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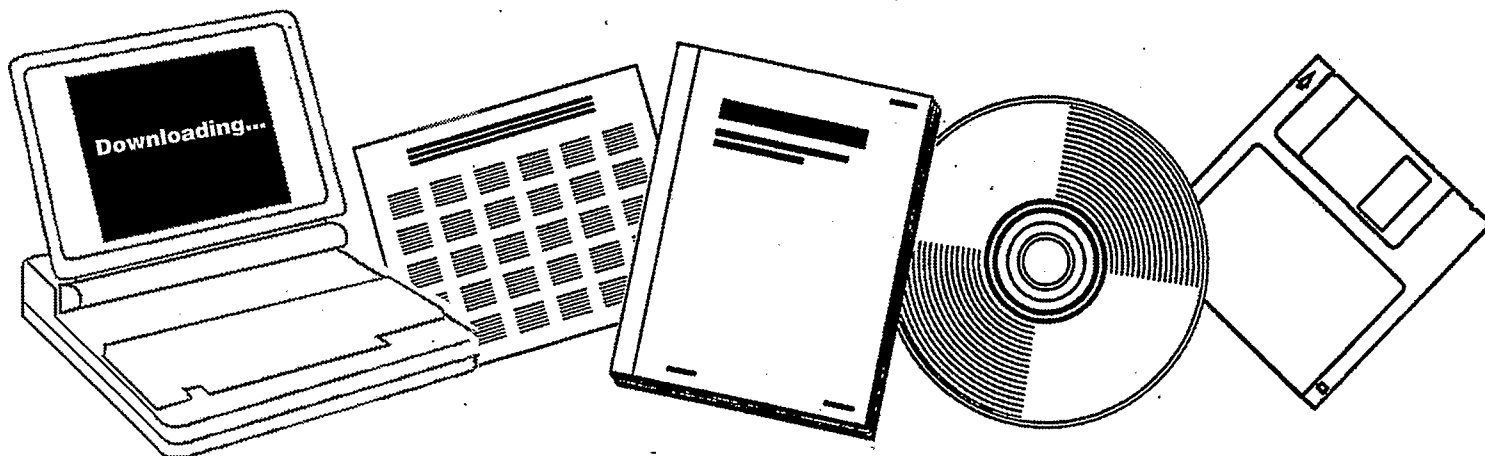
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**PROBE MOLECULE STUDIES: ACTIVE SPECIES IN
ALCOHOL SYNTHESIS. QUARTERLY REPORT NO. 2,
JANUARY 1991-MARCH 1991**

**PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
AND PETROLEUM ENGINEERING**

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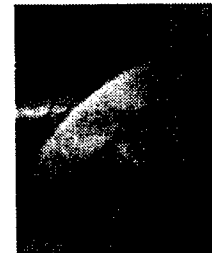
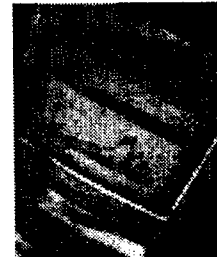
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**PROBE MOLECULE STUDIES:
ACTIVE SPECIES IN ALCOHOL SYNTHESIS**

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2nd Quarterly Report
January 1991 - March 1991

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1. OBJECTIVE AND PLAN OF WORK

The goal of this research is to develop a better understanding of the mechanisms of formation of alcohols and other oxygenates from synthesis gas. Various probe molecules will be added in situ during the reaction to help delineate reaction pathways and identify reaction intermediate species. We will be specifically looking at how the species generated by these probe molecules interact with surface species present during oxygenate formation. Following the incorporation of these species in the reaction products will help us to understand issues including the role of promoter species, the nature of intermediates, the CO insertion reaction, and the apparent A-S-F product distribution of oxygenates over supported metals.

CO hydrogenation reactions will be carried out both in the presence and absence of the probe molecule under conditions which favor the formation of oxygenated products (pressure 1-10 atm, temperature 423-523 K). A reaction and analysis system capable of carrying out the experiments for this research has been set up.

Catalyst studied will include silica-supported Pd and Rh with and without alkali or oxide promoters. The commercially important Cu/ZnO system for methanol synthesis will also be studied for comparison and to see what probe molecule addition can reveal about this type of catalyst.

