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Fischer–Tropsch synthesis: Deuterium labeled ethanol tracer studies on iron catalysts

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ABSTRACT

The addition of D_3- and D_5-ethanol during Fischer–Tropsch synthesis with a promoted iron catalyst gives results that are consistent with ethanol initiating chain growth. However, there is considerable H/D exchange in the alcohol prior to initiating chain growth so that the D/molecule ratios in the alkane and alkene products are in the range 1.3–1.5. The nearly constant D/molecule ratio in the alkane and alkene products in the C_5–C_{14} carbon number range is consistent with ethanol initiating chain growth.

1. Introduction

The Fischer-Tropsch synthesis (FT) can be briefly defined as the catalytic conversion of carbon monoxide and hydrogen to hydrocarbon products. It has long been known that smaller 1-alkene and alcohol molecules may be able to act as a chain initiator under normal FT synthesis conditions [1]. The results from the addition of a C_2 monomer during FT has been reviewed by a number of workers [2–4], who advanced a number of different surface species such as vinyl ($CH_2{=}CH{-}_{(ad)}$) and vinylidene ($CH_2{=}C{=}_{(ad)}$). In the pioneering work of Emmett and co-workers [5,6], ^{14}C labeled ethanol (1.5%) was added to the syngas feed to an iron catalyst operated at 508 K and 1 atm, using a plug-flow reactor. Based on the observed constant radioactivity (^{14}C) of the hydrocarbon products, the authors concluded that ethanol, or an adsorption complex derived from the ethanol, could act as a chain initiator. Schulz et al. [7] probed the mechanism of the FT reaction for a cobalt-thoria-kieselguhr catalyst that was operated at 458 K and atmospheric pressure using ^{14}C alkenes and found that nearly 30% of the ethene and propene added were incorporated into the FT products. Co-feeding ^{14}C-labeled ethene with the syngas over cobalt catalysts demonstrated that the alkene added at concentrations lower than 2 mol% can act as an initiator and also acts as a propagator, when the ethene concentration exceeds 5 mol% [8]. Tau et al. [9] reported that 1- and 2-propanol incorporate into the products of the FT synthesis and claimed that the surface species generated from 1- and 2-propanol are distinct and these initiate chain growth to form different products. Hanlon and Satterfield [10] have reported that the addition of ethanol or ethene to the feed to an iron catalyst increased the olefin to paraffin ratio of the products and observed only a slight degree of chain incorporation upon addition of 1-olefin or ethanol in major amounts. Therefore, it is not only the quantity of the labeled compound that is co-fed along with a syngas during FT synthesis but also the synthesis conditions that may determine the rate of incorporation of the added compound into the FT synthesis products.

In the 1960s, Kryukov et al. [11] used α-deuteroethanol as a tracer to study the mechanism of the FT reaction. The authors concluded that intermediate surface compounds obtained from the alcohol take part in the formation of hydrocarbons and that they retain at least a part of the deuterium of the added alcohol. Brundage and Chuang [12] obtained a two-unequal-hump response for d_1- and d_2-propionaldehyde formation from D_2 and C_2D_4 pulses during ethylene hydroformylation using Mn-Rh/SiO_2 at 513 K and 0.1 MPa. The authors demonstrated using FT-IR/mass spectrometry that the different deuterium incorporation pathways into the propionaldehyde was possibly due to H/D exchange on adsorbed acyl and acyl hydrogenation. The earlier work with ^{14}C-labeled ethanol clearly established the ability of ethanol to initiate chain growth (e.g., 5,9) and that rupture of the C–C bond did not occur to a measurable extent. However, that work could not provide any measure of the lability of the C–H bond during synthesis.

Our previous study added D_2O as a tracer to elucidate the FT mechanism for a cobalt catalyst and these show that there is no measurable H/D exchange in alkanes and the exchange in alkenes appears to be limited to the vinyl positions [13]. In the present study, partially deuterated ethanol (i.e., CD_3CD_2OH and CD_3CH_2OH) was used as a tracer to investigate the iron-catalyzed Fischer–Tropsch mechanism at different synthesis conditions. An attempt has been made to identify the surface intermediates formed from the added D-ethanol through an analysis of FT hydrocarbon products.

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Table 1
Effect of d_5-ethanol co-feeding on olefin–paraffin ratio of hydrocarbon products of Fe-FT synthesis at 543 K and 0.8 MPa using a syngas (H_2/CO: 0.7).

