

Fischer–Tropsch Synthesis catalysed by Ultrafine Particles of Iron: Cessation of Water–Gas Shift Activity

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Slurry-phase hydrocarbon synthesis is affected at 220 °C with reduced ultrafine particles of α -Fe₂O₃ (3 nm) in the absence of water–gas shift activity.

In an effort to develop non-petroleum feedstocks, synthesis of hydrocarbons *via* the Fischer–Tropsch (F–T) reaction continues to be of interest.^{1,2} A few recent reports^{3,4} describe utilization of slurry-phase ultrafine particles (UFP) of traditional F–T metal catalysts to increase space-time-yield (STY). Typically, under F–T conditions, the hydrocarbon producing reaction is complicated by the water–gas shift (WGS) reaction⁵ which controls the H₂O/CO₂ ratio. Described here are results obtained with an iron UFP system which permits F–T catalysis at a lower temperature with concomitant cessation of water–gas shift activity.⁶

A 4.6 wt%† slurry of α -Fe₂O₃ [mean particle diameter (MPD) = 3 nm; surface area (SA) = 255 m² g⁻¹; $d(\text{bulk}) = 0.05 \text{ g ml}^{-1}$] in ethylflopolyolefin-164‡ solvent (406 cm³) was loaded into a 1 l AE stirred autoclave.§ The vessel was flushed several times with CO before pressurizing to 1.43 MPa. The reactor temperature was slowly raised to 280 °C under 0.2 l min⁻¹ CO flow and kept constant for 48 h while monitoring CO₂ evolution.¶ After this period, the temperature was lowered to 220 °C and CO was replaced with preblended syngas containing 65% H₂ and 35% CO to initiate the F–T reaction. At a gas hourly space velocity (GHSV) of 5.59 l_{rt} g_{Fe}⁻¹ h⁻¹,|| CO and H₂ conversions stabilized at 36 ± 1 and 26 ± 2% respectively after 96 h on-line. Thereafter, under steady-state conditions (120–200 h),** H₂/CO consumption ratio was 1.3 (± 0.1): 1 and space-time-yield of hydrocarbons was 0.43 (± 0.03) kg kg_{Fe}⁻¹ h⁻¹. Of interest was the corresponding total product distribution shown in Fig. 1. The total CO₂ generated decreased from a high of 23.9% (at 7 h) to 1.44% after 120 h. Thereafter, no CO₂ was detected in the product stream suggesting no WGS activity. On lowering GHSV to 3.71 l_{rt} g_{Fe}⁻¹ h⁻¹ at 200 h, CO and H₂ conversions increased to 40.9 and 27.7% respectively when measured at 216 h on-line time, but the product stream consisted of only hydrocarbons and aqueous phases. On increasing the temperature to 260 °C, WGS activity was restored and CO₂, hydrocarbon, and aqueous selectivities changed from 0, 44, 56% at 220 °C to 41.7, 39.3, 19% at 260 °C and GHSV of 5.59 l_{rt} g_{Fe}⁻¹ h⁻¹.

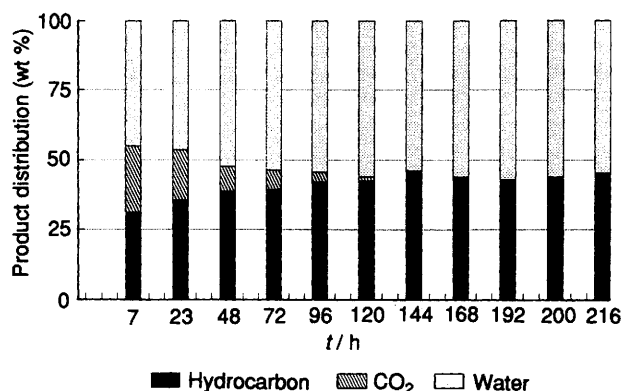


Fig. 1 Total product distribution as a function of time. Reaction conditions: Reduced 4.6 wt% slurry of α -Fe₂O₃ (3 nm) in ethylflopolyolefin-164 (322 g, see text); $T = 220$ °C; $P = 2.77$ MPa; stirring speed = 250 rpm; syngas: H₂/CO = 65%/35%; GHSV = 5.59 l_{rt} g_{Fe}⁻¹ h⁻¹ (0–200 h) and 3.71 l_{rt} g_{Fe}⁻¹ h⁻¹ (200–216 h). The x-axis represents time elapsed after catalyst reduction and syngas introduction. The aqueous phase also contained some oxygenates.

The hydrocarbon product distribution was also measured during this run. These data at 220 °C and GHSV of 5.59 l_{rt} g_{Fe}⁻¹ h⁻¹ are plotted in Fig. 2. The slope of this Schulz–Flory plot yielded α (probability of chain growth) = 0.56 with a break point at C₇ (note that actual values were determined for up to C₁₀ and the C₁₁₊ fraction constituted 41 wt% (at 200 h) of total hydrocarbons produced). This measured α value is atypical of Fe-based catalysts (see below).

