Computational Periodic Trends of Catalysts for Methane to Methanol Conversion

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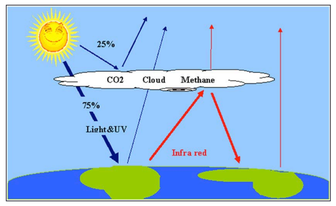
INTRODUCTION



Conversion of a greenhouse gas, methane, into a versatile chemical, methanol, is currently an expensive two-step process.

Step 1: $CH_4 + H_2O \xrightarrow[heat]{[Ni]} CO + 2H_2$

Step 2: $CO + 2H_2 \xrightarrow[high\ pressure]{[cat]} CH_3OH$

$CH_4 + \frac{1}{2}O_2 \longrightarrow CH_3OH$

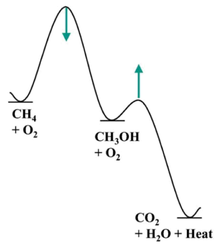
A more economical process of direct conversion of methane to methanol would be highly desirable and allow more efficient transportation and storage of a readily available energy supply.

Unfortunately, current metal catalysts prefer activating the C-H bond in methanol rather than in methane. Methanol is quickly converted to unwanted products such as CO_2.

$CH_4 + \frac{1}{2}O_2 \longrightarrow CH_3OH \longrightarrow CO_2 + H_2O$

Very Reactive with Existing oxidation Catalysts

To solve the problem, research is focused on modifying catalysts to lower the activation barrier to form methanol while raising the barrier to form CO_2.



COMPUTATIONAL DETAILS

Screening large amounts of metal catalysts in an experimental lab is expensive and time consuming. Computers save time and money by calculating energies more quickly and allowing researchers to identify trends.

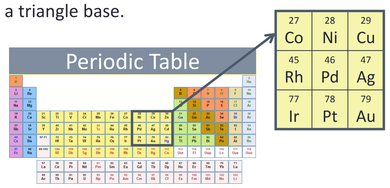
Atom types and positions →  → Energy values

Software: GaussView 5.0.8

Method: DFT (Density Functional Theory)

Basis Set: LanL2DZ

Catalysts Evaluated: 9 metals in various configurations: triangle, square, and pyramid with a triangle base.



Procedure:

1. Build model and create bonds.
2. Use "clean" function to approximate configuration.
3. Calculate Optimization.
4. Calculate Energy and record results.
5. Calculate dissociation energy and plot results.

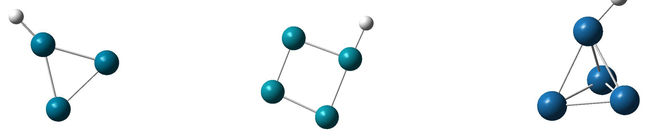
Sample Calculations (Triangle shape)

$$E_{diss\ \text{C-H bond in } CH_4} = \left(\text{Adsorption energy of H} + \text{Adsorption energy of } CH_3\right) - \text{Gas phase energy of } CH_4$$

$$E_{diss\ \text{C-H bond in } CH_3OH} = \left(\text{Adsorption energy of H} + \text{Adsorption energy of } CH_2OH\right) - \text{Gas phase energy of } CH_3OH$$

RESULTS

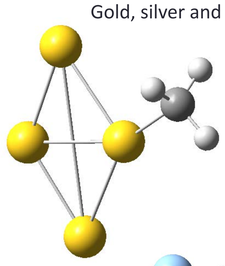
Dissociation Energies for C-H Bond in Methane and Methanol



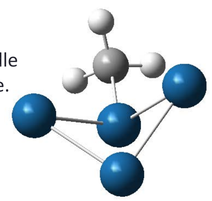
	Triangle			Square			Pyramid		
Co-Ni-Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni	Cu
CH4	1.0694	-2.5634	-0.2912	-9.1922	-4.8628	0.7347	-10.0358	-4.9444	1.9293
CH3OH	0.1497	-3.4287	-0.9579	-10.9392	-5.8424	0.2150	-9.4643	-5.1240	1.0749
Rh-Pd-Ag	Rh	Pd	Ag	Rh	Pd	Ag	Rh	Pd	Ag
CH4	-0.7102	0.5769	1.2300	-1.5973	-1.5212	1.8504	0.5905	-0.9633	2.1688
CH3OH	-1.6164	0.3755	0.6340	-2.3049	-1.9810	1.3307	-0.1170	-1.4232	1.7579
Ir-Pt-Au	Ir	Pt	Au	Ir	Pt	Au	Ir	Pt	Au
CH4	-0.7538	0.9633	-0.2585	-1.6627	-0.3157	1.7334	-0.5306	-2.7158	-0.3238
CH3OH	-2.4436	0.6068	-0.2585	-2.4055	-1.3878	1.3606	-1.3416	-3.2355	-0.5334

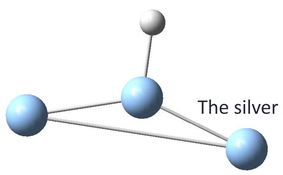
In some cases, the shape of the structure changed drastically upon optimization.

Gold, silver and copper pyramids flattened to form a kite shape.



Many of the square clusters bent in the middle to form a boat-like shape.





The silver and gold triangles compressed.

CONCLUSIONS

The dissociation energy of the C-H bond in methanol is lower than the dissociation energy of the C-H bond in methane matching experimental results of metal catalysis.

Periodic trends are not consistent in metal clusters of very small size.

Future research options include:

- Increasing the metal cluster size until consistent results can be obtained.
- Investigating results on a variety of metal alloys.
- Investigating results with a variety of pre-adsorbed atoms, such as oxygen.

CURRICULUM CONNECTION

Indiana Department of Education Standards

C.7.5 Explain how the rate of a reaction is qualitatively affected by changes in concentration, temperature, surface area and the use of a catalyst

C.9.1 Use structural formulas to illustrate carbon atoms' ability to bond covalently to one another to form many different substances.

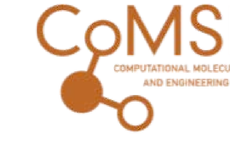
Day 1: Introduction to Rates of Reaction

Experiment: Brown Apples

Enzymes + phenols $\xrightarrow[\text{or inhibitor}]{\text{catalyst}}$ melanin (brown pigment)

Day 2: Catalytic Converters Web Quest

https://sites.google.com/site/catalyticconverterwebquest2014/home



Day 3: Calculating Reaction Rates

One step and multi-step reactions

Rate-determining steps

Simulate multi-step reaction

Day 4: Depletion Board Game

A game for teaching reaction rate theory

http://people.brandeis.edu/~herzfeld/games/Deplete.html

Day 5: Concentration and Reaction Rates

Experiment: The Clock Reaction

Day 6: Check for Understanding

Who Wants to Be a Millionaire Game

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The Official Gaussian Website, 18 July, 2014. Web. 21 July 2014. <www.gaussian.com>.

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NSF

CoMSEL COMPUTATIONAL MOLECULAR SCIENCE AND ENGINEERING LABORATORY

ND Energy CENTER FOR SUSTAINABLE ENERGY AT NOTRE DAME