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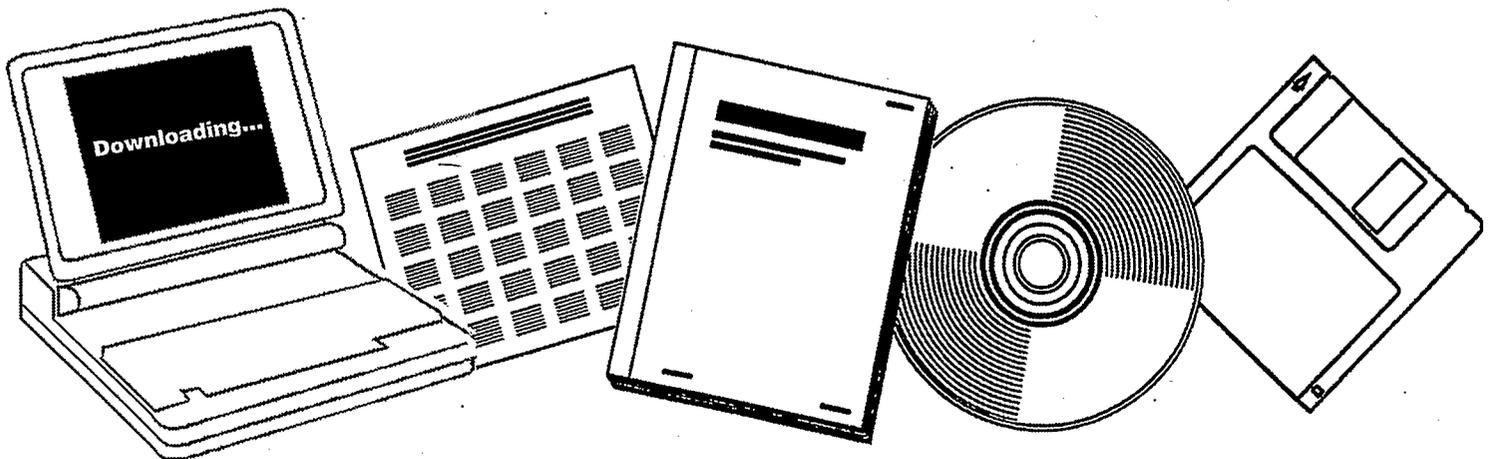
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**EFFECT OF CHEMICAL ADDITIVES ON THE  
SYNTHESIS OF ETHANOL. TECHNICAL PROGRESS  
REPORT NO. 4, JUNE 16, 1988--SEPTEMBER 15,  
1988**

**AKRON UNIV., OH. DEPT. OF CHEMICAL  
ENGINEERING**

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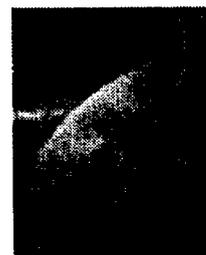
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THE EFFECT OF CHEMICAL ADDITIVES ON THE STABILITY OF ETHANOL

SCIENCE & APPLICATIONS  
ACQUISITION & ASSISTANCE

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Technical Progress Report 4  
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by

Steven S.C. Chuang

Department of Chemical Engineering  
University of Akron  
Akron, OH 44325

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## SUMMARY

The objective of this research is to elucidate the role of various chemical additives on ethanol synthesis over Rh- and Ni-based catalysts. Chemical additives used for this study will include S, P, Ag, Cu, Mn, and Na which have different electronegativities. The effect of additives on the surface state of the catalysts, heat of adsorption of reactant molecules, reaction intermediates, reaction pathways, reaction kinetics, and product distributions is/will be investigated by a series of experimental studies including temperature programmed desorption, infrared study of NO adsorption, reactive probing, steady state rate measurement, and transient kinetic study. A better understanding of the role of additive on the synthesis reaction may allow us to use chemical additives to manipulate the catalytic properties of Rh- and Ni-based catalysts for producing high yields of ethanol from syngas.

