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Effect of CoPd and PdCo Core-Shell Catalysts on Fischer-Tropsch Reactions

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Introduction

The increasing need for clean energy sources has led to the study of Fischer-Tropsch (FT) synthesis for the production of liquid hydrocarbons from synthesis gas (H_2 and CO). Currently, the most effective catalysts for the production of hydrocarbons are Co, Fe, Ni, and Ru transition metals. Recent studies indicate that Pd could also be a good promoter when added to Co in such reactions.

Objectives

- Study preferred adsorption sites and binding energies of a carbon monoxide molecule on CoPd core-shell and PdCo core-shell nanostructured catalysts of 13, 19, and 38 atoms in total

- Determine energy barriers of the different steps involved in the FT reactions on the modeled nanostructured catalysts

- Investigate the dynamics of the FT reactions at 25 ºC and 200 ºC

Methods

Density Functional Theory (DFT) and DFT-coupled Molecular Dynamics (DFT-MD) calculations were used to study Fischer-Tropsch reactions on CoPd core-shell nanostructured catalysts

Materials Studio 6.0
Module: DMol3
Theory Level: LDA-PWC

1. Built and optimized core-shell models of CoPd and PdCo catalysts of 13, 19, and 38 atoms total containing approximately 10%, 50% and 80% elemental core (ex. Pd7Co6 = 13 atoms, ~50% Pd core)

2. Built and optimized systems of the lowest energy catalysts in the presence of 1 CO molecule to determine preferred adsorption site of the CO molecule on the shell (top, bridge, or hollow position)

3. Calculated binding energy of CO to the nanocluster

4. Calculated the activation barriers for the following syngas ($CO+H_2$) conversion to octane over the most favorable CoPd or PdCo core-shell catalyst according to: $8CO + 17H_2 \rightarrow C_8H_{18} + 8H_2O$
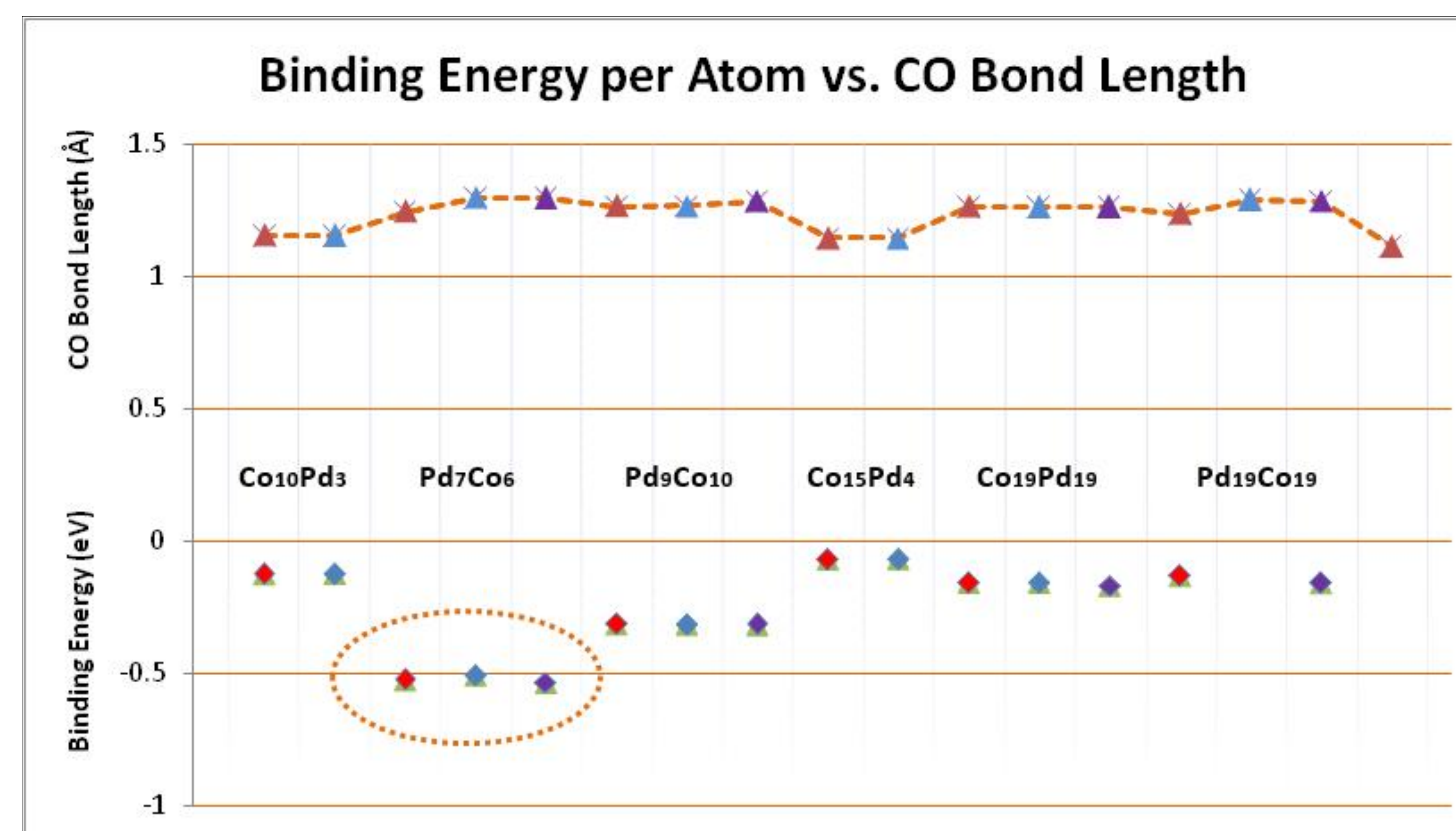
Pd7Co6 Core-Shell Nanoclusters for FTS

