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

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Introduction

• Due to the limitation of easily accessible fossil fuels, there has been a stimulation to many researchers for the search for alternative energy sources.

• Natural gas and biomass can be used for the production of fuels via Fischer-Tropsch synthesis.

•FTS was first industrially used in Germany during WWII, converting synthetic gas from gasification of coal into synthetic oil.

• Natural gas and biomass can be utilized to produce synthesis gas, which is a mixture of carbon monoxide and hydrogen.

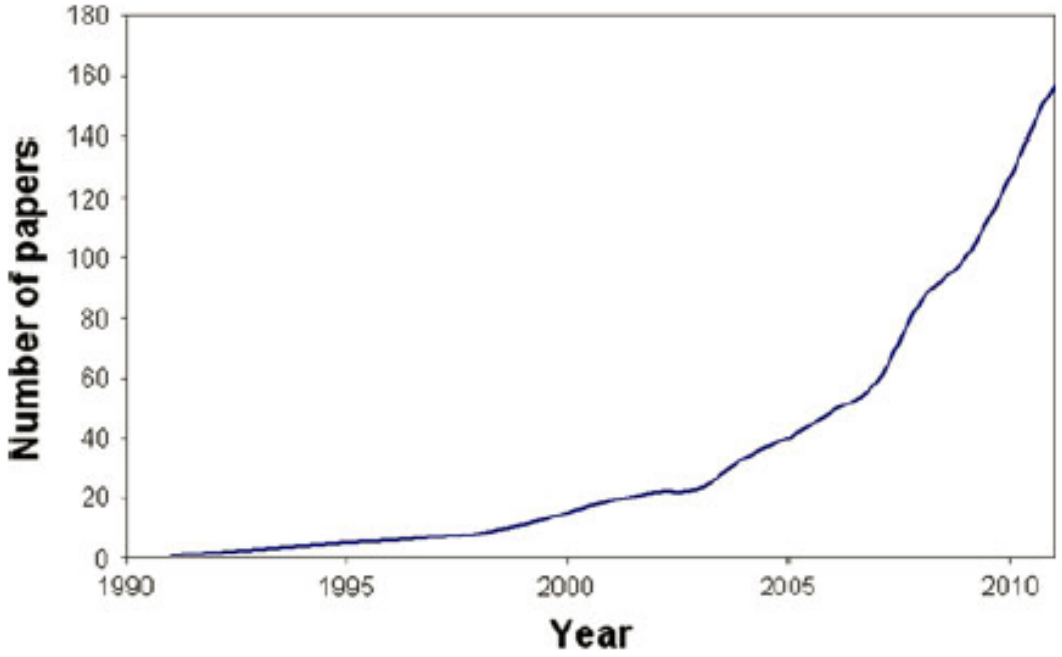


Fig. 1 Cumulated number of papers since 1990 in the field of computational chemistry and the Fischer–Tropsch synthesis. Topic = (Fischer–Tropsch) and ((Density Functional Theory) OR DFT OR (ab initio)) source: Web of Knowledge (c) Thomson Reuters

Introduction Cont'd

• This synthesis gas can be used to produce highly aliphatic hydrocarbons in the presence of transition metal catalysts; the synthetic oil can then be directly used in refineries

• This reaction process is catalytic, in which transition metals like Cobalt, Ruthenium, Nickel, and Iron are the active catalysts.

• The Fischer-Tropsch reaction is based on the following chemical reaction:

$$n\mathrm{CO} + m\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2(m-n)} + n\mathrm{H_2O}$$

• In this research, the production of C_8H_{18} (octane) via FTS is studied using CoPd and PdCo core-shell nanostructure catalysts:

$$8\mathrm{CO} + 17\mathrm{H_2} \rightarrow \mathrm{C_8H_{18}} + 8\mathrm{H_2O}$$

Other examples of FTS reactions:

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow (\mathrm{CH_2})_n + n\mathrm{H_2O} \quad (1)$$

$$n\mathrm{CO} + (2n+1)\mathrm{H_2} \rightarrow \mathrm{H}(\mathrm{CH_2})_n\mathrm{H} + n\mathrm{H_2O} \quad (2)$$

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow \mathrm{H}(\mathrm{CH_2})_n\mathrm{OH} + (n-1)\mathrm{H_2O} \quad (3)$$