Runs	Sample no.	Olefin/Paraffin ratio		
		$C_2^=/C_2$	$C_3^=/C_3$	$C_4^=/C_4$
Without C_2D_5OH	3	1.59	5.80	6.50
	4	1.62	5.70	6.60
With C_2D_5OH	5	1.98	7.01	7.41
	6	1.98	6.20	7.02
Without C_2D_5OH	7	1.64	5.80	6.54
	8	1.60	5.52	6.53
	9	1.62	5.50	6.56

2. Experimental

The Fischer–Tropsch runs were conducted using a 1-L CSTR. The experimental apparatus and materials used are described elsewhere [14]. The iron catalyst has a composition of 4.4 wt% Si, 56 wt% Fe, 0.5 wt% K (i.e., a low α catalyst). The ethanol-D_5 (CD_3CD_2OH) and ethanol-D_3 (CD_3CH_2OH) were purchased from Cambridge Isotope Laboratory, Inc., with an isotopic purity of 98%. For each run, 20 g of crushed catalyst was mixed with 310 g of C_{30} oil and pretreated for 24 h using a syngas (H_2/CO = 0.7) at 543 K and 0.10 MPa. The initial conditions for the FT reaction were 0.8 MPa and 543 K using a syngas feed at 60 slph with a percentage composition of 41.2 H_2 and 58.8 CO. About 1.50 mol% of ethanol-D_5 or ethanol-D_3 (5 g of labeled ethanol was mixed with 17 g of n-heptane) was introduced into the reaction system during a period of 300 min using a MiltonRoy mini-piston pump. The D-ethanol was introduced into the reaction system along with a syngas stream after reaching a steady CO conversion (∼40%) at a feed rate of 0.926 slph. In order to see the effect of pressure on the D-distribution of hydrocarbon products, a separate FT reaction was performed at the same reaction conditions as mentioned above except that the pressure was set at 2.2 MPa. The gaseous products were analyzed by an online-gas chromatograph (GC) during and following D-ethanol addition. Hot (373 K) and cold (273 K) traps were emptied before the addition of deuteroethanol. At the end of the addition, both oil and wax products were collected from the cold and hot traps, respectively, and further separated from the aqueous phase. The aqueous phase was analyzed by GC using a Q-Porapack column at 373 K. The detailed experimental procedures are described elsewhere [14]. Quantitative analysis of ethanol in an aqueous solution was determined using a standard calibration procedure and the D-distribution in ethanol was quantified using GC–MS. It is known that fragments of deuteroethanol could interfere with a parent peak of another D isotopomer of D-ethanol [15], a correction factor was introduced based on the GC–MS pattern obtained using standard D_5-ethanol or D_3-ethanol compounds. The D-distribution of various hydrocarbons present in the oil and wax samples were analyzed using GC–MS. Complications are involved in analyzing the C_1–C_4 gaseous hydrocarbon products due to exchange and scrambling of deuterium among FT products during the FT reaction. The D isotopomers for different carbon numbers were calculated after correcting ^{13}C for their parent ion peak (m^+ ion); the details are described elsewhere [16].

3. Results and discussion

3.1. d_5-Ethanol

There is a significant increase of olefin-to-paraffin ratio for C_2, C_3, and C_4 with D_5-EtOH addition as shown in Table 1 and Fig. 1; this suggests that deuteroethanol can compete with CO and hydrogen for adsorption sites on the catalyst surface. Kummer et al. [5] also noted this decrease in the hydrogenation activity of the catalyst with added ethanol, which causes an increase in the C_2, C_3, and C_4 olefin/paraffin ratios. Nearly constant CO conversion and a linear increasing trend in the selectivity to methane were observed upon D_5-ethanol addition and this suggests that the adsorbed D_5-ethanol is not involved in C–C bond breaking. These results are consistent with the conclusions made from other studies where the small amounts of added ethanol did not significantly affect the CO conversion and methane selectivity [10]. A considerable increase in selectivity to ethylene with D_5-ethanol addition (Table 2) suggests that this is due to the dehydration of D_5-ethanol.

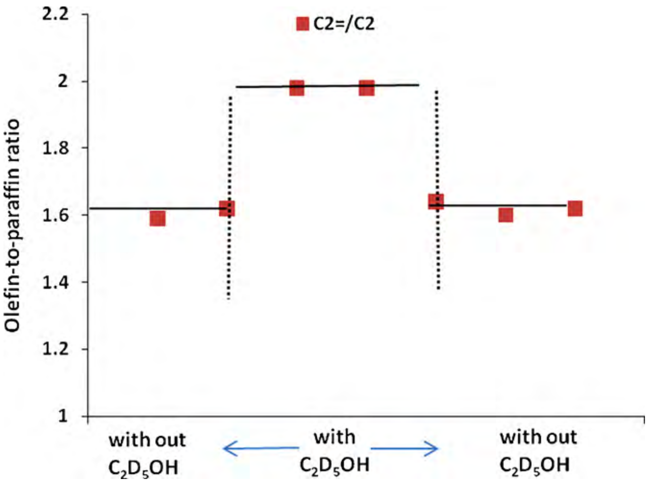


Fig. 1. Effect of D_5-ethanol co-feeding on C_2 olefin-to-paraffin ratio.