For comparative performance, a run was also conducted with UCI catalyst.†† This supported catalyst contained larger particles ($\approx 10,000$ times) but had a similar surface area. After F–T synthesis at 260 °C for 72 h, the temperature was lowered to 220 °C. At GHSV of 8.0 and 5.74 l_{rt} g_{Fe}⁻¹ h⁻¹, CO and H₂ conversions were 23.5 and 15.5% respectively, with H₂/CO consumption ratio of 0.7:1 and hydrocarbon productivity (STY) was 0.46 kg kg_{Fe}⁻¹ h⁻¹ at 31 h on-line time. The Schulz–Flory plot yielded $\alpha = 0.53$. Interestingly, the overall product distribution: 35.6% hydrocarbons, 53.1% H₂O and 11.3% CO₂, clearly shows WGS activity at 220 °C with the UCI catalyst. It is to be noted that F–T synthesis has been reported⁷ with unpromoted as well as alkali (K)-promoted iron catalysts of 1–5 μm MPD under conditions reported herein but WGS activity was observed in these cases.

In summary, though the STY data for unsupported Fe UFP and UCI catalysts are similar at 220 °C, the absence of WGS activity with UFP under STY values of interest is demonstrated. Moreover, volumetric efficiency with Fe UFP is about 33% higher (0.12 vs. 0.09 kg l catalyst⁻¹ h⁻¹).‡‡ A higher H₂/CO consumption ratio (1.3:1 vs. 0.7:1) also supports absence of WGS activity and more saturated products production with Fe UFP. Preliminary identification of the catalyst phase *via* EXAFS and Mössbauer⁸ in a related run suggests iron to be predominantly in the magnetite phase. Several runs are presently under way to further confirm these findings.⁹ Given the environmental importance of non-CO₂ producing pro-

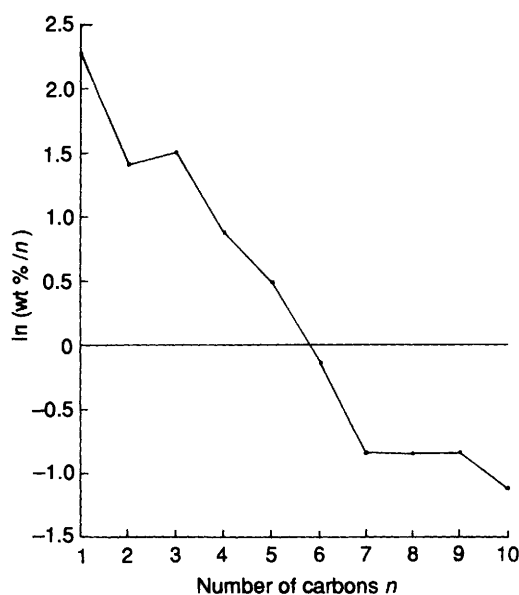


Fig. 2 Schulz–Flory plot of data obtained at 220 °C and GHSV of 5.59 l_{rt} g_{Fe}⁻¹ h⁻¹. Other conditions were identical to those listed in Fig. 1.

cesses, this concept is being extended to Co and Ru based F-T catalysts.

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Footnotes

† To avoid mass transfer problems at low gas feed rates, low loading was selected.

‡ This high molecular mass hydrocarbon solvent, a homopolymer (89.4 trimer and 14.5% tetramer) of dec-1-ene, was obtained from Ethyl Corporation.

§ This commercially available unit, manufactured by Autoclave Engineers (AE) and rated at 40 MPa at 343°C was customized to handle F-T synthesis.

¶ The concentration of CO₂ peaks at 4.3 vol% in 5 h and finally decreased to 0.3 vol%. At this time, the catalyst was assumed to be >95% carbided.

|| l_{rt} Corresponds to litres of gas at room temperature.

** Since no liquid was directly drained from the reactor during the run, small fluctuations observed during steady-state are attributed to liquid volume change.

†† UCI catalyst (69.6% Fe₂O₃, 5.1% K₂O, 8.3% SiO₂, 2.6% CuO, 14.8% loss on ignition; MPD = 32.5 μ m; SA = 232 m² g⁻¹). Reaction conditions in this run were identical except that stirring speed was 1000 rpm.

‡‡ Catalyst loading in slurry-phase operation is a critical parameter.

References

- 1 M. E. Dry, in *Catalysis—Science and Technology*, ed. J. R. Anderson and M. Boudart, Springer-Verlag, Berlin, Heidelberg, 1981, vol. 1, ch. 4.
- 2 J. P. Hindermann, G. J. Hutchings and A. Kiennemann, *Catal. Rev. Sci. Eng.*, 1993, **35**(1), 1 and references cited therein.
- 3 H. Itoh and E. Kikuchi, *Appl. Catal.*, 1990, **67**, 1.
- 4 E. Kikuchi and H. Itoh, in *Methane Conversion*, ed. D. M. Bibby, C. D. Chang, R. F. Howe and S. Yurchak, Elsevier Science Publishers B.V., Amsterdam, The Netherlands, 1988, 517.
- 5 *Catalysis in C1 Chemistry*, ed. W. Keim, D. Reidel Publishing Co., Dordrecht, 1983; C. N. Satterfield, *Heterogeneous Catalysis in Practice*, McGraw-Hill, New York, 1980, 292.
- 6 D. Mahajan, Record of Invention filed at Brookhaven National Laboratory, July 7, 1993.
- 7 R. A. Dictor and A. T. Bell, *J. Catal.*, 1986, **97**, 121.
- 8 K. Pandya (EXAFS) and K. R. P. M. Rao (Mössbauer), personal communications.
- 9 D. Mahajan, K. Pandya and A. Kobayashi, manuscript in preparation.