EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL: TECHNICAL PROGRESS REPORT NO. 1, SEPTEMBER 15, 1987-DECEMBER 15, 1987

AKRON UNIV., OH. DEPT. OF CHEMICAL ENGINEERING

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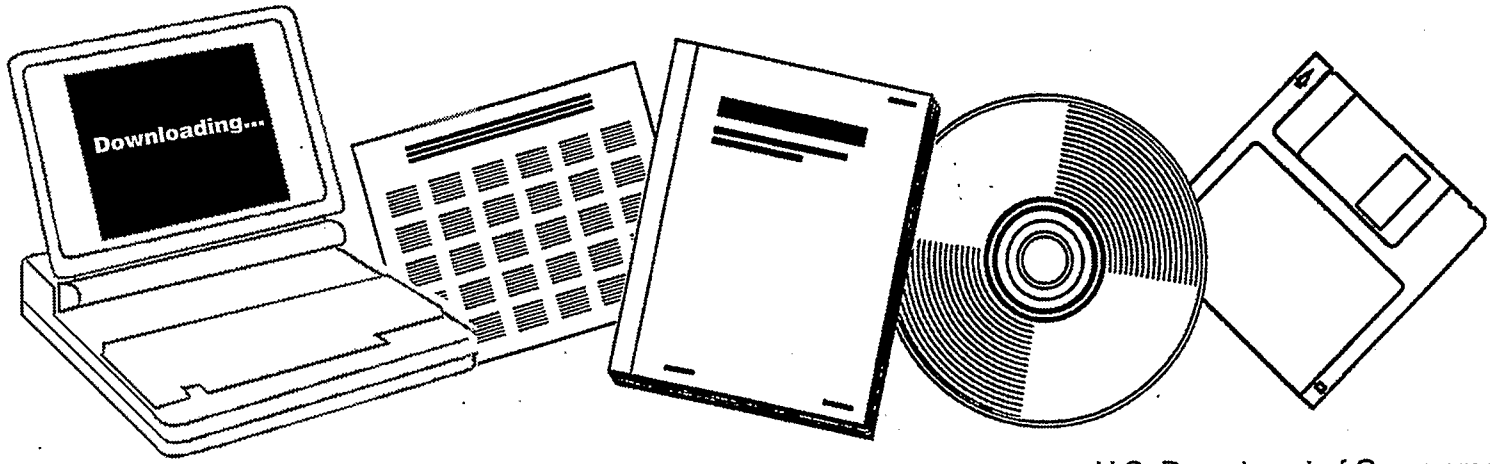

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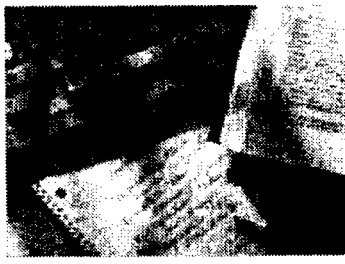

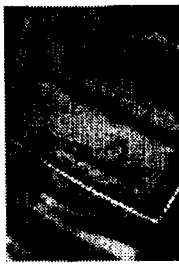

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THE EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL

Technical Progress Report 1
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by

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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. This comprehensive research program includes investigation of 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. A series of experimental studies consisting of temperature programmed desorption, infrared study of NO adsorption, reactive probing, steady state rate measurement, and transient kinetic study is/will be performed to expand current knowledge in this area. 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 first quarter of the project, a micro-reactor system has been built. Rh/SiO_2 and $Cu-Rh/SiO_2$ catalysts have been prepared for ethanol synthesis and reactive probing studies.

Cu, with an electronegativity similar to Rh, may decorate the surface of Rh particle (1). Study of Cu-Rh catalyst may provide a deeper insight into the structure sensitivity of ethanol

synthesis.

EXPERIMENTAL

Catalyst Preparation

3 wt % Rh/SiO_2 was prepared by incipient wetness impregnation of SiO_2 using Rh chloride. The $Cu-Rh/SiO_2$ was prepared by using co-impregnation of Cu nitrates. The ratio of Rh to Cu additive is 2.

