“I had not known what research meant until I saw it. We were babes compared to what I saw.”:

Modeling and simulation of Fischer–Tropsch GTL Energy Conversion

Abstract

•Fischer-Tropsch process for gas-to-liquid (GTL) conversion was developed in 1925 by German scientists and used extensively by Nazi Germany during World War II and subsequently in times of petroleum shortages.

•Various catalysts are used to achieve less methanation and more moderate sized hydrocarbons.

• Computational chemistry is used to calculate the surface of cobalt, creating many different surface structures, and determining how the structure influences the mechanism for the catalytic reaction.

•When CO dissociates on the surface of cobalt, does it first react with a H atom to form CHO, and then dissociate, or does it dissociate itself?

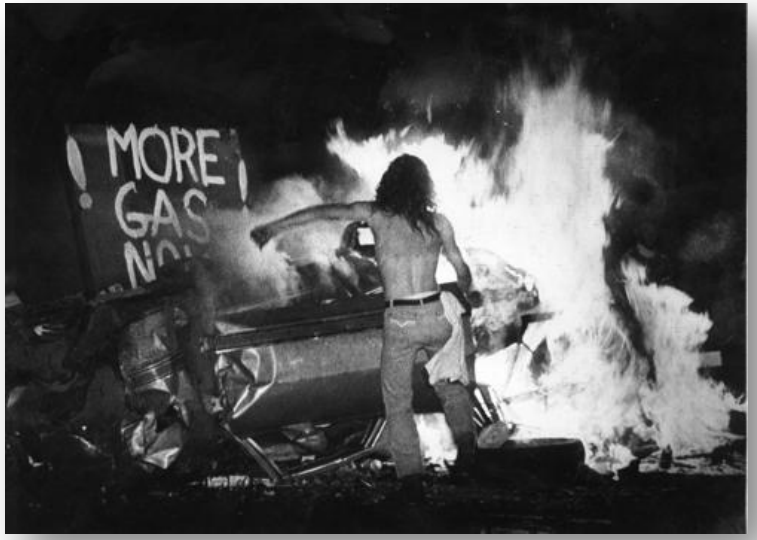
•Furthermore, once there are C atoms on the surface, how do they react to form either methane gas or longer chains of carbons (C-C bonds)?

•Investigators attempted to model the tips to see how they promote the formation of carbon-carbon bonds.

Source: “I had not known…” Walter C. Teagle, president of Standard Oil of NJ, 1926. Quoted in “Fischer-Topsch Fuels: Historical Review”

Gas shortages in war & peace

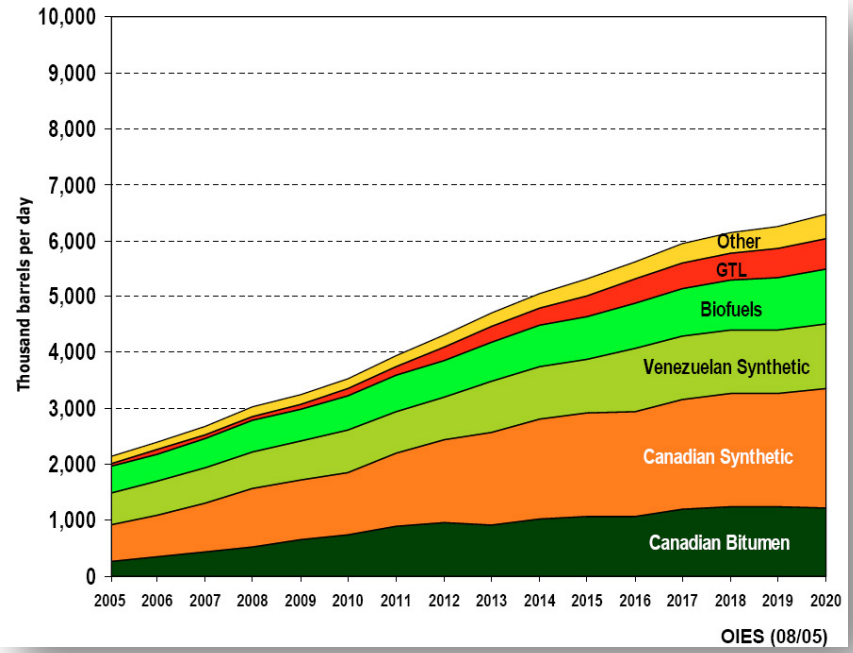
Operation Tidal Wave: B-24 bomber "Sandman" over Astra Romana refinery during the Ploesti Oil Campaign, 1943.



"Levittown is Burning!" 1979 Five Points Gas Riots. Levittown, PA.

