Catal Lett (2012) 142:190–194
DOI 10.1007/s10562-011-0750-8

Deuterium Exchange Study for Hydrogenation of D_5-1-Pentene (4,4,5,5,5) Over Conventional Cobalt Fischer–Tropsch Catalyst

Muthu Kumaran Gnanamani · Wilson D. Shafer ·
Burtron H. Davis

Received: 7 September 2011 / Accepted: 24 November 2011 / Published online: 13 December 2011

Abstract The hydrogen–deuterium exchange reaction was performed for hydrogenation of D_5-1-pentene (4,4,5,5,5) under realistic cobalt Fischer–Tropsch synthesis conditions. In the presence of CO, the added deutero-1-pentene did not show any significant H/D exchange but a step-wise H/D exchange occurs when CO was replaced with N_2. The inhibition effects of CO and other FT products on H/D exchange of D_5-1-pentene and a pressure dependency effect on H/D exchange are observed.

Keywords Deutero-1-pentene · Hydrogenation · Fischer–Tropsch · Cobalt · Deuterium exchange

1 Introduction

Fischer–Tropsch synthesis (FTS) is a process that converts syngas into a variety of products including hydrocarbons (methane, paraffins, olefins, aromatics), oxygenates and water as a by-product using Fe and cobalt-based catalysts [1–5]. Even though FT synthesis has been widely studied since 1923, there is still controversy in the literature about the mechanism of CO hydrogenation and the reaction pathway for the formation of hydrocarbons and oxygenates [6–8]. Isotopic tracer techniques have been widely used to study the reaction mechanism of FT synthesis. Emmett, who was a pioneer in this field, used ^{14}C-labeled alkenes and alcohols for studying FT mechanisms [9–12] and later, Tau et al. [13] co-fed ^{14}C-labeled pentenes during iron FT synthesis and concluded that alkenes do participate to a limited extent in chain initiation.

Tracer compounds containing deuterium have also been used in FT synthesis, in particular deuterium labeled alkenes and alcohols, in order to show that these compounds could participate in the FT reaction [14–16]. However, H/D exchange process is often observed under FT synthesis conditions that make the application of this technique very complex. In the viewpoint of H/D exchange of alkanes over a metal surface, Taylor and his co-workers [17] established that paraffin hydrocarbons, methane to propane, underwent exchange with deuterium on nickel at 180 °C. Later, Thompson et al. [18] demonstrated that while methane is quite stable toward interaction with deuterium, ethane, propane, and butane are labile on a FT cobalt catalyst under synthesis conditions. The authors speculated that the species (alkyl) mean life on the surface is very much greater than the rate of exchange of an individual C–H bond so that all the hydrogen will be exchanged before these alkyl groups can desorb as alkanes. Miller and Moskovits [15] reported that deuterium from deuterated ethylene ($CD_2{=}CD_2$) was incorporated in the hydrocarbon products without any H/D scrambling either as CD_2 or C_2D_4 using an iron catalyst at 603 K and 0.69 MPa. Shi et al. [19] concluded that there is no measurable H/D exchange in octane under iron-catalyzed FT reaction conditions where CO conversion is not complete. The authors further showed that H/D exchange does occur in alkenes but even here it is limited to the vinyl positions. Therefore, for a given deuterated 1-alkene (below), the deuterium on carbon C_4 and higher carbon positions will not be subject to H/D exchange and its behavior will be similar to that of the paraffin under typical FT synthesis conditions.

M. K. Gnanamani · W. D. Shafer · B. H. Davis (✉)
Center for Applied Energy Research, University of Kentucky,
2540 Research Park Dr, Lexington, KY 40511, USA
e-mail: burtron.davis@uky.edu

$$\overbrace{CD_3 - CD_2} - \overbrace{CH_2 - CH = CH_2}$$

Recently we have reported that D_5-1-pentene (4,4,5,5,5) initiates chain growth without H/D scrambling for both iron and cobalt FT synthesis [20]. In the present study, we investigated the effect of CO on H/D exchange between H_2 and D_5-1-penetene over Pt promoted cobalt FT catalysts.

