Deuterium tracer study of Fischer–Tropsch synthesis: A method to eliminate accumulation problems

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Abstract

Product accumulation in Fischer–Tropsch synthesis (FTS) occurs not only in large continuously stirred tank reactors, but also in small fixed bed reactors. Thus, in order to obtain the correct product distribution data and paraffin to olefin ratio for a FTS reaction test, it is necessary to eliminate the accumulation effect even for reactions conducted in fixed bed reactors. This study shows that the D_2/H_2 switching method is a way to obtain the correct data for the FTS reactions. In a Co catalyzed FTS reaction, the α value determined by the D_2/H_2 switching method was close to 0.88 from C_9 to C_{20}. After accumulation and secondary hydrogenation corrections, the paraffin to olefin ratio for the hydrocarbons produced by this reaction was found to increase with increasing molecular size by a rate of $e^{0.15n}$, in which n is the number of carbon atoms. This is much smaller than the values obtained by the conventional method.

1. Introduction

The Fischer–Tropsch synthesis (FTS) is a practical way of converting coal or natural gas to fuels and chemicals [1]. The starting materials of this reaction are carbon monoxide (CO) and hydrogen (H_2), which can be produced from coal, natural gas or biomass.

The major products of FTS are linear hydrocarbons, which decrease exponentially with chain length, a distribution usually refers to as Anderson–Schulz–Flory (ASF) distribution [2]. However, as early as 1956, Anderson [3] observed that ASF plots fell on two straight lines. Since then, the two α distribution phenomenon have been reported by many research groups for FT synthesis conducted in different types of reactors, using different catalysts, and over a range of different reaction conditions [4–15]. The deviations from ASF distribution fall into two categories: positive deviation in which higher-than-expected yield of longer chain hydrocarbons was observed [3,9–15], and negative deviation in which lower-than-expected yield of longer chain hydrocarbons was observed [4–8].

Such chain-length related problems were also observed in isotope tracer experiments and in paraffin to olefin ratio analysis. According to the definition of initiation, the molar activity should be a constant for all the hydrocarbons if a labeled initiator is used in a tracer experiment. However, many research groups found that the measured molar activity decreased with increasing molecular size [16–20], and the paraffin to olefin ratio also increased with increasing carbon number [14,15].

To explain these chain-length related problems, several theories and models were proposed during the 1980s and 1990s [5,8,14]. However, none of these theories can adequately explain all of these chain-length related problems. In 2001, Shi and Davis [21,22] found that if the accumulation factor (Δ) was taken into consideration, the isotope data could be explained. By using the D_2/H_2 switching method, Shi and Davis [23] measured the amount of hydrocarbons from C_7 to C_{16} accumulated in the reactor, and then they proposed a new model for accounting for the chain-length related phenomena. This model states that the apparent amount of products for a FTS reaction, *S*, in a defined time interval is a mixture of the products produced

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during this time (Φ) and the products accumulated in the reactor (Δ), $S_n = \Phi_n + \Delta_n$. By using this model, all of the chain-length related problems in FT synthesis could be explained without using any assumption. This model also implies that in order to obtain the true product distribution and the paraffin to olefin ratio for a FTS reaction test, it is necessary to find a way to eliminate the term Δ; and the D_2/H_2 switching experiment is a way to achieve this goal.

Shi and Davis model is based on the data obtained from the D_2/H_2 switching experiments conducted in a 1 L continuously stirred tank reactor (CSTR) [23]. When a FT reaction was conducted in supercritical conditions in a fixed bed reactor, Jacobs et al. [24] found that when switching from normal fixed bed testing to a feed containing supercritical hexane/pentane mixture, considerable more wax was produced in the initial period following the switch, clearly demonstrating that higher molecular weight products are accumulated in the catalyst bed. Since a large volume of data was generated from fixed bed reactor (FBR) testing over the past 80 years, it will be helpful to know if there are accumulated products in the experiments conducted in the fixed bed reactor. If there are, how will they affect the data interpretation? In order to address these questions, we conducted a Co catalyzed FT synthesis test in a FBR as well as in a CSTR using the D_2/H_2 switching method.

