Task 5. Oxygenates

The objective of this task is to obtain a better understanding of the factors that affects catalyst selectivity toward oxygenates for iron-based Fischer-Tropsch catalysts.

No scheduled activity to report.

Task 6. Literature Review of Prior Fischer-Tropsch Synthesis with Co Catalysts

The objective of this task is to prepare a critical review of prior work on cobalt Fischer-Tropsch catalysts.

No scheduled activity to report.

Task 7. Co Catalyst Preparation

The objective of this task is to prepare a limited number of cobalt-based Fischer-Tropsch catalysts that can be used to obtain baseline data on cobalt-based Fischer-Tropsch synthesis.

No scheduled activity to report.

Task 8. Cobalt Catalyst Testing for Activity and Kinetic Rate Correlations

The objective of this task is to conduct initial screening of the cobalt catalysts prepared in Task 7 to select three baseline catalysts that will then be used to generate a data base on the performance of cobalt-based Fischer-Tropsch catalysts in slurry reactors.

No scheduled activity to report.

Task 9. Cobalt Catalyst Life Testing

The objective of this task is to obtain life data on baseline cobalt Fischer-Tropsch catalysts.

No scheduled activity to report.

Task 10. Cobalt Catalyst Mechanism Study

The objective of this task is to determine the impact of secondary reactions on the relationship of cobalt Fischer-Tropsch catalysts under conditions appropriate to slurry bubble column reactors.

A. D_2O Tracer Studies in Co Catalyzed Fischer-Tropsch Reaction

Introduction

The Fischer-Tropsch (FT) reaction can be summarized by Equation 1.

$$nCO + (2n + 1)H_2 \text{ ---> } C_nH_{2n+2} + nH_2O \quad (1)$$

Under FT reaction conditions, the water-gas shift reaction also can occur as the side reaction (eq. 2).

$$H_2O + CO \rightleftharpoons CO_2 + H_2 \quad (2)$$

The amount of water converted to hydrogen depends on the reaction conditions and the catalyst used. It has been reported that water can affect the FT reaction rate and the selectivity [1].

According to eq. 2, water can be converted to hydrogen, which can be used by FT reaction to produce hydrocarbons. The question of how effective a hydrogen source the H_2O can be in FT reaction is still not answered. In this study, we use D_2O as the probe to study the deuterium distribution of FT products. The H/D ratio of the products shall give us some clue about H/D ratio of the surface H-D pool and quantitative measure of the effectiveness of H_2O as the hydrogen source.

Experimental

The FT reaction was carried out in a 1-L continuously stirred autoclave reactor (CSTR) as described previously [2]. Fourteen grams of catalyst (Co (10)/ Ru (0.2)/TiO2) was activated using H_2 at 300ºC and the synthesis was conducted at 350 psig and 230ºC using 300 g of Pw

3000 as the startup oil. Three traps follow the reactor and are held at 200°C, 130°C and 0°C. For the D_2O tracer run, D_2O was co-fed with syngas (D_2O, 4.19 SLPH; H_2, 17.09 SLPH; CO, 8.50 SLPH) for 7 hours. Immediately prior to addition of the tracer, the three products traps were emptied. At the end of the addition of D_2O, the products traps were again drained and the contents were analyzed using our normal procedures as well as the GC/MS analysis. During the tracer run gas samples were taken every one and half hours for analysis.

The relative amounts of the isotopomers of the hydrocarbons were determined by GC/MS. The data were corrected for the ^{13}C content of the products. Because of the inverse isotope effect of the deuterated compounds on gas chromatography, the relative amount of the total area of the molecular ion of each isotopomer were used to calculate the molar ratio [3].

The relative amount of H_2, HD and D_2 were measured using VG mass spectrometry. A series of standard mixtures of H_2 and D_2 were measured by scanning the corresponding mass for at least 50 times, and the average of abundance of the compound were compared with the known mole ratio of that compound. The corresponding factors thus obtained were used to calculate the relative amount of H_2, HD and D_2 of the gas sample of the D_2O tracer experiment.

The relative amounts of H_2O, HDO and D_2O were analyzed using GC/MS. The ratio of H/D obtained using this method has a standard deviation of 0.12.

Results and Discussions

Table 1 shows the deuterium distribution of alkane products of the D_2O tracer products of a Co catalyzed FT reaction. The relative amount of the isotopomers of each carbon number from C_{15} to C_{16} were determined using the GC/MS method [3]. As can be seen from Table 1, the relative amount of d_0 isomer of each carbon number is unusually higher than expected if we assume the binomial distribution of H and D atoms in a compound. Also, the relative amount of

the d_0 isomers of alkanes increases as the carbon number increasing. These results indicate the presence of the accumulated products (Δ) [4, 5].

