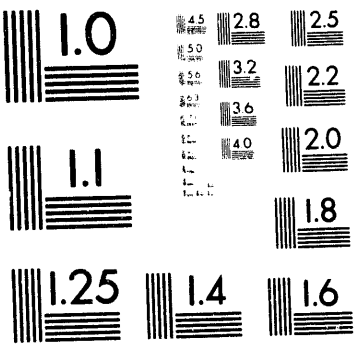
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1 of 1

BNL-49390

DEVELOPMENT OF NON-PETROLEUM FEEDSTOCKS--

THE ROLE OF CATALYSIS

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For Presentation at

WINTER SCHOOL-CUM-WORKSHOP ON

ORGANOMETALLIC CHEMISTRY

(Sponsored by The Department of Science and Technology (DST))
Department of Chemistry
Indian Institute of Technology (IIT) Delhi
New Delhi, India 110016

December 6-8, 1993

INTRODUCTION

A recent report (1) from the Worldwatch Institute emphasizes "Continual Expansion through Sustainable Development" to accommodate projected population increase. Though the emphasis is on renewables (solar, wind, etc.), non-petroleum feedstocks indigenous to developing countries will still play a major role on the future energy science. The utilization of natural gas and coal feedstocks was initiated in the 1970s' in response to volatility in availability and price of petroleum. This concerted effort led to the development of processes based on C_1 chemistry (2) through which synthesis gas (a mixture of CO and H_2) could be catalytically converted to hydrocarbons and oxygenates. The catalytic conversion to hydrocarbons via the Fischer-Tropsch (F-T) reaction (Scheme 1) continues to be of

Scheme 1

$$xCO + yH_2 \longrightarrow \begin{cases} (CH_2)_l + mH_2O + nCO_2 \\ \text{Oxygenates} \end{cases}$$

commercial interest (3) but further improvements in reaction rates and product selectivity are sought. To this effect, recently a liquid phase Fe (slurry) F-T catalyst has replaced the traditional solid Fe (4).

For oxygenates synthesis (Scheme 1), the utilization of organometallic complexes is established. Examples include homogeneously catalyzed commercial synthesis of acetic acid (Monsanto process) and acetic anhydride (Eastman Kodak process) catalyzed presumably by $Rh(CO)_2I_2^-$ species at ~180°C and ~50 atm (5,6). These examples indicate

$$CH_3OH + CO \xrightarrow{Rh} CH_3COOH \qquad (1)$$

$$CH_3CO_2CH_3 + CO \xrightarrow{Rh} (CH_3CO)_2O \qquad (2)$$

that organometallic complexes will find increasing applications as catalysts in new and improved processes.

ONGOING BNL CATALYSIS EFFORT

Since economical processes for direct conversions of coal (direct liquefaction) and natural gas (direct methane conversion) are yet to be targeted for commercial applications, synthesis of oxygenates via the "Indirect Route," i.e. through synthesis gas, is carried out. The stoichiometry of synthesis gas produced from these two sources is of interest:

$$\text{Coal} \xrightarrow{\text{Gasification}} CO + xH_2 + CO_2 \; (x < 1) \qquad (3)$$

$$CH_4 \xrightarrow{\text{Partial Oxidation}} CO + 2H_2 \qquad (4)$$

$$CH_4 \xrightarrow{\text{Steam Reforming}} CO + 3H_2 \qquad (5)$$

Thus, the H_2/CO ratio varies from < 1 for coal-derived syngas to 3 for syngas from steam-reforming of natural gas. In order to maximize C utilization, the Catalyst-By-Design (CBD) approach for synthesis of methanol and higher oxygenates is ongoing under the "BNL Catalyst Development" program. The central theme of this effort is to achieve:

- ideal syngas source/product match
- favorable thermodynamic parameters
- high activity
- enhanced product selectivity
- liquid phase performance
- one-step synthesis
- low temperature and pressure operation
- better process economics

Since methanol (see for example, Equations 1 and 2) and methyl formate are two oxygenates which are potential building blocks for several downstream processes (2), improved syntheses of these molecules is of interest. Described here is a study initiated to understand chemistry associated with methyl formate synthesis.

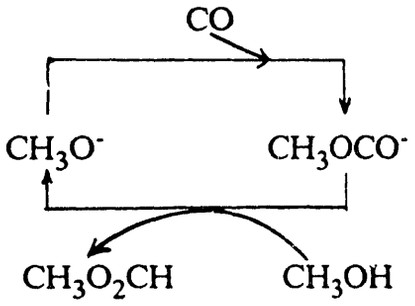
Homogeneously catalyzed synthesis of methyl formate via carbonylation of methanol has been studied (7):

$$CH_3OH + CO \xrightarrow[<100°C]{MOR} CH_3O_2CH \qquad (6)$$

(MOR is alkali metal alkoxide)

and the following two-step mechanism is proposed (Scheme 2):

Scheme 2



Carbon monoxide is activated by alkoxide anion to generate an alkyl formate anion followed by protonation of this anion with alcohol. Obviously, bases other than alkoxides must work if proton abstraction from the solvent (alcohol) is feasible. In our study, representative bases used, other than alkoxides, are listed in Table 1. As expected, no methyl formate is produced in the absence of a catalyst (Run 1) whereas K_2CO_3 affects this synthesis (Run 2). The activity observed with $KHCO_2$, a weak base, is of interest (Run 3).

Potassium methyl carbonate ($KOCO_2Me$), synthesized by the reaction of KOMe with CO_2, is active (Run 4) and establishes the possibility of using CO feedstock containing CO_2. This aspect is being studied in detail.

A better understanding of this simple carbonylation process (Equation 6) is critical to designing a homogeneous catalyst capable of synthesizing methyl formate and/or methanol directly from synthesis gas. A heterogeneous/homogeneous combination catalyst (Cu chromite/RO^-) is already known (8) but an elusive homogeneous system is the goal. To date, substantial breakthrough has been achieved at BNL in the design of such a catalyst.

Table 1

Base Catalyzed Synthesis of Methyl Formate via Carbonylation of Methanol

Run	Catalyst, mmol	Reaction Time, min	MF Yield, mmol
1	---	70	0
2	K_2CO_3, 20	91	3.4
3	$KHCO_2$, 20	40	6
4	$KOCO_2Me$, 20	60	15

Solvent: 60% Peg-400/40% MeOH = 120 mL; Syngas: H_2/CO = 65%/35%; T: 130°C; P_I: 130 psig; Stirring Speed: 1200 rpm.

ACKNOWLEDGEMENTS

The author thanks the Electric Power Research Institute (EPRI RP 8003-8) and Department of Applied Science, BNL (US DOE Contract No. DE-AC02-76CH00016) for the financial support.

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