It is well-known from ethanol and ethylene co-feeding studies during FT synthesis using iron catalysts that the rate of incorporation of ethanol is much higher than the rate of incorporation of ethylene [10]. In the present system, about 55.4% of the added D_5-ethanol was recovered from the aqueous phase; thus, up to 44.6% of D_5-ethanol could be converted into various hydrocarbons by entering into the growing hydrocarbon chain. It is hard to predict the exact amount of D_5-ethanol that is incorporated into the growing hydrocarbon chains as evidenced by the lack of increase of C_3 hydrocarbon selectivity (Table 1) with added D_5-ethanol. Kokes et al. [17] applied ^{14}C tracer experiments to define the mechanism for a doubly promoted iron catalyst used at varying pressures and temperatures and found that the percentage incorporation of ethanol falls from 18% to 7%, and then from 7% to 2.2% as the pressure increased from 0.1 to 0.75 to 2.1 MPa, respectively. The authors compared their results to Kummer's work and concluded that less incorporation occurred over a doubly promoted catalyst containing potassium and magnesium than over a singly promoted catalyst without potassium. In our system, a singly promoted Fe catalyst at low potassium content and at low pressure (0.8 MPa) may favor more D_5-ethanol incorporation.

Table 2
Effect of d_5-ethanol co-feeding on hydrocarbon product selectivity of Fe-FT synthesis at 543 K and 0.8 MPa using a syngas (H_2/CO: 0.7).

Runs	Sample no.	Selectivity, %C						
		CH_4	$C_2^=$	C_2	$C_3^=$	C_3	$C_4^=$	C_4
Without C_2D_5OH	3	8.21	4.68	2.93	10.46	1.57	9.08	1.39
	4	7.87	4.45	2.74	9.80	1.72	8.45	1.28
With C_2D_5OH	5	8.38	5.78	2.92	10.70	1.77	8.40	1.08
	6	8.21	5.63	2.88	10.51	1.69	8.22	1.17
With out C_2D_5OH	7	8.63	4.88	2.97	10.61	1.83	9.14	1.40
	8	8.45	4.68	2.92	10.39	1.88	8.84	1.35
	9	8.40	4.66	2.87	10.28	1.93	8.75	1.34

Table 3
Distribution of deuterium in paraffins for co-feeding D_5-ethanol during Fe-FT synthesis at 543 K and 0.8 MPa using a syngas (H_2/CO: 0.7).

Paraffin	mol%						D/molecule*
Carbon no.	D_0	D_1	D_2	D_3	D_4	D_5	
5	67.62	22.93	7.21	1.64	0.60	0.00	1.38
6	62.31	28.3	7.15	1.39	0.68	0.00	1.31
8	53.68	32.72	10.07	3.06	0.47	0.00	1.38
9	48.77	34.44	11.33	5.02	0.25	0.00	1.43
10	45.04	35.91	12.92	4.01	1.45	0.00	1.45
11	45.46	34.8	12.41	4.75	1.88	0.00	1.49
12	44.8	31.18	16.53	5.15	2.21	0.00	1.60

* The D/molecule were calculated without including d_0.

Table 4
Distribution of deuterium in 1-olefins from co-feeding D_5-ethanol during Fe-FT synthesis at 543 K and 0.8 MPa using a syngas (H_2/CO: 0.7).

1-olefin	mol%						D/molecule*
Carbon no.	D_0	D_1	D_2	D_3	D_4	D_5	
5	69.60	25.36	4.13	0.74	0.11	0.00	1.19
6	64.08	28.35	6.16	1.13	0.20	0.00	1.25
8	56.80	33.06	9.74	2.00	0.14	0.00	1.35
9	50.36	34.87	11.42	2.48	0.70	0.00	1.37
10	49.25	35.15	11.87	3.59	0.15	0.00	1.38
11	42.06	34.81	15.90	4.97	2.14	0.00	1.55
12	43.76	33.61	17.65	4.30	0.68	0.00	1.50

