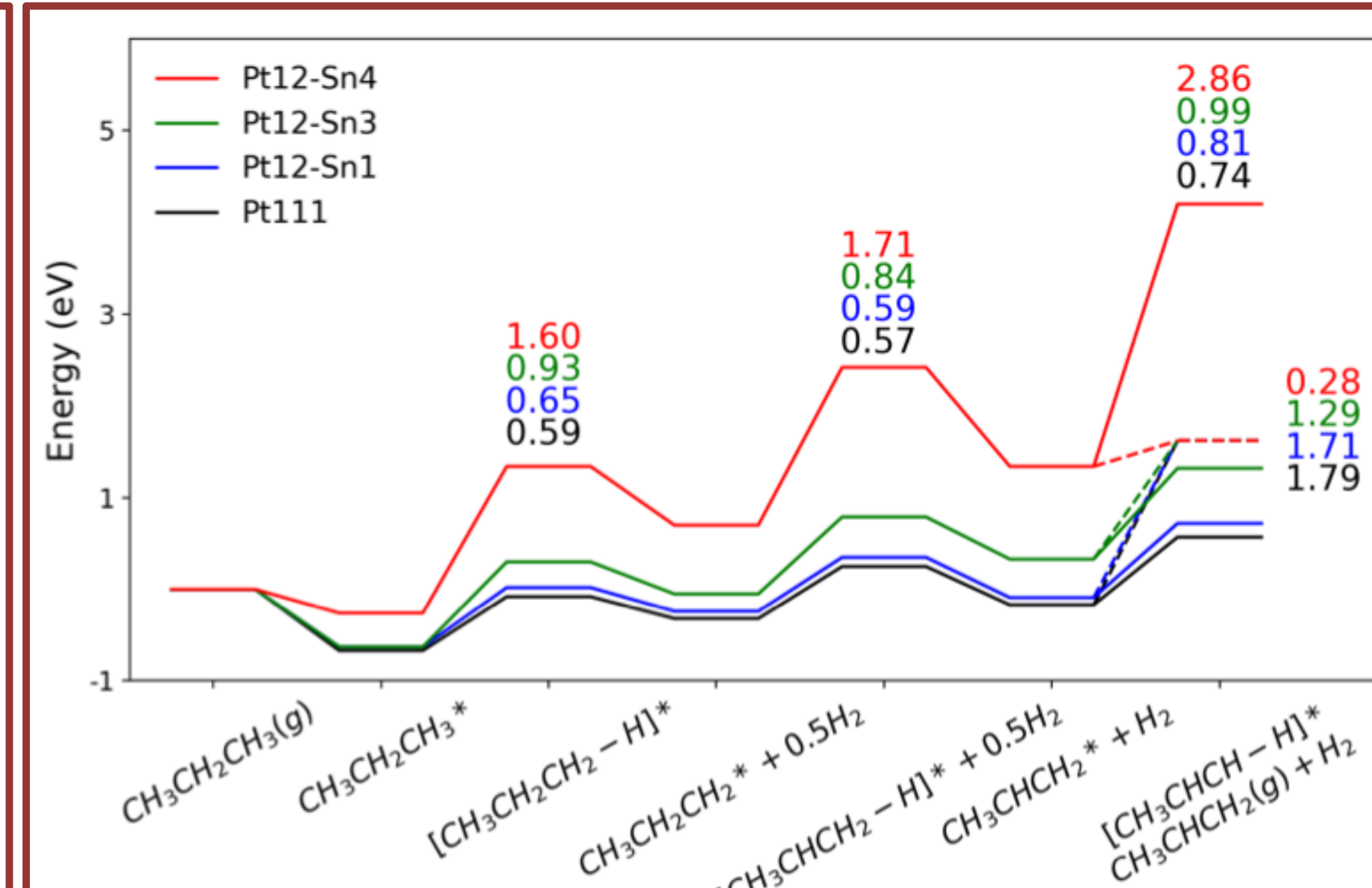