| 50% Core | -0.52 eV Top | -0.50 eV Bridge | -0.53 eV Hollow |
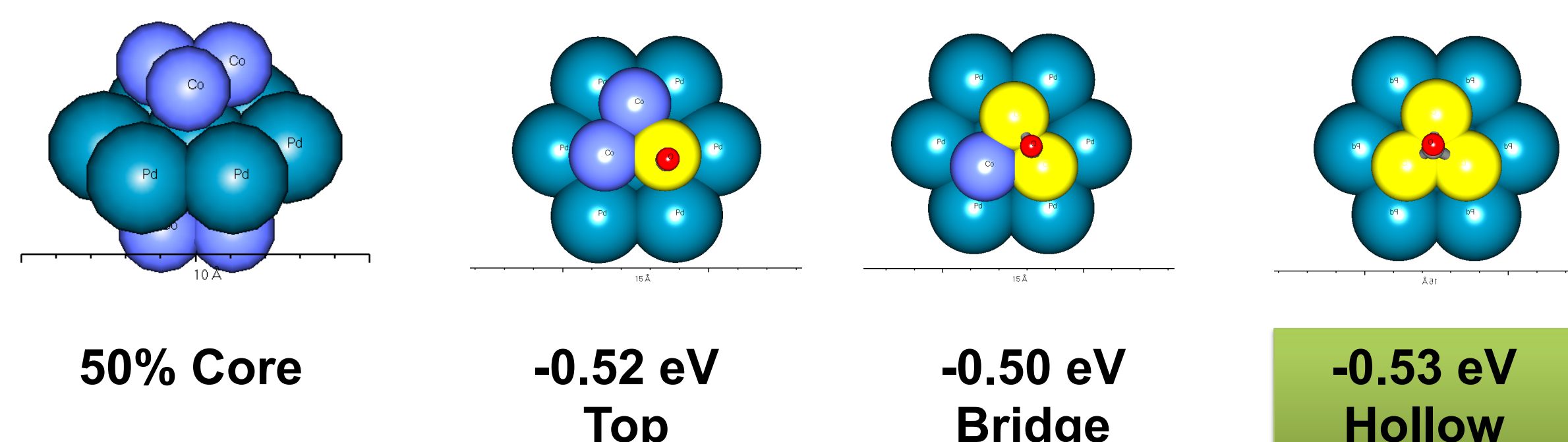
Geometry optimized core-shell models concluded that Pd7Co6 had the lowest cohesive energy; therefore, Pd7Co6 was selected as one of the models used to determine preferred adsorption site of the CO molecule

Calculation of Binding Energy

Binding Energy (BE) = Energy (catalyst + CO molecule) – Energy (catalyst) – Energy (CO molecule)

Binding Energy per Atom vs. CO Bond Length

CO Position: Top, Bridge, Hollow

Calculation of Activation Barriers

Transition State — Activation Barrier Energy 61.794 kcal/mol

Reactant — Product

Calculation of the activation barrier of Pd7Co6 core-shell catalyst according to $8CO + 17H_2 \rightarrow C_8H_{18} + 8H_2O$

Conclusions

- For both CoPd and PdCo Core-Shell nanoclusters, clusters with ~50% core-shell ratio expressed the lowest binding energy of CO to the cluster (and longest CO bond length)

- Preferred binding site on the Co or Pd shell of the nanocluster were more often the bridge or hollow positions

Future Work

- Continue to calculate activation barriers for the following syngas ($CO+H_2$) conversion to octane over the most favorable CoPd or PdCo core-shell catalysts according to: $8CO + 17H_2 \rightarrow C_8H_{18} + 8H_2O$

- Run Density Functional Theory coupled molecular dynamics (DFT-MED) simulations at 25 °C and 200 °C to investigate the conversion of CO and $2H_2$ molecules to octane over the most favorable CoPd and PdCo core-shell catalysts