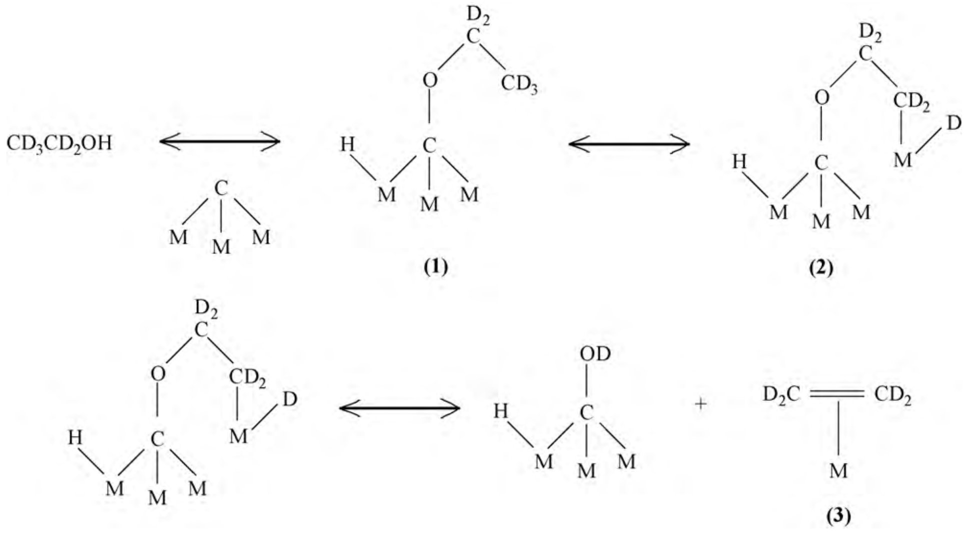
* The D/molecule were calculated without including d_0.

The detailed relative amounts of isotopomers in alkanes and 1-olefins produced in the D_5-ethanol tracer run are summarized in Tables 3 and 4, respectively. The important characteristics of these data are: (1) more than 60% of the alkanes and 1-olefins are D_0 isotopomer, and D_1 is the most abundant D isotopomer of all the FT products formed irrespective of carbon number; (2) the relative mol% of D_1, D_2, D_3 and D_4 isotopomer increased with increasing carbon number; and (3) the total D content per molecule for both alkanes and 1-olefins was between 1.2 and 1.6 in the carbon range C_5–C_{12}.

If the added D_5-ethanol is only involved in initiating the hydrocarbon chain one would expect the maximum number of deuterium atoms that an alkane or 1-olefin could have is 5; however, our experimental results show that there is no evidence for the presence of D_5 isotopomer in any of the hydrocarbons. The D/molecule for each hydrocarbon can be calculated based on the GC–MS analysis of oil and wax samples, and is shown in Tables 3 and 4. The D/molecule for alkanes was nearly constant (~1.4) up to C_{10} and may increase slightly with increasing carbon number after C_{10}. However, the D/molecule ratio for 1-olefin exhibits an increasing trend starting from 1.2 for C_5 and increases to 1.5 for C_{12}. The D_0 isotopomer for each compound comes from two sources: a normal FT synthesis during the tracer period and from the accumulated product. The predominance of the D_1 isotopomer in all hydrocarbons suggests that considerable H/D exchange occurred during the interaction of D_5-ethanol on the catalyst surface and this would create a pool of deuterium which may eventually be introduced into hydrocarbon products.

If a C_2 species derived from D_5-ethanol acts as an initiator, the D/molecule must be a constant for all compounds. It appears that ethanol competes with the reactants (CO and H_2) as well as products (H_2O, alkenes, etc.) for adsorption sites. The amount of ethanol added is small compared to the added CO; thus, the added ethanol does not impact the total conversion of CO to a measurable extent. The added ethanol does impact the secondary hydrogenation reaction so that the alkene/alkane ratio increases and the amount of methane decreases.

