Optimum Catalytic Process for Fuel Alcohols from Syngas

DE-AC22-86PC90013

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The purpose of our research is to develop and evaluate novel catalytic systems for the selective conversion of syngas into a mixture of alcohols useful as a fuel additive. These systems include both homogeneous and heterogeneous catalysts, and may involve two-stage operation through methanol.

We have mainly investigated three catalytic approaches from syngas to higher alcohols. A novel methanol homologation process discovered under our previous contract has been a subject of continued study. This homogeneous catalyst converts methanol (with syngas) into ethanol under lower pressures than previously possible; good rates and selectivities are obtained below 1000 psi. Homogeneous ruthenium-based catalysts have been developed which can produce a mixture of C_1-C_4 alcohols from syngas under pressures of 3000 to 5000 psi. Certain novel catalyst additives have been found to increase the activity and selectivity to higher alcohols. Heterogeneous molybdenum sulfide-based catalysts have also been investigated. A major objective in these studies is to discover new modifications of the catalyst with improved performance.

Novel Methanol Homologation Catalyst System

K. G. Moloy and R. W. Wegman, *J. Chem. Soc., Chem. Commun.*, 620 (1988)

U. S. Patent 4,727,200 (1988), to Union Carbide.

U. S. Patent application filed on preparation of ligands for this system (1988).

Work on this system originated from an interest in improving on the known cobalt catalyst for conversion of methanol to acetaldehyde and ethanol, and the following question:

Could Rhodium be a Better Methanol Homologation Catalyst?

- Rhodium catalyzes a variety of carbonylation reactions with faster rates under milder conditions than cobalt.

  Compare:

  Rhodium vs. cobalt catalyzed olefin hydroformylation.

  Rhodium vs. cobalt catalyzed methanol carbonylation.

- Rhodium had been investigated for methanol hydrocarbonylation and homologation, but very high ratios of H_2/CO were required — 40:1. Carbonylation to acetic acid highly favored.

Key Difference Between Cobalt- and Rhodium-Catalyzed Methanol Carbonylation

- Cobalt acetyl complex reacts with hydrogen to produce acetaldehyde.
- Rhodium acetyl complex rapidly eliminates acetyl iodide.
- Rhodium acetyl not stable enough to be intercepted by hydrogen. A means of stabilizing the acetyl must be found.

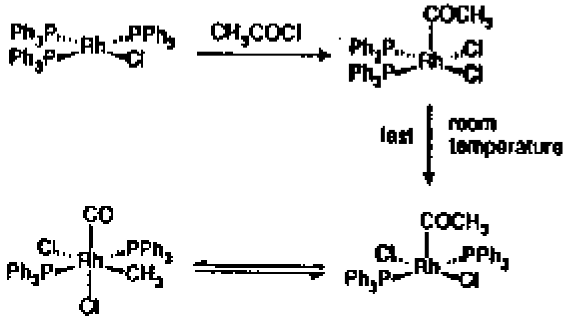
RHODIUM ACETYLS ARE STABILIZED WITH DIPHOSPHINE LIGANDS

Baird, et al. *J. Organometal. Chem.* 1978, *146*, 71-76.
Pignolet, et al. *Ibid.* 1980, *185*, 241-249.

Thermally very stable

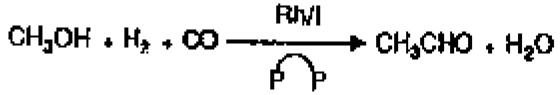

= $Ph_2P(CH_2)_nPPh_2$

Contrast with monodentate phosphines:



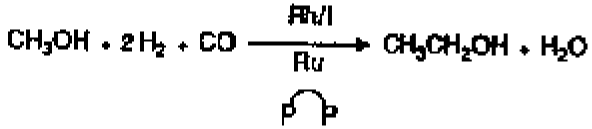
REDUCTIVE CARBONYLATION OF METHANOL WITH DIPHOSPHINE MODIFIED RHODIUM CATALYSTS

Methanol hydroformylation:



$$CH_3OH + H_2 + CO \xrightarrow[P\frown P]{Rh/I} CH_3CHO + H_2O$$

Addition of ruthenium results in methanol homologation:



$$CH_3OH + 2H_2 + CO \xrightarrow[Ru,\ P\frown P]{Rh/I} CH_3CH_2OH + H_2O$$

Temperature: 130-160 °C
Pressure: 1000 psig
Rate: 2-6 mol L^{-1} h^{-1}
Selectivity: **Up to 85 %**