2 Experimental

The tracer compound, D_5-1-pentene (4,4,5,5,5) was prepared in our laboratory following a published procedure [21] and the details about the procedure are described elsewhere [20]. The cobalt catalyst (0.5% Pt–25%Co/γ-Al_2O_3) was prepared using a slurry impregnation method that utilized an aqueous solution of cobalt nitrate. After multiple impregnations with cobalt to give a 25 wt% Co loading, the catalyst was dried at 373 K for 24 h and then 0.5 wt% Pt was added using an aqueous solution of tetraammine platinum(II) nitrate (Alfa Aesar, purity: 99.9%). It was then dried in an oven at 373 K and calcined in flowing air at 773 K for 5 h.

In a typical cobalt FT synthesis run, about 10 g of calcined Pt promoted cobalt catalyst were reduced ex situ using an H_2:He (1:3) mixture at 623 K for 10 h. The reduced catalyst was transferred under flowing nitrogen to a 1 L CSTR which already contained 310 g of melted Polywax 3000. The catalyst was further reduced in situ using pure H_2 (20 slph) for 24 h at 503 K. The FT synthesis was conducted at 493 K, 2.08 MPa with a syngas space velocity of 2.0 and at a constant H_2/CO of 2.0. About 0.53 mol% D_5-1-pentene (4,4,5,5,5) (4.8 g D_5-1-pentene (4,4,5,5,5) + 30 g of *o*-xylene), based on total carbon in the feed, was introduced into the reaction system using a MiltonRoy Mini-pump for a period of 5 h. The co-feed was introduced after reaching a steady CO conversion of about 30%. Hydrogenation of D_5-1-pentene was carried out separately under similar conditions as described above by replacing CO in the feed gas mixture with an inert gas N_2.

The gaseous products were analyzed by online gas chromatography before, during and following D_5-1-pentene (4,4,5,5,5) addition. Hot (373 K) and cold (273 K) sample collection traps were emptied before the addition of D_5-1-pentene (4,4,5,5,5). At the end of the addition, both traps were emptied again and the oil and wax products were separated from the aqueous phase. The liquid products that condensed in the hot and cold traps were analyzed separately using a HP 5890 GC with DB-5 capillary column and a HP 5790 GC with Porapak Q packed column. The hydrogenated product of D_5-1-pentene (i.e., pentane-d_x) may contain different deuterium isotopomers only if they undergo any H/D exchange under the conditions followed. A 5973 N MSD coupled to the 6890 GC from Agilent was employed for product identification. A ^{13}C correction was introduced to the mass spectral data for ascertaining the presence of deuterium isotopomers. In order to avoid the necessity of correcting for ion fragments from species of greater molecular weight, sufficiently low energy ionizing electrons were used to suppress dissociation processes.

3 Results and Discussion

Table 1 summarizes the reaction conditions utilized. The H/D exchange of D_5-1-pentene (4,4,5,5,5) was performed at two different pressures over a conventional cobalt based FT catalyst (Pt promoted Co/γ-Al_2O_3) by replacing CO with N_2. Under a typical FT synthesis condition nearly 27.3% of the added deutero-1-pentene was converted to products. Among the reactions the added deutero-1-pentene underwent were: (i) mainly hydrogenation to deuteropentane (48.5%), (ii) isomerization (42.5%) and (iii) in initiating FT chain growth (8.6%). Analysis of the deuterium content in the pentane recovered after reaction shows that no measurable H/D exchange occurs under the conditions followed (Table 2; Fig. 1). The calculated H/D of the recovered pentane in the presence of CO was 1.4 which is equal to the theoretical value obtained based on a complete lack of H/D exchange and we did not observe any d_1,d_2, or d_3 mass fractions in pentane.

