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Fischer–Tropsch synthesis: The paraffin to olefin ratio as a function of carbon number

Buchang Shi, Burtron H. Davis *

Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511, USA

Abstract

The Fischer–Tropsch synthesis (FTS) reaction mechanism has been studied by establishing a steady-state operation using a syngas comprised of H_2 and CO and then switching to a syngas feed comprised of D_2 and carbon monoxide. The products made during the 24-h period following switching from a hydrogen-containing syngas to a deuterium-containing one are analyzed for deuterium content. The paraffin/olefin (P/O) ratio of the highly deuterated products represent primary FTS products. The data show that the P/O ratio increases much more slowly with carbon number than the O/P ratio of the total products exiting the reactor. The data show that diffusion limitations for the olefin products and their subsequent re-incorporation as chain initiators does not make a major impact on the product distribution.

Keywords: FTS; Fischer–Tropsch synthesis; Isotopic tracer; Deuterium; Catalyst; Cobalt; Reaction mechanism

1. Introduction

Mechanism studies of the Fischer–Tropsch synthesis (FTS) present a demanding task. First, the products cover an extremely wide range, including alkanes, alkenes and oxygenates ranging from C_1 to greater than C_{100}. Secondly, except for the fluid bed operation, three phases are present: gas, liquid and solid catalyst. Mechanisms are nearly always based upon the products collected after exiting the reactor. However, as the results of this study show, the products collected may not be representative of those formed during the sampling period and this may significantly impact the mechanism that is proposed.

One area of uncertainty is the impact of diffusion and/or solubility (vapor–liquid equilibrium) upon secondary reactions that alter the initial product distribution. This issue has been summarized as follows by Van der Laan and Beenackers [1], and they emphasize solubility over diffusion as the main contributor: Iglesia and co-workers [1–8] studied the influence of chain length dependent diffusion coefficients on secondary reactions. They reported an empirical equation describing a strong influence of chain length on diffusivity for olefins and paraffins,

$$D_n \propto e^{-0.3n} \tag{1}$$

which was not verified by experimental data. This carbon number dependency is a factor of three higher than determined by Erkey et al. [9] and apparently is wrong (see Fig. 1). Iglesia et al. [4] modelled diffusion-limited removal of olefins and diffusion limitation of CO on a cobalt and ruthenium catalyst in a packed bed reactor. No reactant depletion was observed at particle diameters smaller than 0.2 mm. However, selectivity changes due to product limitations are still present. They concluded that olefin re-adsorption and chain initiation is the most important secondary reaction. Their transport model includes the rate of diffusion-enhanced olefin re-adsorption and its effect on detailed product distributions. However, Iglesia et al. [4] were not able to explain the strong exponential decrease of the olefin/paraffin (O_n/P_n) ratio on their catalyst ($c = 0.19$–0.49) in the following equation:

$$\frac{m_{O_n}}{m_{P_n}} = e^{-cn} \tag{2}$$

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* Corresponding author. Tel.: +1 859 257 0251; fax: +1 859 257 0302.
E-mail address: davis@caer.uky.edu (B.H. Davis).

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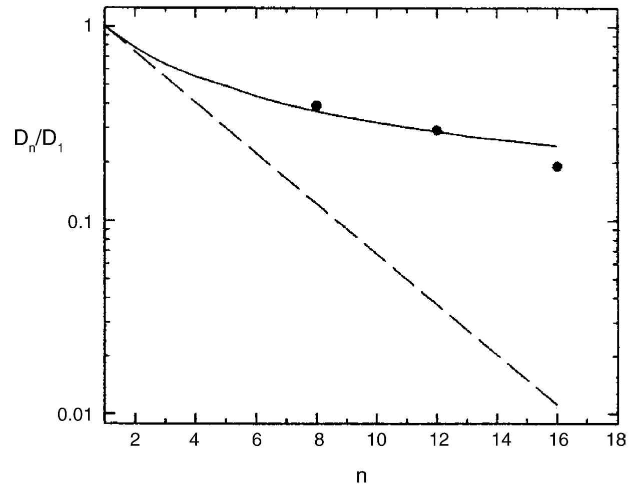

Fig. 1. Diffusivities of *n*-paraffins in FT-wax: (●) experimental data at $T = 504$ K from ref. [9], (—) Wilke–Chang correlation at $T = 540$ K, (- - -) correlation from ref. [4] {from ref. [1]}.

with diffusion effects only. Especially, when the more realistic lower dependency of the diffusion coefficients with chain length, as observed by Erkey et al. [9] (Fig. 1), is used their model underestimates the olefin to paraffin ratio.