Product accumulation (Δ) is a special phenomena of isotope tracer studies in FT reactions and its presence is determined by the tracer experiment procedure of FT reaction. In most tracer studies of the FT synthesis, the unlabeled syngas conversion is conducted until the catalytic activity has stabilized and then the labeled compound is added for some time period. Usually the products are collected during the period of labeled addition. The products thus collected will consist of three fractions: (1) the products derived from the labeled compounds, which will contain at least one labeled atom; (2) the products from the normal FT synthesis that are derived from the unlabeled syngas, and (3) any products formed from unlabeled synthesis gas during the period of activity stabilization or period when the labeled compound is not added.

It has been reported [6] that the relative amount of Δ of a carbon number increases as the carbon number increasing. It also has been reported that the product accumulation (Δ) can affect the data interpretation of all of isotope tracer studies in FT reaction runs at both small fixed bed and large CSTR reactors [4]. Failing to include this factor in the data analysis could led to wrong conclusion [4, 7].

Since the presence of product accumulation is the nature of the isotope tracer experiment in FT reaction, this factor can not be removed completely. However, the effect of the accumulated products can be minimized by applying some experimental techniques. For example, by collecting the gas sample of a tracer experiment after the experiment has run for a period of time (3 hours, for instance) and using the data derived from gas sample only, the accumulation factor can be minimized. In ^{13}C and deuterium labeled tracer experiments, this factor can be removed by the way that utilize only the products that contain ^{13}C or deuterium for

all carbon numbers. This method has been used to reinterpret the ^{13}C labeled tracer data [4]. In this study, we are going to use this method to reinterpret the data that obtained from the D_2O tracer experiment as shown in Table 1.

The d_0 isomers of each carbon number in Table 1 come from two sources: the product accumulation (Δ) and the products from normal FT synthesis that are derived from the unlabeled syngas. In D_2O tracer experiment, the amount of d_0 isomer of each carbon number from normal FT synthesis during the tracer experiment is determined by the H/D ratio of the surface pool as well as the carbon number. As can be seen from Table 2 that assuming the H/D ratio of 4 as the surface H-D pool, the amount of d_0 isotopomer of C7 alkane produced during the tracer experiment is only 2.8%. As the carbon number increases, the amount of d_0 isotopomer decreases, with the amount of d_0 isomer of C16 alkane only 0.05%. These values are smaller than the experimental error of GC/MS analysis [3]. Therefore, if we eliminate the d_0 isomers in Table 1 and recalculate the deuterium distribution of the remaining isotopomers of each alkane, we will remove all of the products left in the reactor before the tracer experiment since all of the Δs are d_0 isomers. Also, based on the above analysis and the data in Table 2, removing all of the d_0 isomer in each carbon number introduces a very small additional experimental error. The amounts of d_0 isomers of C5 and C6 alkane shown in Table 2 are larger than the standard deviation of GC/MS method [3]. However, since what we are interested the average H/D ratio of all of the compounds analyzed, the error introduced by these two isomers will not alter our conclusions.

Table 3 is the deuterium distribution of the isotopomers of each carbon number after eliminating the d_0 isotopomers. As can be seen from this table that the deuterium distribution of each compounds is close to binomial distribution with a H/D ratio of 4.4. For example, the

Figure 1 is the deuterium distribution of octane (d_0 isomer was eliminated). Based on the mole% of each isotopomer, the H/D ratio of octane (Table 3) was calculated to be 4.4. Assuming binomial distribution of the deuterium with a H/D ratio of 4.4 in the surface H-D pool, the calculated mole% of each isotopomer were fitted with the experimental value nicely.

Figure 2 is the H/D ratio of alkanes measured from carbon number C_5 to C_{16}. When d_0 isomer was included in each carbon number, the H/D ratio increases as the carbon number increases, indicating the presence of the accumulated products. While the d_0 isomers were not included in each carbon number, the H/D ratio was close to a constant (in this case, 4.4), indicating that all of the deuterium (hydrogen) of the compounds came from the same H-D source: the surface H-D pool, and the H/D ratio of it is 4.4.