Sources: S. L. Wuestoff. The utility of targeting the petroleum-base of a nation's economic infrastructure. Air University, 1993. D.M. Anderson. Levittown is Burning! *Labor*. 2005

Unconventional Oil

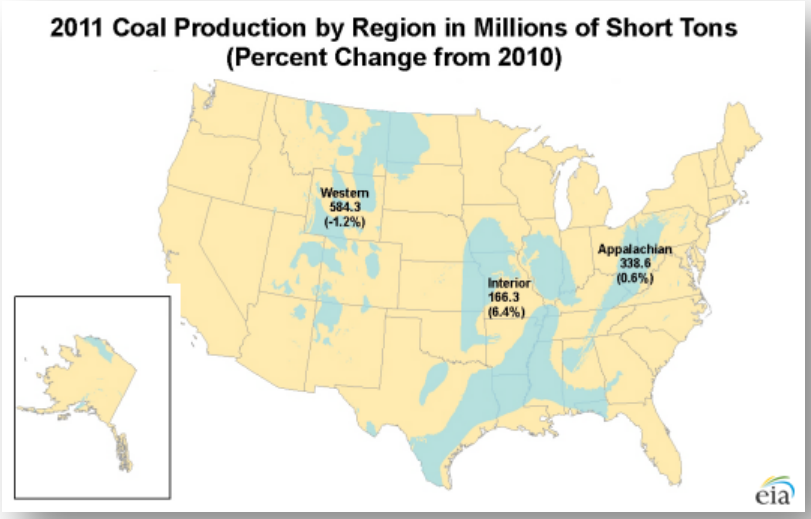


- Extra heavy oil & oil sands
- Shale oil
- Oil shale
- Thermal depolymerization
- Coal & gas conversion

Source: Unconventional Oil Forecast- Oxford Institute of Energy Studies

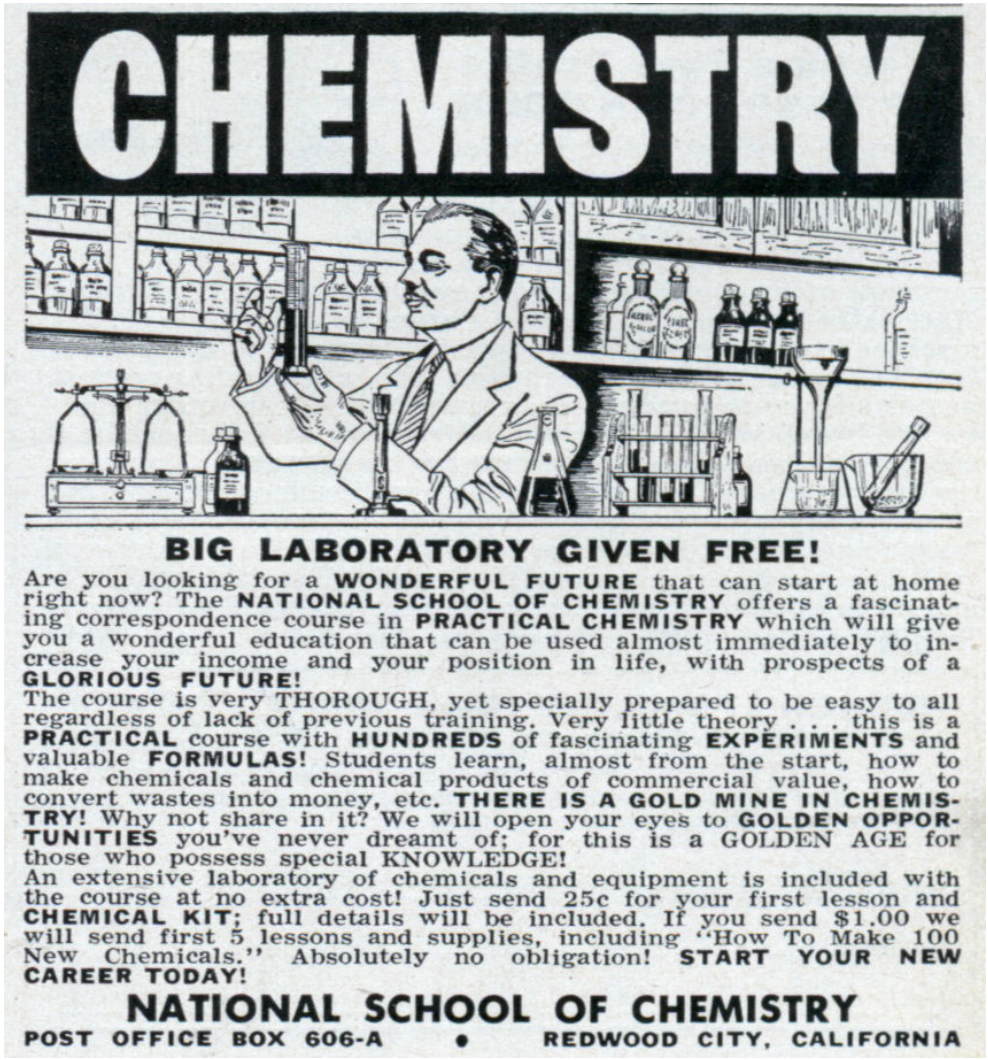
American Unconventional Oil Resources

U.S. Coal Reserves



U.S. Natural Gas Reserves

Source: U.S. Energy Information Administration



Use of chemistry to solve energy issues

- Organic chemistry - reactions of organic (C) compounds
- Analytical chemistry
- Computational chemistry – use of computer simulation to calculate structure & properties of molecules
- Physical chemistry – application of physics to chemical reactions, such as quantum mechanics & thermodynamics