US 4,594,463 1986 to Union Carbide
US 4,727,200 1988 to Union Carbide

EXAMPLE

Catalyst Charge:

Rh(CO)2(acac)	1 mmol
$Ph_2P(CH_2)_3PPh_2$	1 mmol
$RuCl_3 \cdot 3H_2O$	4 mmol
CH_3I	40 mmol

Reaction Conditions:

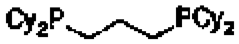
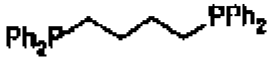
MeOH	40 ml.
Pressure	1000 psig $2H_2$/CO
Temperature	140°C
Time	2.5 h

Conversion: 60-70 %

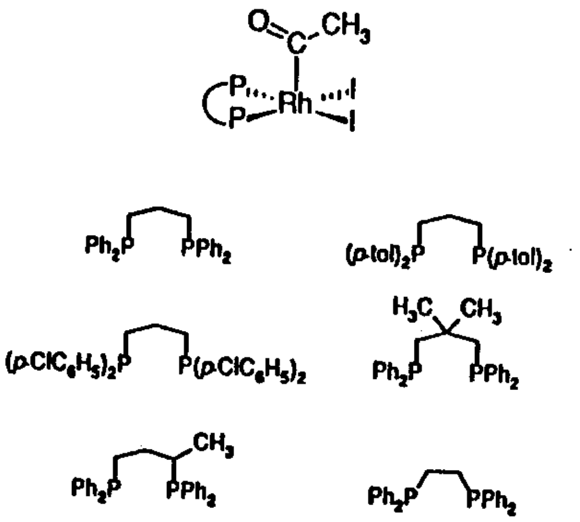
Selectivity: 85 % Total Ethanol
15 % Total Acetic Acid

Diphosphine modified rhodium catalysts reductively carbonylate methanol at low pressure and temperature with rates that rival those of the best cobalt catalysts

REACTION SELECTIVITY IS HIGHLY DEPENDENT ON THE DIPHOSPHINE LIGAND

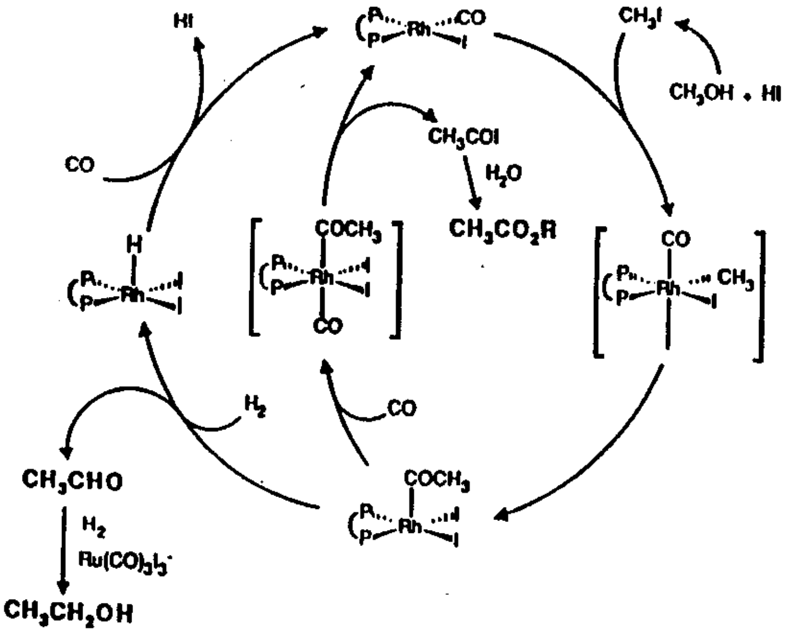
Diphosphine	*Selectivity*
	80 %
	4 %
	26 %
	4%
	20 %
2 PPh_3	6%

CRYSTALLINE ACETYL COMPLEXES ARE ISOLABLE AFTER CATALYSIS



- All complexes isolated and characterized by ^1H and ^{31}P NMR, IR, and elemental analysis.
- These complexes account for > 95 % of the rhodium and diphosphine charged to the reactor.
- These complexes can be reused for catalysis and *again* be isolated in high yield.

