Fischer–Tropsch Product Distribution for Rh/TiO$_2$

The Fischer–Tropsch synthesis shows a wide range of product distribution. This reaction is considered to occur through a kind of polymerization mechanism in which a basic monomeric unit is produced on the catalyst surface from CO and H$_2$ and the product results from the polymerization of this monomer. The hydrocarbon and alcohol products typically show a logarithmic (Shultz-Flory or Anderson (*1*)) distribution frequently indicating a constant ratio of propagation and termination rates especially in molecular range above C$_3$ (*1–4*).

$$\log(\text{mole\% } C_n) = K + C_n \log \alpha$$

where $\log(\text{mole\% } C_n)$ shows linear relation to C_n (carbon number of product). The probability of chain growth is α; $(1 - \alpha)$ is the probability of chain termination, i.e., product formation (*1–4*).

We have studied the mechanism of alcohol formation catalyzed by Rh/TiO$_2$ using the isotopic tracer method and have shown that methanol is produced by a nondissociative (CO) mechanism (*5*). Related isotopic tracer studies have shown that ethanol is not produced by an enol condensation mechanism nor by a CO insertion into an adsorbed methyl species; a CO insertion into carbene mechanism which explains the isotopic composition of the product ethanol has been proposed (*6*). The majority of the ethanol is produced from CO + H$_2$ directly; the homologation of product methanol is a minor route (*7*). Carbon atoms deposited on Rh are not readily hydrogenated to form methane, methanol, or ethanol, in contrast to the behavior on Ni (*8*).

In this paper, total product distribution from CO hydrogenation catalyzed by Rh/TiO$_2$ is considered. CO hydrogenation was catalyzed by 3.0 wt% Rh/TiO$_2$ at 423 K; the catalyst (0.10 g) was prereduced at 473 K (*5*). The logarithm of mole percent of hydrocarbon and alcohol products is plotted versus their carbon number in Fig. 1. Curve a is the carbon number distribution for hydrocarbons, curve b is the carbon number distribution for alcohols, and curve c is the carbon number distribution for the total products (hydrocarbons plus alcohols). C$_2$ in the hydrocarbon distribution falls seriously below the curve.

This type of undershooting of C$_2$ has been observed for Ni, Fe, and Co catalysts and has usually been explained by invoking the rapid insertion reaction of product ethylene leading to higher carbon number products and reduced C$_2$ product concentration (*3, 4, 9*). Carbon number distribution for alcohols does not show an extended linear behavior because, in these experiments, higher molecular weight alcohols were not detectable; the product was composed mainly of methanol and ethanol. Higher pressure CO hydrogenation experiments produced alcohols in decreasing concentration through C$_6$ (*10*).

If the total products, hydrocarbons plus alcohols, are plotted for the Rh/TiO$_2$, the product distribution shows Schultz-Flory and Anderson type behavior as shown by curve c in Fig. 1. Curve c shows a curvature indicating the change in the value of α from about 0.22 at C$_2$ to an apparently constant value of about 0.54 above C$_4$. There were essentially no olefins, indicating complete hydrogenation to their respective paraffins. Thus we infer that the large deficit in C$_2$ hydrocarbons cannot be attributed to reaction of product ethylene but appears to be due to the formation of ethanol. This result suggests that a common intermediate may
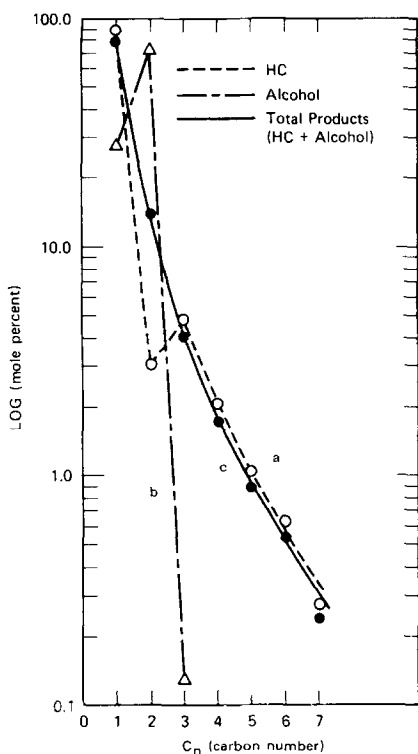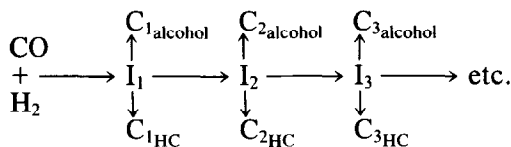
FIG. 1. Product distribution from CO hydrogenation on Rh/TiO$_2$. Curve a C$_n$(HC) as mole% of total hydrocarbons; curve b C$_n$(alcohol) as mole% of total alcohols, curve c C$_n$ (HC + alcohols) as mole% total product.

be involved in the formation of hydrocarbons and alcohols from CO + H$_2$ catalyzed by Rh/TiO$_2$. We suggest that the behavior observed may be explained by

$$CO + H_2 \longrightarrow I_1 \overset{\overset{C_{1\,alcohol}}{\uparrow}}{\underset{\underset{C_{1\,HC}}{\downarrow}}{}} \longrightarrow I_2 \overset{\overset{C_{2\,alcohol}}{\uparrow}}{\underset{\underset{C_{2\,HC}}{\downarrow}}{}} \longrightarrow I_3 \overset{\overset{C_{3\,alcohol}}{\uparrow}}{\underset{\underset{C_{3\,HC}}{\downarrow}}{}} \longrightarrow etc.$$

This is consistent with the reaction mechanism proposed for Fischer–Tropsch synthesis catalyzed by Rh/TiO$_2$ (6). Therein, methanol and methane were assumed to be formed from CHOH$_{ad}$, although it is possible that the common intermediate for C$_1$ products is adsorbed CO. The ethanol, ethane, and ethylene are assumed to be produced from an adsorbed ketene or oxirene intermediate formed by CO insertion into a surface carbene. These results indicate that reaction mechanisms are open to further evaluation and require careful, detailed examination over a broad range of catalysts to establish appropriate mechanisms and their generality to a range of Fischer–Tropsch catalysts.

REFERENCES

1. Anderson, R. B., "Catalysis" (P. H. Emmett, Ed.), Vol. 4, p. 257. Reinholt, New York, 1956.
2. Master, C., Adv. Organomet. Chem. 17, 61 (1979).
3. Biloen, P., and Sachtler, W. M., H., Adv. Catal. 30, 165 (1981); Sachtler, W. M. H., Mechanism of Hydrocarbon Synthesis over Fischer–Tropsch Catalysts, in "Chemistry and Chemical Engineering of Catalytic Processes," R. Prins and G. C. A. Schuit, Eds.), p. 583. Sijthoff & Noordhoff, The Netherlands, 1980.
4. Henrici-Olivé, G., and Olivé, S., Angew. Chem. Int. Ed. Engl. 15, 136 (1976).
5. Takeuchi, A., and Katzer, J. R., J. Phys. Chem. 85, 937 (1981).
6. Takeuchi, A., and Katzer, J. R., J. Phys. Chem. 86, 2438 (1982).
7. Takeuchi, A. Katzer, J. R., and Crecely, R. W., Mechanism of Ethanol Formation: The Role of Methanol," in press.
8. Takeuchi, A., and Katzer, J. R., "Inactivity of Surface Carbon to Hydrogenation on Supported Rhodium," in press.
9. Biloen, P., Helle, J. N., and Sachtler, W. M. H., J. Catal. 58, 95 (1979).
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