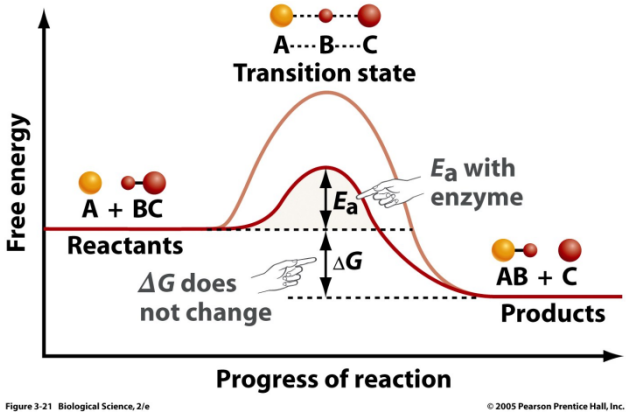
$$n\mathrm{CO} + (2n-1)\mathrm{H_2} \rightarrow (\mathrm{CH_2})_n\mathrm{O} + (n-1)\mathrm{H_2O} \quad (4)$$

$$n\mathrm{CO} + (2n-2)\mathrm{H_2} \rightarrow (\mathrm{CH_2})_n\mathrm{O_2} + (n-2)\mathrm{H_2O}, n > 1. \quad (5)$$

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 ^{o}C and 200 ^{o}C

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

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Methods Cont'd

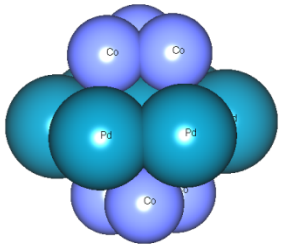
1. Built and optimized core-shell models of CoPd and PdCo catalysts of 13, 19, and 38 atoms total containing approximately 10%, 50% and 80% elemental core (ex. Pd7Co6 = 13 atoms, ~50% Pd core)

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)

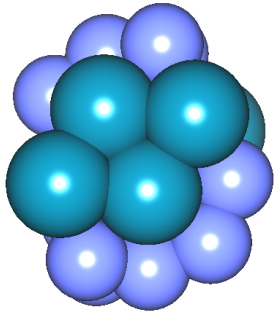
3. Calculated binding energy of CO to the nanocluster

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: $8CO + 17H_2 \rightarrow C_8H_{18} + 8H_2O$

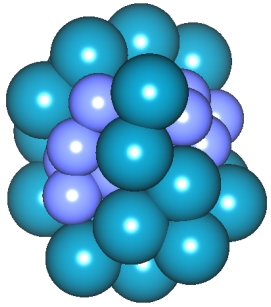
Core-Shell Nanoclusters for FTS



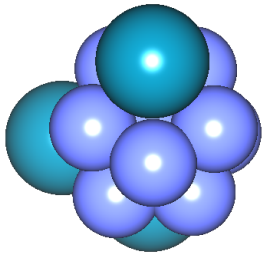
Pd_7Co_6
(13 atoms | 50% Core)



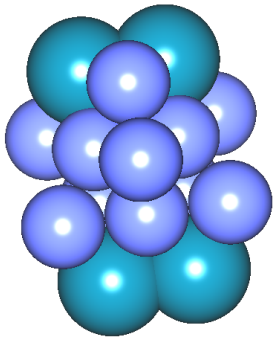
Pd_9Co_{10}
(19 atoms | 50% Core)



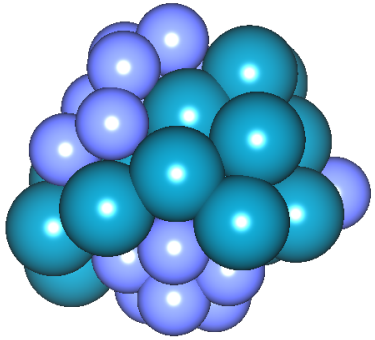
$Co_{19}Pd_{19}$
(38 atoms | 50% Core)



$Co_{10}Pd_3$
(13 atoms | 80% Core)

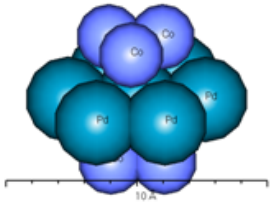


$Co_{15}Pd_4$
(19 atoms | 80% Core)

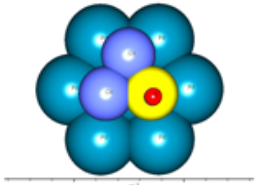


$Pd_{19}Co_{19}$
(38 atoms | 50% Core)