PROPOSED REACTION MECHANISM



Methanol Homologation - Conclusions

- Novel system with superior performance to previously known systems.
- Diphosphine ligands stabilize rhodium acyl complexes under catalytic conditions.
- Kinetic, mechanistic, and labeling studies have been used to elaborate the reaction mechanism. All steps of the proposed mechanism have been verified.
- Catalytic reactions studied only in small-scale batch reactions.
- Catalyst stability appears good in these tests.
- Significant improvements in rate/productivity required.
- Experimental work concluded until further concepts for catalyst improvement developed.

Direct Syngas Conversion with Homogeneous Catalysts

- Homogeneous ruthenium catalysts previously found to be active.
- Novel catalyst additives found which improve catalyst activity and selectivity to C_2+ alcohols.
- Improved activity allows operation at lower pressure.
- U. S. patent application filed (1988).

Effects of Catalyst Additives

Mol/l/hr		
Total Rate	C_2+ Rate	Additives
1.9	0.8	KI
4.1	1.9	KI, A16, A92
6.7	2.5	LiI, A16, A111

All runs at 5000 psi 1:1 H_2/CO, 230°C with Ru catalyst, NMP or DMI solvent.

Effects of Reaction Pressure

	Mol/l/hr	
Pressure, psi	Total Rate	C_2+ Rate
5000	6.7	2.5
4000	6.4	2.2
3000	4.8	1.0

All runs with 1:1 H_2/CO, 230°C with Ru catalyst, LiI, A16, A111 additives, DMI solvent.

Recent Experiments with the Ruthenium-Based Homogeneous System

- A number of additives tested for their potential as rate or selectivity promoters.
- Most of the additives tested had negative effects on activity.
- Ratio of higher alcohols to methanol can be increased significantly by longer reaction times (greater contact time).

Effect of Reaction Time on Product Selectivity

Reaction Time, Hrs.	1.5	3.0
Methanol, g	5.6	4.9
Ethanol, g	5.7	10.2
n-Propanol, g	0.9	2.1
n-Butanol, g	0.4	1.6
Total Rate, M/l/hr	5.9	4.04
C_2+ Alcohols, wt %	43	61

Conditions: 4.7 mmol $Ru_3(CO)_{12}$, 7 mmol A16, 1 mmol A9, 30 mmol KI, 93 mmol A93, 38 mL DMI, 5000 psi 1:1 H_2/CO, 230°C.

Direct Syngas Conversion with Homogeneous Catalysts

Experimental Status

- Studied in small-scale batch reactions; 35-75 mL total solution.
- Substantial improvements in ruthenium catalyst activity at lower pressures attained.
- Further enhancements selectivity to higher alcohols attained.
- Improvements in activity needed.
- Experimental work being suspended until new approaches are identified.

Direct Syngas Conversion with Heterogeneous Catalysts

- Molybdenum sulfide-based catalysts being investigated.
- Alkali-promoted MoS_2 catalysts can produce up to 85% C_1 - C_4 linear alcohols.

	K-MoS_2	**Target**
Rate to Alcohols	15-20 lb/cf/hr	>25 lb/cf/hr
% Oxygenates	70-85	>85
Wt.% C_2+ Alcohols	35-45	50

Typical conditions: 1200 psi, 300°C, 6000 GHSV

Objectives

- Obtain increased activity.
- Gain information on catalyst stability.
- Reduce methane formation.

Approaches

- Understand present catalysts - physical factors affecting performance.
- Study alternative catalyst preparations.
- Explore modifications of the catalyst.

Test Facilities

- U-Tube microreactors, continuous flow without recycle.
- 1-3 cc catalyst charge.
- Liquids condensed and analyzed by GC.
- Effluent gas analyzed directly by GC.

Alkali Impregnation Step Investigated

- High potassium levels needed for good selectivity to alcohols.
- Lowers surface area: 65 m^2/g to 5 m^2/g.
- Potassium acetate wets catalyst surface and appears to fill most of the small pores.
- Leaching with water removes the potassium and restores most the the original surface area, even with used catalysts.

Effects of Potassium Loading

K / Mo	Alcohol Rate	Select to HC	C_2 / C_2+	Schulz-Flory alpha alcohols	Schulz-Flory alpha hydrocarbons
0.09	4.93	87.9	50.6	0.356	0.405
0.1	7.75	78.3	59.	0.405	0.376
0.2	18.4	25.7	71.9	0.228	0.223
0.35	19.1	20.9	78.6	0.210	0.141

Evaluations at 300°C, 1200 psi, GHSV = 6000, $H_2/CO = 1$.

