



# Boosting Hydrodeoxygenation reaction over molybdenum carbide by means of reactivity descriptors: A DFT study

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## Background

- Search for alternatives to fossil-based resources.
- Conversion of biomass derived long-chain fatty acids to value-added chemicals.
- Heterogeneous catalyst for biomass conversion: easily separable, recyclable, and robust.<sup>1</sup>
- Transition metal carbides (TMCs) as viable alternatives to platinum group metals (PGMs).<sup>2</sup>
- Intrinsic descriptors of reactivity.<sup>3</sup>

### Noble metal catalysts Vs Transition metal carbides



Scarce  
Expensive  
S/N Poisoning

Abundant  
Relatively cheaper  
Resists S/N Poisoning



Figure 1. Differences between noble metal catalysts and transition metal catalysts.

## Objectives

- To study the reaction mechanism of butyric acid hydrodeoxygenation (HDO) on  $\beta$ -Mo<sub>2</sub>C (101) surface.
- To elucidate structure-activity relationships.
- To identify the descriptors responsible for governing the activity of  $\beta$ -Mo<sub>2</sub>C, and ways for further optimization of activity.

## Methods

All the DFT calculations are performed using the VASP.5.4.4, and VASP.6.2.1 packages. CI-NEB method was used for identification of transition states. The kinetic-energy cutoff: 500 eV, SCF energy convergence threshold: 10e-5 eV, and force convergence: geometry optimization (0.05 eV/Å), NEB (0.10 eV/Å),  $\Gamma$ -centered k-mesh of size 6\*6\*6 for optimizing bulk, and 2\*2\*1 for optimizing the supercell. MKMCXX package was used for performing microkinetic modeling, based on DFT data.