2. Experimental

2.1. Apparatus

The FTS reactions were carried out in a 1 L CSTR and in a 60 cm long FBR with 2 cm internal diameter. The hydrogen and carbon monoxide gases were introduced into the reactor by Brooks 5850 mass flow controllers, which were calibrated over a wide range of pressure for each of the gases. The products collected were analyzed using an Agilent 6890N gas chromatograph and an Agilent 5973N gas chromatograph–mass spectrometer (GC/MS) with HP-5 column.

2.2. Catalyst preparation

The calcined SiO_2 (pore size of 5–8 nm, Qingdao Meigao Chemical Co.) was impregnated with the appropriate amount of $Co(NO_3)_2$ solution, and then dried at 383 K for 12 h, and finally calcined in air at 673 K for 6 h. The surface area and the pore volume of the catalyst are 359.3 m²/g and 0.59 cm³/g.

2.3. Reaction procedure

Six grams of catalyst were reduced in a stainless steel tube at 450 °C and under atmospheric pressure of H_2 with a flow rate of 35 SL h⁻¹ for 10 h, and then transferred to the CSTR in the absence of air. The catalyst was reduced again at 280 °C for 18 h in a H_2 flow of 30 SL h⁻¹. For FBR runs, six grams of catalyst were mixed with 36.0 g of carborundum (the surface area of 4.75 m²/g, the pore volume of 0.0118 cm³/g) and 80.0 g of glass beads to minimize the temperature gradient and then reduced in atmospheric pressure of H_2 with a flow rate of 35 SL h⁻¹. After

reduction, the reactor temperature was decreased to 180 °C, and then the syngas was introduced to the reactor and the pressure was increased to 1.0 MPa. The temperature was then raised to 230 °C, and the syngas flow rate was adjusted to 2 SL h⁻¹ g⁻¹. The products were collected in three traps, the temperature of which were 130, 50 and −2 °C, respectively.

2.4. D_2/H_2 switching experiment

The general procedure for the D_2/H_2 switching experiment is the same as described previously [23]. The FT synthesis was started using $CO/H_2/N_2$ (1:2:2) as the synthesis gases. Several days later, the feeds were switched to $CO/D_2/N_2$ (1:2:2). Twenty-four hours later, the samples were collected and then the feeds were switched back to $CO/H_2/N_2$, and the samples were collected every 24 h. The quantitative analysis of deuterated compounds was the same as described previously [23].

3. Results and discussion

3.1. Product accumulation in CSTR and FBR

The Co catalyzed FTS reaction was conducted in a 1 L CSTR and FBR. The reaction conditions are given in Table 1. For the CSTR runs, the reaction was started using $CO/H_2/N_2$ as reagents for 7 days, and then the feed was switched to $CO/D_2/N_2$ for a duration of 24 h, and then switched back to $CO/H_2/N_2$. After switching back to $CO/H_2/N_2$, the samples were collected every day until no deuterium-containing compounds were found in the high molecular weight hydrocarbons. The products accumulated in the reactor are estimated by analyzing the sample collected prior to switching back to $CO/H_2/N_2$. After switching to $CO/D_2/N_2$, the deuterium-containing hydrocarbons are the products freshly produced by FTS (Φ), while the hydrogen-containing hydrocarbons are the products accumulated in the reactor (Δ). The relative amount of Φ and Δ in each hydrocarbon are given in Table 2. Under similar reaction conditions and using the same catalyst, the FTS reaction was conducted in a FBR. After the reaction was run using $CO/H_2/N_2$ for 5 days, the feeds were switched to $CO/D_2/N_2$ for 24 h, and then switched back to $CO/H_2/N_2$. The samples were analyzed in the same manner as in CSTR runs. The results are also given in Table 2.