## RESULTS TO DATE

During the fourth quarter of the project, a high pressure infrared (IR) reactor cell capable of operating at 260°C and 50 atm was constructed. The schematic diagram of the reactor cell is shown in Figure 1. Infrared spectroscopic studies of CO adsorption at various pressures and temperatures were carried out for Rh/SiO<sub>2</sub> and Ag-Rh/SiO<sub>2</sub>. In-situ infrared studies of CO hydrogenation and

ethylene addition were conducted at 240°C and pressures from 30 to 430 psig. These studies are aimed at developing a better understanding of the effect of Ag on CO adsorption and reaction intermediates during the synthesis of oxygenated hydrocarbons. Ag additive is generally considered as an inert additive on the Rh catalyst due to their similarity in electronegativity (1). It has been shown that methanation decreases linearly with the increasing Ag coverage on the Rh surface. In contrast, our preliminary study on Ag-Rh/SiO<sub>2</sub> showed that Ag is an effective promoter in enhancing C<sub>2</sub> oxygenate selectivity in CO hydrogenation. To elucidate the role of Ag on the synthesis, CO adsorption, CO hydrogenation, and ethylene addition over Rh/SiO<sub>2</sub> and Ag-Rh/SiO<sub>2</sub> were studied in a high pressure IR reactor cell. Reported here are the results of in situ infrared observations.

## EXPERIMENTAL

### Catalyst Preparation

Three wt. % Rh/SiO<sub>2</sub> was prepared by impregnation of SiO<sub>2</sub> (Strem) using rhodium nitrate. Ag-Rh/SiO<sub>2</sub> was prepared by coimpregnation of SiO<sub>2</sub> using rhodium nitrate and silver nitrate. Hydrogen flow chemisorption and hydrogen temperature programmed desorption technique were used to determine metal surface area of the catalysts.

### Reaction Studies

CO hydrogenation was carried out in an infrared reactor cell at 240°C and pressures from 30 to 240 psig. The product distribution was determined by a HP-5890A gas chromatograph. Ethylene was added to CO/H<sub>2</sub> reactant mixture after steady state CO hydrogenation. The amount of ethylene added ranged from 2-10 %. Added ethylene serves as a probe molecule to determine the effect of Ag on hydrogenation and CO insertion capabilities of the catalysts. Infrared spectra were measured by a Nicolet 5SXC Fourier transform infrared spectrometer with a DTGS detector. Spectral resolution was fixed at 4 cm<sup>-1</sup>.

### RESULTS AND DISCUSSIONS

The effect of temperature of the infrared spectrum of CO adsorption on Rh/SiC<sub>2</sub> is shown in Figure 2. At 30°C, the band near 2077 cm<sup>-1</sup> corresponds to linearly bonded CO and the band at 1887 cm<sup>-1</sup> corresponds to bridge-bonded CO. Infrared bands of gas phase CO were not eliminated due to the difficulty in subtracting background CO absorbance exactly from the catalyst absorbance spectrum. As temperature increased to 240°C, the band for linear CO decreased to 2056 cm<sup>-1</sup> and the band for bridge CO decreased to 1844 cm<sup>-1</sup>. Similar temperature effect on the shift of CO adsorption bands has been observed for Rh/Al<sub>2</sub>O<sub>3</sub> under low pressure and temperature conditions (2). Infrared spectra

of CO hydrogenation over Rh/SiO<sub>2</sub> and Ag-Rh/SiO<sub>2</sub> are shown in Figure 3. The band for linear CO on Rh/SiO<sub>2</sub> appears to overlap with gas phase CO. The distinct linear CO band on Ag-Rh/SiO<sub>2</sub> indicates that Ag may promote adsorption of CO in the linear form. It appears that the concentration of linear CO on Ag-Rh/SiO<sub>2</sub> is higher than that of linear CO on Rh/SiO<sub>2</sub>. Ethylene was added as a probe molecule to determine the effect of Ag on the CO insertion. Infrared spectra of reaction of ethylene with syngas are shown in Figure 4. The band for linear CO is not easily discernible on Rh/SiO<sub>2</sub>. The bands near 1920, 2950 and 3120 cm<sup>-1</sup> are the gas phase ethylene. The bands near 1735 and 2985 cm<sup>-1</sup> correspond to propionaldehyde. The major differences in infrared spectrum between these two catalysts are: (1) a distinct linear CO bands on Ag-Rh/SiO<sub>2</sub> and (2) strong bands near 1415 and 1443 cm<sup>-1</sup> on Ag-Rh/SiO<sub>2</sub> which may be assigned to carboxylates.

The general requirements for a catalyst to catalyze the formation of higher oxygenates from syngas are:

- (i) moderate CO dissociation ability permitting the existence of both surface carbon and nondissociatively adsorbed CO the catalyst surface.
- (ii) ability to catalyze CO insertion into C<sub>y</sub>H<sub>x</sub> species.