Furthermore, Kuipers et al. [10] measured the (O_n/P_n) ratio for the FTS on a polycrystalline cobalt-foil (without diffusion limitations) and still obtained an exponential decrease of this ratio with chain length. So, we can conclude that the chain length dependency of the olefin to paraffin ratio can hardly be due to diffusion effects only, but the preferential physi-sorption and increase of the solubility with chain length influences the selectivity as well.

In this report, we use the products formed when one switches from a syngas composed of H_2/CO to D_2/CO to provide a measure of the primary products of the synthesis.

2. Experimental

The general apparatus and procedure for the FTS synthesis have been provided in earlier publications (e.g., [11]). The cobalt-alumina catalyst was first reduced ex situ in a plug flow reactor at 350 °C and atmospheric pressure in a flow of hydrogen for 14 h and again after transferring to the continuously stirred autoclave reactor (CSTR) under an inert gas blanket at 280 °C for 24 h. The general procedure we follow to determine the initial paraffin and olefin products from using the deuterium tracer in the FTS is as follows: (1) the FTS was started in a 1 L CSTR using H_2/CO as the synthesis gas; (2) after a few days of operation during which the FTS approaches and attains a steady-state operation the sample collection vessels are emptied and the feed switched from H_2/CO to D_2/CO; (3) a sample is collected about 24 h after switching to the D_2/CO feed.

In carrying out deuterium tracer studies in FTS, the following requirements must be kept in mind: (1) there must be no H/D exchange in the paraffin and (2) the hydrogen (or deuterium) exchange in the olefin is limited (the 1–3 positions of an olefin). The Co catalyst (19% Co) used in this study is qualified to conduct H_2/D_2 switching experiments since measurable exchange in the alkanes is not obtained [11]. Hence, the isotopes in paraffin left in the reactor will remain the same after switching to D_2/CO, and the olefins left in the reactor will undergo H/D exchange and generate D_1 to D_5 isotopomers of an olefin. The total amount of olefin left in the reactor is equal to $\sum_{i=0}^{5} C_nH_iD_{2n-i}$. Due to hydrogenation of the olefin, the total amount of paraffin left in the reactor equals to $\sum_{i=0}^{7} C_nH_iD_{2n+2-i}$. The quantitative analysis of the isotopomers of products by GC/MS method has been described previously [11].

3. Results

The deuterium-containing compounds in the first sample collected after switching from H_2/CO to D_2/CO will be the "true products" of FTS reactions. For the higher carbon number hydrocarbons, the vapor pressure of the same carbon number alkenes and alkane do not vary appreciably so that the alkene/alkane ratio obtained from the deuterium analysis of the products exiting the reactor in the vapor phase will be representative of the primary products of the FTS.

The paraffin to olefin ratios (P/O) of hydrocarbons from C_8 to C_{16} for a Co-catalyzed FTS reaction determined by the conventional method show that the ratio increases with increasing molecular weight by a rate of $e^{0.3n}$ (see Fig. 2); this is the value for the constant c in Eq. (1) that was discussed in the introduction and that was reported in ref. [4].

Similar results for the constant, based on analysis of products exiting the reactor, were reported by other groups but these values are not representative of the true ratios of the reaction due to the presence of the accumulated products

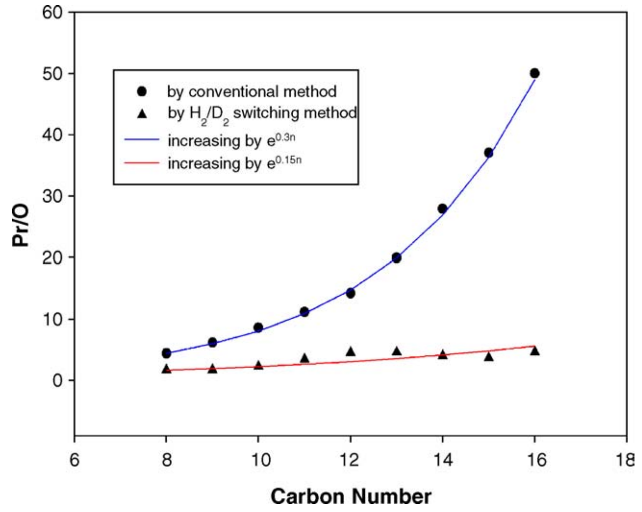

Fig. 2. The paraffin to olefin ratio of products of a Co-catalyzed FT reaction.