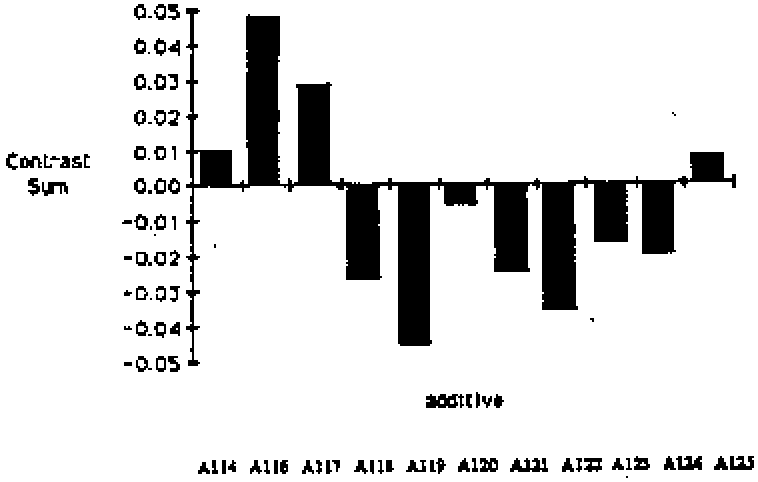
Some Approaches Investigated

- Standard procedure involves precipitation of ammonium thiomolybdate from ammonium paramolybdate and H_2S, decomposition to amorphous MoS_2, and impregnation with K salt.
- Various procedures investigated for preparation of ammonium tetrathiomolybdate (ATM) precursor (temperature, time, solvent, etc.).
- Potassium incorporated during the ATM precipitation step.
- Catalysts prepared by low temperature calcination of ATM to produce MoS_3, then impregnated and calcined.
- Catalysts prepared by precipitation of ATM to give finer particles.
- Catalysts prepared from $(NH_4)_2MoO_2S_2$.
- KMo_6S_8 (Chevrel phase) used as catalyst precursor.

Modified Catalysts

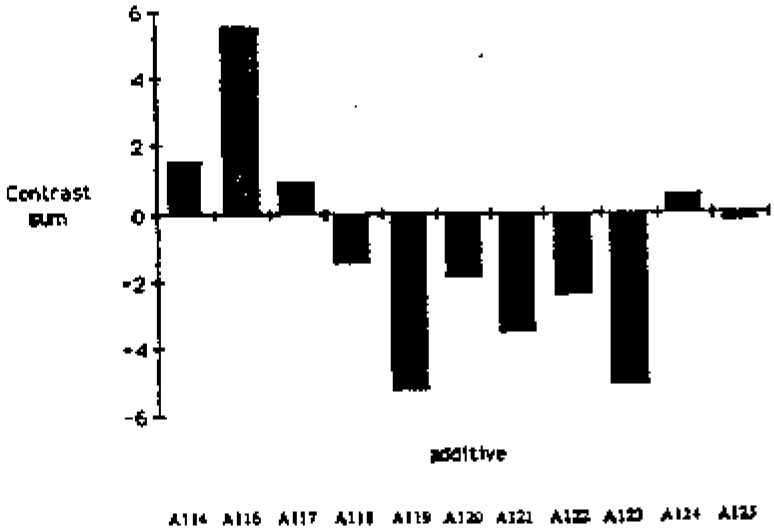
- Catalyst supports investigated, especially high surface-area carbon.
- Carbon-supported K-MoS_2 show lower activity than the bulk catalyst, although rates on a contained Mo basis are higher.
- Metal additives investigated in a statistically designed approach.
- Eleven additives investigated at two levels in 12 experiments.

Effects of Additives on Rate to Alcohols (lb/kg/hr)



(Contrast sum represents the total difference in rates between catalysts containing the high level of the component and those containing the low level of the component.)

Effects of Additives on Selectivity to Alcohols (Wt %)



Modified Catalyst Composition and Preparation

- A new procedure needed to be developed for preparation of A116-containing catalysts.
- These modified catalysts appear to have a 10-15% advantage in rate over previous best catalysts.
- Product selectivities are not negatively affected.

Direct Syngas Conversion with Heterogeneous Catalysts

Experimental Status

- No direct correlation observed between catalyst surface area and activity.
- No significant improvements attained through modified preparations of K-MoS_2 catalyst.
- Incorporation of metal additive A116 appears to significantly improve the activity.
- Experimental approaches with other heterogeneous catalysts are being formulated and will be pursued in the next year.