

Secondary Reactions of Low-Molecular Weight Olefins  
During Fischer-Tropsch Synthesis

Deborah S. Jordan and Alexis T. Bell  
Materials and Molecular Research Division  
Lawrence Berkeley Laboratory

and  
Department of Chemical Engineering  
University of California, Berkeley, CA 94720

INTRODUCTION

Low molecular weight olefins formed during Fischer-Tropsch synthesis can undergo secondary reactions and thereby influence the distribution of the final products. In the case of Ru catalysts, it has been postulated (1) that the low yields of  $C_2$  and  $C_3$  olefins over these catalysts may be due to the reincorporation of these products into growing chains. Ekerdt and Bell (2) observed that the addition of 2% ethylene to an  $H_2/CO$  mixture resulted in an enhanced yield of propylene. Subsequent studies by Kellner and Bell (1) demonstrated that at concentrations above 1% ethylene addition enhanced the rates of  $C_3$  and  $C_4$  formation but suppressed the synthesis of  $C_{6+}$  hydrocarbons. Kobori et al. (3) have examined the effects of ethylene, propylene, and 4-octene addition. When  $^{12}C$ -labeled olefins were added to a  $^{13}CO/H_2$  mixture, the isotopic distribution of products showed that the carbon from the additives was incorporated randomly into the products. Very recently Morris et al. (4) investigated the effects of ethylene and propylene addition on the hydrogenation of CO over Ru supported on silica, 13x-zeolite, titania, and magnesia. For  $Ru/SiO_2$  and  $Ru/13x$ -zeolite, ethylene addition markedly increased the rates of higher hydrocarbon formation without greatly influencing the methanation rate, whereas for  $Ru/TiO_2$  and  $Ru/MgO$ , ethylene addition enhanced the rate of higher hydrocarbon formation by a factor of less than two and reduced the methanation rate. With increasing proportion of ethylene in the feed, the yield of methane decreased and the yield of  $C_{3+}$  products increased. Propylene addition to CO hydrogenation over  $Ru/SiO_2$  increased the rates of  $C_2$  and  $C_{4+}$  hydrocarbon formation, without markedly affecting the methanation rate.

The objectives of this study were to investigate the influence of ethylene addition on the hydrogenation of CO over  $Ru/SiO_2$ , and to compare the product distribution obtained with those for CO hydrogenation in the absence of ethylene and ethylene homologation in the absence of CO. To enable identification of the source of carbon in the products,  $^{13}C$ -labeled CO and unlabeled  $C_2H_4$  were used. Products were analyzed by isotope-ratio gas chromatography-mass spectrometry. Among the issues investigated were the influence of ethylene addition on the reactions of CO and the participation of ethylene in processes of hydrocarbon chain initiation and growth. The influence of ethylene addition on methane formation was also examined.

EXPERIMENTAL

A 4.3%  $Ru/SiO_2$  catalyst is used in this investigation. Details concerning its preparation and initial reduction are presented elsewhere (5). The dispersion of the catalyst is 0.27 as determined by  $H_2$  chemisorption at 373 K.

Hydrogen is purified by passage through a Deoxo unit (Engelhard Industries) and 5-Å molecular sieve. Helium (99.999%) and ethylene (99.95%) are used without further purification. Isotopically labeled carbon monoxide (Isotec, Inc.) consisting of 89.3%  $^{13}\text{C}$ , 9.86%  $^{13}\text{C}^{18}\text{O}$ , and 0.36%  $^{12}\text{C}$  is used as received.

Reactants are supplied from a gas flow manifold at a pressure of 1 atm to a stainless steel microreactor heated by a fluidized sand bath. The catalyst (0.51 g) is reduced in flowing  $\text{H}_2$  for 12 h at 573 K prior to each series of experiments. Reduction is continued at the reaction temperature of 493 K for 2 h before initiating an experiment. The reactant stream is then introduced, and the reaction allowed to continue for 15 min before product samples are taken for analysis. Reduction is resumed and maintained for at least 2 h between experiments. The activity of the catalyst was checked periodically by returning to base case conditions. The activity remained constant to within five percent of its standard activity.

The reactor effluent is analyzed by a combination of gas chromatography and mass spectrometry, to determine the product distribution and the  $^{13}\text{C}$  content of each of the products. The products are first separated by gas chromatography and then each eluted product is combusted to  $\text{CO}_2$ . The  $^{13}\text{C}$  content of the  $\text{CO}_2$  is determined by mass spectrometry. This analytical approach has been described by Sano et al. (6) and Matthews and Hayes (7), and is termed isotope-ratio gas chromatography-mass spectrometry.