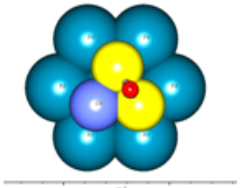
Core-Shell Nanoclusters for FTS



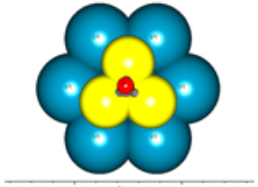
50% Core



-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

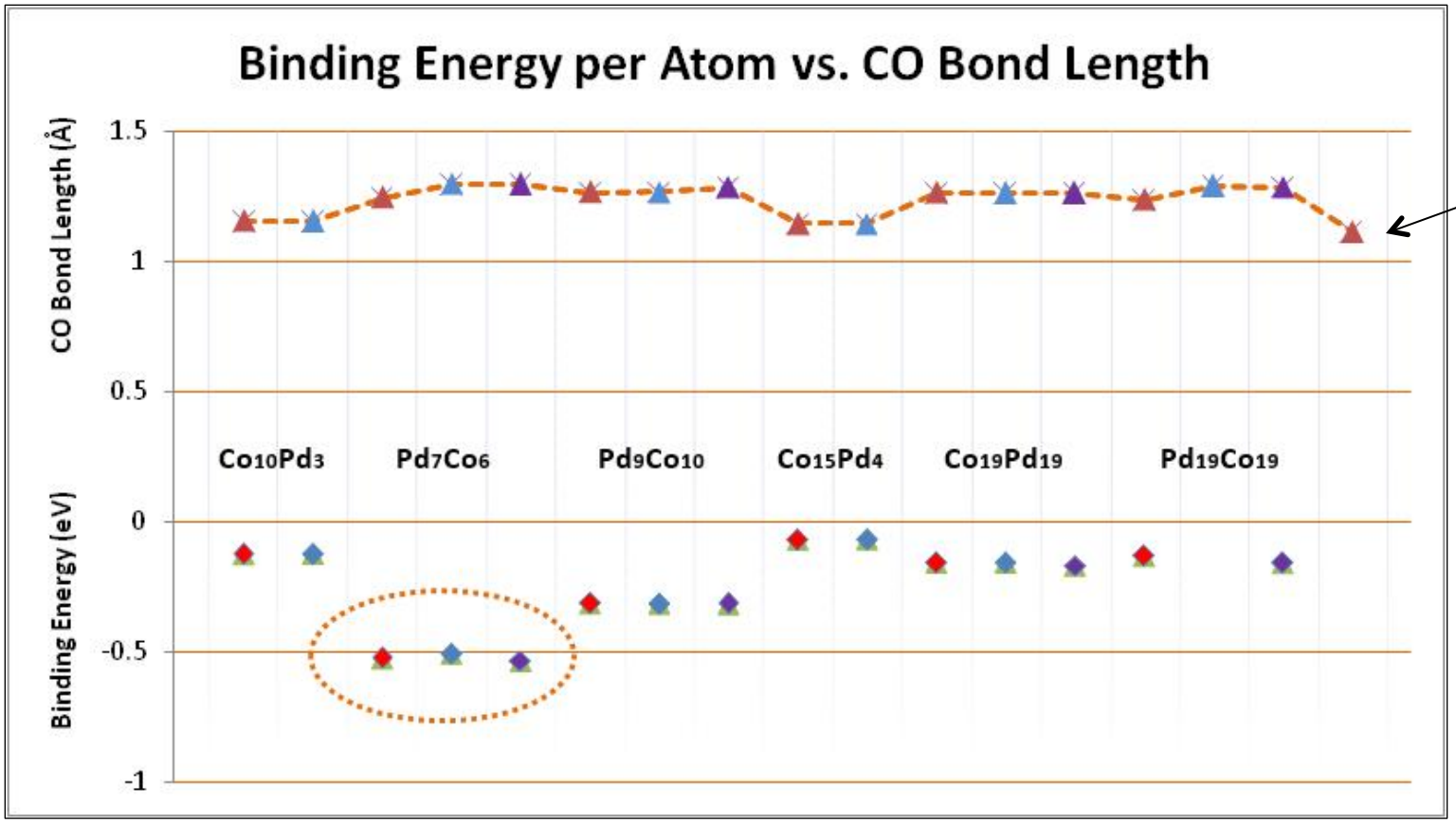
Binding Energies

CALCULATION:

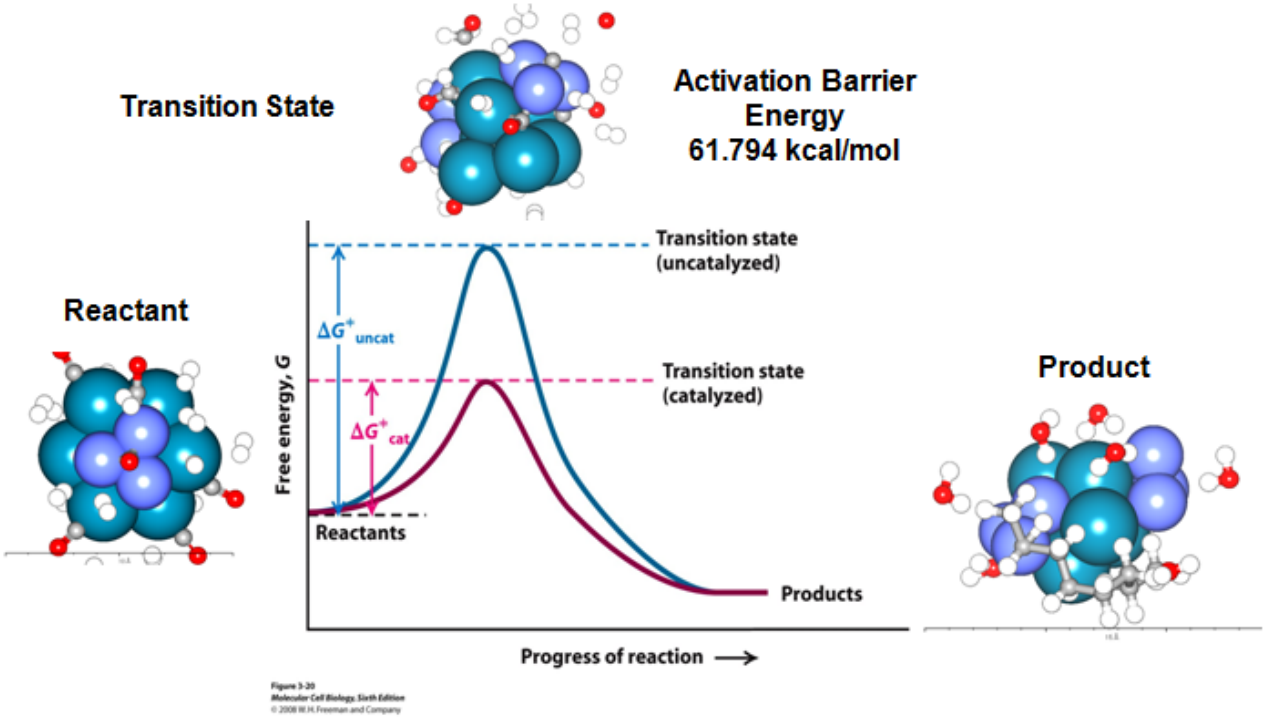
Binding Energy (BE) = Energy (catalyst + CO molecule) – Energy (catalyst) – Energy (CO molecule)

Catalyst	Position	E(CO+Surface) (Ha)	E(surface) (Ha)	E(CO) (Ha)	BE (Ha)	27.21139	BE per atom	CO Bond Length	
Co10Pd3	Top	-28726.12716	**-28613.57236**	-112.4953	-0.0594955	-1.61895	-0.12	1.155	
	Bridge	-28726.12697	-28613.57236		-0.0593127	-1.61398	-0.12	1.155	
Pd7Co6	Top	-42946.32914	**-42833.58363**		-0.2502031	-6.80837	-0.52	1.246	
	Bridge	-42946.32023	-42833.58363		-0.2412952	-6.56598	-0.51	1.298	*became hollow
	Hollow	**-42946.33394**	**-42833.58363**		**-0.2550047**	**-6.93903**	**-0.53**	1.296	
Pd9Co10	Top	-58340.49448	**-58227.7799**		-0.2192721	-5.96670	-0.31	1.266	*became bridge
	Bridge	-58340.49461	-58227.7799		-0.2194063	-5.97035	-0.31	1.267	
	Hollow	-58340.49587	-58227.7799		-0.2206655	-6.00461	-0.32	1.284	
Co15Pd4	Top	-40565.06519	**-40452.52156**		-0.0483176	-1.31479	-0.07	1.143	*became bridge
	Bridge	-40565.06514	-40452.52156		-0.0482752	-1.31364	-0.07	1.143	
Co19Pd19	Top	-123679.0008	**-123566.2859**		-0.2195924	-5.97541	-0.16	1.264	*became hollow
	Bridge	-123679.0003	-123566.2859		-0.219072	-5.96125	-0.16	1.263	*became hollow
	Hollow	-123679.0168	-123566.2859		-0.235558	-6.40986	-0.17	1.263	
Pd19Co19	Top	-120123.9670	**-120011.2862**		-0.1854753	-5.04704	-0.13	1.237	
	Bridge	*error in outmol: ran out of memory						1.289	*became hollow
	Hollow	-120124.0045	-120011.2862		-0.2229457	-6.06666	-0.16	1.287	
								1.111	<--CO Opt

Binding Energies



Calculation of Activation Barriers



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

Acknowledgments

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