Table 1

Reaction conditions in Co catalyzed FT reaction conducted in a continuously stirred tank reactor (CSTR) and a fixed bed reactor (FBR)

	CSTR	FBR
Catalyst	15%Co/SiO₂	15%Co/SiO₂
Temperature (°C)	230	230
Pressure (bar)	10	10
Flow rate (SL h⁻¹ g⁻¹)	2	2
CO/H₂/N₂ ratio	1:2:2	1:2:2
CO/D₂/N₂ ratio	1:2:2	1:2:2
Time of CO/H₂/N₂ run (h)	89	117
Time of switching to CO/D₂/N₂ run (h)	24	24
Time of CO/H₂/N₂ run (h)	312	216

Table 2
The Percentages of the accumulated products and the freshly produced products obtained in CSTR and FBR runs

		C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19
CSTR	$\Delta\%$	19	26	32	41	51	61	69	75	80	84	87	90
	$\Phi\%$	81	74	68	59	49	39	31	25	20	16	13	10
FBR	$\Delta\%$	21	13	10	9.3	10	11	12	15	18	23	28	35
	$\Phi\%$	79	87	90	91	90	89	88	85	82	77	72	65

As shown in Table 2, in the CSTR runs, the amount of accumulated products for C_8 is about 19%, the percentage of accumulated products increases with molecular size and increases up to 90% for C_{19}. These results are in agreement with the results reported by Shi and Davis [23], indicating that the products obtained by the conventional method are not the true FTS products, instead, they are the mixture of FTS products and the products accumulated in the reactor. As for the FBR runs, the relative amount of accumulated products for C_8 is 21%, the percentage of accumulated products increases as the carbon number and increases up to 35% for C_{19}. Clearly, the product accumulation problems do exist in FBR runs even though they are less problematic than in CSTR runs.

In each sample collection period (the sample was collected every 24 h), only a fraction of products produced during this period (f_n) can be collected, the rest ($1 - f_n$) of them are accumulated in the reactor. The f_n for each hydrocarbon are calculated by the following equation:

$$f_n = \frac{a_1}{a_t} \tag{1}$$

where a_1 is the amount of deuterium-containing compound (C_n) collected during $CO/D_2/N_2$ run and a_t is the total amount of deuterium-containing compounds (C_n) collected during $CO/D_2/N_2$ run and after switching back to $CO/H_2/N_2$ run. During $CO/D_2/N_2$ run, only a fraction of the freshly produced FTS products can be collected. After switching back to $CO/H_2/N_2$ run, the amount of deuterium-containing compounds were measured for every sample in each sample collection period until no deuterium-containing compounds were found for C_{20} (for CSTR runs, there are still significant amounts of deuterated compounds in the sample collected even after 13 days; for FBR runs, it takes 9 days).

The f_n value is a function of Henry's law constant and the reaction conditions such as gas flow and the reactor type [23]. Fig. 1 shows the f_n values of Fe and Co catalyzed FTS reaction at different reaction conditions. Under the same reaction temperature and the same sample-collecting interval, the f_n value obtained in a large CSTR reactor is smaller than that in the FBR reactor. Using the same reactor, the f_n value obtained at higher temperature run are larger than that in low temperature runs. These results indicate that the major contribution to the accumulation is from the Henry's law constant which is a function of temperature and the size of the reactor and other reaction conditions. The Henry's law constants for hydrocarbons at 250 °C are also plotted in Fig. 1, in which the Henry's law constants have been converted to percentage of vapor phase, assuming that the percentages of vapor phase for C_1–C_7 were 100% and the percentage of

vapor phase for C_8–C_{20} were adjusted accordingly. The values thus obtained have a trend that is similar to the f_n obtained from CSTR reactor, suggesting that vapor–liquid equilibrium effect is partly responsible for the chain-length dependent accumulation factor.

