

## Iron Catalyzed CO<sub>2</sub> Hydrogenation to Liquid Hydrocarbons

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Many of the catalysts which are useful in Fischer-Tropsch synthesis are also capable of catalyzing the hydrogenation of CO<sub>2</sub> to hydrocarbons. Our structure-function studies have shown that it is possible to control the selectivity of CO<sub>2</sub> hydrogenation by specific iron-based catalysts to generate yields of C<sub>5</sub>+ hydrocarbons that are comparable to those produced with conventional CO based feedstocks.

### 1. INTRODUCTION

Catalyst structure-function studies have shown that alpha-olefins are the primary products of CO<sub>2</sub> hydrogenation, with normal paraffins being formed by secondary hydrogenation. Catalysts that contain mainly iron oxide, or iron carbide with substantial concentrations of matrix carbon, favor secondary reactions and limited chain growth. The relative concentrations of these phases depend on the ease of reduction of the starting catalyst precursor, which can be changed to some degree by substitution of various cations into the initial formulation. In cases where excess matrix carbon is introduced into the reduced/carbided catalyst system, we are able to demonstrate the importance of diffusion constraints on overall process selectivity. We have developed proprietary iron catalysts that are essentially free of metal oxide and/or matrix carbon phases, with unprecedented selectivity toward C<sub>5</sub>+ olefinic products.

### 2. BACKGROUND ON CO AND CO<sub>2</sub> HYDROGENATION

Studies on CO<sub>2</sub> hydrogenation can be traced back to the early 1900's [1] with emphasis on cobalt, nickel and iron-based catalysts. While this work clearly demonstrated the overall reactivity of CO<sub>2</sub> under a wide range of reaction conditions, the primary product(s) consisted of methane, CO and other light hydrocarbons. Emmett and others have evaluated the large body of experimental work that was performed through the early 1960's and concluded that CO<sub>2</sub> hydrogenation to higher molecular weight hydrocarbons remained a significant challenge.

Selectivity control continues to be a critical issue in Fischer-Tropsch chemistry, a catalytic process that dates back more than seventy years [1]. Operating conditions can be adjusted to control selectivities but overall effects are limited [2-4]. During Fischer-Tropsch synthesis with conventional bulk iron catalysts, various phases, including metal, metal carbides and metal oxides are present at steady-state catalytic conditions [5-7].

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Previous studies indicate that alkali increases the heat of CO chemisorption while decreasing the heat of H<sub>2</sub> chemisorption [8,9]. As a result of alkali promotion on iron catalysts, the average chain length and the olefin content of the products increase, whereas the activity and methane selectivity decrease [10,11].

Recent studies indicate that  $\alpha$ -olefins, the major primary products formed during Fischer-Tropsch synthesis, participate in secondary reactions [12]. Chains can terminate either by  $\beta$ -hydrogen abstraction to form an  $\alpha$ -olefin or by H-addition to form a paraffin [13,14]. Olefins can undergo secondary reactions by subsequent readsorption leading to isomerization or hydrogenation. We observe selectivity relationships that are consistent with Egiebor's proposal that significant secondary hydrogenation reactions can occur on iron catalysts [12].

### 3. EXPERIMENTAL ON CO AND CO<sub>2</sub> HYDROGENATION

The details of the preparation of the iron oxide catalyst precursors are described elsewhere [15-17]. For those carbides made by exsitu carburization, the oxide was loaded into a 1" diameter quartz tube and heated in a 1/1 H<sub>2</sub>/CO mixture at a space velocity of 10,000 v/v/hr at 350°C for 24 hours. Iron carbide catalysts were also prepared by laser pyrolysis of iron carbonyl and ethylene using a 150 watt continuous wave CO<sub>2</sub> laser to provide both a rapid high temperature reaction (~.1 sec with T~1000°C) and quench [18].

The procedures used to produce the wet chemical and laser generated iron carbides of this paper have been disclosed in detail [22]. Catalyst tests were performed in a 300 cc Parr stirred tank reactor with octacosane as the slurry medium. Wide-angle powder x-ray diffraction identified catalyst phases present. Thermogravimetric reductions were recorded on a Mettler TA-2000°C using 100-200 mg of sample and a heating rate of 8 deg/min. Gravimetric titrations were performed using a specially designed heated entry port enabled injection of the pyridine titrant [19]. Mossbauer spectra were collected with an Austin Sciences instrument with a radiation source consisting of Co<sup>57</sup> diffused into Rh (New England Nuclear).