The distinct linear CO band on Ag-Rh/SiO<sub>2</sub> suggest that the

concentration of linear CO on Ag-Rh/SiO<sub>2</sub> is higher than that of linear CO on Rh/SiO<sub>2</sub>. Ag has essentially little effect on the adsorption state of CO. The enhancement in the activity for CO insertion, when Rh/SiO<sub>2</sub> is promoted with Ag, may be due to the higher concentration of linear CO on Ag-Rh/SiO<sub>2</sub>.

#### REFERENCES

1. Goodman, D. W. in Heterogenous Catalysis (Ed. Shapiro, B. L.) Texas A & M Unil Press 1984.
2. Yates, J. T., Jr. J Chem. Phys. 71 (10) 3908, 1979.

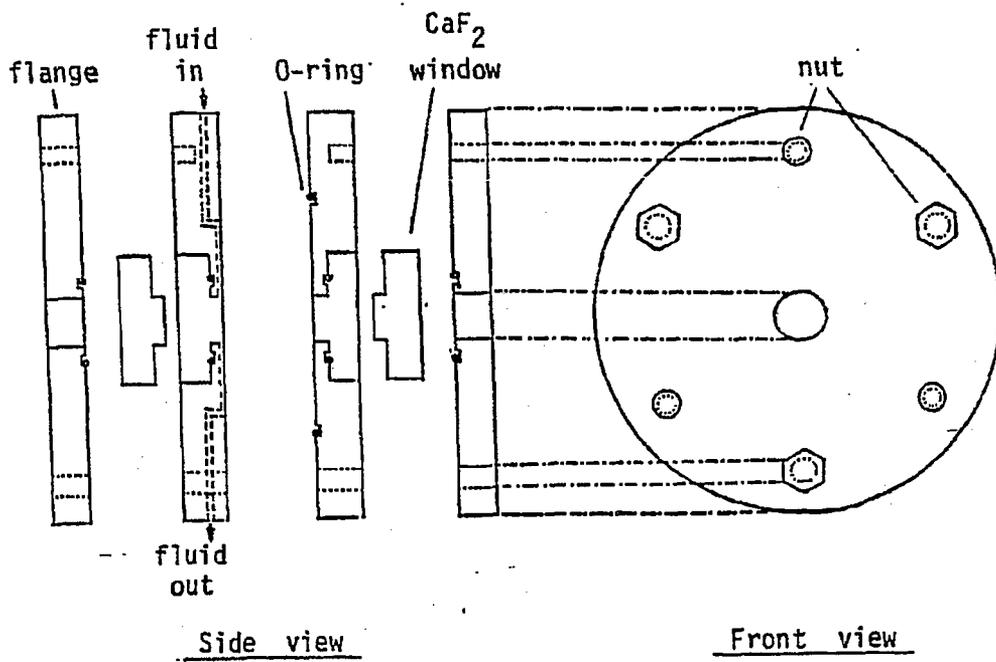


Figure 1. High Pressure and Temperature IR Cell

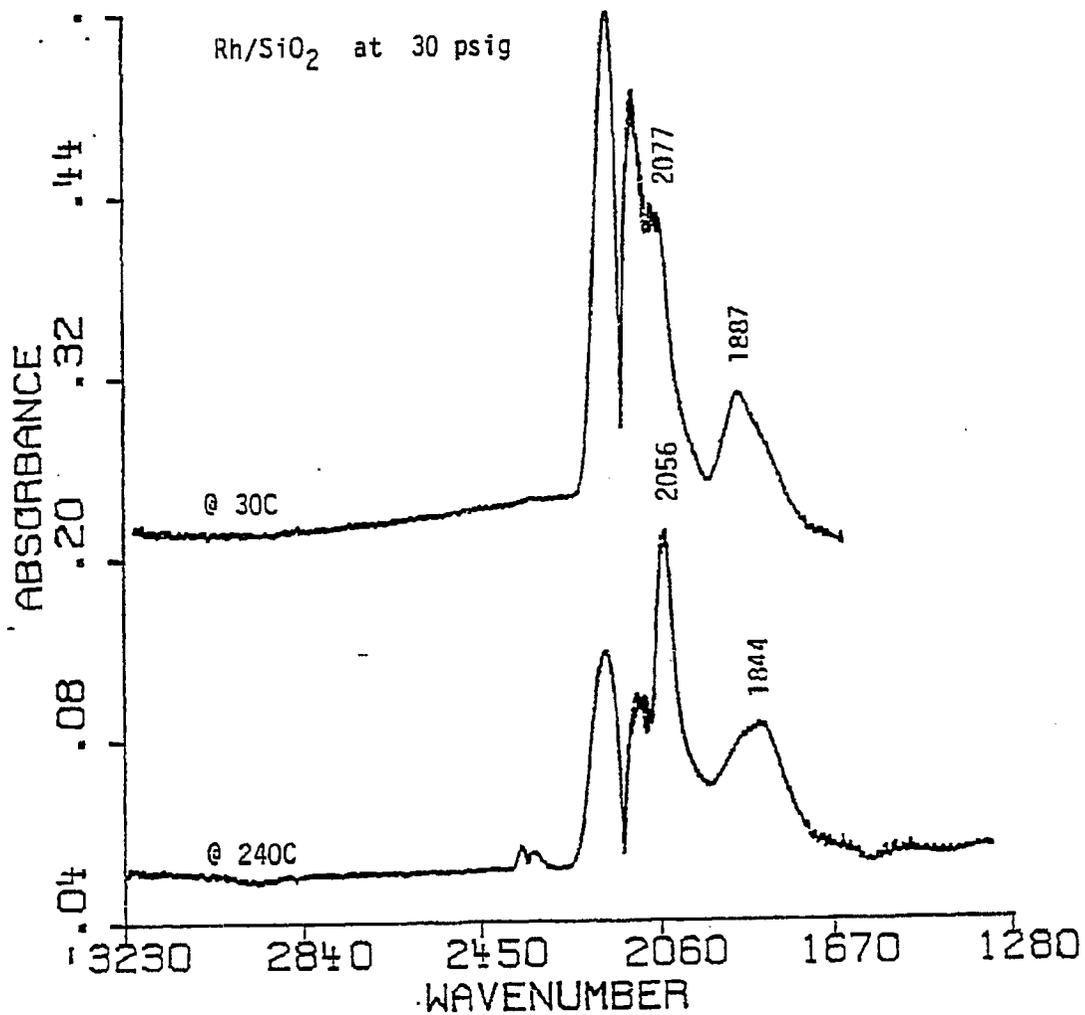


Figure 2 Effect of temperature on the infrared spectrum for Rh/SiO<sub>2</sub>