## Results

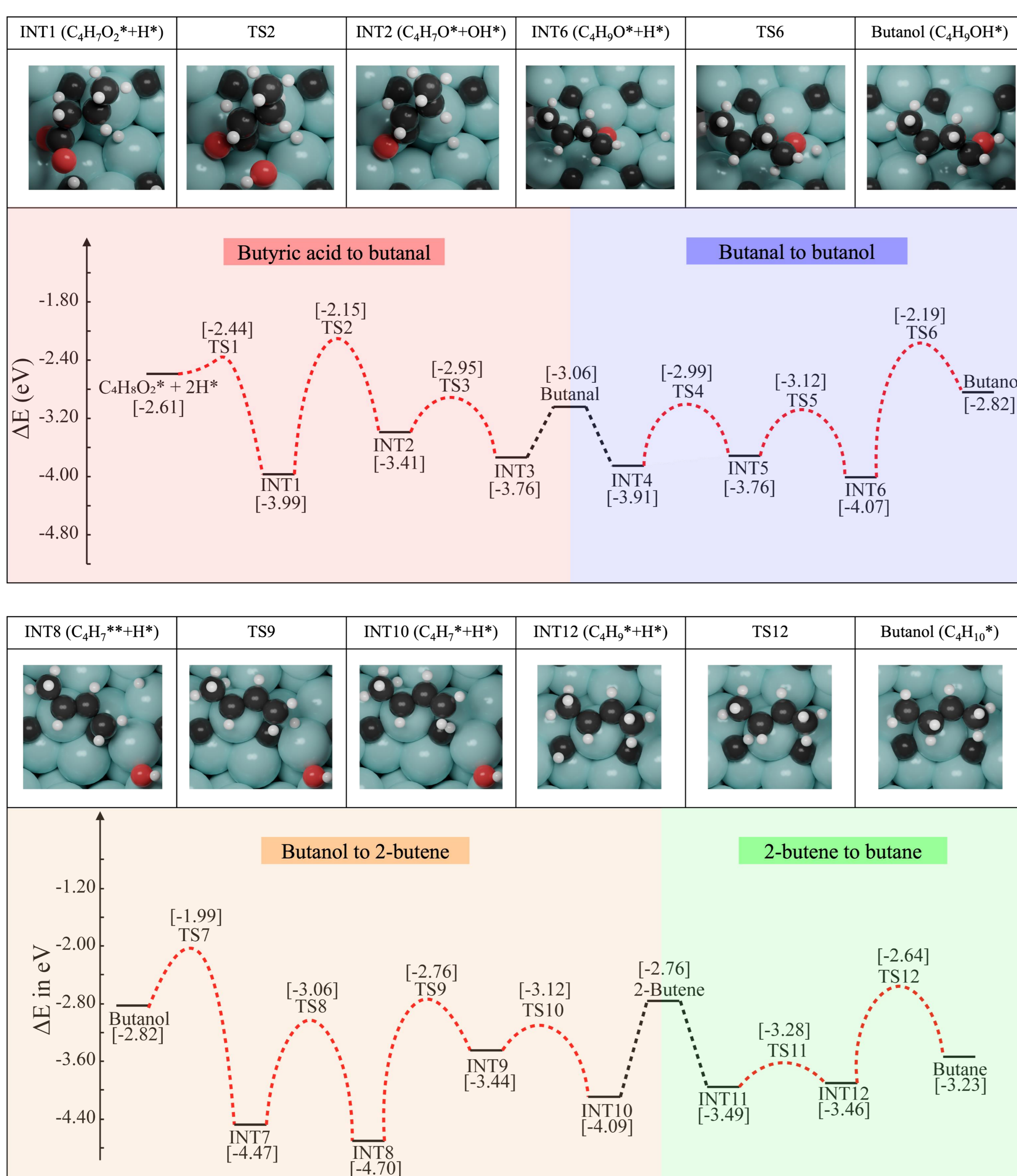


Figure 2. Reaction energy profile for the formation of butanal, butanol, 2-butene and butane from butyric acid over the (101) surface of  $\beta$ -Mo<sub>2</sub>C. The local geometries of intermediates and transition states of the key reaction steps are highlighted on top.

## Conclusions

- The reaction pathway for HDO of butyric acid to butane on  $\beta$ -Mo<sub>2</sub>C (101) has been identified using DFT modeling.
- Butanol dissociation is the rate-determining step, as verified by DFT & MKM.
- Dopants' d-band filling and dopants' radius are the key descriptors governing the activity of Mo<sub>2</sub>C catalyst.

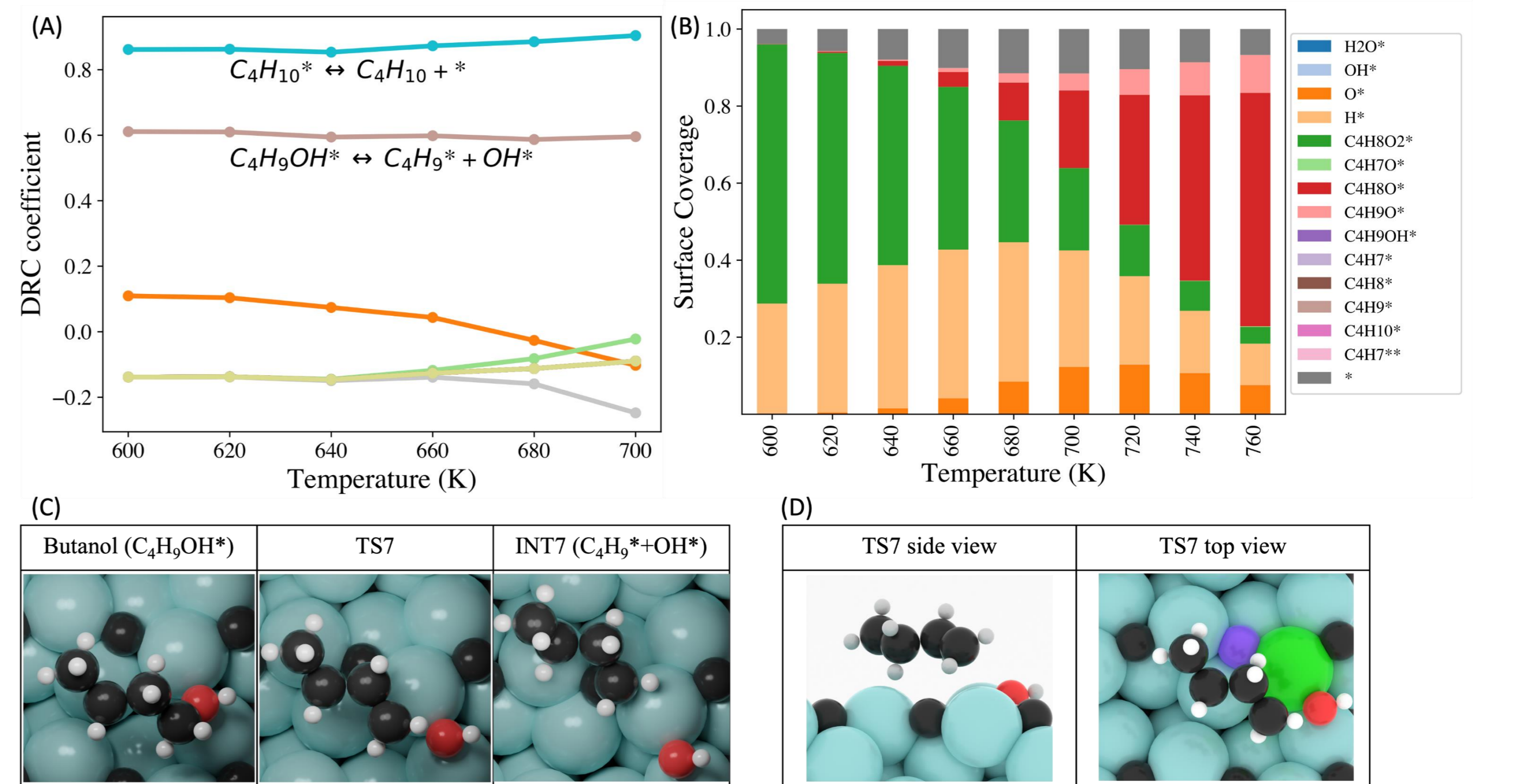


Figure 3. (A) The DRC coefficients for all the elementary reaction steps as a function of temperature; (B) surface coverage as a function of temperature; (C) local geometries of the rate-determining step identified by DRC analysis; (D) side and top view of the transition state of the RDS with active sites for heteroatom doping highlighted (Green: Mo active site for metal doping, Purple: C active site for nonmetal doping).