The relative amounts of D_2O, DHO and H_2O were determined using the GC/MS method and the H/D ratio in water was calculated. The relative amount of unreacted H_2, HD and D_2 were also measured. These results were compiled in Table 4. As can be seen from this table that the tracer experiment started from a H_2/D_2O ratio of 4.1; the H/D ratio in the alkanes was measured to be 4.4; in water, 2.5; and in unreacted gas, 16. These results indicated that the H/D ratio obtained from using D_2O as the tracer differs from using D_2. If D_2 gas was used as the tracer and the H_2/D_2 ratio is 4, then the H/D ratio in hydrocarbons, in water and in unreacted gas will be the same, and the value will be 4, ignoring a small inverse isotope effect. These results also indicated that the D_2O was used in FT reaction as the hydrogen source before it becomes D_2.

The mass balance calculation showed that 80% of total deuterium that is put in the reactor in the form of D_2O was recovered from the hydrocarbons, water and unreacted gas. The deviation from 100% may come from the analysis of hydrogen gas.

The H/D ratio in hydrocarbons is 4.4, which is close to the H_2/D_2O ratio. This suggests that as the hydrogen source, the water can be as effective as the H_2 under these reaction conditions. More experiments are needed to show the limitations.

In studying the mechanism of FT reaction, almost all of the possible carbon-14 and carbon-13 labeled compounds suitable for studying the mechanism of FT reaction have been used as the probes [8]. Only a few deuterium tracer experiments have been conducted to study the mechanism of FT reaction before we published an article dealing with the isomerization of 1-alkenes under FT reaction conditions [2]. The D_2O tracer study reported in this paper provided a way to study the behavior of hydrogen. To understand the role of D_2O fully, further study under different reaction conditions are underway.

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Table 1

Deuterium Distribution of the Alkane Products of the FT Reaction (Tracer: D_2O)

# of C[a]	C5[c]	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16
# of D[b]												
0	41.7	45.9	49.4	61.0	70.2	73.5	78.0	80.7	84.2	87.7	91.0	94.1
1	16.1	9.8	7.3	6.2	4.4	4.1	3.4	2.9	2.5	1.9	1.6	0.7
2	17.6	12.7	10.6	7.4	4.9	3.3	2.3	2.0	1.4	1.2	0.8	0.5
3	13.9	13.1	12.3	8.4	5.8	4.3	3.1	2.4	1.8	1.2	0.8	0.5
4	7.5	9.8	9.9	7.7	5.9	4.9	3.9	3.0	2.2	1.6	0.9	0.7
5	2.4	5.5	6.1	5.1	4.4	4.3	3.6	3.2	2.5	1.7	1.2	0.8
6	0.8	2.3	3.0	2.8	2.7	3.0	2.7	2.6	2.2	1.7	1.3	0.8
7	0.12	0.8	1.0	1.1	1.2	1.6	1.7	1.7	1.6	1.4	1.0	0.8
8		0.2	0.3	0.4	0.5	0.7	0.9	1.0	1.1	0.9	0.8	0.7
9				0.1	0.1	0.3	0.4	0.5	0.6	0.6	0.5	0.4
10							0.1	0.2	0.2	0.2	0.3	0.3
11									0.1	0.2	0.1	
H/D	7.6	7.7	8.8	12.8	17.8	20.5	25.5	29.9	37.3	49.5	69.2	104

a: Carbon number.
b: Number of deuterium.
c: The values in all the alkanes are mole%.

Table 2

Mole% of d_0 Isomers of Each Carbon Number in a Binomial Distribution with a H/D Ratio of 4.

Carbon Number	d0 isomer (mol%)
C5	6.9
C6	4.4
C7	2.8
C8	1.8
C9	1.2
C10	0.7
C11	0.5
C12	0.3
C13	0.2
C14	0.1
C15	0.08
C16	0.05

Table 3

Deuterium Distribution of the Alkane Products of the FT Reaction (Tracer: D_2O; after eliminated d_0 isomers of each carbon number of Table 1)