On the other hand, hydrogenation of the added deutero-1-pentene yields selectively deuteropentane (100%) in the absence of CO at 473 K and 2.09 MPa pressure over Pt–Co/γ-Al_2O_3 catalyst. Furthermore, the H/D ratio of recovered pentane was 1.9 and the calculated D/molecule dropped to 4.2. This shows that some H/D exchange of the added D_5-1-pentene (4,4,5,5,5) occurs on metal surfaces during hydrogenation. As shown in Table 2, the degree of H/D exchange increases with decreasing reaction pressure (0.10 MPa) and thereby the D/molecule dropped to 3.8 from 5.0. The distribution of d-isotopomers in the recovered pentane is shown in Fig. 1. It can be see that there is a distribution of d-isotopomers of pentane formed in the absence of CO during hydrogenation of added D_5-1-pentene and the relative abundance (mol%) of pentanes formed increase with increasing deuterium content. It is noticed from Fig. 2 that the number of deuterium in deutero-1-pentene that exchanges with hydrogen declined logarithmically with increasing number of such atoms. In other words, H/D exchange occurs in a step-wise manner. Similar phenomenon was observed with hydrogenation (deuterium) of lower alkenes like ethene on a Ni wire catalyst at 363 K [22]. The authors concluded the stepwise

Table 1 Hydrogenation of D_5-1-pentene (4,4,5,5,5) over Pt–Co/γ-Al_2O_3

	P_{CO} (MPa)	P_{H_2}(MPa)	P_{N_2}(MPa)	% CO conversion	Amount of D_5-1-pentene co-fed (mmol)	% conversion of D_5-1-pentene	Selectivity (mol%)			
							S_{HYD}	S_{ISO}	S_{INC}	Unacc.
With CO										
2.08 MPa[a]	0.69	1.39	0	22.0	43.0	27.3	48.5	42.5	8.6	6.3
Without CO										
2.08 MPa	0	1.39	0.69	–	43.0	100	100	–	–	–
0.10 MPa	0	0.067	0.033	–	43.0	100	100	–	–	–

[a] Reaction conditions: Co catalyst, T = 493 K, P = 2.09 MPa, H_2/CO = 2.0, SV = 2.0 slph/g cat

Table 2 H/D exchange during hydrogenation of D_5-1-pentene (4,4,5,5,5) over Pt–Co/γ-Al_2O_3

	Pressure (MPa)	H/D in D_5-*n*-pentane	D/molecule (*n*-pentane)	Degree of H/D exchange (%)
With CO	2.08	1.4	5.0	0
Without CO	0.10	2.2	3.8	24.0
	2.08	1.9	4.2	16.0

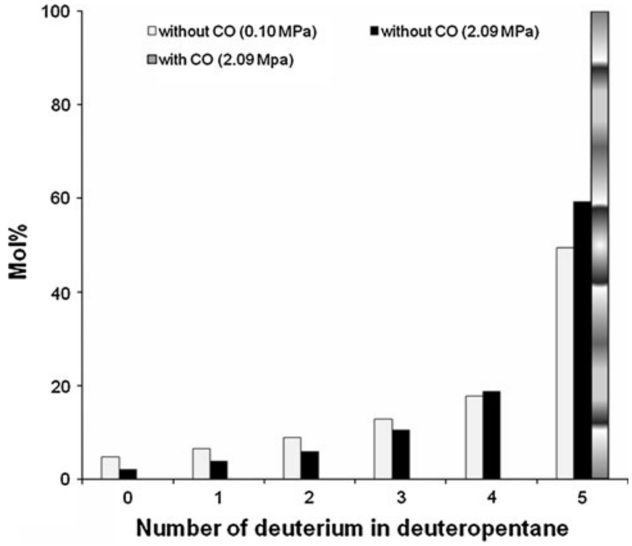


Fig. 1 Deuterium distributions in pentane obtained during hydrogenation of D_5-1-pentene (4,4,5,5,5) over Pt–Co/γ-Al_2O_3 catalyst