[12]. By using the H_2/D_2 switching method, more reliable values are obtained, as displayed in Fig. 2. The ratios obtained by the conventional method are much larger than the true paraffin to olefin ratios of the reaction. For instance, the paraffin to olefin ratio of hydrocarbon C_{16} measured by the conventional method is 10 times higher than the value obtained by considering only the deuterium-containing compounds. Although the true paraffin to olefin ratio of the hydrocarbons from C_8 to C_{16} increases with increasing molecular size, the rate of the increase ($e^{0.15n}$) is much smaller than most of the rates reported in the literature. The true value of the paraffin to olefin ratio will be even smaller than shown in Fig. 2 because accumulation of deuterated products during the 24-h period may impact the distribution shown in Fig. 2. A comparison of the curves in Figs. 1 and 2 show that the c value obtained from the deuterium/hydrogen switch agrees more closely with the data generated by Erkey et al. [9] than reported by Iglesia et al [4].

Many studies have been made where isotopically labelled compounds have been added to the feed to the FTS reactor [13]. However, any diffusion effects that impact the primary FTS products as they exit the pore structure of the catalyst particle will operate for added tracer compound as it diffuses into the pore structure. In the present case, deuterium and carbon monoxide diffuse into the pore in a manner that is, or is nearly, identical to that of hydrogen and carbon monoxide. Since the deuterated products are formed in the catalyst pores, they must diffuse out of the catalyst pore structure just as the normal hydrogen products do. Thus, for FTS mechanism studies, the switch from hydrogen to deuterium-containing syngas is preferred to that of adding a labelled compound such as an alkene or an alcohol.

The smaller value for the impact of diffusion of heavier alkenes means that the earlier models utilizing diffusion limitations as a means to account for the two-alpha distribution through re-adsorption and chain initiation will grossly over-estimate the impact of alkene re-incorporation when the catalyst is operated under the conditions used in this study. However, there are many factors that may impact the product selectivity and much additional work is needed before a generalization to the wider range of conditions and catalysts can be made.

References

[1] G.P. Van der Laan, A.A.C.M. Beenackers, Kinetics and selectivity of the Fischer–Tropsch synthesis: a literature review, Catal. Rev. Sci. Eng. 41 (1999) 255.

[2] E. Iglesia, S.C. Reyes, S.L. Soled, Reaction-transport selectivity models and the design of Fischer–Tropsch catalysts, in: E.R. Becker, C.J. Pereira (Eds.), Computer-Aided Design of Catalysts, Marcel Dekker, New York, 1993, pp. 199–257.

[3] R.J. Madon, E. Iglesia, S.C. Reyes, Non-flory product distributions in Fischer–Tropsch synthesis catalyzed by ruthenium, cobalt, and iron, in: S.L. Suib, M.E. Davis (Eds.), Selectivity in Catalysis, ACS Symposium Series, American Chemical Society, 1993 , pp. 382–396.

[4] E. Iglesia, S.C. Reyes, R.J. Madon, S.L. Soled, Selectivity control and catalyst design in the Fischer–Tropsch synthesis: sites, pellets and reactions, in: E.E. Eley, H. Pines, P.B. Weisz (Eds.), Advances in Catalysis, vol. 39, 1993, pp. 221–301.

[5] E. Iglesia, S.C. Reyes, R.J. Madon, Transport-enhanced α-olefin re-adsorption pathways Ru-catalyzed hydrocarbon synthesis, J. Catal. 129 (1991) 238–256.

[6] R.J. Madon, I. Eglesia, The importance of olefin readsorption and H_2/CO reactant ratio for hydrocarbon chain growth on ruthenium catalysts, J. Catal. 139 (1993) 576–590.

[7] R.J. Madon, S.C. Reyes, E. Iglesia, Primary and secondary reaction pathways in ruthenium-catalyzed hydrocarbon synthesis, J. Phys. Chem. 95 (1991) 7795–7804.

[8] R.J. Madon, E. Iglesia, Hydrogen CO interpellet diffusion effects in ruthenium-catalyzed hydrocarbon synthesis, J. Catal. 1949 (1949) 428–437.

[9] C. Erkey, J.B. Rodden, A. Akgerman, Diffusivities of synthesis gas in alkanes in Fischer–Tropsch wax, Energy Fuels 4 (1990) 275–276.

[10] E.W. Kuipers, I.H. Vinkenburg, H. Oosterbeek, Chain length dependence of α-olefin re-adsorption in Fischer–Tropsch synthesis, J. Catal. 152 (1995) 137–146.

[11] B. Shi, R.J. O'Brien, S. Bao, B.H. Davis, J. Catal. 199 (2001) 202.

[12] B. Shi, B.H. Davis, Fischer–Tropsch synthesis: accounting for chain-length related phenomena, Appl. Catal. A: Gen. 277 (2004) 61.

[13] A. Raje, B.H. Davis, Fischer–Tropsch synthesis. Mechanism studies using isotopes, in: J.J. Spring (Ed.), Catalysis, vol. 12, The Royal Society of Chemistry, Cambridge, 1996, pp. 52–131.