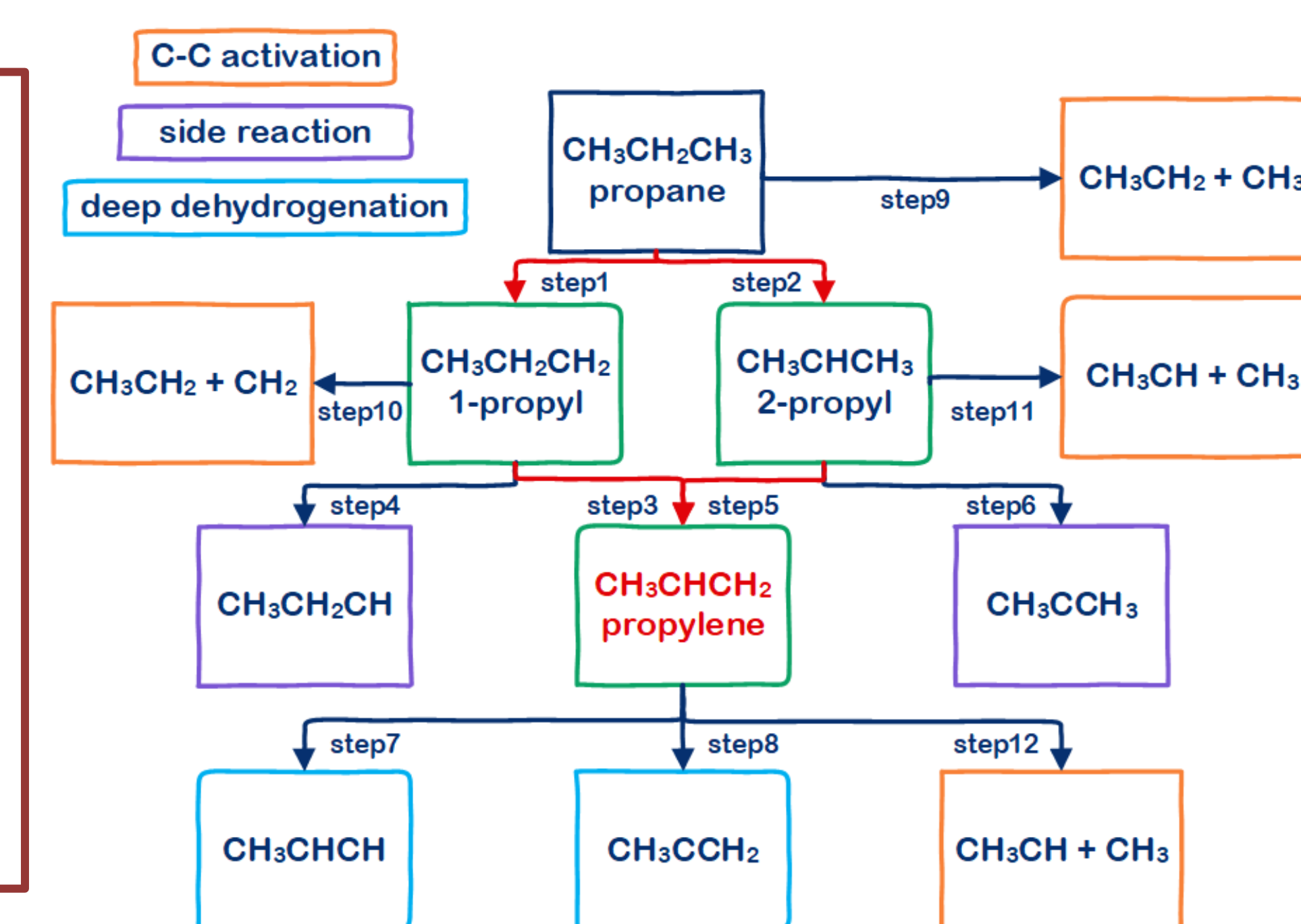