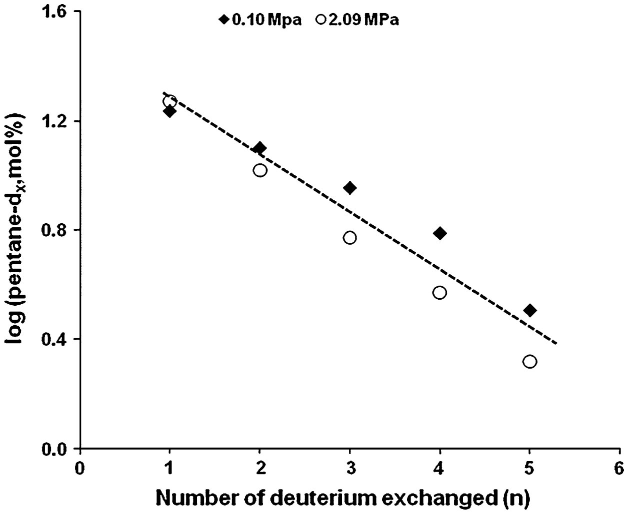
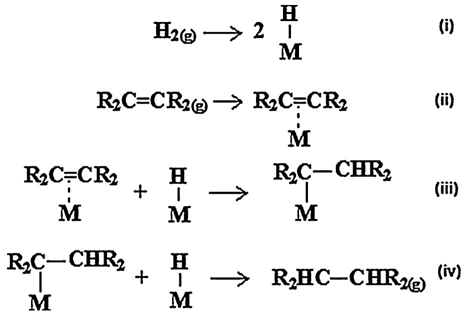


Fig. 2 Logarithmic plots of deuteropentane distributions obtained for the hydrogenation of D_5-1-pentene (4,4,5,5,5) over Pt–Co/γ-Al_2O_3 catalyst at different pressure

character of the ethene exchange implied a rapid desorption (and adsorption) of ethene molecules. In another study, Bond [23] showed that the distribution of deuteroethene did not change much with ethene conversion at temperatures in the range of 273–333 K over Pt/SiO_2.

As can be seen from the above results there is no H/D exchange in the deuterated pentane in the presence of CO (i.e., a typical FT synthesis condition) and that a considerable H/D exchange occurs under the same reaction conditions when CO was replaced with N_2. The occurrence of H/D exchange on remote carbons (C_4, and C_5) during hydrogenation of D_5-1-pentene without CO can be explained as follows. As proposed by Horiuti and Polanyi [24], hydrogenation of alkenes on metal surfaces generally consists of four steps as shown in Scheme 1: (i) dissociation of H_2 to form M-H bonds, (ii) coordination of alkene to the metal, (iii) the migratory insertion reaction between H and the coordinated alkene to form an alkyl-metal, and (iv) the reductive elimination reaction between H and alkyl to produce an alkane.

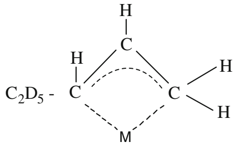
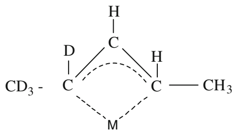
In addition to hydrogenation, olefins can undergo double bond migration (isomerization) and H/D exchange [25, 26]. Depending on the specific catalytic system and reaction conditions the extent of isomerization, and thereby H/D exchange, may vary. For example, the extent of H/D exchange (M-deuterohexane distribution) increases with an increase of 1-hexene conversion during hydrogenation (addition of deuterium) over Ni/SiO_2 at 378 K [27]. On