# of C[a]	C5[c]	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16
# of D[b]												
0												
1	27.5	18.1	14.5	15.9	15.0	16.0	16.2	16.5	17.5	18.0	20.5	15.1
2	30.2	23.5	21.1	19.2	16.6	13.0	11.1	11.1	10.0	11.3	10.7	9.9
3	23.8	24.3	24.5	21.9	19.9	17.0	15.2	13.7	12.5	10.9	10.7	11.2
4	12.9	18.2	19.8	19.9	20.2	19.3	18.8	17.0	15.8	14.8	12.0	13.4
5	4.1	10.2	12.1	13.2	14.9	16.7	17.4	17.8	17.5	16.0	16.1	16.8
6	1.3	4.3	6.1	7.2	9.3	11.9	13.0	14.6	15.7	15.8	16.9	16.2
7	0.2	1.4	2.0	2.9	4.2	6.2	8.4	9.4	11.2	13.3	13.2	17.5
8		0.3	0.6	0.9	1.7	2.9	4.2	5.9	7.6	8.3	10.6	14.0
9			0.1	0.1	0.3	1.1	2.1	2.9	4.1	6.0	6.6	8.3
10						0.2	0.4	0.9	1.7	2.1	3.2	5.6
11								0.2	0.5	1.4	1.8	0.8
H/D	4.0	3.7	3.9	4.4	4.6	4.7	4.8	5.0	5.2	5.4	5.6	5.5

a: Carbon number.
b: Number of deuterium.
c: The values in all the alkanes are mole%.

Table 4

H/D ratio of Starting Reagents, Products and Unreacted Gas

Category	Compounds Analyzed	H/D
Starting Reagents	D_2O; H_2	4.1
Products	Alkanes	4.4
Products	H_2O; HDO; D_2O	2.5
Unreacted Gas	H_2; HD; D_2	16

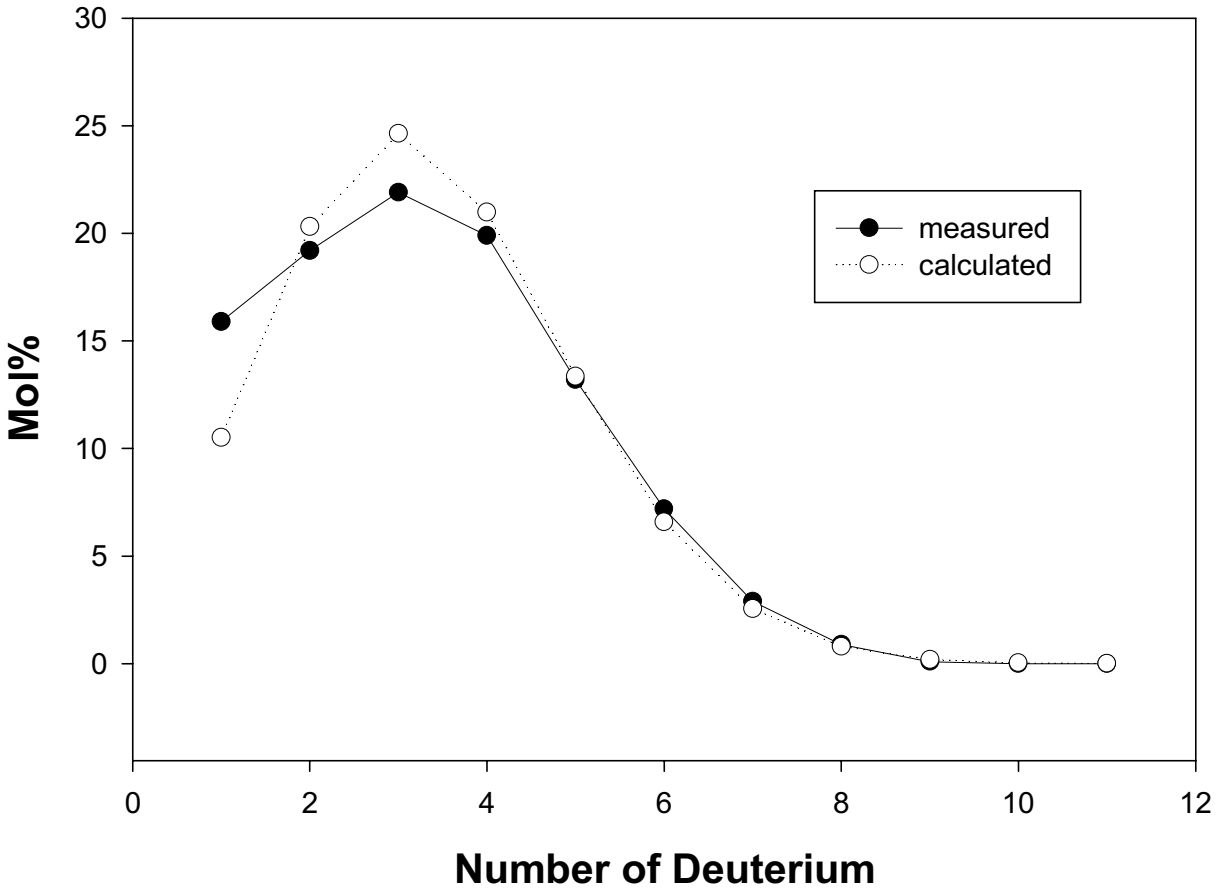

Figure 1. The deuterium distribution of the isotopomers of octane.

