ELSEVIER

Catalysis Today 84 (2003) 59–65

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Direct synthesis of middle *iso*-paraffins from synthesis gas

Xiaohong Li [a,*], Kenji Asami [a], Mengfei Luo [a], Keisuke Michiki [a],
Noritatsu Tsubaki [b], Kaoru Fujimoto [a]

[a] *Department of Chemical Processes and Environments, Faculty of Environmental Engineering, The University of Kitakyushu,*
1-1, Hibikino, Wakamatsu-ku, Kitakyushu, Fukuoka 808-0135, Japan
[b] *Department of Material System and Life Science, School of Engineering, Toyama University,*
Gofuku 3190, Toyama 930-8555, Japan

Abstract

This paper focuses on the synthesis of *iso*-paraffin-rich hydrocarbons by Fischer–Tropsch synthesis (FTS) over Co/SiO_2 catalyst. The basic concept was to secondarily isomerize and/or hydrocrack the primary FTS hydrocarbon products.

A physical mixture of a small amount of added H-ZSM-5 in the Co/SiO_2 catalyst enhanced the formation of C_4–C_{10} *iso*-paraffins while suppressing the formation of longer hydrocarbons, probably because of the selective cracking of higher hydrocarbons on ZSM-5. The three-component catalyst (Co/SiO_2–Pd/SiO_2–ZSM-5) promoted the formation of paraffins, whereas the yield of isomerized products was not high enough.

For a two-step reaction, the first step catalyst was the Co/SiO_2 + ZSM-5 catalyst and the second step catalyst was Pd/SiO_2 + ZMS-5 catalyst where additional hydrogen was added. The selectivity of *iso*-paraffins was markedly promoted and the molecular weight of the product decreased while the syngas conversion was kept constant.

The hydrocracking of *n*-octane (which is the model compound of FTS reaction) over hybrid catalyst composed of Pd/SiO_2–zeolite and showed high and stable activity giving *iso*-paraffin-rich hydrocarbons. The isomerization was favored for Pd rich catalyst. The role of Pd was thought to be the port hole of hydrogen spillover to zeolite.

Keywords: *iso*-Paraffin; Fischer–Tropsch synthesis; Catalyst

---

1. Introduction

Synthesis of hydrocarbons by Fischer–Tropsch synthesis (FTS) has been industrialized for producing clean diesel fuel because of its high *n*-paraffin and low sulfur content.

It is well known that the FTS product is mostly *n*-hydrocarbons, either olefins or paraffins. Recently, the production of hydrocarbons rich in *iso*-paraffins has gained attention because of its excellent gasoline fuel properties. Several groups have tried to make *iso*-paraffins by utilizing FTS catalyst supported acidic zeolite [1–3]. However, acidic zeolites are not a stable support for FTS catalysts, typically results in low activity and high methane selectivity [4]. Chen reported light hydrocarbon synthesis at 0.1 MPa from syngas using three kinds of NaY zeolite-supported ruthenium catalyst prepared by impregnation, ion exchange and CVD, respectively. Due to low reaction pressure, methane was the main product but isobutene predominated in C_4 fraction [5]. Nijs and Jacobs [6,7] also reported similar phenomenon on Ru/NaY. Kong et al. [8,9] used a NaOH washed Co/Y zeolite catalyst to do FTS. The selectivity of isomers was 20–30%.

---

[*] Corresponding author.

0920-5861/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0920-5861(03)00301-8