### 4. RESULTS AND DISCUSSION

Unpromoted iron oxide catalysts (surface area 30-50m<sup>2</sup>/gm) and iron oxide converted ex-situ to iron carbide were compared under standard reaction conditions. Figure 1 illustrates the sequential conversion of an iron surface in 1:1 H<sub>2</sub>:CO at 1 atm under programmed heating conditions. In region 1 CO adsorbs onto the metal surface. At about 300°C, Fe begins to convert to (Haag) carbide and at slightly higher temperature amorphous carbon begins to grow. Gravimetric acidity titrations with 3,5 dimethylpyridene at 250°C showed an acid site concentration of 99  $\mu$ -moles/gm catalyst for the oxide and only 27 for the carbided catalyst. These numbers compare with ~250  $\mu$ -moles/gm for a solid acid like  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Figure 2 summarizes the different product selectivities measured at CO conversions of ~50%. In the carbided system we find ethylene present as well as a higher olefinic content in C<sub>4</sub>, apparently as a result of inhibited secondary hydrogenation. Consequently, a carbided iron surface produces a more olefinic, heavier product, consistent with the observations of Egiebor and Cooper who suggest that acid sites on a precipitated FeOx/SiO<sub>2</sub> catalyst lead to secondary reactions of  $\alpha$ -olefins [12].

Alkali titrates acid sites on the iron surface and also increases the strength of the CO-surface interaction. Figure 3 compares the effect of potassium promotion on the iron carbide catalyst where we had substantial amounts of matrix carbon. A cementite  $\text{Fe}_3\text{C}$  phase was synthesized by laser pyrolysis with a carbon content corresponding closely to the  $\text{Fe}_3\text{C}$  stoichiometry, i.e., without any excess matrix carbon. Some of it was heated in  $\text{H}_2/\text{CO}$  mixtures (1/1) at  $350^\circ\text{C}$  in order to introduce 40-50% by weight matrix carbon. Figure 4 shows that the excess carbon reduced olefin selectivity while favoring  $\text{CH}_4$  and lighter products. The pure carbide, as prepared, does not respond to alkali treatment, Figure 5, suggesting that potassium is only needed when removal of the olefins is not fast enough to prevent secondary hydrogenation. The oxide catalyst reduces at lower temperature with substitution of Co into  $\text{Fe}_3\text{O}_4$ . Figure 6 shows the onset of reduction is initiated  $20^\circ\text{C}$  lower with the cobalt substitution. This may explain the enhanced olefin selectivity attributed to iron-cobalt catalysts in the literature [20,21].

Mossbauer spectroscopy on spent catalysts suggests that oxide/carbide phase formation in iron catalysts is also sensitive to reactor configuration (extent of backmixing). In integral fixed bed reactors, we find that iron has partitioned into carbide in the front of the bed but shows increasing amounts of oxide near the exit, whereas the same catalyst in the stirred tank reactor remains all iron carbide, Figure 7.

Comparative tests were conducted on  $\text{CO}_2$  hydrogenation over a conventional coprecipitated Fe/Cu/K/Si catalyst versus a wet chemical derived sample of  $\text{Fe}_3\text{C}_2$ , see Figure 8. At 7/1  $\text{H}_2/\text{CO}_2$  feed ratio, the carbide exhibits significantly higher selectivity to  $\text{C}_2^+$  products and higher olefin yields than the conventional catalyst.

The higher molecular weight fractions produced from the 7/1  $\text{H}_2/\text{CO}_2$  feed consisted of a mixture of alpha- and beta-olefins, n-paraffins and n-alcohols together with large fraction of methyl-branched and internal olefin isomers, see Figure 9, while a 2/1 mixture of  $\text{H}_2/\text{CO}$  operated at >80% CO conversion (i.e., effective  $\text{H}_2/\text{CO}$  ratios >10/1) over this catalyst would produce nearly 65% alpha-olefin, 15% n-paraffin, 1-3% n-alcohol and 15% methyl-branched and internal olefin isomers.