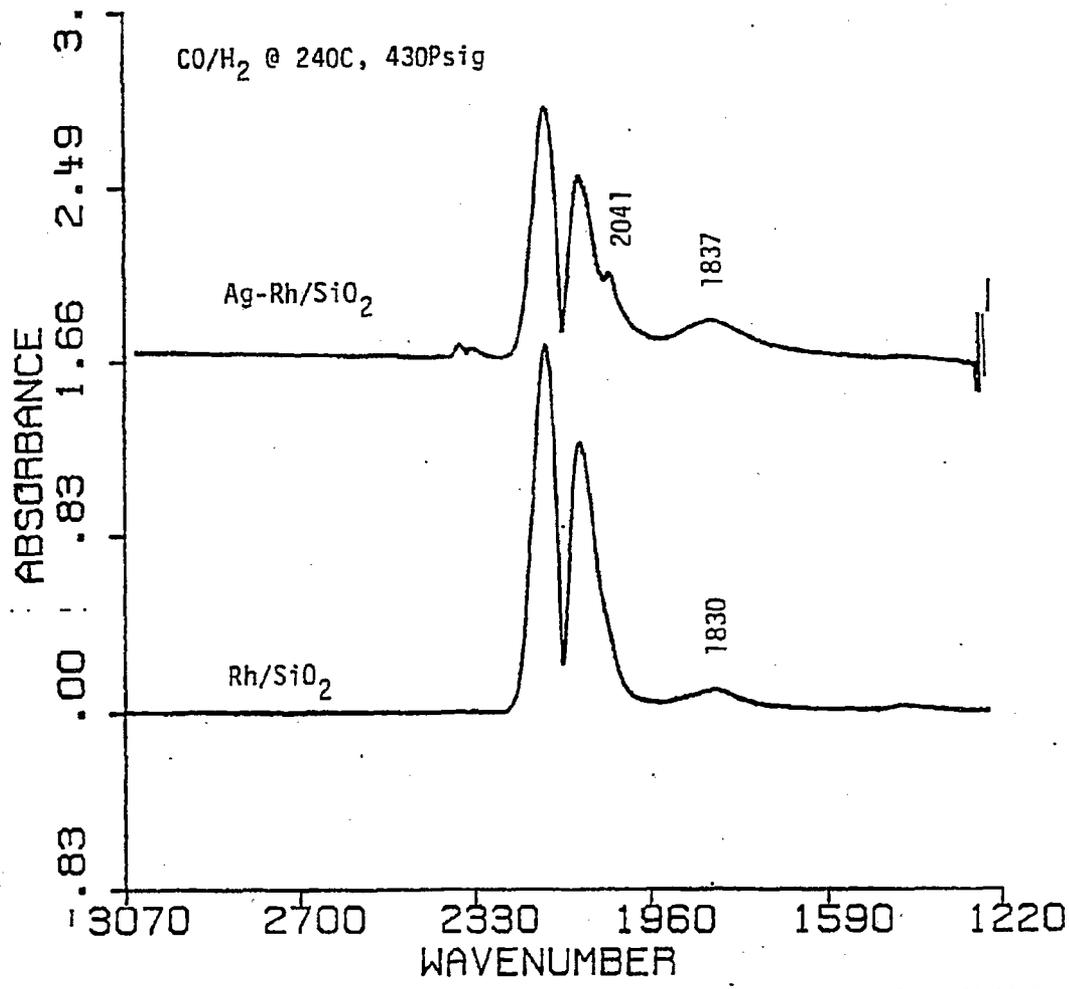


Figure 3 Infrared spectrum for CO/H<sub>2</sub> reaction on Rh/SiO<sub>2</sub> and Ag-Rh/SiO<sub>2</sub>

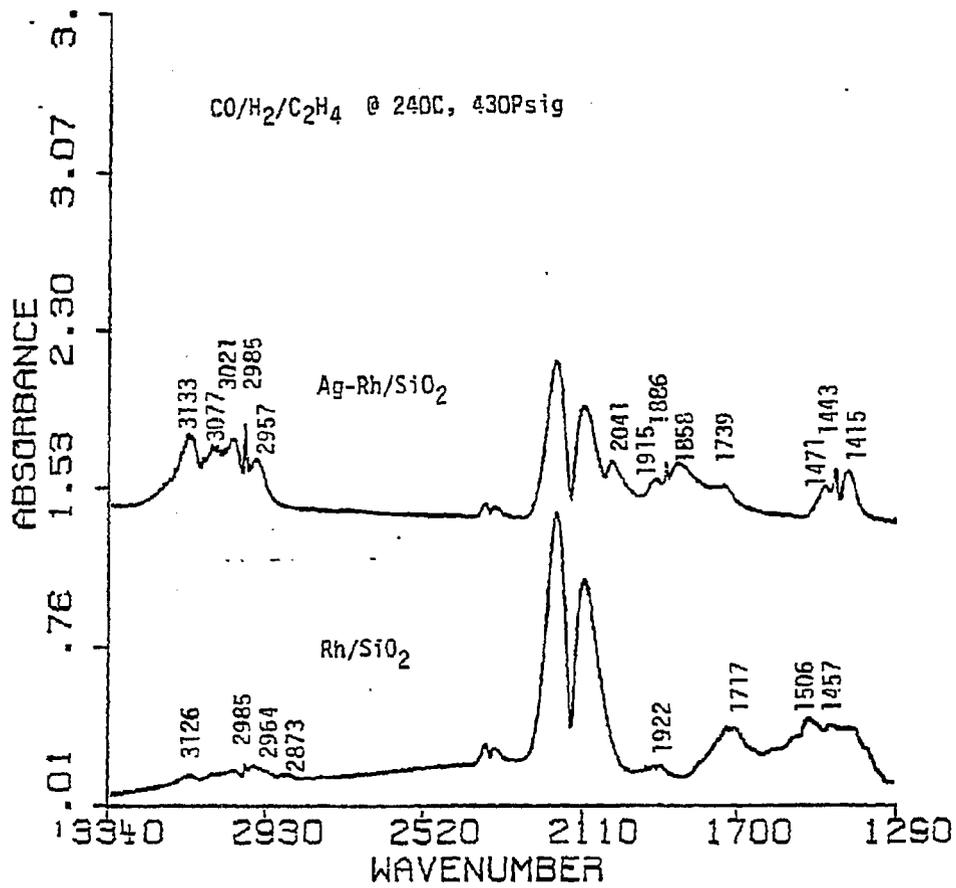


Figure 4 Infrared spectrum for CO/H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> reaction on Rh/SiO<sub>2</sub> and Ag-Rh/SiO<sub>2</sub>

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