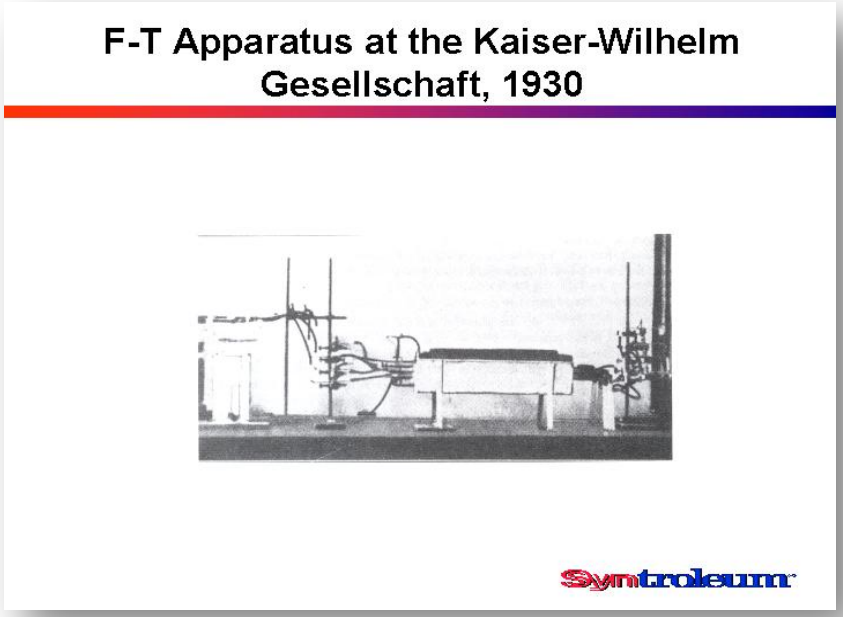
Who were Fischer & Tropsch?

Franz Fischer (1877-1947)

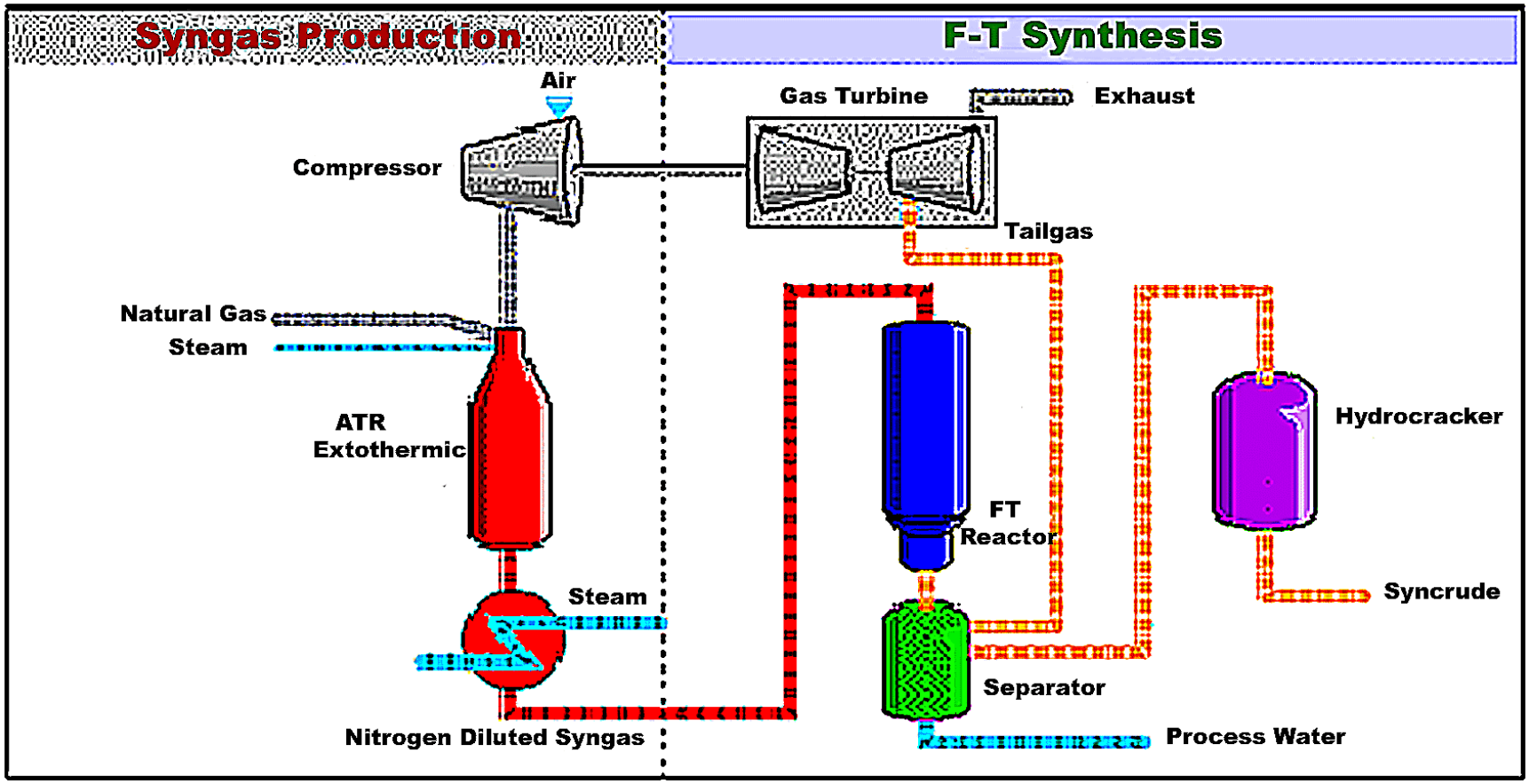
Hans Tropsch (1889-1937)

