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CATALYTIC REDUCTION OF CARBON MONOXIDE-- SELECTIVE SYNTHESIS OF C1 AND HIGHER OXYGENATES

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ABSTRACT

The "BNL Homogeneous Catalyst Development Program" to convert synthesis gas to oxygenates is aimed at utilizing domestic coal and abundant natural gas via the indirect route. To this effect, the synthesis of methanol utilizing the promising Liquid Low Temperature Methanol (LLTMeOH) technology is of interest due to benefits inherent to this process: the synthesis takes place under thermodynamically favorable temperature of < 150°C resulting in > 90% syngas conversion per pass with > 95% selectivity to methanol. An extension of this concept resulted in the development of a new catalyst (LLTMF) for the synthesis of methyl formate, a C_2 oxygenate. The ultimate aim is to identify the ideal synthesis gas source/product match thereby enhancing carbon conversion and product selectivity. The latest results obtained with the LLTMF catalyst are presented. The mechanistic implications of base catalyzed methanol carbonylation reaction to produced methyl formate and its relevance to the LLTMF system are described.

INTRODUCTION

Though a concerted effort in the development of processes based on C1 chemistry was initiated in the U.S. after the first energy crunch in the 1970s (1,2), interest in this approach slowly waned due to availability of plentiful inexpensive petroleum in the world market. With revision of environmental laws in the past few years that curb burning of fossil fuels and expand the role of oxygenates, development of processes based on coal and natural gas is being revitalized. To name a few, the C1 effort has resulted in coal to acetic anhydride process (3) and methanol to acetic acid process (4). More processes are likely to come on-stream in the coming years (5,6). To affect oxygenates synthesis, the chemistry associated with synthesis gas catalysis is being studied at Brookhaven National Laboratory (BNL) under the "BNL Catalysts Development Program." The thrust of this approach is:

- New catalysts development to attain higher rates and product selectivity.
- Liquid phase performance for better process heat management.
- Syngas source/product match to maximize carbon utilization.
- Better process economics.

The result of this BNL effort is the development of a family of catalysts for methanol synthesis under mild conditions (7,8). Specifically, a liquid phase catalyst, formed by dissolving

$$CO + 2H_2 \xrightarrow{Cat.\ 1} CH_3OH \qquad (1)$$

a nickel complex and a base in a high boiling solvent and methanol, affects > 90% syngas conversion per pass with > 95% selectivity to methanol. If pilot studies are successful, this process is of commercial interest due to favorable economics. Several aspects of this system have appeared (9,10,11). Methanol is of interest due to its potential use as a neat fuel, fuel additive as well as a building block for several downstream process.

In an effort to enhance carbon conversion of coal-derived synthesis gas, a process to synthesize methyl formate is under development at BNL (9-12).

$$2CO + 2H_2 \xrightarrow{Cat.\ 2} CH_3O_2CH \qquad (2)$$

It is of interest to note that methyl formate, a C2 molecule, is a promising building block (13,14). This paper deals with the BNL approach and its relationship to existing literature.

METHODOLOGY

All batch runs were conducted in a 0.5 L AE Zipperclave stirred reactor. Data collection and analysis procedures are described elsewhere (9). Of particular interest is methanol/methyl formate separation and quantification that was achieved on a Perkin-Elmer 8500 gas chromatograph in a TCD mode and fitted with a 10′ × 1/8″ (80/100) chromosorb 101 column.

For gas-phase infrared studies, a 1-inch cylindrical cell fitted with NaCl windows was used. Methyl formate concentration as a function of time was monitored by periodically analyzing gas phase of the reactor during a run.

RESULTS AND DISCUSSION

BNL Data

Methyl formate is commercially manufactured via carbonylation of methanol:

$$CH_3OH + CO \overset{RO^-}{=} CH_3O_2CH \qquad (3)$$

$$\Delta H^\circ = -29.1 \text{ kJ/mol}$$

Thus the overall transformation of syngas to methyl formate (Equation (2)) is a combination of Equations (1) and (3) but occurs in two distinct processes. The BNL approach utilizes a catalyst comprised of nickel/base for activating CO and H_2 to synthesize methyl formate in one-step. A few preliminary runs showed that with this catalyst in p-Dioxane/MeOH solvent, methyl formate selectivity varied from 23% to 78% between 80° - 112°C under syngas (H_2/CO) of 1:1 ratio (10). This approach represents a promising technology because the low reaction temperature employed is favorable for equilibrium (3) to maximize methyl formate yield. The following features of this Liquid Low Temperature Methyl Formate (LLTMF) technology, developed at BNL, are of interest:

- Synthesis of methyl formate in one-step directly from synthesis gas.
- Catalyst system employed consists of nickel/base combination and produces methyl formate under mild conditions.
- Selectivity to methyl formate was up to 78 mol%.
- Methanol was the main by-product.
- The process utilizes twice as much carbon compared to that used in methanol synthesis.