- Perform a literature review on FTS and current challenges; compare simulation results with work found in literature
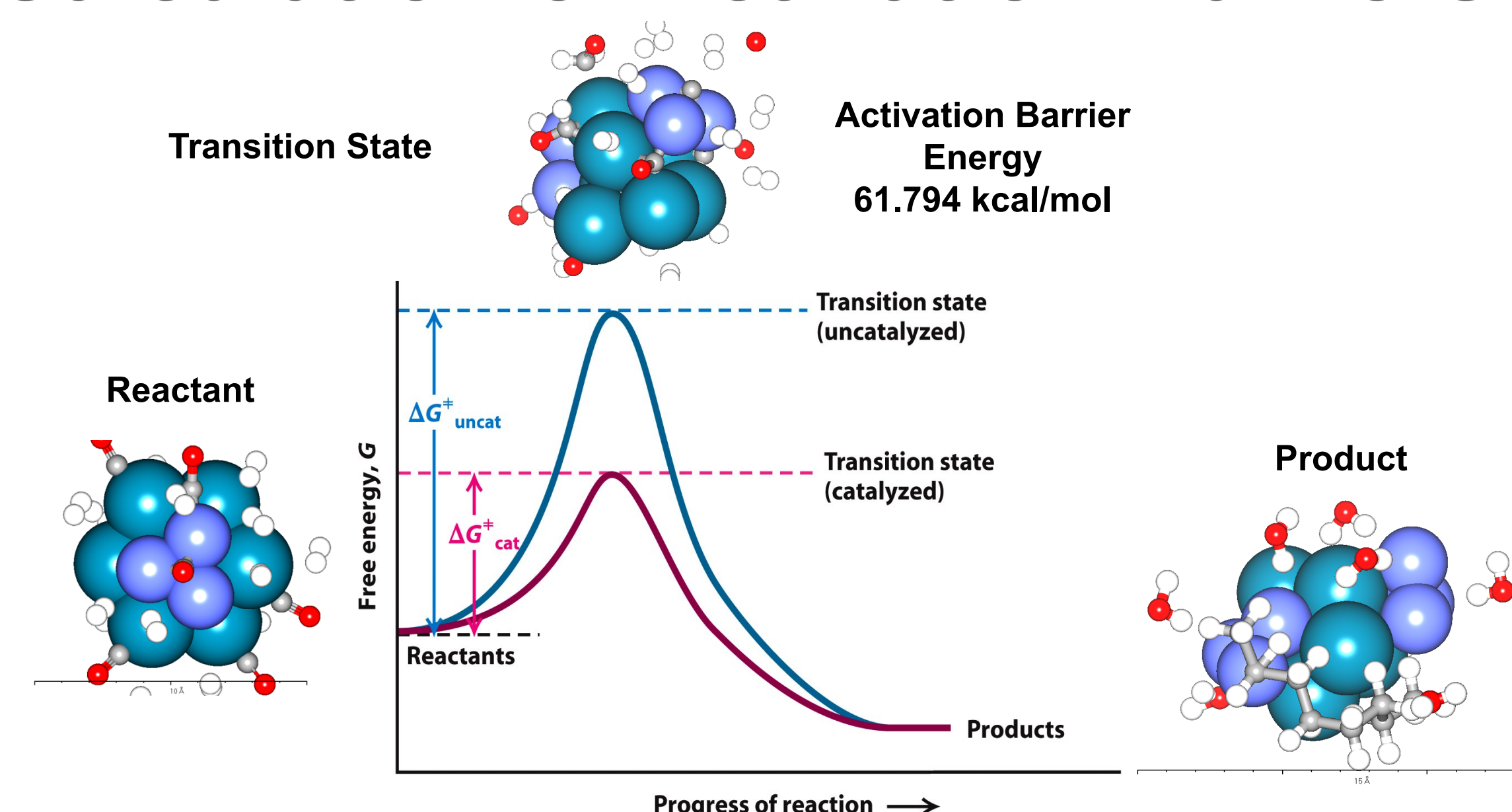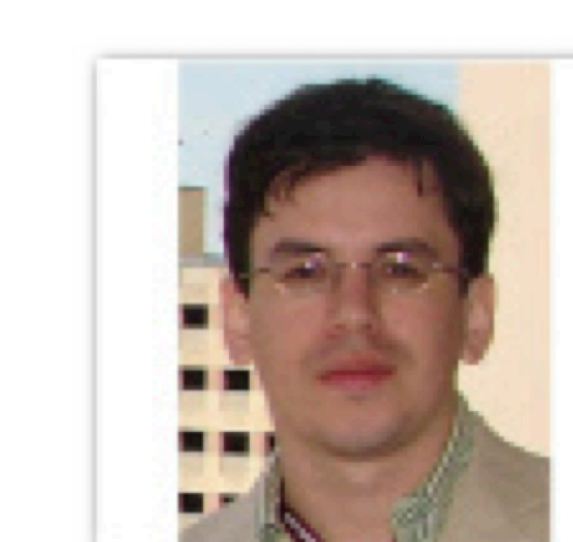
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Acknowledgements

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