Nitromethane will be one of the probe molecules which will be studied since it was demonstrated in a previous study that it

is effective as a source of CH_2 groups. Changes in the product distribution of CO hydrogenation brought about by CH_3NO_2 addition took place without any significant disturbance of the main reaction pathways leading to hydrocarbon formation. Furthermore, the fragments generated by the decomposition of this probe molecule did not poison the catalyst.

Other probe molecules such as some acetylenic compounds will also be used. These compounds have been shown by other workers to be effective as a source of chain initiators.

2. SUMMARY OF PROGRESS

A well characterized commercial methanol synthesis catalyst has been selected. CO hydrogenation reaction was carried out over this catalyst under various conditions of pressure and temperature in order to determine the optimum conditions for our experiments.

A silica-supported Pd catalyst for methanol synthesis was also prepared.

3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Catalyst Selection and Preparation

Cu/ZnO has been extensively studied for both methanol and higher alcohol formation. The addition of probe molecules may

provide a better understanding of a number of issues including the type of active sites and the role of CO_2 .

A well characterized Cu/ZnO methanol synthesis catalyst was selected for this study. Its characteristics are as follows:

Properties the Commercial Methanol Synthesis Catalyst

Manufacturer : United Catalysts, Inc.

Composition	CuO	:	55%
	ZnO	:	36%
	Al_2O_3	:	8%
	SiO_2	:	1%

Specific Area : $92 \text{ m}^2/\text{g}$

Pore Volume : $0.43 \text{ cm}^3/\text{g}$

Particle size : sieved to -140 mesh

The second methanol synthesis catalyst to be used in this study is a SiO_2 -supported Pd catalyst. Reaction conditions will be adjusted so that the catalyst selectively produces methanol.

SiO_2 was used as a support. A 10 g batch of supported Pd catalyst was prepared by incipient wetness impregnation using an aqueous solution of Palladium (II) nitrate hydrate ($\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$) (Aldrich). A nominal 3 weight % Pd loading was used. The catalyst precursor was then dried overnight in air at 80°C . Finally, the catalyst is reduced in flowing hydrogen at 400°C for 16 h.

The catalyst will be characterized by hydrogen and CO static

chemisorption to determine the metal dispersion. Depending on the reaction results which will be obtained with this catalyst, a small batch will be promoted with an alkali or a rare earth oxide to improve its catalytic properties for methanol synthesis.

Reaction Studies

During this quarter, much of the time spent on the reaction system was used to calibrate the gas chromatograph and develop a procedure for reaction product analysis.

Some preliminary CO hydrogenation reactions were carried out over the Cu/ZnO catalyst in order to determine optimum conditions for this study. 0.5 g of catalyst was used for this reaction.

First, the catalyst which was obtained in its unreduced form had to be reduced to its active state before reaction. Since the reduction process is highly exothermic, the catalyst is reduced at 4 atm very slowly with a dilute mixture of hydrogen (5%) in helium flowing at 100cc/min to avoid local hot spots and sintering. The temperature is raised slowly (0.5°C/min) to 400°C, between each 100°C step at which it was held for 30 min. After the last 30 min step at 400°C the catalyst was cooled down to reaction temperature.

In order to obtain a satisfactory methanol yield under moderate temperature and pressure conditions different from those used in industrial application, CO hydrogenation reaction was carried at 25 atm pressure and temperatures ranging from 200 to 250°C. A CO/H₂ ratio of 1:1 and a total reactant flow rate of 180

cc/min were used. Preliminary results indicate that CO conversion between 0.5-1% may be obtained under these conditions. More reaction experiments are being run to optimize these conditions and check for reproducibility before addition of probe molecules. Details of the reaction results will be reported in the next quarterly report.

4. PLANS FOR THE NEXT REPORTING PERIOD

In the next quarter, more methanol synthesis reactions over the commercial Cu/ZnO catalyst will be carried out to determine the optimum conditions for a satisfactory yield of methanol.

1-Hexyne will be used as a probe molecule in the first stages of this study. The probe molecule will be added to the reactant flow after optimum conditions were established with just CO and H₂.

The Pd/SiO₂ catalyst will be characterized by H₂ and CO chemisorption.

CO hydrogenation will be carried out over the latter catalyst to adjust the conditions for methanol synthesis.

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