Encouraged by these results, the data base was expanded to establish the effect of reaction parameters. The data are presented in Table 1. In tetrahydrofuran (THF), 84% syngas was consumed in 37 minutes yielding a rate of 55 mmol/min and 41 mol% selectivity to methyl formate with the rest being methanol (Run 1). A continuation of previous work was done in

p-Dioxane/MeOH solvent mixture and with 1/1 (H_2/CO) syngas (Runs 1-4). Runs 1 and 2 were conducted to establish the effect of stirring speed. The data show that rates were not diffusion controlled. From these data, run reproducibility was also established (78% syngas conversion in 75 minutes in both runs). On lowering the temperature to 80°C, methyl formate productivity increased to 73 mol% (Run 3). During this run, 65% syngas conversion was achieved in 145 minutes. When the catalyst loading was increased to 6%, only a slight increase in syngas conversion (from 78% in 75 minutes during Run 1 to 85% in 15 minutes) was obtained, but the rate increased by a factor of five (Run 4). Methyl formate selectivity also increased to 40%. With syngas containing high CO (H_2/CO = 37%/63%), selectivity to methyl formate approached 100%, but rate was slow (50% syngas conversion in 120 minutes in Run 5). In tetrahydrofuran solvent containing no initial methanol, the rate and methyl formate selectivity was somewhat higher (Run 6). During this run, 84% syngas was consumed in 37 minutes.

The above data unequivocally establish that the BNL approach to produce methyl formate directly from synthesis gas is workable. The chosen reaction conditions are such that maximization of methyl formate yield is thermodynamically allowed. More runs are under way to generate a kinetic model for the system.

Mechanistic Studies

As part of the LLTMF technology development at BNL, an effort is dedicated to establishing the mechanism of reaction (2). The carbonylation of methanol reaction (3) has been studied by several groups (15), and the following mechanism is proposed:

$$CO + RO^- \rightarrow ROCO^- \qquad (4)$$

$$ROCO^- + R'OH \rightarrow RO_2CH + R'O^- \qquad (5)$$

Thus Reaction (3) is a sum of (4) and (5) where carbon monoxide is activated by alkoxide anion to generate an alkyl formate anion followed by protonation with alcohol. To understand the contribution of these reactions to the LLTMeOH system, a study was carried out at BNL with different bases listed in Table 2. No methyl formate was produced when methanol was heated under syngas (H_2/CO = 2/1) at 130°C (Run 7, blank). In the presence of potassium carbonate, methyl formate was produced (Run 8). In this run, the pressure maximized to 249 psig at 130°C and the gas phase of the reactor contained 4% CO_2. With potassium formate, no CO_2 was detected but the final solution contained 6 mmol methyl formate (Run 9). With potassium methyl carbonate, 15 mmol methyl formate was produced (Run 10). In this run, the gas phase analyzed for 5.1% CO_2 (12 mmol) corresponding to about 60% carbonate decomposition. Methyl formate synthesis with bases other than alkoxides has been previously shown to be

effective (16): in this study, 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU), K_2CO_3, $KHCO_3$, $KOCO_2Me$, Na_2CO_3, and others were tested. It appears that these bases work by:

- abstraction of a proton from methanol solvent to generate methoxide base.
- generated base catalyzes methyl formate synthesis

$$MeOH + Base \rightarrow {}^{-}OMe + Base.H^{+} \qquad (6)$$

In our runs (Table 2), catalysis by a weak base ($KHCO_2$) is of interest. In any case, more data need to be taken to establish a data base.

To monitor the reaction sequence proposed (Reactions (4) and (5)), a run was conducted in 50% Triglyme/50% MeOH solvent with potassium methoxide (KOMe) catalyst under 1/1 (H_2/CO) syngas.

Interestingly, when the reactor was heated at 130°C under 500 psig syngas, a sharp gas uptake was observed in the first few minutes. Thereafter, the pressure stabilized. The gas-phase infrared was used to follow methyl formate formation (Figure 1). It is interesting to note that no methyl formate was present even after 24 minutes of heating at 130°C. Slowly, the peak attributed to methyl formate peaked after almost three hours. These results indicate that a fast gas uptake initially observed is due to Reaction (4). The protonation reaction (Reaction (5)) is extremely slow under these conditions (Rate Determining Step). Further work is in progress to establish the mechanism operating in the LLTMF system and its relationship to the above data.

CONCLUSIONS

A one-step synthesis of methyl formate, a C2 oxygenate, has been developed at BNL. The following features of the LLTMeOH technology and related studies are of interest:

- The BNL approach exemplifies a synergistic effect of two combined catalysts.
- The chosen reaction conditions favor methyl formate synthesis. The only identified by-product is methanol.
- The effect of stirring speed, temperature, solvent, catalyst loading, and syngas composition is noted. Of particular interest is a run with H_2/CO = 37%/63% in which methyl formate selectivity approached 100%.
- Bases (K_2CO_3, $KHCO_2$, $KOCO_2Me$) other than alkoxide have been used for methyl formate synthesis.
- A gas phase infrared mechanistic study of methanol carbonylation reaction, carried out with methoxide catalyst at 130°C under 1/1 (H_2/CO) syngas, showed that the fast alkyl formate anion formation was followed by an extremely slow protonation step. It appears that under these conditions, protonation step is rate determining (RDS).