Figure 3. The energy profile for PDH on Pt(111) and Pt(111) with Sn adatoms

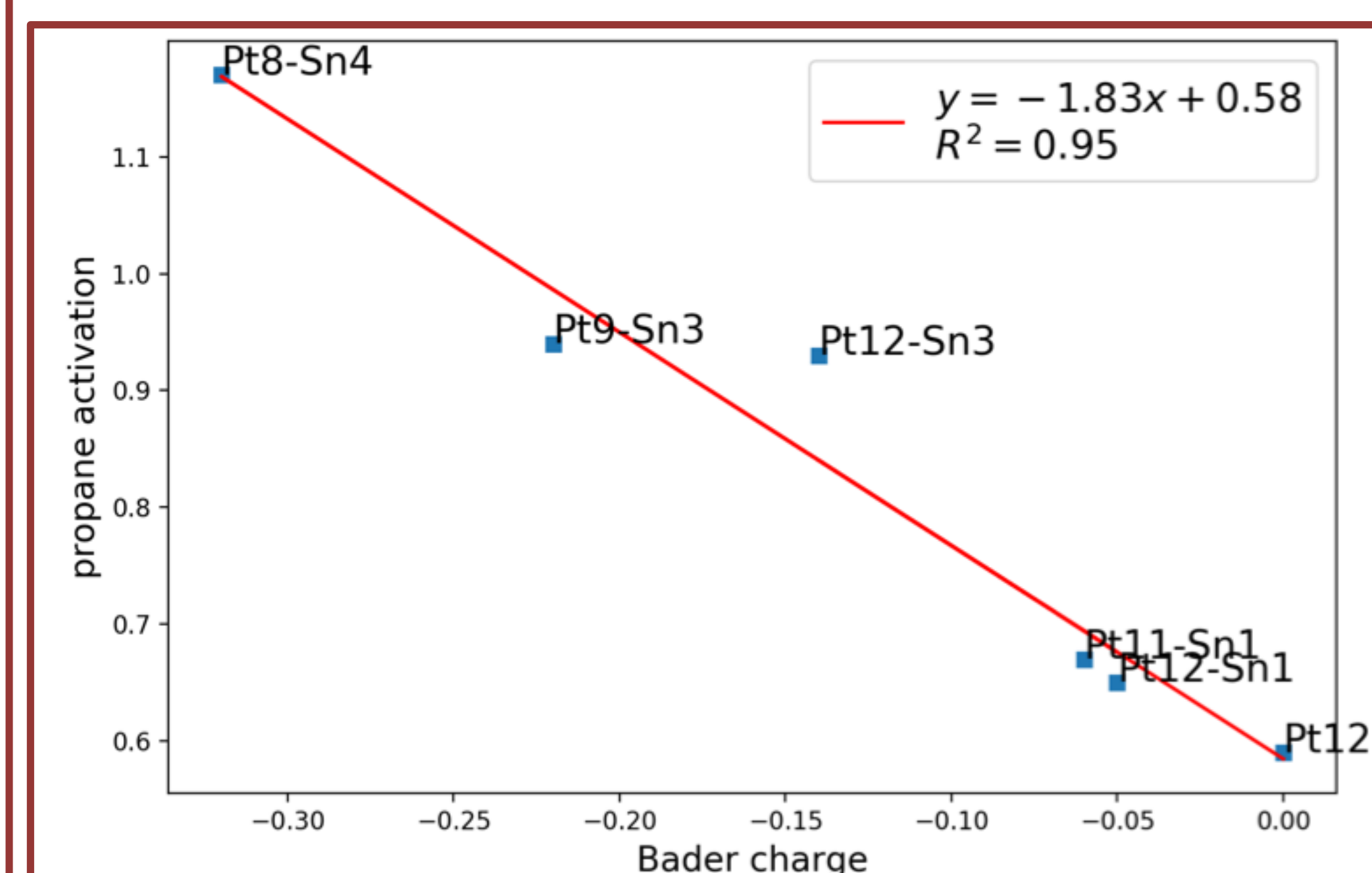


Figure 4. A linear relationship between propane activation energies and Bader charge of surface Pt atoms

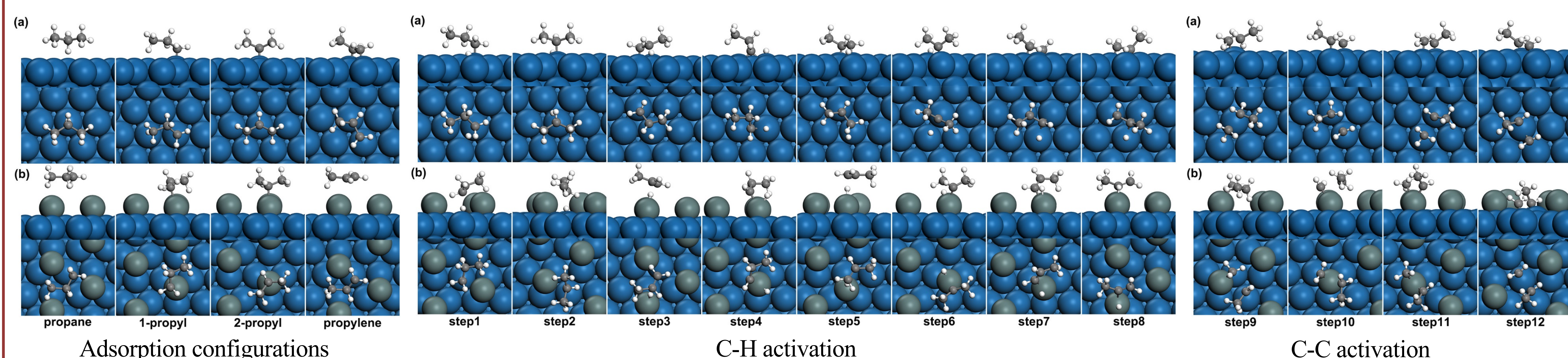


Figure 5. Adsorption configurations and geometrical structures transition state in each step of PDH (a) Pt(111), (b) Pt12-Sn4. Pt12-Sn1, Pt12-Sn3 have similar structures as Pt(111)

Conclusions

- Sn is the best candidate to modify Pt's properties for propane dehydrogenation, because it can reduce the Pt exposed area most efficiently and have weakest propylene affinity.
- The selectivity for PDH is improved at the cost of losing activity when increasing Sn.
- The changed Bader charge of surface Pt when introducing Sn is responsible for the changed energy barrier of each step in PDH.