Reaction Studies

Ethanol synthesis over both Rh and Cu-Rh catalysts was carried out in a differential reactor system under 300 °C and 10 atm. The product distribution was determined by a HP-5890A gas chromatograph.

The addition of probe molecules such as ethylene during CO hydrogenation could produce ethyl species which may undergo (a) hydrogenation to form ethane, (b) CO insertion to form propionaldehyde (2-4), (c) chain incorporation to form higher hydrocarbons, and (d) hydrogenolysis to form methane (2,3).

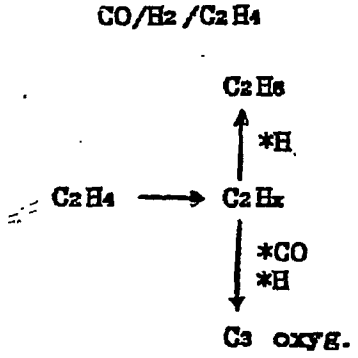
A small amount of ethylene (3-4 mole %) was added to CO/H_2 reactant mixture after steady state kinetic study. The relative hydrogenation, CO insertion, chain incorporation, and hydrogenolysis activities were estimated by careful determination of the product distribution before, during, and after the addition of the probe molecule. The effect of Cu additive on the specific reaction steps during the synthesis reaction was

determined.

RESULTS AND DISCUSSION

CO hydrogenation was carried out in a differential reactor at 300 °C, 10 atm, and $CO/H_2 = 1$. Figure 1 shows results of CO hydrogenation over Rh/SiO_2 and $Cu-Rh/SiO_2$ catalysts. The major products of CO hydrogenation over Rh/SiO_2 catalysts are methane, C_2-C_4 hydrocarbons, and C_2 oxygenated compounds (acetaldehyde and ethanol). The addition of Cu to Rh/SiO_2 increased the rate of CO conversion and the selectivity for methane but decreased the selectivity for C_2 oxygenated compounds.

After CO hydrogenation study, 3-4 mole % of ethylene was added to CO/H_2 reactant stream under synthesis conditions. Figure 2 shows rate of ethylene conversion and the selectivity for the product formation from ethylene. The major products for the $C_2H_4/CO/H_2$ reaction over Rh/SiO_2 are ethane and C_3 oxygenated compounds (propionaldehyde and 1-propanol). The reaction scheme for the formation of these products is shown as follows (3,4):



C_3 oxygenated compounds appear to be formed from the insertion of CO into adsorbed C_2 hydrocarbon species. The presence of Cu on Rh/SiO_2 catalysts decreased the rate of ethylene conversion and the selectivity for C_3 oxygenate formation. The decrease in the selectivity for C_3 oxygenate formation and the increase in selectivity for ethane formation appear to result from a lower rate of CO insertion step compared with the rate of hydrogenation. The substantial decrease in rate of CO insertion brought about by the Cu additive indicates that the CO insertion is a step which appear to be more structure sensitive than ethylene hydrogenation.

Ethylene hydrogenation was studied over both Rh/SiO_2 and $Cu-Rh/SiO_2$ catalysts. The presence of Cu inhibits the ethylene conversion. The decrease in rate of ethylene conversion may be due to the site blocking. Further study on the effect of Cu on activation energy of hydrogenation is required to reveal the role of Cu on hydrogenation over Rh/SiO_2 catalysts.

FUTURE PLAN FOR THE NEXT QUARTER

A temperature programmed desorption system will be constructed for studying the effect of additives on the adsorption of hydrogen. A series of $Cu-Rh/SiO_2$ catalysts with the ratio of Cu to Rh of 1 - 10 will be prepared for studying the structure sensitivity of CO insertion step in ethanol synthesis.