The data obtained in this study display a constant D/molecule for alkanes indicating that the added D_5-ethanol could initiate the carbon chain growth, but only after extensive H/D exchange on the catalyst surface. The D-content per molecule for the 1-olefin increased linearly from 1.2 to 1.5 with increasing carbon number in the C_5–C_{12} range, suggesting that 1-olefin readsorption that was followed by some H/D exchange could cause this observation. It is known that iron catalysts readily effect hydrogenation–dehydrogenation of alcohols and so it is common to relate the participation of alcohol in H/D exchange by reverse dehydrogenation of alcohol. Scheme 1 shows that more than one step likely exists where H/D exchange could take place at the α and β positions of adsorbed d_5-ethanol. Thus, the intermediate compound (1), (2) will readily exchange deuterium with adsorbed hydrogen on the catalyst surface leading to a spectrum of D-ethanols (D_0, D_1, D_2, D_3, D_4 and D_5). As shown in Fig. 2, the recovered ethanol contains D_0, D_1, D_2, D_3, and D_5 isotopomers. After the rapid elimination-addition reactions, the ethanol that participates in the chain growth is actually the partially deuterated ethanol (C_2H_5DO, $C_2H_4D_2O$, $C_2H_3D_3O$), and not the added D_5-ethanol. GC–MS analysis of ethanol after the FT run shows the presence of the following D isotopomers (mole, %): C_2H_6O = 22.8, C_2H_5DO = 14.3,



Scheme 1. Hydrogenation–dehydrogenation of d_5-ethanol on Fe catalysts.

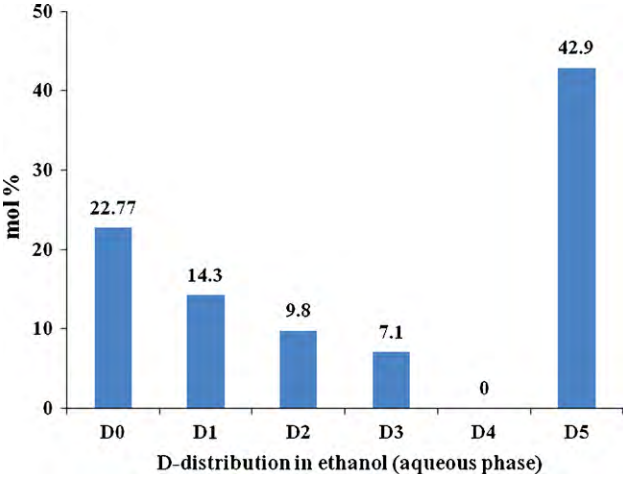


Fig. 2. The D-distribution of ethanol in aqueous phase during Fe-FT synthesis D_5-ethanol co-feeding at 543 K and 0.8 MPa using a syngas (H_2/CO: 0.7).

$C_2H_4D_2O = 9.8$, $C_2H_3D_3O = 7.1$, $C_2H_2D_4O = 0$, $C_2D_5HO = 42.9$. It reveals that hydrogenation–dehydrogenation takes place readily during adsorption of D_5-ethanol (CD_3CD_2OH) and this leads to deuterium exchanging with hydrogen of the reaction mixture on the catalyst surface.

It is also possible that intermediate surface species could be an ethene π-complex derived from the dehydration of added deuteroethanol (Scheme 2). After the metal bonds to one carbon in ethene to produce (4), it then undergoes a hydrogen atom shift to produce (5). Finally, the carbon-metal double bond is formed (6) which can initiate chain growth. The intermediates (4) and (5) can also undergo H/D exchange with surface adsorbed hydrogen atoms and this leads to a total deuterium atoms are less than 4 in the C_2 unit. Furthermore, the co-feeding experiments [18] have revealed that ethanol and propanol are to a considerable extent converted to ethene and ethane or to propene and propane, respectively. It has been reported [17] that ^{14}C labeled ethene addition also initiates chain growth but that the molar radioactivity in the products is significantly smaller than observed in ethanol co-feeding runs. These results suggest that it is more difficult to form the chemisorbed surface structure (3) in Scheme 2 in the case of ethene addition than for ethene produced from added ethanol. Another possibility is that the ethanol incorporation mechanism may follow more than one pathway. At present, we do not have any direct experimental evidence to show the specific C_2 intermediate derived from the added deuteroethanol which is incorporated into the growing hydrocarbon chain. However, the fact that under the same reaction conditions ethanol initiates chain growth about 50-100 times greater than ethene suggests that most of the H/D exchange occurs prior to loss of the oxygen–carbon bond.