3.2. The true product distribution for a Co catalyzed FTS reaction

Due to accumulation, the products obtained by the conventional method cannot be considered as the "true products" of the FTS reactions since the olefins can undergo secondary reaction under FTS reaction conditions. As discussed by Shi and Davis [23,25], before a reaction has reached steady state, the product distribution will show a negative deviation from ASF distribution; after the reaction has reached the steady state, the change in Φ_n/Δ_n due to catalyst deactivation or reaction condition changes such as syngas flow rate will give a positive deviation from ASF distribution. Therefore, in order to obtain the correct product distribution for a FTS reaction, it is necessary to eliminate the term Δ. The D_2/H_2 switching experiment provides a way to obtain the correct product distribution data. After switching to $CO/D_2/N_2$ run for 24 h and then switching back to $CO/H_2/N_2$, the deuterium-containing compounds obtained can be considered as the true FTS products and their distribu-
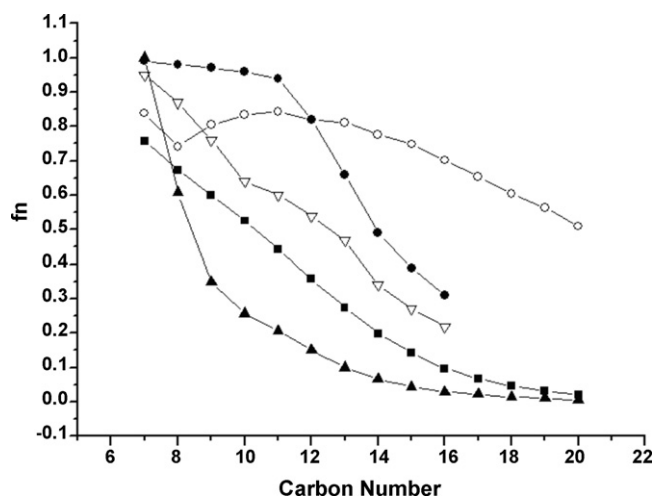

Fig. 1. The f_n values for reactions conducted in different reaction conditions: (■) f_n values obtained in CSTR runs at 230 °C; (○) f_n values obtained in FBR runs at 230 °C; (●) reported f_n values in Ref. [23] for a Fe catalyzed FTS reaction conducted in CSTR at 270 °C; (□) reported f_n values in Ref. [23] for a Co catalyzed FTS reaction conducted in CSTR at 210 °C; (▲) the values calculated based on Henry's law constant at 250 °C (see text for calculations).
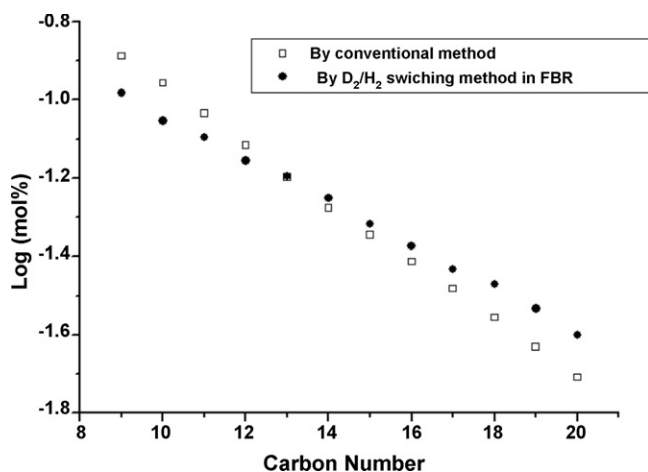
Fig. 2. The product distributions of Co catalyzed FTS reactions conducted in FBR.

tion can be considered as the true product distribution of a FTS reaction.

Fig. 2 is the product distribution obtained by the conventional method and the D_2/H_2 switching method for a Co catalyzed FTS reaction conducted in a FBR. Using the D_2/H_2 switching method, the α value based on the mole fraction from C_9 to C_{20} is 0.881. By conventional method, the α value is 0.844, a negative deviation from the true product distribution. These results are in agreement with results reported previously [23] where there was no or very little deviation from an ASF distribution in Fe and Co catalyzed FTS reactions after accumulation factor is accounted for. Many evidences show that 1-olefin produced by a FTS reaction can be readsorbed onto the surface of catalysts and can undergo secondary reaction. The reasons why readsorbed olefin cannot alter the ASF distribution may be due to following facts: (1) the amount of readsorbed olefin incorporating into high carbon number compounds are small especially for olefins with carbon number greater than C_{10} [25]; (2) the percentage of regrowth of readsorbed olefin is decreased not increased as the molecular size is increased [25]; and (3) the secondary hydrogenation of readsorbed olefin to the corresponding paraffin with same carbon number will not alter the mole fraction of that carbon number.