Recently mesoporous molecular sieves were used as FTS catalyst supports but the stability under high pressure water vapor in FTS was harmful [10,11]. Calejia studied the physical and chemical properties, activity, and selectivity of Co/HZSM-5 zeolite bifunctional catalyst for FTS prepared by incipient wetness impregnation with different conditions of drying, calcination and reduction. The Co content of the catalyst and the effect of Th, as promoter, were also studied. Maximum activity of the catalyst was obtained with 1.5 wt.% Th, resulting in an increase of C_6+ selectivity. This was explained in terms of a shift in chemisorption properties of the catalyst. The basic character of the promoter affected the zeolite acidity, decreasing the aromatic proportion in the liquid hydrocarbon fraction [12]. Bessell studied the catalytic activity and product selectivity of a series of FTS Co catalysts, supported on kieselguhr, SiO_2, Al_2O_3, bentonite, zeolite Y, mordenite, and ZSM-5 which were correlated with catalyst reproducibility and adsorptive properties (e.g., with H, CO, and NH_3), as well as support acidity, surface area, and structure [13]. The nature of the higher hydrocarbons depended strongly upon support acidity, with the non-zeolitic low-acidity supports producing the classic straight-chain Fischer–Tropsch product. Of the zeolite-supported catalysts, the most strongly acidic ZSM 5-supported catalyst produced the most highly branched products, followed by the zeolite Y-supported catalyst. The straight-chain character of the product from the mordenite-supported catalyst was explained by the inaccessibility of primary Fischer–Tropsch products to the mordenite acid sites, due to the mordenite channel system and ion exchange properties, thereby preventing secondary reactions (e.g., isomerization). Jothimurugesan reported a 50:50 wt.% ratio Co–Ni catalyst physically mixed with HZSM-5 (5% Co–5% Ni/TiO_2 + HZSM-5) gave the highest CO conversion (45.2%) at the conditions tested. This compared to conversion of 8.9 and 10.5% with Co-only and Ni-only catalysts, respectively. Mixing the Co–Ni catalyst with HZSM-5 resulted in a significant reduction in methane selectivity and a significant increase in C_4+ selectivity. The aromatic fraction increased from 1.5 to 8.1 wt.%, the C_2+ olefins were nearly eliminated, and isobutane increased from 2.3 to 58.5 wt.% in the C_4 fraction [14]. Part of the authors have shown that a hybrid catalyst composed of a physical mixture of supported Co catalyst and zeolite gives excellent catalytic activity and high selectivity of middle *iso*-paraffins [15].

In this research, the selective synthesis of C_4–C_6 *iso*-paraffins from synthesis gas was aimed.

The fundamental concept in this research is the synthesis of hydrocarbon mixtures rich in C_4–C_6 *iso*-paraffins by hydrocracking and isomerization, the primary hydrocarbons which are produced by FTS. Catalysts used were physical mixtures of a Co/SiO_2 FTS catalyst, Pd/SiO_2 and a zeolite. In this reaction system product hydrocarbons on the FTS catalyst diffuse to the hydrocracking catalyst either in the gas phase (volatile products) or on the surface (products such as wax, which is hard to be vaporized under reaction conditions) and are hydrocracked or isomerized to *iso*-paraffins. It was interesting that higher hydrocarbons such as wax were exclusively cracked when the hydrocracking catalyst existed nearby to the FTS catalyst. The hydrocracking catalysts used were a physical mixture of Pd/SiO_2 and zeolite, which showed excellent activity because of hydrogen spillover from Pd. Hydrogenation catalyst in the Pd/SiO_2–zeolite promoted isomerization reaction while itself has no isomerization activity. On the other hand, the cracking reaction was not affected by hydrogenation.

2. Experimental

2.1. Catalyst preparation

A 20 wt.% Co on SiO_2 catalyst was selected as an FTS catalyst. The Co/SiO_2 catalyst was prepared by the incipient wetness method with the silica gel (Fujisilicia Q-10 whose surface area and pore volume were 300 m^2/g, and 1.0 ml/g, respectively) and an aqueous solution of $Co(NO_3)$. In certain runs, a small amount of powdery H-ZSM-5 was physically mixed with the Co/SiO_2 catalyst.

Catalysts with hydrocracking and/or hydroisomerization activity were prepared by physically mixing H-ZSM-5, USY, or H-mordenite with 2.5 wt.% Pd on SiO_2 by pressure-molding the zeolite powder and the Pd/SiO_2. All catalysts were reduced in flowing hydrogen at 673 K for 10 h.

The hydrocracking catalyst was activated in hydrogen gas flow at 673 K for 1 h under atmospheric pressure.