Fischer-Tropsche Research at Kaiser Wilhelm Institut für Kohlenforschung

Kaiser Wilhelm (now Max Planck) Institute at Mülheim an der Ruhr in 1943.

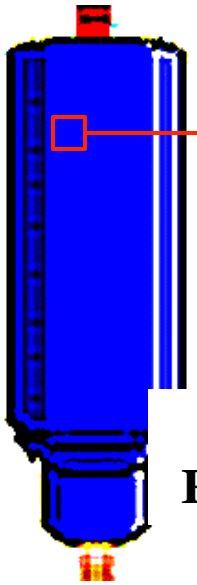


Fischer-Tropsche Flow Chart: $2\,CO(g) + H2(g) \rightarrow (-CH2-)n(l) + CO2(g) + H2O$

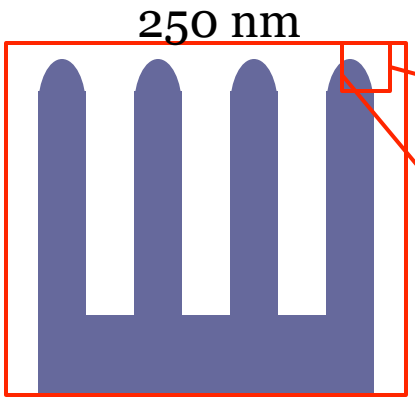


Fischer-Tropshe Catalysts: Fe Ru Co

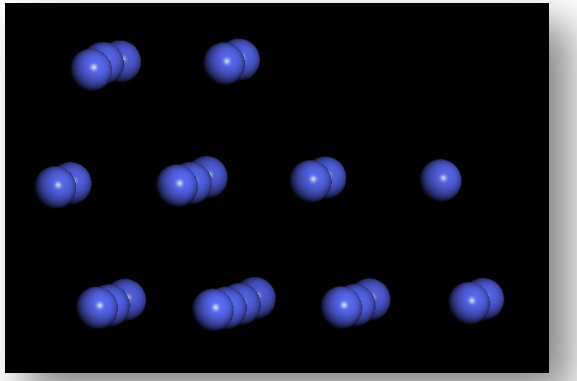
Use of Co as a F.T. Catalyst

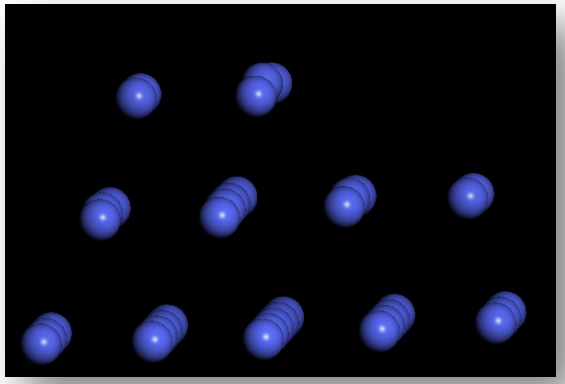


FT Reactor



Cobalt nanowires are used as a catalyst





Cobalt (Co) frustums, resembling the nanowires, model catalysts for H & CO molecules reactions . Single (above) and double (below), upon which the various C molecules are attached.

This structure has been found to form longer chained hydrocarbons (important for gasoline).

Methodology: How do we simulate and model the Fischer-Tropsch process?