3.3. The paraffin to olefin ratio (Pr/O) of a FTS reaction

The paraffin to olefin ratio of a hydrocarbon produced in a FTS reaction (Pr/O) is given by $Pr/O = \Phi_n(P)/\Phi_n(O)$, where $\Phi_n(P)$ is the amount of paraffin, $\Phi_n(O)$ the total amount of 1-alkene, trans-2-alkene and *cis*-2-alkene, and n is the number of carbon atoms. Early studies recognized that olefins and paraffins are the major primary products of FTS reactions. The accurate measurement of the Pr/O ratio for each carbon number produced by FTS is crucial for understanding both the nature of the catalyst and the mechanism of the FTS reactions. It is assumed that the Pr/O ratio of hydrocarbons with different carbon number produced in FTS reaction for a given catalyst has the same value, and it is the characteristic of the catalyst. However, all reported data show that the paraffin to olefin ratios increased with increas-

ing molecular size exponentially as expressed by $P_n/O_n \propto e^{cn}$, where n is the number of carbon atoms and c is a constant, the value of which varies from 0.15 to 0.59 depending on catalyst type and reaction conditions [15]; and these value increased with increasing bed residence time [14,26]. To account for these experimental facts, several theories were proposed. Schulz and Gokcebay [27] proposed that FTS catalyst sites preferably produce olefins, and to a lesser extent, paraffins; and that olefins can be adsorbed and hydrogenated on hydrogenation sites other than FTS growth sites. Iglesia et al. [14] proposed that olefin transport rates decrease with increasing molecular size, leading to increasing paraffin to olefin ratio as the carbon number of the product molecules increases. Shi and Davis [23] proposed that the Pr/O ratio increases with increasing carbon number because the olefins left in the reactor undergo secondary hydrogenation and the higher carbon number olefins stay in the reactor longer than the lower ones do. This model suggests that unlike the measurement of α value of a FTS reaction, the correct Pr/O ratio cannot be obtained by conducting the FTS reaction using the conventional method even through the reaction has reached steady state. A D_2/H_2 switching method was thus proposed.

The true Pr/O ratio of a FTS reaction can be obtained by eliminating both the accumulation effect and the effect of secondary hydrogenation of olefin. By analyzing the very first sample after switching to $CO/D_2/N_2$ run, the accumulation effect on Pr/O ratio can be eliminated. The ratio of freshly produced deuterium-containing paraffin and olefin that are free of accumulation can be considered as the Pr/O ratio of the FTS reaction for a given catalyst. The values are listed in Table 3. The Pr/O ratios obtained in this way are close to the true values of paraffin to olefin ratio, but they are not the values of paraffin and olefin produced at the moment when these compounds were desorbed from the surface of the catalyst because the samples were collected during a period of 24 h and the desorbed olefin can readsorb onto the catalyst surface and undergo secondary hydrogenation during this period, resulting in an apparent Pr/O ratio larger than the true ratio. To obtain the correct Pr/O ratio, both the accumulation effect and the secondary hydrogenation effect must be
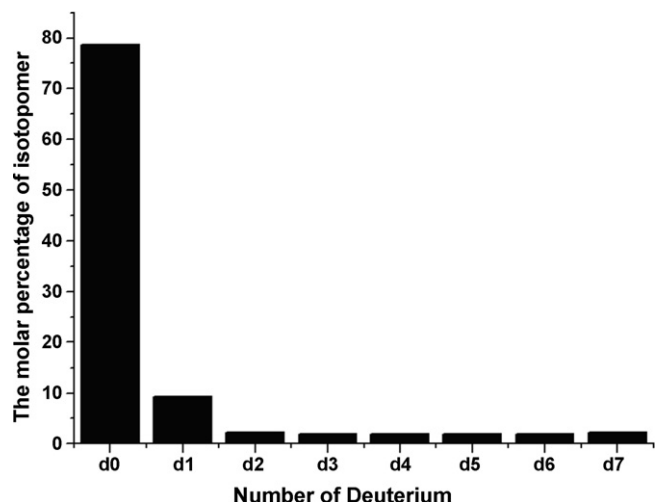

Fig. 3. The molar percentage of isotopomers of $C_8H_{18-x}D_x$ obtained in a CSTR run.