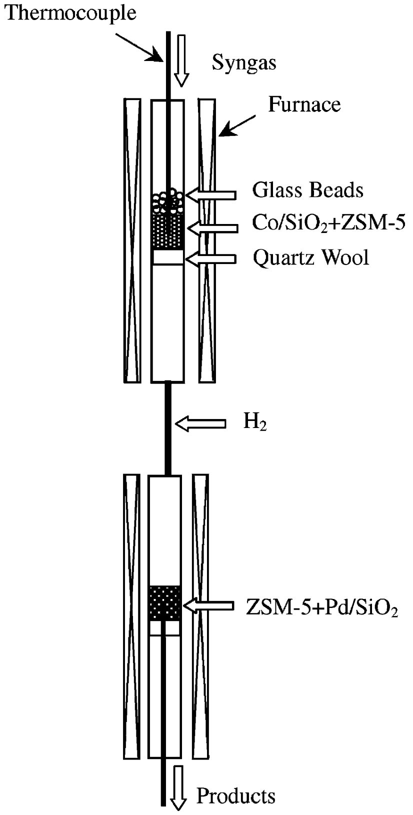


Fig. 1. Illustration of the two-step reactor.

2.2. Reaction apparatus and procedure

Fig. 1 shows the reaction apparatus. The first reactor (upper one) contains the FTS catalyst and the second reactor (lower one) contains the hydrocracking/hydroisomerization catalyst. In the 2-stage reaction operation, additional hydrogen was injected to promote the hydrocracking/hydroisomerization reaction.

FTS reaction was conducted under pressurized conditions 0.5–2.0 MPa, 513–573 K by using a flow type fixed bed reactor (SUS-316 tube, 8 mm ID). The catalyst amount was 1.0 g and the H_2/CO ratio of the feed gas was 3.0 or 1.8. In some experiments, the hydrocracking catalyst (zeolite or Pd/SiO_2 + zeolite) was mixed with the Co/SiO_2 FTS catalyst in first stage. In other experiments, the two were separated. Reaction conditions were: pressure, 0.5–2.0 MPa; H_2/hydrocarbons mole ratio, 9/1; reaction temperature, 543–553 K.

3. Results and discussion

3.1. FTS reaction

3.1.1. Single step reaction

Fig. 2 shows the hydrocarbon distribution obtained for Co/SiO_2 only or for a physical mixture of Co/SiO_2 + ZSM-5. CO conversion of both reactions was 100%. CO_2 selectivity was only about 2%. For the conventional FTS on Co/SiO_2 catalyst, $C_{15}+$ hydrocarbons were formed and there were no olefins. Because the syngas used here was hydrogen-rich (H_2/CO = 3), olefin formation was suppressed. However, in the product distribution of the modified FTS on the Co/SiO_2 + ZSM-5, heavy hydrocarbons disappeared and C_4–C_{10} fractions increased as expected. These facts agree well with the reported findings that longer chain hydrocarbons are easily hydrocracked [16]. Formed *iso*-paraffins were accompanied by small amount of olefin. The isomerization reaction between *iso*-paraffin and normal paraffin is at equilibrium state and it is impossible to exclude the formation of normal paraffin. The disappearance of $C_{10}+$ can be explained as follows: the waxy product from the conventional FTS catalyst stays on the surface of the catalysts and is subjected to the secondary hydrocracking, forming lighter hydrocarbons

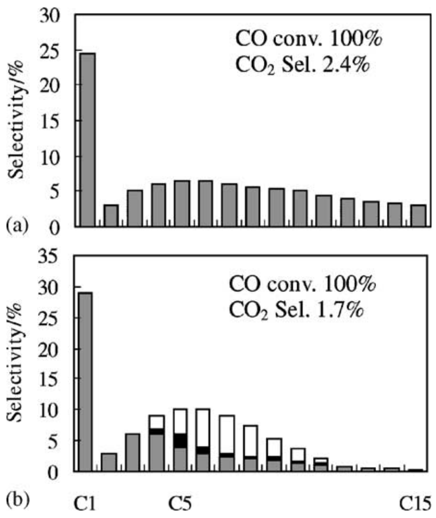
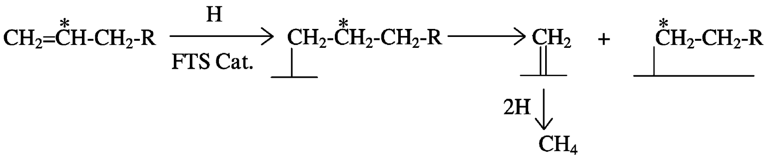