- In-situ density functional theory (DFT) calculations were performed with the DMol3 code in Materials Studio using the double numerical with polarization (DNP) basis.
- Allows the efficient calculation of energetics associated with moderately large clusters with modest resources (4 processor computers)

Source: J. Gao, E. de Smit, G. Fitzgerald et al. Dynamic characterization of Co/TiO2 Fischer-Tropsch catalysts with infrared spectroscopy and DFT calculations. 22nd North American Catalysis Society Meeting, Detroit. 2011

We Need to Understand the Mechanism for Hydrocarbon Formation

$CO + Cobalt \rightarrow CO\ (ads)$

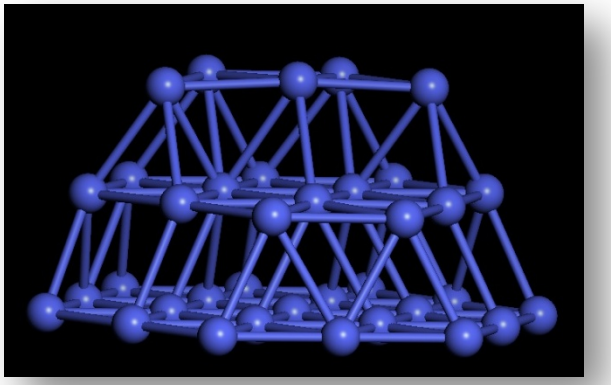
$CO\ (ads) \rightarrow C(ads) + O(ads)$

$C(ads) + H_2 \rightarrow CH_2(ads)$

$CH_2(ads) + CH_2(ads) \rightarrow H_2C\text{-}CH_2(ads)$

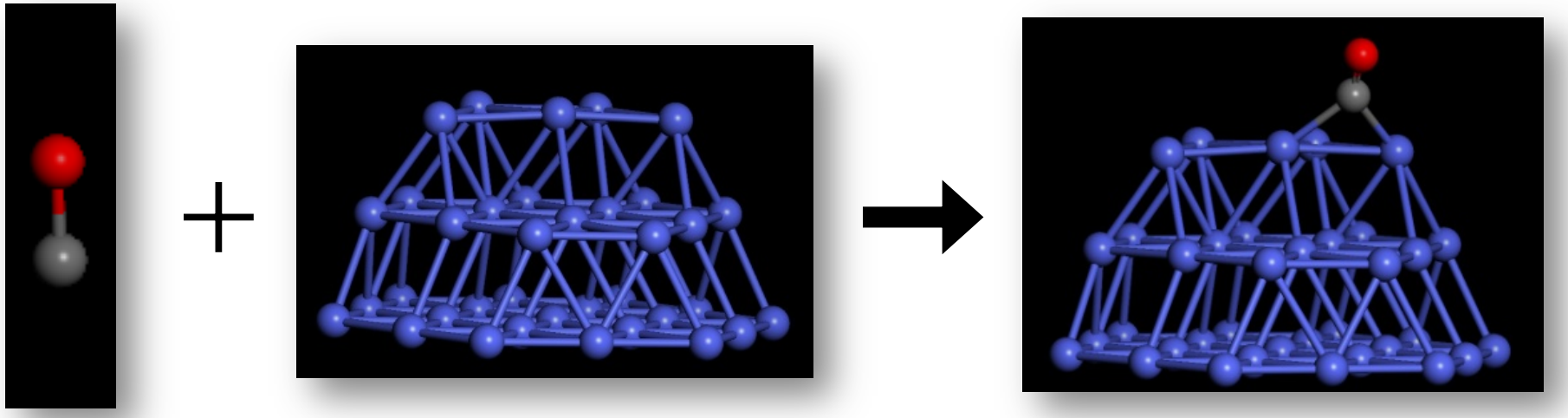
$H_2C\text{-}CH_2(ads) + CH_2(ads) \rightarrow$ larger and larger chains (until around 8 Cs)

We did not address larger chains because of the limited nature of this study. We investigated a larger frustum (right), which took too long to study (around a week to get a good answer for each calculation)



The CO appears to prefer binding to the ‘bridge’ site, where it is bound to two cobalt atoms