Table 3
The Paraffin to olefin ratios and the percentage of the secondary reduction of olefin in runs conducted in CSTR and FBR

Carbon number	CSTR				FBR			
	Conventional	Corrected for Δ	Reduction (%)	Corrected for 2nd hydrogenation	Conventional	Corrected for Δ	Reduction (%)	Corrected for 2nd hydrogenation
C8	4.1	3.7	51	1.3	3.7	3.0	8.7	2.6
C9	4.8	4.3	41	2.1	4.7	3.7	13	3.3
C10	6.4	5.0	46	2.2	5.9	5.7	16	4.9
C11	6.8	6.4	34	3.9	7.3	6.4	19	4.8
C12	11	9.7	33	6.1	8.8	10	29	6.7
C13	10	8.6	26	6.1	11	11	26	7.4
C14	18	12	27	8.3	22	18	32	12
C15	26	13	22	9.7	35	23	31	15
C16	31	13	14	11	46	28	26	21
C17	38	13	18	10	53	33	41	19
C18	51	15	19	12	120	39	38	24
C19	165	22	66	13	191	41	42	23

corrected. The corrections for secondary hydrogenation can be made from the result of the D_2/H_2 switching experiment.

Under FTS reaction conditions, olefin can undergo isomerization and hydrogenation; and the hydrogen atoms on carbon 1–3 of the olefins are subjected to deuterium/hydrogen exchange [28] which does not occur in alkanes [23,28]. After switching to $CO/D_2/N_2$ run, the olefin left in the reactor (hydrogen-containing olefin, Δ(o)) will undergo secondary hydrogenation to produce paraffin that could contain 1–7 deuterium atoms. Figs. 3 and 4, for instance, illustrate the molar percentage of isotopemers of $C_8H_{18-x}D_x$, where $x = 0 \rightarrow 7$. Clearly, the compound C_8H_{18} is the octane left in the reactor before switching to $CO/D_2/N_2$ run; and $C_8H_{17}D$, $C_8H_{16}D_2$, $C_8H_{15}D_3$, $C_8H_{14}D_4$, $C_8H_{13}D_5$, $C_8H_{12}D_6$, and $C_8H_{11}D_7$ are the compounds produced by the secondary hydrogenation of C_8H_{16}. The percentage of secondary reduction of olefin during the period of 24 h can be obtained by the following equation:

$$\text{Reduction } (r_n)\% = \frac{\sum_{x=1}^{7} C_n H_{2n+2-x} D_x}{\sum_{x=1}^{7} C_n H_{2n+2-x} D_x + \sum_{y=0}^{5} C_n H_{2n-y} D_y} \quad (2)$$
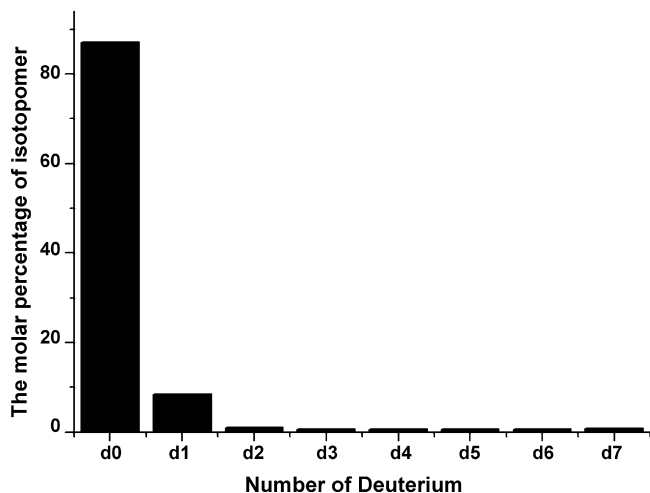
Fig. 4. The molar percentage of isotopemers of $C_8H_{18-x}D_x$ obtained in a FBR run.

The percentage of secondary reduction of olefin from C_8 to C_{19} during the period of 24 h is shown in Table 3. The true amount of freshly produced deuterium-containing olefins is equal to $\sum_{y=0}^{5} C_n D_{2n-y} H_y / 1 - r_n$, and the true amount of freshly produced deuterium-containing paraffins is equal to $\sum_{x=0}^{7} C_n D_{2n+2-x} H_x - \left(\sum_{y=0}^{5} C_n D_{2n-y} H_y / 1 - r_n \right) r_n$, by assuming that the percentage of secondary reduction of freshly produced olefins during the period are the same as that of the olefins left in the reactor. The Pr/O ratios corrected for secondary reaction are also listed in Table 3.