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Figure 1. CO HYDROGENATION

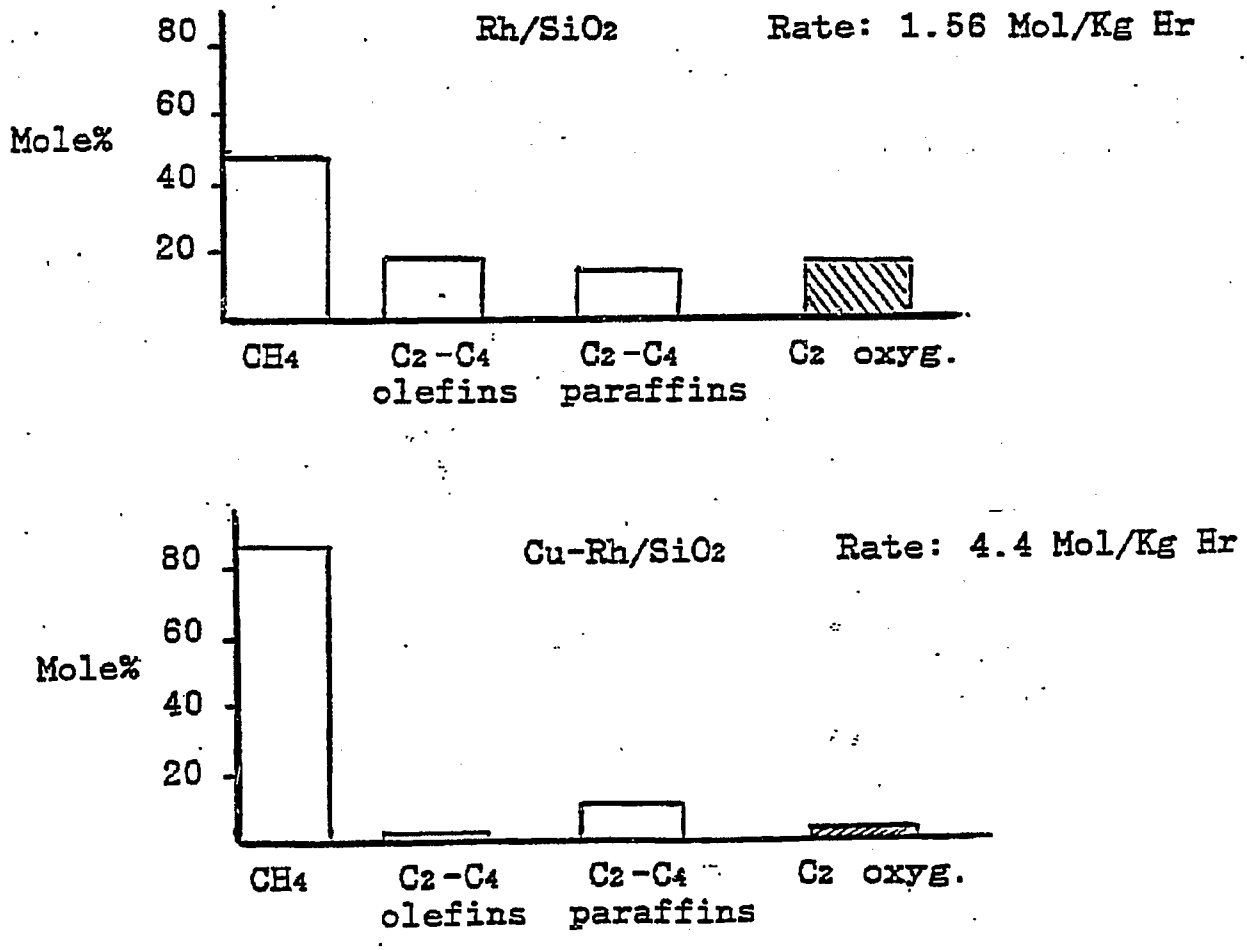


Figure 2. $CO/H_2/C_2H_4$