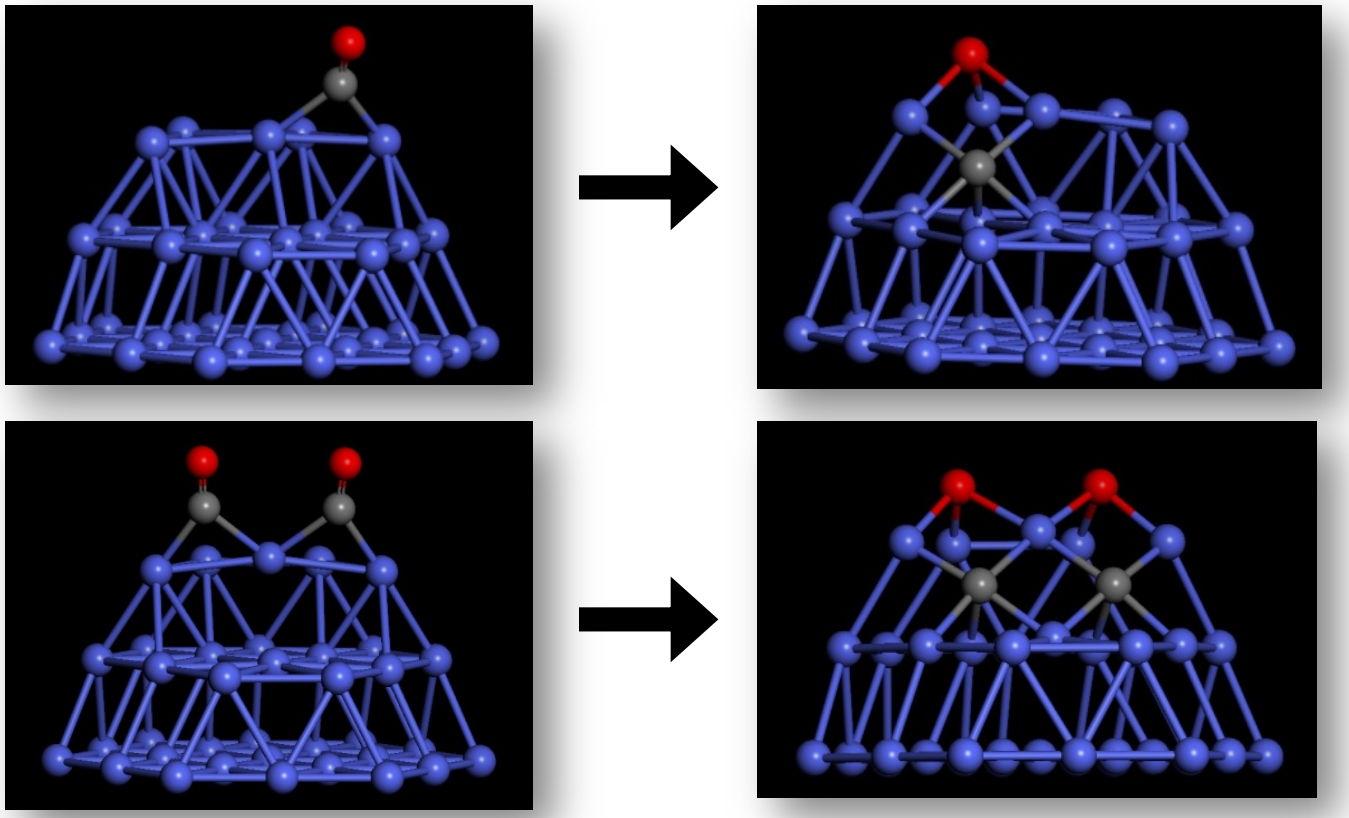
$$CO + Cobalt \rightarrow CO\ (ads)$$



- Many sites were trialed, but this one had the lowest energy
- The energy for adsorption was strongly negative or exothermic, so it is strongly energetically favorable

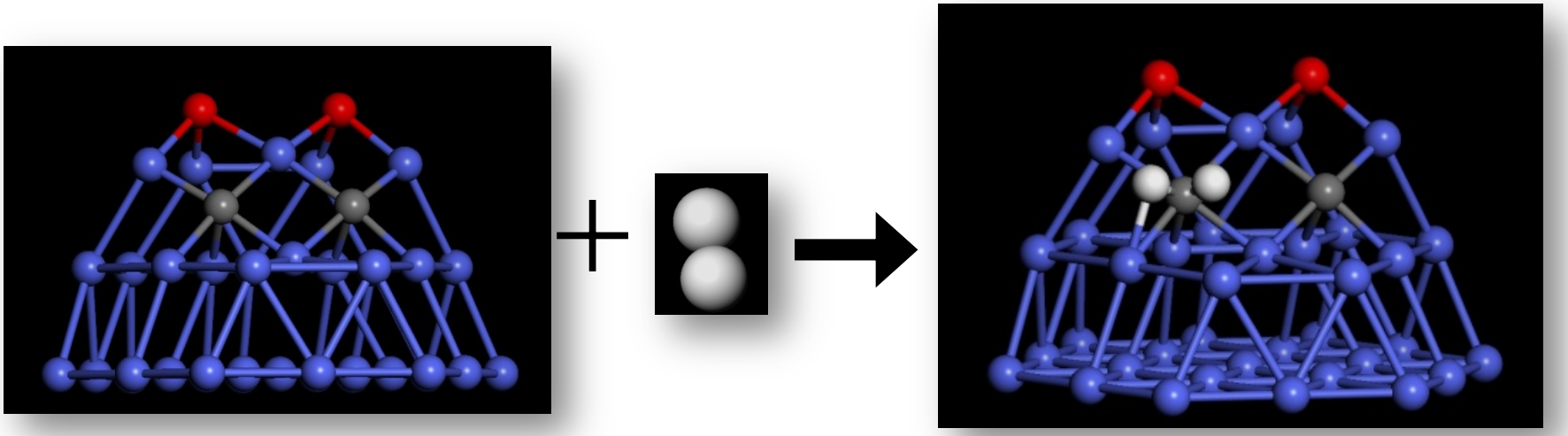
CO atoms dissociate into highly coordinated atoms