Fig. 5 shows the paraffin to olefin ratio against carbon number on a Co catalyst conducted by the conventional method and the D_2/H_2 switching method in a CSTR reactor as well as in a FBR reactor. The correct Pr/O ratios obtained by the D_2/H_2 method are much smaller than the ratio obtained by the conventional method either in a CSTR reactor or in a FBR reactor. The correct Pr/O ratio of Co catalyzed FTS reaction increases with increas-
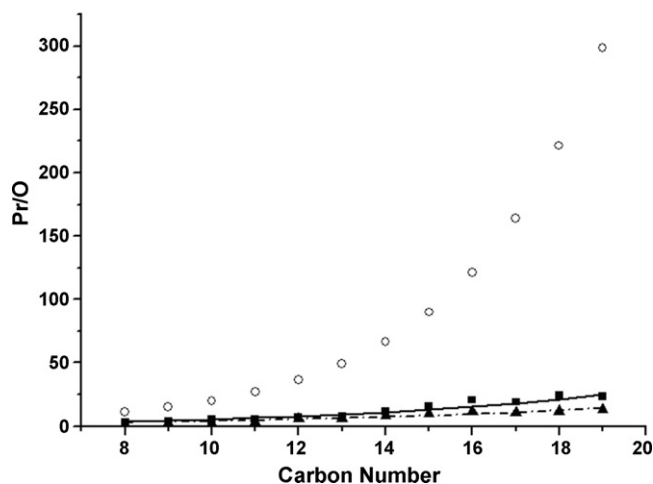
Fig. 5. The paraffin to olefin ratio of hydrocarbons with carbon number: (■) values obtained in FBR run by the D_2/H_2 switching method showing Pr/O ratio increasing at a rate of $e^{0.17n}$; (▲) values obtained in CSTR run by the D_2/H_2 switching method showing Pr/O ratio increasing at a rate of $e^{0.14n}$; (○): the average values obtained in CSTR runs by conventional method showing Pr/O ratio increasing at a rate of $e^{0.3n}$.

ing molecular size exponentially by a rate of approximately $e^{0.15n}$, which is much smaller than the enhanced readsorption model suggested value of $e^{0.3n}$ [14].

If we assume that both olefins and paraffins are primary products of the FTS reaction and the Pr/O ratio is independent of the molecular length, the fact that Pr/O ratios increase as the molecular size increasing even after accumulation factor is removed by the D_2/H_2 switching method would suggest that 1-olefins produced in FTS reaction can be readsorbed onto the surface of catalysts and can undergo secondary hydrogenation. The question why Pr/O ratios increase as the carbon number increasing has been the subject of debating over the past two decades, several models has been proposed [14,15,26,29–31]. The diffusion limitation model [14,29,30] argues that the 1-olefin of longer chain length will take longer time to diffuse, resulting in more longer chain 1-olefin being readsorbed. On the other hand, the viewpoint of solubility model [26,31] is that high solubility of longer chain hydrocarbons will enable them to reside in the liquid layer longer, so that they can be readsorbed. In a similar argument to solubility model, the physisorption model's conclusion is that the readsorption rate is governed by the concentration of the physisorbed interface [15]. All of these models can be used to qualitatively discuss the secondary reduction that result in Pr/O ratios increasing with carbon number increasing. However, in order to quantitatively explain these results, the diffusion limitation model needs to be modified to account for the facts that there is no or very little deviation from ASF distribution and Pr/O ratio increasing at a much slower rate than that the model intended to explain initially.

4. Conclusions

For the FTS reaction, the product accumulation (Δ) not only exists in larger CSTR reactor, but also in small fixed bed reactor. In some cases, even in microscale fixed bed reactor, the accumulation can also complicate the data interpretation. The positive and negative deviation from ASF distribution, the strong dependency of olefin content on molecular size and the negative deviation from a constant molar activity for an initiator in FT synthesis were caused mainly by the product left in the reactor. Therefore, the product distribution and Pr/O ratio data generated in CSTR and FBR cannot be considered as the true product distribution and the correct Pr/O ratio for a given catalyst. In order to obtain the correct production distribution and the paraffin to olefin ratio, it is necessary to eliminate the term Δ by using the D_2/H_2 switching method. Using this method, it is not necessary to conduct the FTS reaction for a long period in order to reach steady state so that the correct product distribution can be obtained. This is the only way so far to obtain the correct Pr/O ratio for a FTS reaction.