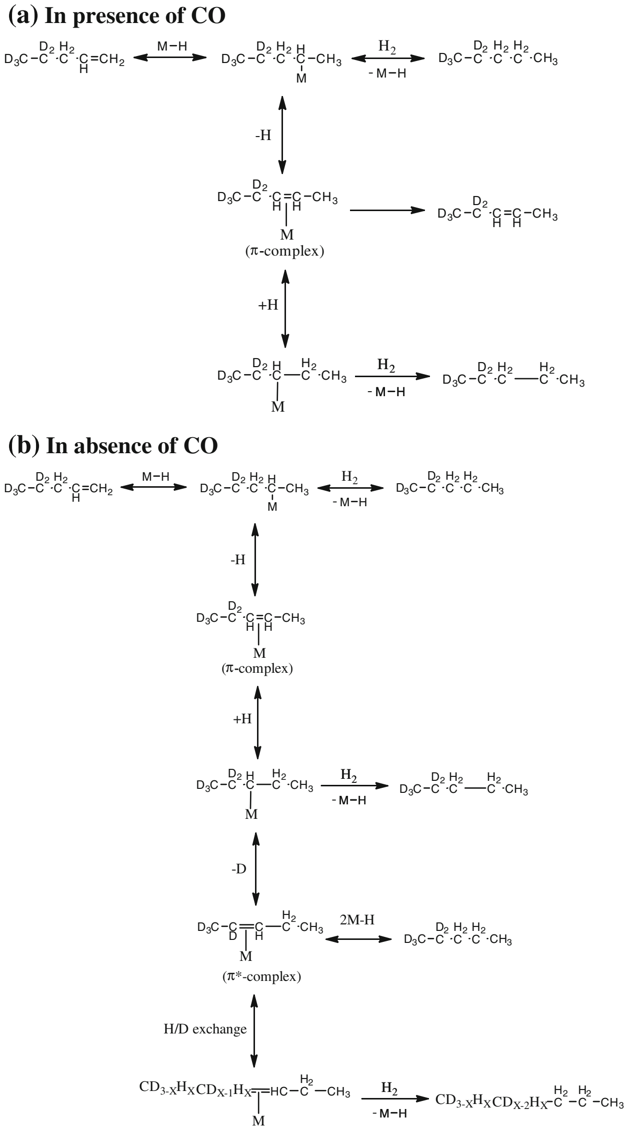


Scheme 1 Horiuchi-Polanyi hydrogenation mechanism for alkene

Raney Ni at 296 K, with cyclohexane as solvent, 1-hexene rapidly isomerizes, first to the 2-hexenes and afterwards to the 3-hexenes [28]. Extensive isomerization is also shown with liquid 1-pentene on Pd/C, Rh/C and Rh/Al_2O_3 and with Ru/Al_2O_3 [29].

For our reaction conditions, the two observable processes are: (i) addition of hydrogen leading to D_5-pentane, and (ii) isomerization (double-bond migration of pentene). In the presence of CO, even an isomerized π-complex intermediate that leads to hydrogenation (Scheme 2a) does not lead to H/D exchange on carbon C_4 and C_5 (Fig. 1). On the other hand, H/D exchange occurs on remote carbons (C_4 and C_5) in the absence of CO, indicating that the intermediate π-complex undergo further isomerization to produce π^*-complexes as shown in Scheme 2b. It is reasonable to argue that this π^*-complex could be involved in H/D exchange and thus eventually produce a distribution of deuteropentane. One can expect two things when CO was replaced by N_2: (1) an increase in hydrogen surface coverage and thereby an increase for the local H_2/D_5-1-pentene ratio and (2) increased surface coverage by hydrogen due to lack of inhibition effects from CO and other FT products.

The formation of  involves the breaking of a vinyl C–H bond on carbon C_3; this will require less energy than the breaking of the remoter C–D bond of the CD_2 groups. In addition, the breaking of the C–D bond to form  may require more metal surface sites than to form the initial π-bonded structure involving the R–CH_2–CH=CH_2 unit. The competitive adsorption of CO may decrease the number of sites with the needed grouping and/or decrease the electron concentration, and thereby inhibit the breaking of the C–D bond of the C_2D_5 group.



