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Formation of 2-alkenes as secondary products during Fischer–Tropsch synthesis

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ABSTRACT

The H_2/D_2 switching experiments showed that there is an inverse isotope effect during iron catalyzed Fischer–Tropsch (FT) reactions. The rate of hydrocarbon production (r) increased when syngas CO/H_2 was switched to CO/D_2 with the ratio of r_H/r_D being 0.55–0.58. The inverse isotope effect in every propagation step was calculated to be 0.88, which is a reasonable value for an inverse isotope effect at 270 °C that originates from the C–H (D) bond hybridization change from sp^2 to sp^3. These results are similar to cobalt catalyzed FT reactions that were explained by the modified alkylidene mechanism by which 1-alkenes and n-alkanes are the primary products of the FT reaction and the others are products of secondary. The detailed analysis of products produced during iron catalyzed FT reactions with CO/H_2 or CO/D_2 as the syngas feeds showed that while the ratios of $[\text{1-alkenes}]_H/[\text{1-alkenes}]_D$ are less than 1, the ratios of $[\text{2-alkenes}]_H/[\text{2-alkenes}]_D$ are more than 1; this indicates that 2-alkenes are produced through a pathway that is different from 1-alkenes. These results also suggest that there is a normal isotope effect during the formation of 2-alkenes through the corresponding 1-alkenes, which will result in the ratio of $[\text{1-alkenes}]_H/[\text{1-alkenes}]_D$ being less than 1. The formation of 2-alkenes is explained by the alkylidene mechanism.

1. Introduction

The Fischer–Tropsch (FT) reaction is a non-selective process in which CO and H_2 are converted to fuels and chemicals such as n-alkanes, 1-alkenes, 2-alkenes and oxygenates as well as branched hydrocarbons. The commercial importance of this reaction is that it provides a route for the production of liquid fuel from coal or biomass via gasification to CO and H_2. With the prospect of oil supplies drying up completely in the foreseeable future and the environmental concern in desiring to have a renewable energy source, there is a great revival of interest in FT reactions [1,2]. Furthermore, the theoretical significance of FTS is that it is invoked to explain the formation of abiogenic hydrocarbons in the Earth's crust [3], precursors of life essential building blocks [4], and organic matters in the solar nebula [5]. Therefore, studying the mechanism of FT reactions is of importance both commercially and fundamentally. However, nearly 100 years of studies show that it is a challenge to propose a mechanism that can explain formation of all FT products. The reason for this difficulty is that there are still many disagreements within scientific community regarding the basic aspects of the reaction.

One of the controversial topics is what the primary and secondary products are in FT reactions. Through many years of outstanding studies, there is substantial agreement that the linear 1-alkenes and part of n-alkanes are the primary products [6–13], and the branched hydrocarbons are produced through the re-adsorption and re-growth of 1-alkene [8]. However, the formation of the internal alkenes during FT reactions is still a subject of some debate. Experiments showed that the selectivity of 2-olefin decreased (i.e., 1-olefin selectivity increased) with an increase in gas-hourly-space-velocity (GHSV) [10]. The same trends were also observed in experiments with different syngas feed compositions [11]. These results suggest that while 1-alkenes and some alkanes are the primary products, the internal alkenes are products of the secondary reactions. While most researchers considered the internal alkenes as secondary products [6,7,10,11], some research groups concluded that, similar to 1-alkenes and n-alkanes, the internal alkenes are the primary products that are produced through surface reaction of alkyl group on the metal surface [12,13]. Furthermore, there is no consensus at the present time whether some of the n-alkanes and 2-alkenes are formed on FT-sites or on sites where chain growth cannot take place.

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We have shown that the deuterated octene can be converted to deuterated trans-2-octene, cis-2-octene and octane when octene-d_{16} was used as the probe in an iron catalyzed FT reaction [14]. This experiment clearly showed that it is possible that 1-alkenes can be isomerized to 2-alkenes under FT reaction conditions.

During iron catalyzed FT reactions, significant amounts of trans-2-alkene and cis-2-alkene of each carbon number are produced. The question of whether the internal alkenes are primary or secondary products is very important theoretically and practically, and the understanding of how the internal alkenes being formed will enable us to gain insight into mechanism of the FT reaction.

Based on results of H_2/D_2 switching and competition experiments in cobalt catalyzed FT reactions, we proposed a modified alkylidene mechanism. This mechanism has been used to explain the inverse isotope effect, the deuterium enrichment in hydrocarbons, and the formation of 1-alkenes, alkanes [15,16] and branched hydrocarbons [8]. In this study, we provide evidence to show that the formation of 2-alkenes is through a different pathway from 1-alkenes based on results of H_2/D_2 switching experiments of FT reactions over iron catalysts. The formation of 2-alkenes is explained by the alkylidene mechanism.

2. Experimental

The iron catalyst (Fe:Si:K = 100:4.6:1.4) was synthesized based on a procedure reported in the literature without modification [17]. The Fischer–Tropsch synthesis procedure is the same as described previously [15]. In a typical run, 1.5 g of iron catalyst (Fe:Si:K = 100:4.6:1.4) is used. A mixture of H_2 (60%), CO (30%) and N_2 (10%) was used as the syngas feed. The reactions were conducted at 1.3 MPa and 270 °C. It usually takes about 24 h in order to have constant CO conversion after the synthesis begins. The liquid samples were collected every 24 h and the gas samples were measured four times every day. Three days later, the syngas was switched to a mixture of D_2 (60%), CO (30%) and N_2 (10%). Four hours after the switching, the CO conversion was measured. In the same manner as during CO/H_2 run, the liquid samples were collected every 24 h and the gas samples were analyzed four times a day. The syngas was switched back to CO/H_2/N_2 again after 3 days of running the D_2/CO syngas feed. This procedure was usually repeated two times under one set of reaction conditions.