## RESULTS AND DISCUSSION

The reaction of  $\text{C}_2\text{H}_4$  and  $\text{H}_2$  over Ru produces, in addition to  $\text{C}_2\text{H}_6$ ,  $\text{CH}_4$  and  $\text{C}_{3+}$  olefins and paraffins. A large fraction of the  $\text{C}_{4+}$  hydrocarbons are branched. As shown in fig. 1, the carbon number distribution of the  $\text{C}_{3+}$  products does not decrease monotonically, but rather, oscillates so that products with an even number of carbon atoms predominate. The formation of  $\text{CH}_4$  is ascribed to the hydrogenolysis of  $\text{C}_2\text{H}_4$  and the formation of  $\text{C}_{3+}$  hydrocarbons to homologation of  $\text{C}_2\text{H}_4$  via chain growth, involving  $\text{C}_1$  and  $\text{C}_2$  monomer units. An accurate description of the product distribution is achieved using the mechanism illustrated in Fig. 2 (8).

The addition of  $\text{C}_2\text{H}_4$  to synthesis gas has a strong influence on the hydrogenation of CO. Figures 3 and 4 show that above a  $\text{C}_2\text{H}_4/\text{CO}$  ratio of 1.0, the formation of hydrocarbons from CO is completely suppressed and only the hydroformylation of  $\text{C}_2\text{H}_4$  to form propanal (and some propanol) is observed. The presence of CO suppresses the hydrogenation of  $\text{C}_2\text{H}_4$  to  $\text{C}_2\text{H}_6$  but has relatively little effect on  $\text{C}_2\text{H}_4$  hydrogenolysis and homologation. The selectivities to  $\text{CH}_4$  and  $\text{C}_{3+}$  products are influenced by the partial pressures of  $\text{C}_2\text{H}_4$ , CO, and  $\text{H}_2$ . High selectivity to  $\text{C}_{3+}$  products and low selectivity to  $\text{CH}_4$  are observed for high  $\text{C}_2\text{H}_4$ , CO, and  $\text{H}_2$  partial pressures and low reaction temperatures. The observed distribution of products can be described theoretically using a modified version of the mechanism for  $\text{C}_2\text{H}_4$  homologation (8).

The results of the present study clearly indicate that ethylene formed via the hydrogenation of CO can undergo extensive secondary reaction. The presence of CO inhibits the hydrogenation of ethylene to ethane, and hence the formation of a stable  $\text{C}_2$  hydrocarbon product. A major portion of the readsorbed ethylene will participate in the initiation and propagation of chain growth. A significant fraction will react with adsorbed CO and hydrogen to form propanal (or propanol). Ethylene readsorption will also result in a suppression of  $\text{CH}_4$  formation. This would explain why the yield of  $\text{CH}_4$  produced over Ru catalyst is observed to decrease as the conversion of CO to products increases.

### ACKNOWLEDGMENT

This work was supported by the Division of Chemical Sciences Office of Basic Energy Sciences, United States Department of Energy, under contract DE-AC03-76SF00098.

### REFERENCES

1. Kellner, C. S., and Bell, A. T., *J. Catal.* **70**, 418 (1981).
2. Ekerdt, J. G., and Bell, A. T., *J. Catal.* **62**, 19 (1980).
3. Kobori, Y., Yamasaki, H., Naito, S., Onishi, T., and Tamaru, K., *Chem. Soc. Faraday Trans. 1* **78**, 1473 (1982).
4. Morris, S. R., Hayes, R. B., Wells, P. B., and Whyman, R., *J. Catal.* **96**, 23 (1985).
5. Winslow, P., and Bell, A. T., *J. Catal.* **86**, 158 (1984).
6. Sano, M., Yotsui, Y., Abe, H., and Sasaki, S., *J. Biomed. Mass Spec.* **3**, 1 (1976).
7. Matthews, D. E., and Hayes, J. M., *Anal. Chem.* **50**, 1465 (1978).
8. Jordan, D.S., and Bell, A. T., *J. Phys. Chem.*, submitted.

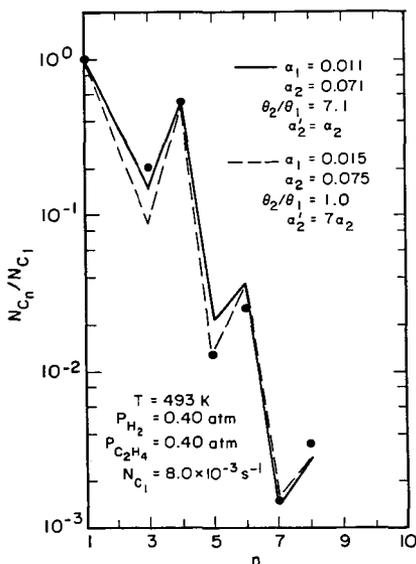


Fig. 1 Distribution of  $\text{C}_1$  through  $\text{C}_8$  hydrocarbons produced by reaction of  $\text{H}_2$  and  $\text{C}_2\text{H}_4$  at 493K.  $P_{\text{H}_2} = P_{\text{C}_2\text{H}_4} = 0.40 \text{ atm}$ . Solid and dashed lines represent a theoretical description of the data for two sets of parameters.