Scheme 2 H/D exchange of D_5-1-pentene (4,4,5,5,5) during hydrogenation over Pt promoted Co/γ-Al_2O_3 catalyst: **a** in presence of CO, **b** in absence of CO

4 Conclusions

Under Co-FT synthesis condition, D_5-1-pentene (4,4,5,5,5) did not show any H/D exchange even though it was hydrogenated to D_5-n-pentane and isomerized to D_5-2-pentenes as well as being involved in initiating FT chain growth. When D_5-1-pentene was hydrogenated under similar Co-FT synthesis conditions by replacing CO with N_2 the deuteropentane had undergone a considerable H/D exchange. In the presence of CO, the lack of H/D exchange on remote carbons (C_4 and C_5) can be explained based on inhibition effects of CO for adsorption of added D_5-1-pentene in a form that requires C–H bond rupture of the CD_3CD_2 group. Thus, CO does not strongly inhibit the adsorption of the double bond to form a π-bonding involving the sp^2 1,2 or 1,3 carbons but inhibits rupture of the sp^3 bonds.

Acknowledgments The work was supported by funding from the Commonwealth of Kentucky.

References

1. Dry ME (1990) Catal Lett 7:241
2. Schulz H (1999) Appl Catal A 186:3
3. de Smit E, Weckhuysen BM (2008) Chem Soc Rev 37:2758
4. Khodakov AY, Chu W, Fongarland P (2007) Chem Rev 107:1692
5. Dry ME (2004) Appl Catal A 276:1
6. Dry ME (2004) Stud Surf Sci Catal 152:533
7. Hindermann JP, Hutchings GJ, Kiennemann A (1993) Catal Rev-Sci Eng 35:1
8. Adesina AA (1996) Appl Catal A 138:345
9. Kummer JT, Podgurski HH, Spencer WB, Emmett PH (1951) J Am Chem Soc 73:564
10. Kokes RJ, Hall WK, Emmett PH (1957) J Am Chem Soc 79:2989
11. Kummer JT, Emmett PH (1953) J Am Chem Soc 75:5177
12. Hall WK, Kokes RJ, Emmett PH (1960) J Am Chem Soc 82:1027
13. Tau LM, Dabbagh HA, Davis BH (1990) Energy Fuels 4:94
14. Kryukov YB, Bashkirov AN, Fridman RA, Liberov LG, Smirnova RM, Pegov AA (1965) Neftekhimiya 5:62
15. Miller D, Moskovits M (1989) J. Am Chem Soc 111:9250
16. Gnanamani MK, Keogh RA, Shafer WD, Shi B, Davis BH (2010) Appl Catal A 385:46
17. Morikawa K, Benedict WS, Taylor HS (1936) J Am Chem Soc 58:1795
18. Thompson SO, Turkevich J, Irsa AP (1951) J Am Chem Soc 73:5213
19. Shi B, O'Brien RJ, Bao S, Davis BH (2001) J Catal 199:202
20. Gnanamani MK, Keogh RA, Shafer WD, Davis BH (2011) Appl Catal A 393:130
21. Lorenz B, Heinrich KH, Herrmann M, Moebius G (1981) Isotopenpraxis 17:437
22. Turkevich J, Bonner F, Schissler DO, Irsa AP (1950) Discuss Faraday Soc 8:352
23. Bond GC (1956) Trans Faraday Soc 52:1235
24. Horiuchi, J, Polanyi M (1934) Trans Faraday Soc 30:1164
25. Farkas A (1939) Trans Faraday Soc 35:906
26. Eley DD (1955) In: Emmett PH (ed) Catalysis, Chap 5. Reinhold, New York
27. Burwell RL Jr, Tuxworth RH (1956) J Phys Chem 60:1043
28. Horner L (1969) Ann NY Acad Sci 158:456
29. Philipson JJ, Burwell RL Jr (1970) J Am Chem Soc 92:6125