References

[1] F. Fisher, H. Tropsch, Brennst. Chem. 4 (1923) 276.
[2] R.A. Friedel, R.B. Anderson, J. Am. Chem. Soc. 72 (1950) 1212.
[3] R.B. Anderson, in: P.H. Emmett (Ed.), Catalysis, vol. IV, Reihold, New York, 1956, pp. 123–163.
[4] G. Henrici-Olive, S. Olive, Angew. Chem. Int. Ed. Engl. 15 (1976) 136.
[5] C.N. Satterfield, G.A. Huff, J.P. Longwell, Ind. Eng. Chem. Process. Des. Dev. 21 (1982) 465.
[6] C.N. Satterfield, G.A. Huff, J. Catal. 73 (1982) 187.
[7] P.B. Pannell, C.L. Kibby, K.S. Chung, Proceedings of the Advances in Catalytic Chemistry, vol. II, Salt Lake City, UT, May 18–21, 1982.
[8] R.A. Dictor, A.T. Bell, Ind. Eng. Chem. Process Des. Dev. 22 (1983) 678.
[9] H. Pichler, H. Schulz, M. Elstner, Brennst. Chem. 48 (1967) 78.
[10] H.E. Atwood, C.O. Bennett, Ind. Eng. Chem. Process Des. Dev. 18 (1979) 163.
[11] R.J. Madon, W.F. Taylor, J. Catal. 69 (1981) 32.
[12] L. Koning, J. Gaube, Chem. Eng. Technol. 55 (1983) 14.
[13] G.A. Huff, C.N. Satterfield, J. Catal. 85 (1984) 370.
[14] E. Iglesia, S.C. Reyes, R.J. Madon, J. Catal. 129 (1991) 238.
[15] E.W. Kuipers, C. Scheper, J.H. Wilson, I.H. Vinkenburg, H. Oosterbeek, J. Catal. 158 (1996) 288.
[16] L.-M. Tau, H.A. Dabbagh, B. Chawla, B.H. Davis, Catal. Lett. 7 (1990) 141.
[17] L.-M. Tau, H.A. Dabbagh, B.H. Davis, Energy Fuels 5 (1991) 174.
[18] L.-M. Tau, H.A. Dabbagh, B. Bao, B.H. Davis, Catal. Lett. 7 (1990) 127.
[19] H. Schulz, Erdoel Kohle Erdgas Petrochem. 30 (1977) 123.
[20] M.L. Turner, H.C. Long, A. Shenton, P.K. Byers, P.M. Maitlis, Chem. Eur. J. 1 (1995) 549.
[21] B. Shi, B.H. Davis, Catal. Today 58 (2000) 255.
[22] B. Shi, B.H. Davis, Catal. Today 65 (2001) 95.
[23] B. Shi, B.H. Davis, Appl. Catal. A: Gen. 277 (2004) 61.
[24] G. Jacobs, K. Chaudhari, D. Sparks, Y. Zhang, B. Shi, R. Spicer, T.K. Das, J. Li, B.H. Davis, Fuel 82 (2003) 1251.
[25] B. Shi, G. Jacobs, D. Sparks, B.H. Davis, Fuel 84 (2005) 1093.
[26] T. Komaya, A.T. Bell, J. Catal. 146 (1994) 237.
[27] H. Schulz, H. Gokcebay, in: J.R. Kosak (Ed.), Catalysis of Organic Reactions, Marcel Dekker, New York, 1984, pp. 153–169.
[28] B. Shi, R.J. O'Brien, S. Bao, B.H. Davis, J. Catal. 199 (2001) 202.
[29] R.J. Madon, E. Iglesia, J. Catal. 139 (1993) 576.
[30] R.J. Madon, S.C. Reyes, E. Iglesia, J. Phys. Chem. 95 (1991) 7795.
[31] E.W. Kuipers, I.H. Vinkenburg, H. Oosterbeek, J. Catal. 152 (1995) 137.