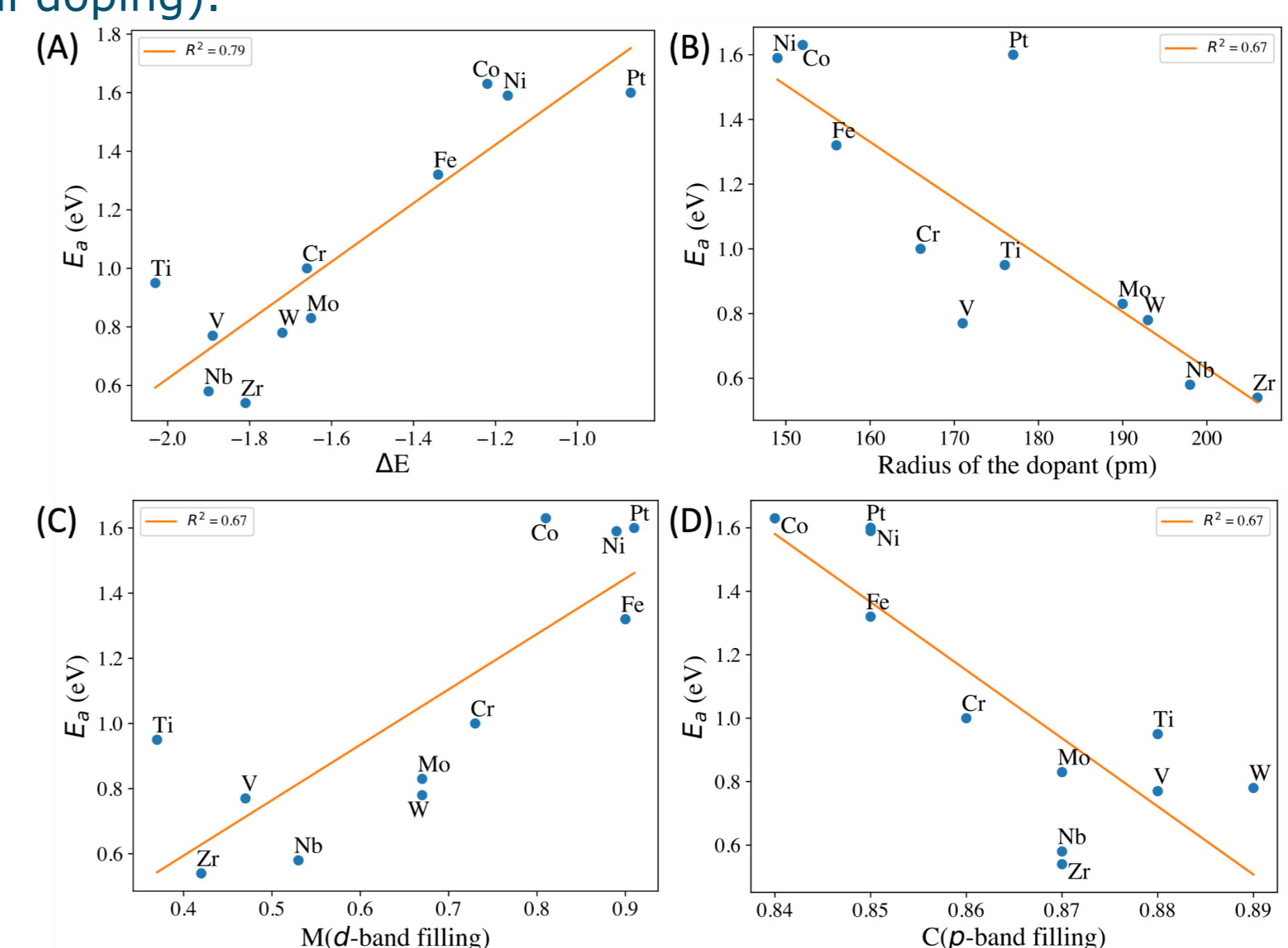


Figure 4. Linear-scaling relationships of potential descriptors of reactivity with reaction barriers required in the RDS.



## References

1. Feng et al. Chemical Society Reviews 2021, 50 (10), 6042–6093.
2. Oyama, S. T. Catalysis Today 1992, 15 (2), 179–200.
3. Hammer, B.; Nørskov, J. K. Advances in Catalysis 2000; Vol. 45, pp 71–129.