$$CO\ (ads) \rightarrow C(ads) + O(ads)$$



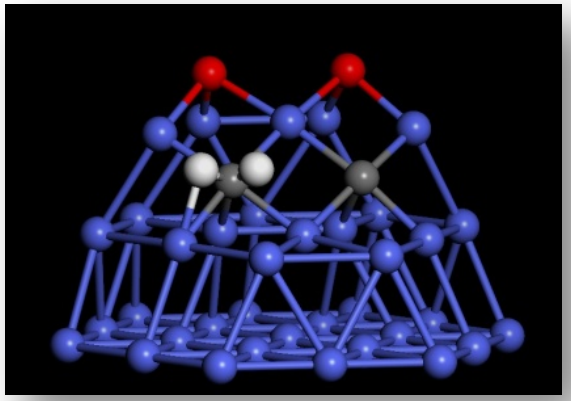
***Positive Energy for these steps**

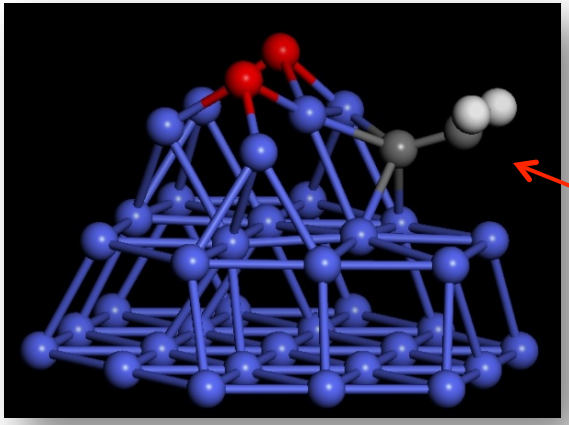
Hydrogenation of carbons occur fairly readily

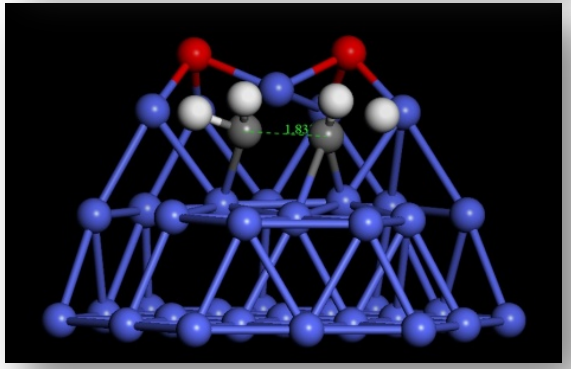


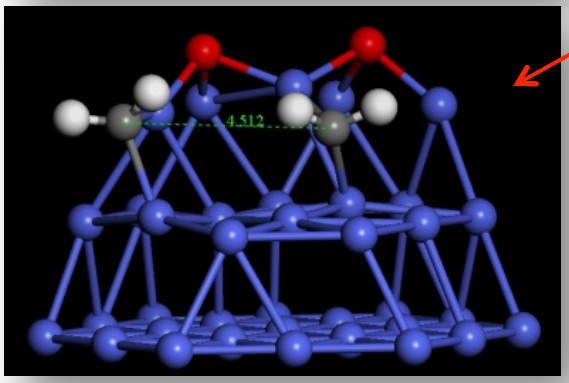
- The energy for hydrogenation is strongly negative
- The carbon moves away from the Cobalt a bit after hydrogenation (weaker carbon-cobalt bonding)

