

Reaction Pathways in Catalytic CO Hydrogenation

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The Need for Fischer-Tropsch Catalysis

New compact, efficient, and selective GTL Plants (gas to liquid plants that combine steam reforming of methane with Fischer-Tropsch) are needed at the production sites to allow transport of natural gas in liquefied form.

Planned Facilities

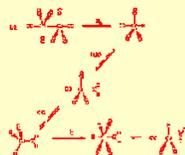
In Qatar	
Conoco Phillips	146,000 BPD
Shell	140,000 BPD
Sasol/Chevron Texaco	34,000 BPD

In Alaska

BP Reformer tests

On the Homogeneous Mechanistic Front

- $\text{HCo}(\text{CO})_4$ was the first demonstrably homogeneous CO hydrogenation catalyst
- Proved to be mononuclear when conventional wisdom required multiple metal centers
- Rate law: $d[\text{CH}_2\text{O}]/dt = P_{\text{H}_2}[\text{HCo}(\text{CO})_4]$
- The overall mechanistic features are generally accepted for Co, Rh, and Ru complex catalysts
- The initial products are from formaldehyde, followed by homologation and transesterification
- Reaction conditions: 220°C at 300 atm



Early Steps

Hydrogen activation, formation of coordinated formaldehyde

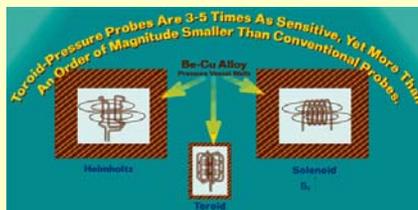
Product-Determining Steps

Produce the primary reaction products: Methanol, methyl formate, ethylene glycol

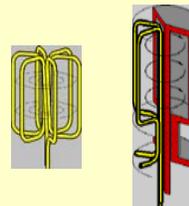


Secondary Products

Stem from catalytic alcohol homologation and transesterification of formate esters



The Relationship Between Toroid Coils and Toroid Cavities



Toroid Cavity Imager



Toroid Cavity Pressure Probe



Problems Associated with Autoclave Kinetic Methods

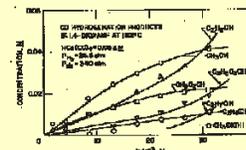
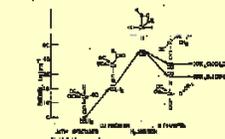
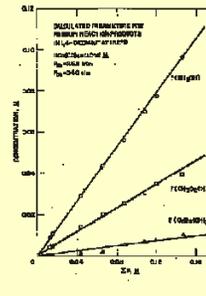
- Uncertain quenching of samples containing high-pressure species
 - $\text{HCo}(\text{CO})_4$ and its derivatives are extremely labile. The concentrations of such species can change when the pressure and temperature are lowered during sampling.
- Sampling itself changes catalyst concentration
 - $\text{HCo}(\text{CO})_4$ evaporates more and more into the autoclave headspace, which increases as liquid samples are removed.

Solution

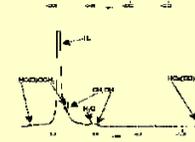
- In situ spectroscopic methods
 - Allow direct measurement of catalytic intermediates
- Improved theoretical methods
 - Density functional calculations can be used to complement experimental data
- Supercritical fluids
 - Gas-like media highly amenable to calculations
 - Problems associated with gas/liquid mixing, solvent expansion, and partitioning between phases are all alleviated
 - NMR signals of quadrupolar nuclei are narrower and less temperature-dependent in supercritical media

Autoclave Results

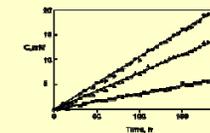
Prog. Inorg. Chem. 39, 113-180, 1991



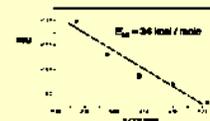
In Situ NMR Results



In situ ^{59}Co NMR (upper trace) and ^1H NMR (lower trace) during CO hydrogenation in supercritical CO at 80°C and 260 atm



Rate plot showing the production of methanol (▲), methyl formate (■) and their sum (×) in supercritical CO at 180°C and 260 atm



Arrhenius plot for $\text{HCo}(\text{CO})_4$ catalyzed CO hydrogenation: data in supercritical CO (▲); in liquid benzene, (○)

Conclusions

- Homogenous catalytic carbon monoxide hydrogenation was measured in situ in an NMR probe and in a supercritical fluid, both for the first time.
- Rates measured using a toroid NMR probe in supercritical carbon monoxide are comparable to those measured in liquid benzene solution using earlier autoclave methods.
- Alcohol homologation is suppressed in supercritical CO, thereby greatly simplifying the product mixture.
- The preliminary experimental NMR determination of E_{act} (~34 Kcal/mol) for CO hydrogenation in supercritical CO is significantly lower than earlier theoretical results calculated using modified extended Hückel theory.

Future Work

- Design and fabricate a new toroid cavity high-temperature/high-pressure cell for in situ CO hydrogenation experiments
- Measure (1) activation parameters, (2) methanol, methyl formate, and ethylene glycol branching ratios, and (3) deuterium kinetic isotope effect for CO hydrogenation in supercritical CO
- Compare results with calculated values for formyl, hydroxycarbene, coordinated formaldehyde, hydroxymethyl, and methoxy intermediates (density-functional calculations in collaboration with L. Curtiss at Argonne)