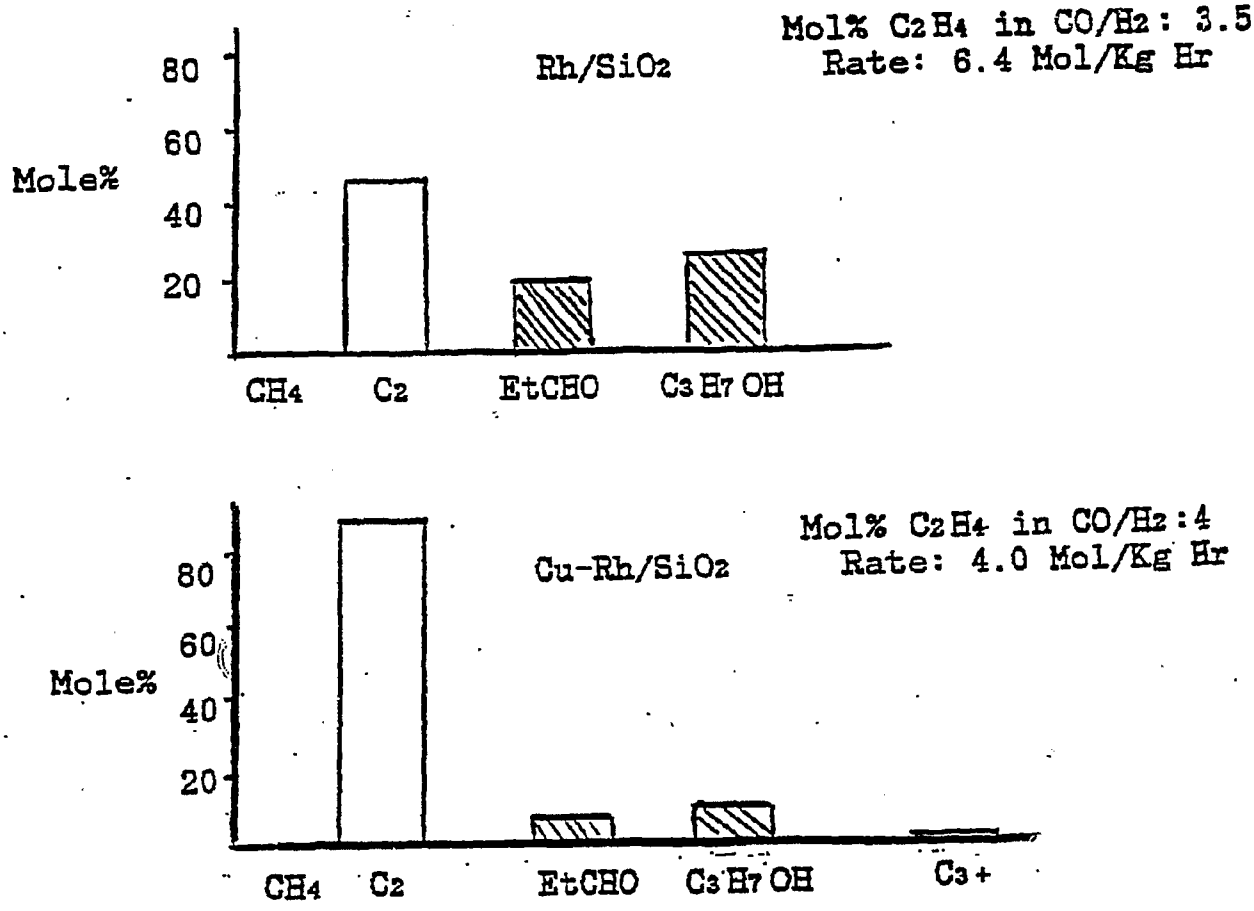
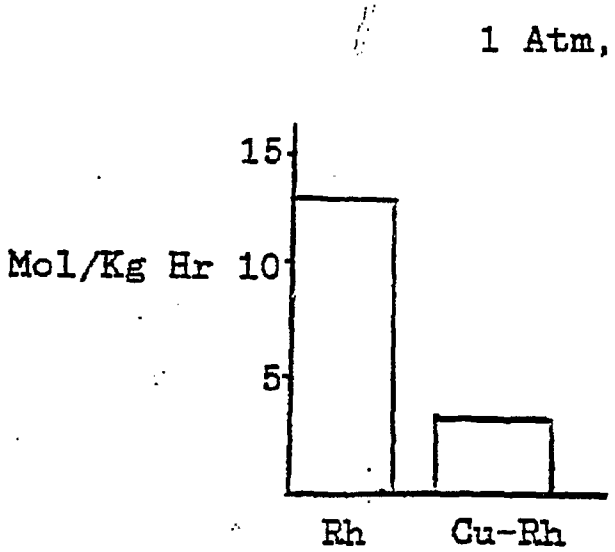


Figure 3. ETHYLENE HYDROGENATION



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