Liquid samples were analyzed by GC and the identities of products were confirmed by GC/MS [15,18].

3. Results and discussion

3.1. Inverse isotope effect during iron catalyzed FT reaction

According to the Anderson–Shultz–Flory (ASF) equation $r_n = r_1\alpha^{n-1}$, if $n = 1$, the r_n is the rate of formation of methane, which suggests that methane was formed through the FT reaction only. In fact, methane could be formed through the methanation reaction. If we separate the methanation reaction from the “Fischer–Tropsch” reaction and consider the FT reaction only, the ASF equation can be rewritten as equation (1), where C_1^H is the rate of formation of C_1 monomer [8]. In the case of the alkylidene mechanism, it is M≡CH.

$$r_n^H = C_1^H a_H^{n-1}\ (n > 1) \tag{1}$$

The r_n^H in equation (1) is the rate of formation of a hydrocarbon with a carbon number n. Under the same reaction conditions, r_n^D is the rate of formation of a hydrocarbon with a carbon number n when using CO/D_2 as the syngas feed. According to equation (1), the ratio of r_n^H/r_n^D can be represented by equation (2), and equation (3) if the formation of C_1 monomer is not rate determining and $C_1^H/C_1^D = 1$. The k_p^H and k_p^D in equation (3) are the rate constants of propagation, and k_t^H and k_t^D are the rate constants of termination of the FT reactions when H_2/CO and D_2/CO are used as the syngas feeds, respectively.

$$\frac{r_n^H}{r_n^D} = \frac{C_1^H a_H^{n-1}}{C_1^D a_D^{n-1}} \tag{2}$$

$$\frac{r_n^H}{r_n^D} = \frac{C_1^H a_H^{n-1}}{C_1^D a_D^{n-1}} = \left(\frac{a_H}{a_D}\right)^{n-1} = \left(\frac{k_p^H(k_p^D + k_t^D)}{k_p^D(k_p^H + k_t^H)}\right)^{n-1} \tag{3}$$

Equation (3) indicates that the rate of the formation of a FT product with a carbon number n is determined by k_p, k_t and the carbon number n, which determines how many propagation steps $(n-1)$ are needed to produce this compound. Unlike most organic reactions in which the isotope effect originates from one step of the reaction, the ratio of r_n^H/r_n^D in equation (3) measures the overall isotope effect that originates from every propagation step during formation of the FT products. According to equation (3), the r_n^H/r_n^D ratio is a function of the carbon number n.

The isotope effect of a reaction should be a constant. However, the values of r_n^H/r_n^D become smaller (larger inverse isotope effect) when carbon number n increases. In order to remove the effect of carbon number, equation (3) is converted to equation (4), where the α_H/α_D is used to represent the isotope effect of a FT reaction. This value is a constant and independent of the carbon number of the compound measured.

$$\frac{\alpha_H}{\alpha_D} = \sqrt[n-1]{\frac{r_H}{r_D}} \tag{4}$$

The rate of hydrocarbon formation in a FT reaction can be represented by r_k, where k is the carbon number of a hydrocarbon whose molecular weight is the average molecular weight of the FT reaction. The average molecular weight of a FT reaction can be estimated by its α value of the reaction or measured experimentally, and k equals the average molecular weight divided by 14. Therefore, the isotope effect of a FT reaction can also be determined by the hydrocarbon formation rates of the reaction as shown in equation (5).

$$\frac{\alpha_H}{\alpha_D} = \sqrt[k-1]{\frac{r_k^H}{r_k^D}} \tag{5}$$

The hydrocarbon formation rates (r_k^H or r_k^D) can be determined by equation (6), where the CO conversion rate and the rate of formation of CO_2 can be experimentally measured.

$$r_k = \text{rate of CO conversion} - \text{rate of } CO_2 \text{ formation} \tag{6}$$

By using the H_2/D_2 switching method, the Fe catalyzed FT reactions were conducted. Fig. 1 is an example of these results. The top of Fig. 1 is the percent of CO conversion. The average CO conversion from time-on-stream (TOS) 119 h to 167 h is 59.3% with a standard deviation of 2.0% when the FTS was run using H_2/CO as the syngas. When switched to D_2/CO, the average CO conversion from TOS 210 h to 258 h increased to 70.8%. After switching back to H_2/CO, the CO conversion decreased to 61.9%. The bottom of Fig. 1 is the hydrocarbon production rate (r_k) in mol/s-per gram of catalyst. When the syngas was switched from H_2/CO to D_2/CO, the hydrocarbon production rate increased from 1.52×10^{-7} mol/g s to 2.76×10^{-7} mol/g s. After switching back to H_2/CO, the rate decreased again to 1.71×10^{-7} mol/g s.

Table 1 lists the CO conversions and the rates of hydrocarbon formation during Fe catalyzed FT reactions at different CO conversion levels when H_2/CO and D_2/CO were used as the syngas feeds. The α value for these reactions is 0.81, with the average molecular weight of 75.7 and the carbon number $k = 5.41$. At 15–30% conversion level, the ratio of $[CO]_{conv}^H/[CO]_{conv}^D$ is 0.62, indicating that the CO conversion rate is much faster when the D_2/CO mixture was used as the