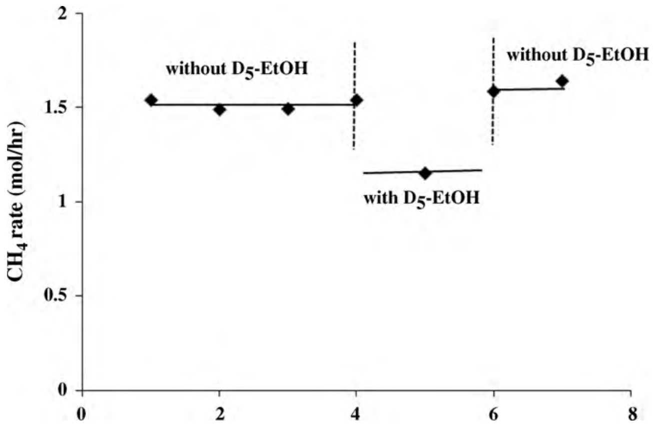


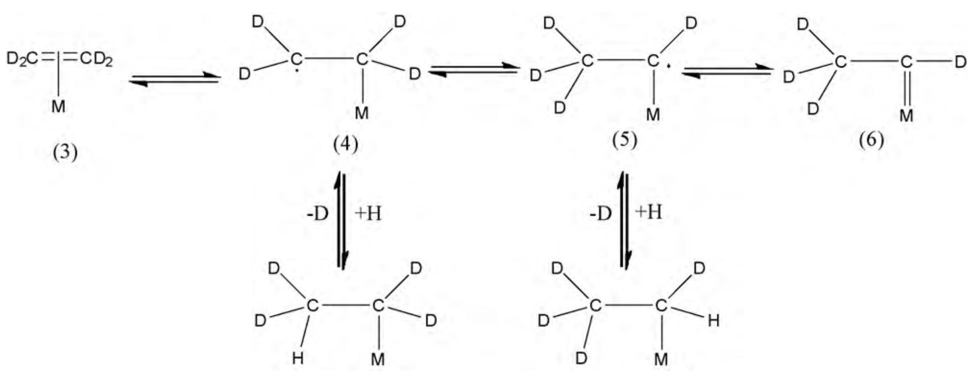
Fig. 3. Effect of methane production rate during D_5-ethanol addition at 2.2 MPa and 543 K using a syngas ratio of H_2/CO = 0.7.

Table 5
Effect of D_5-ethanol co-feeding on olefin–paraffin ratio of products from D_5-ethanol co-feeding during Fe-FT synthesis at 543 K and 2.2 MPa using a syngas (H_2/CO: 0.7).

Feed	Olefin-to-paraffin ratio		
	$C_2^=/C_2$	$C_3^=/C_3$	$C_4^=/C_4$
Without C_2D_5OH	0.462	2.614	3.408
	0.458	2.555	3.415
With C_2D_5OH	0.802	5.232	4.689
Without C_2D_5OH	0.408	2.267	3.257
	0.400	2.181	3.189

3.2. Effect of pressure on d_5-ethanol incorporation

Quantitatively, the picture for D_5-ethanol co-feeding at high pressure (2.2 MPa) is not significantly different from the results obtained at lower pressure (0.8 MPa). As shown in Fig. 3 and Table 5 there is a depression of methane formation and an increase of olefin-to-paraffin ratio of C_2, C_3 and C_4 hydrocarbons at higher pressure which could suggest that some hydrogenation sites were occupied by the added deuteroethanol. Hanlon and Satterfield [10] also observed a similar decrease in methane selectivity with the addition of ethanol during FT synthesis using a fused magnetite catalyst containing potassium at 521 K and 0.78 MPa. Also, Snel and Espinoza [8] observed a substantial decrease in the rate of methane formation that depended on the co-feed concentration as well as the catalyst used. In contrast, a large number of reports indicate little or no influence of ethanol co-feeding on the rate of methane formation. The authors observing suppression of methane



Scheme 2. The possible pathway for the formation of C_2 species.

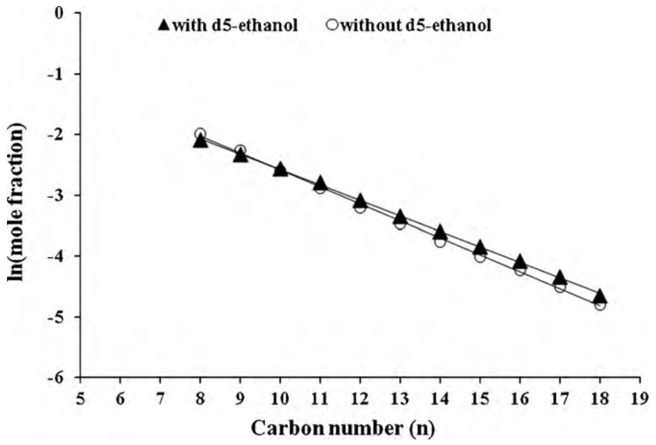


Fig. 4. Anderson–Schulz–Flory product distribution plot for low α-Fe catalyst with and without D_5-ethanol co-feed at 2.2 MPa, 543 K and $H_2/CO = 0.7$.