- This approach results in enhancing carbon conversion of syngas derived from coal or other sources that produce CO-rich gas.

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Table 1

Effect of Reaction Parameters on Rate
of Methyl Formate Synthesis with LLTMeOH Catalyst

Total Solvent Volume: 100 mL
Stirring Speed: 1200 rpm

Run	Syngas		Solvent	% Catalyst Loading	Stirring Speed rpm	T,°C	Batch Rate[1] mmol/min	MF[2] Selectivity mol%
	%H_2	%CO						
1	50	50	98% p-Dioxane 2% MeOH	3	1600	110	22	34
2	50	50	" "	3	800	110	20	35
3	50	50	" "	3	1200	80	4	73
4	50	50	" "	6	1200	110	100	40
5	37	63	96% p-Dioxane 4% MeOH	3	1200	80	3	>100[3]
6	50	50	THF	3	1200	100	55	41

[1]Syngas consumption.
[2]Methyl formate.
[3]Some of initial methanol was also consumed.

Table 2

Base Catalyzed Synthesis of Methyl Formate via Carbonylation of Methanol

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

Run[1]	Catalyst, mmol	Reaction Time, min	MF Yield, mmol
7	---	70	0
8	K_2CO_3, 20	91	3.4
9	$KHCO_2$, 20	40	6
10	$KOCO_2Me$,[2] 20	60	15

[1]During all these runs, the final solution was clear yellow.
[2]Potassium methyl carbonate.

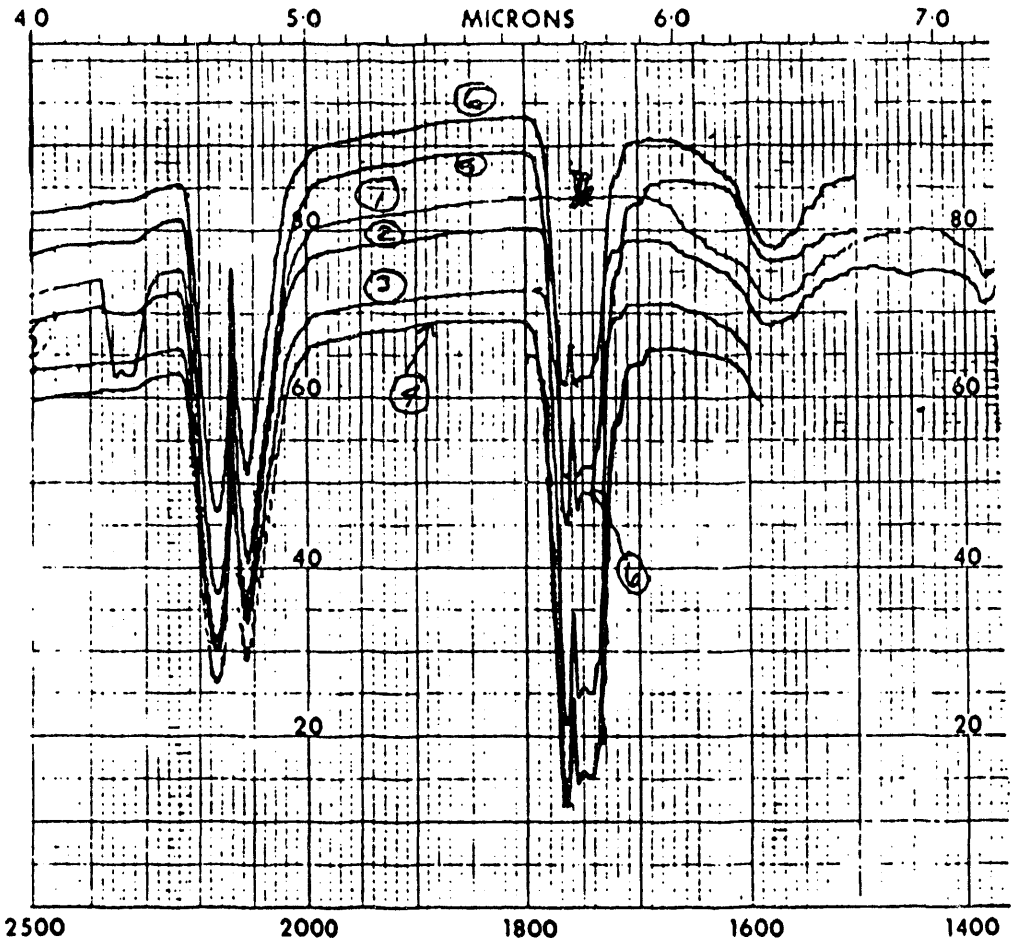

Figure 1. Gas Phase Infrared Monitoring of Methyl Formate Synthesis at T = 130°C with Syngas (H_2/CO = 1/1). 1) 24 min., 2) 49 min., 3) 110 min., 4) 166 min., 5) 173 min., 6) after cooling the reactor to 25°C.

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