Carbon-carbon bond formation only occurs if one carbon releases from Cobalt





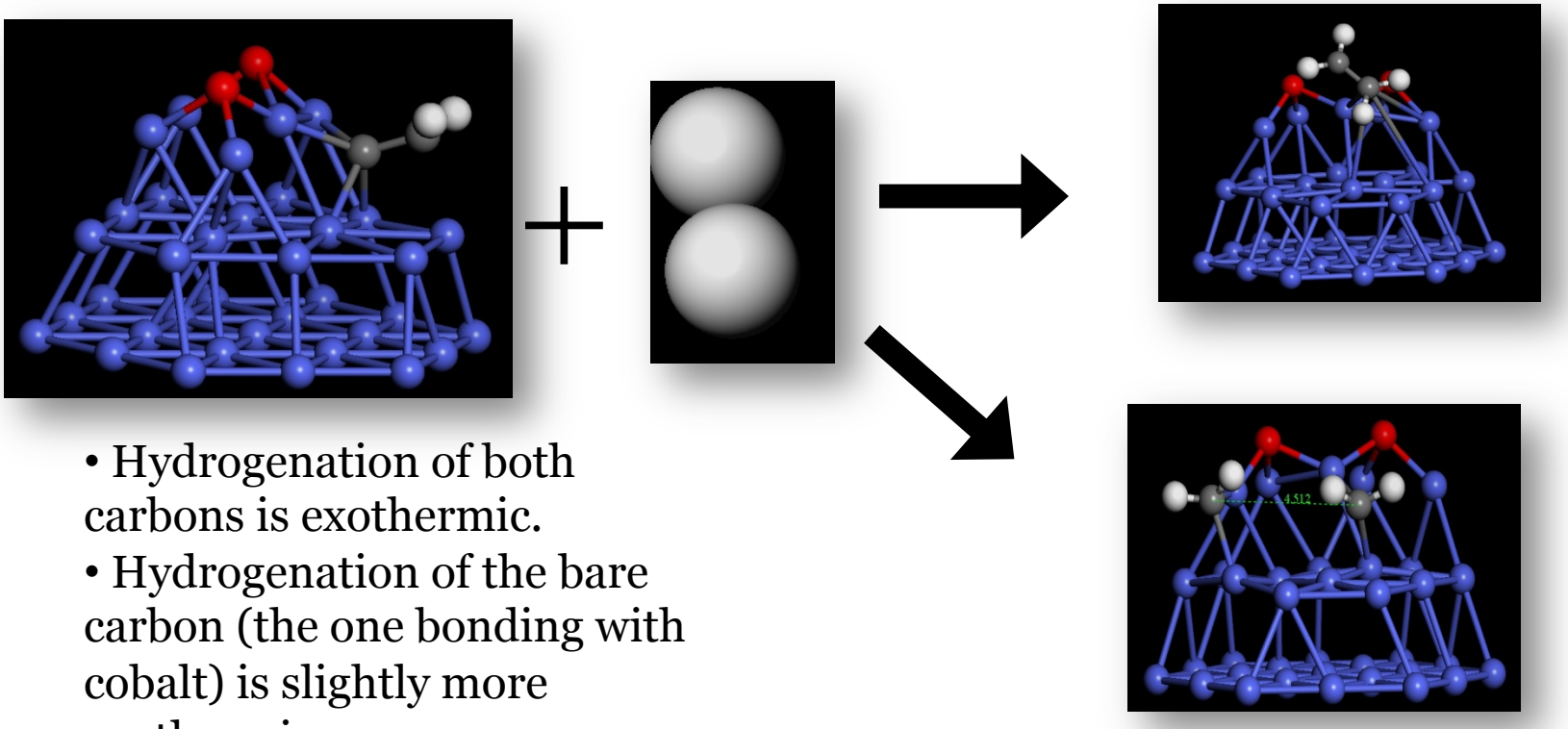




- The formation of a C-CH_2 bond is exothermic

- CH_2-CH_2 when bound with cobalt did not form a bond, but moved away form one another.

Further hydrogenation can occur via one of two routes, but similar in energy

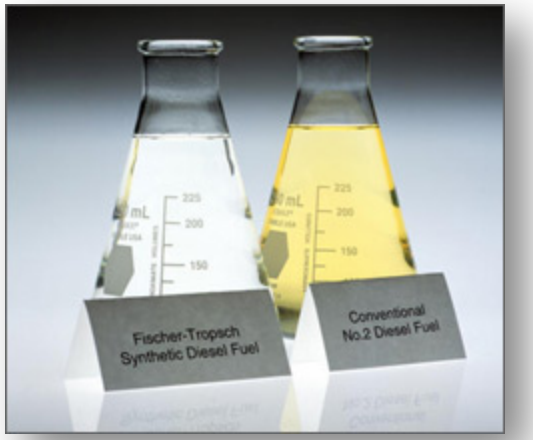


- Hydrogenation of both carbons is exothermic.
- Hydrogenation of the bare carbon (the one bonding with cobalt) is slightly more exothermic

Applications

A USAF B-52H Stratofortress from Minot AFB flying on a mix of synthetic and conventional JP-8 fuel.

Syntroleum plant near Tulsa



Cleaner than conventional Diesel

Conclusions

- GTL takes advantage of plentiful American coal & gas reserves and is a solid move toward energy independence.
- Computational chemistry has provided major advances in the study of catalysts on a molecular level.
- Cobalt reactors prove to be the most successful F.T. catalyst with hydrogenation (dissociation) occurring and avoiding a methanation step in the process.
- Further research is needed in developing improved F.T. catalysts.

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Fini

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