Table 6
Effect of D_5-ethanol co-feeding on hydrocarbon product selectivity during Fe-FT synthesis at 543 K and 2.2 MPa using a syngas (H_2/CO: 0.7).

Runs	Sample no.	Selectivity, %C						
		CH_4	$C_2^=$	C_2	$C_3^=$	C_3	$C_4^=$	C_4
Without C_2D_5OH	3	7.76	2.83	6.11	8.79	3.36	7.48	2.20
	4	7.86	2.59	5.65	8.63	3.38	7.50	2.20
With C_2D_5OH	5	6.36	3.58	4.46	9.72	1.86	7.56	1.61
Without C_2D_5OH	6	8.06	2.71	6.64	8.79	3.88	7.42	2.28
	7	7.78	2.82	7.03	8.76	4.02	8.03	2.52

formation attributed it to scavenging of surface hydrogen and C_1 intermediates. In our study, the rate of methane formation remains unaffected by D_5-ethanol addition at low pressure (0.8 MPa) but a noticeable change is observed at higher pressure (2.2 MPa) and at high CO conversion suggesting that added D_5-ethanol forms surface intermediates which could scavenge a surface hydrogen to form ethane but this was not found to be the case. Also, it cannot be attributed to the reaction of adsorbed ethanol with adsorbed methane precursors, since such a reaction should yield a higher C_3 formation. Fig. 4 shows only a slight variation of the ASF distribution with added D_5-ethanol. As seen from Table 6, the selectivity to propene increased to about the same extent as the propane decreases.

The relative amounts of isotopomers in alkanes and 1-olefins produced in the D_5-ethanol tracer run at high pressure (2.2 MPa) are summarized in Tables 7 and 8, respectively. Compared to the data obtained at low pressure (0.8 MPa), D_5-ethanol co-fed at high pressure (2.2 MPa) exhibited a distinguished D-distribution in hydrocarbon products (alkanes and 1-olefins). The following data were obtained at higher CO conversion (high pressure, 2.2 MPa): (1) more than 80% and 70% of the alkanes and 1-olefins, respectively, are D_0 isotopomer; (2) the relative mol% of D_1 isotopomer of the 1-olefin is almost two times higher than the corresponding alkane and; (3) the D/molecule remains close to a constant value of 1.35 (C_5–C_{12}) for alkanes, perhaps showing an increasing trend from 1.30 to 1.5 for 1-olefins (C_5–C_{12}). Fig. 5 shows the D-distribution of ethanol which was recovered from the reactor during D_5-ethanol addition and it reveals that H/D exchange occurs at the catalytic sites before being involved in the chain growth. As described earlier, the C_2 intermediate species derived from the adsorbed D_5-ethanol are responsible for the observed D-distribution in the hydrocarbon products. A noticeable difference can be seen for D_0 and D_1 distributions between low and high CO conversion. As CO conversion increases the relative mole % of deutero compounds (D_1, D_2, and D_3) decreased irrespective of carbon number due to the fact that most of the catalyst surface will be covered with intermediates which are derived from the normal FT synthesis. This reveals that the possibility for H/D exchange is lower at high pressure and could be a dominating process at low CO conversion. Indeed, the overall D/molecule remains more or less the same at 1.35, which is slightly lower than the D/molecule (1.45) obtained at low CO conversion. It is likely that there may be a considerable difference between the interaction of added D_5-ethanol and the catalyst surface that impacts the D-distribution among hydrocarbon products. Therefore, the probability that D_5-alcohol participates in FT synthesis decreases with increasing pressure, in agreement with previous studies [10]. Similar results were obtained for a CD_3CH_2OH tracer run. As shown in Fig. 6, the D/molecule exhibits a constant value of 1.4, indicating that the C_2 species derived from the ethanol acted as an initiator for the FT synthesis.

Table 7
Distribution of deuterium in paraffins while co-feeding D_5-ethanol during Fe-FT synthesis at 543 K and 2.2 MPa using a syngas (H_2/CO: 0.7).

Paraffin	mol%						D/molecule*
Carbon no.	D_0	D_1	D_2	D_3	D_4	D_5	
5	79.41	16.11	3.33	0.83	0.16	0.00	1.30
6	81.64	13.86	3.25	0.73	0.24	0.00	1.36
8	84.73	10.85	3.15	1.05	0.23	0.00	1.39
9	88.65	8.17	2.56	0.44	0.18	0.00	1.35
10	91.44	6.29	1.76	0.32	0.20	0.00	1.35
11	88.64	8.08	2.73	0.47	0.06	0.00	1.35
12	90.45	5.89	2.69	0.76	0.16	0.00	1.51

* The D/molecule were calculated without including d_0.