Laser generated carbides that contain virtually no matrix carbon overlayer have been tested and show much higher selectivity to desired products than wet chemical analogs. The Zn and Mn containing systems required potassium promoters for optimum selectivity, see Figure 10.

A series of  $^{13}\text{CO}_2$  labeling studies were conducted to determine the extent of  $\text{CO}_2$  conversion to hydrocarbons in the presence of varying quantities of CO, see Figure 11. These studies showed that no  $\text{CO}_2$  was converted in mixtures where >5% carbon atom CO was present, and that  $\text{CO}_2$  conversion to hydrocarbons did not occur until virtually all of the CO was consumed. Preliminary kinetic studies showed that product formation rates in the presence of low levels of unlabeled CO were consistent with a mechanism involving dissociative  $\text{CO}_2$  chemisorption followed by "CO" and surface "C" formation with hydrogenation to hydrocarbons, Figure 12.

## REFERENCES

1. M. E. Dry, "The Fischer-Tropsch Synthesis" in *Catalysis, Science and Technology*. Vol. 1, p. 159, ed. J. R. Anderson and M. Boudart, NY (1981); "The Fischer-Tropsch and Related Synthesis," H. Storch, N. Golumbic and R. Anderson, Wiley NY 1951.
2. C. D. Frohning and B. Cornils, *Hydrocarbon Processing*, p. 143, Nov. 1974.
3. B. Cornils, B. Buessmeier and C. D. Frohning, *Inf. Ser.-Alberta Res. Council*, 85, 126 (1978).
4. B. Buessmeier, C. D. Frohning and B. Cornils, *Hydrocarbon Processing*, p. 105, Nov. 1976.
5. F. Fischer and H. Tropsch, *Brennstoff-Chem.* 7, 97 (1926).
6. V. V. Niemanstuerdiert, A. M. vanderKraan, W. L. Van Dyk and H. S. vanderBaan, *J. Phys Chem.* 84, 3363 (1980).
7. F. Blanchard, J. P. Reymond, B. Pommier and S. J. Teichner, 3rd International Symp on Scient Basis for Prep. of Het. Catal. (Belg), Sept. 1983 and *J. Mol. Catal.* 176, 171 (1982).
8. M. E. Dry, T. Shingles, L. J. Boshoff and G. J. Ostuizien, *J. Cat.* 15, 190 (1969).
9. J. Benziger and R. J. Madix, *Surf. Sci.* 94, 119 (1980).
10. D. L. King and J. B. Peri, *J. Cat.* 79, 164 (1983).
11. H. Storch, N. Golumbic, and R. B. Anderson, "Fischer-Tropsch and Related Synthesis", Chap. 6, Wiley N. Y., 1951.
12. N. O. Egiebor and W. C. Cooper, *Appl. Catal.* 17, 47 (1985).
13. P. Biloen, J. N. Helle and W. Sachtler, *J. Cat.* 58, 95 (1979).
14. G. Henrici-Olive and S. Olive, *Angew. Chem. Int. Ed.* 15, 136 (1976).
15. R. A. Fiato and S. L. Soled, U.S. Pat. 4,618,597 (1986).
16. S. L. Soled and R. A. Fiato, U.S. Pat. 4,544,671 (1985).
17. S. L. Soled and R. A. Fiato, U.S. Pat. 4,584,323 (1986).
18. G. Rice, R. A. Fiato and S. L. Soled, U.S. Pat. 4,788,222 (1988).
19. S. L. Soled, G. McVicker and B. DeRites, Proc. 11th North American Thermal Analysis Conference, 1981.
20. M. Nakamura, B. B. Wood, P. Y. Hou and H. Wise, Proc. 7th Int Conf of Catal., part 7a, June '80.
21. R. M. Stanfield and W. N. Delgass, *J. Cat.* 72, 37 (1981).
22. R. A. Fiato, S. L. Soled, G. W. Rice and S. Misco, U.S. Pat. 4,687,753 (1987) and U.S. Pat. 5,140,049 (1992).

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