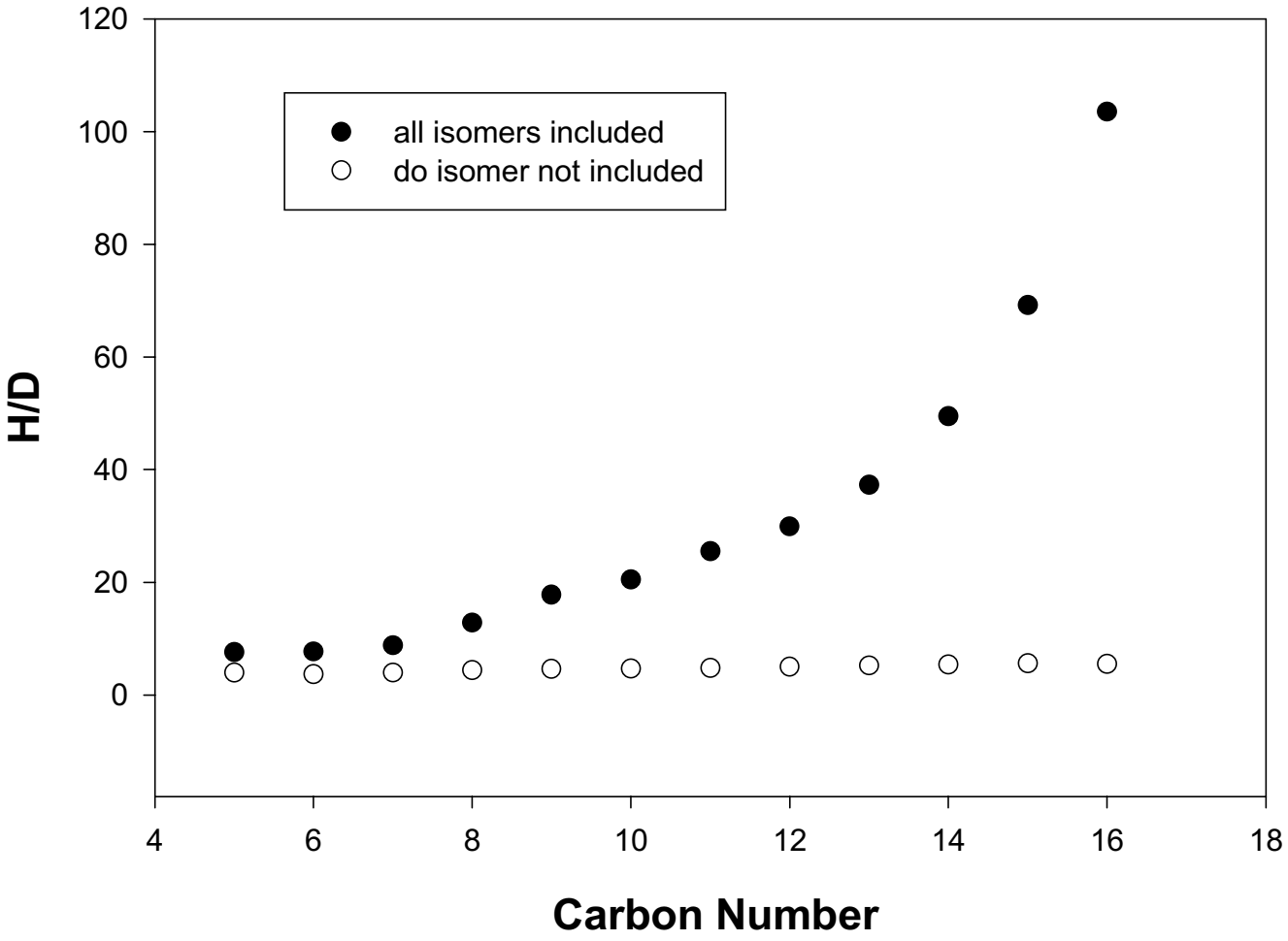

Figure 2. The ratio of H/D of alkanes in Co catalyzed Fischer-Tropsch reactions (tracer: D_2O (H_2:D_2O = 4:1).