Table 8
Distribution of deuterium in 1-olefins while co-feeding D_5-ethanol during Fe-FT synthesis at 543 K and 2.2 MPa using a syngas (H_2/CO: 0.7).

1-olefin	mol%						D/molecule*
Carbon no.	D_0	D_1	D_2	D_3	D_4	D_5	
5	72.27	22.25	4.44	0.80	0.20	0.00	1.30
6	70.64	22.92	5.10	1.05	0.19	0.00	1.30
8	66.44	24.39	6.80	2.15	0.22	0.00	1.35
9	64.99	22.74	9.29	2.61	0.36	0.00	1.45
10	69.32	20.00	6.69	2.60	1.40	0.00	1.52
11	68.02	20.94	7.88	2.64	0.52	0.00	1.46
12	72.56	17.03	7.23	2.38	0.61	0.00	1.53

* The D/molecule were calculated without including d_0.

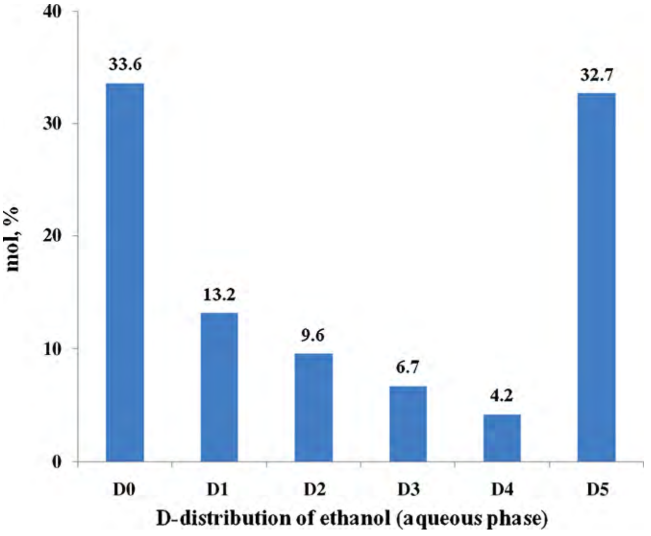


Fig. 5. The D-distribution of ethanol in aqueous phase during Fe-FT synthesis with D_5-ethanol co-feeding at 543 K, 2.2 MPa and a syngas of $H_2/CO = 0.7$.

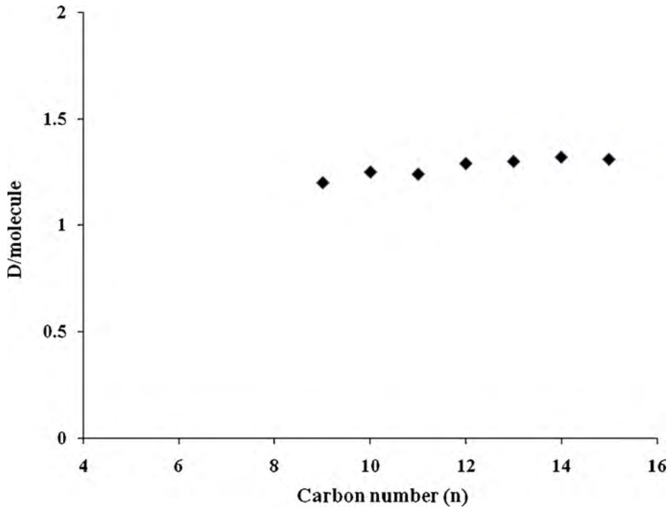


Fig. 6. Variation of total deuterium content with carbon number for paraffins formed during Fe-FT synthesis with D_3-ethanol co-feeding at 543 K, 2.2 MPa and using a syngas of H_2/CO = 0.7.

4. Conclusions

Partially deuterated D_5- and D_3-ethanol were used as a tracer to study the Fe-FT synthesis mechanism. A significant amount of deuterium was found in the hydrocarbon products (alkane, 1-olefin) irrespective of carbon number. Addition of D_5-ethanol during the FT synthesis produces more D_1, D_2, D_3 and to some extent D_4 isotopomers than for D_3-ethanol. The tracer runs (high and low CO conversions) yielded a nearly constant D/molecule for alkanes and 1-olefins suggesting that the C_2 species derived from the partially deuterated ethanol acted as an initiator for the FT synthesis. None of the compounds were found to contain the D_5 isotopomer, indicating extensive H/D exchange of adsorbed D_5-ethanol with hydrogen on the surface of the catalyst before initiating a growing hydrocarbon chain.

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