Fig. 2. FTS product distribution on (a) Co/SiO_2; (b) Co/SiO_2 + ZSM-5 catalyst (H_2/CO = 3.0, 1.0 MPa, W/F = 5.1 g h/mol, 513 K, 60 min). ▨ , paraffin; □, *iso*-paraffin; ■, olefin.

containing *iso*-paraffins. The characteristic features of the Pd/SiO_2-added hybrid catalyst system is the lower methane selectivity and the much lower content of olefins. The high methane and olefin selectivity should be attributed to the different reaction mechanisms on metal free zeolite from that of Pd/SiO_2 containing catalyst. On the metal free system, the mechanism is the single cracking reaction while that on the Pd-containing catalyst is the hydrocracking catalysis. The simple cracking reaction makes lower olefins as well as methane, while hydrocracking gives mostly *iso*-paraffins distributed C_3 to C_6.

In order to stabilize the activity of ZSM-5, Pd/SiO_2 catalyst was added to the Co/SiO_2 + ZSM-5 hybrid catalyst to form a three-component catalyst: FTS, hydrocracking and hydrogenation. In Fig. 3, the effect of Pd/SiO_2 introduction is shown. It is clear that the olefin content in the FTS products of the Co/SiO_2 + ZMS-5 + Pd/SiO_2 catalyst mixture decreased significantly. More importantly, no olefinic products were formed, meaning that not simple cracking but hydrocracking occurred. However, here the feed gas ratio was H_2/CO = 1.8 and most of the hydrogen was consumed in the FTS reaction. The hydrogen used in hydrocracking was not enough and little olefin existed even though Pd was presented. For a syngas ratio of H_2/CO = 3, no olefins appeared in the products on the Pd-containing catalyst at the same reaction condition.

When Pd/SiO_2 was added, methane decreased from 18 to 11%, as shown in Fig. 3. Here methane formed from not only FTS itself but also from olefins, produced from the cracking reaction (Fig. 3(a)). However, because 1-olefins were hydrogenated on Pd effectively, methane derived from the secondary reaction of 1-olefin hydrocracking disappeared:



$$CH_2{=}\overset{*}{C}H\text{-}CH_2\text{-}R \xrightarrow[\text{FTS Cat.}]{H} \underline{CH_2\text{-}\overset{*}{C}H_2\text{-}CH_2\text{-}R} \longrightarrow \underline{CH_2} + \underline{\overset{*}{C}H_2\text{-}CH_2\text{-}R}, \quad CH_2 \xrightarrow{2H} CH_4 \tag{1}$$

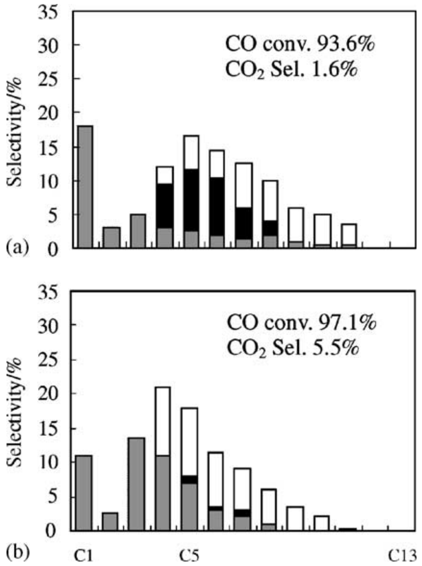


Fig. 3. Pd/SiO_2 addition effect on hybrid catalyst: (a) Co/SiO_2 + SiO_2 + ZSM-5; (b) Co/SiO_2 + Pd/SiO_2 + ZSM-5 catalyst (H_2/CO = 1.8, 1.0 MPa, W/F = 5.1 g h/mol, 513 K). ▨, paraffin; ☐, *iso*-paraffin; ■, olefin.

3.1.2. Two-step reaction

In Fig. 4 is shown the product distribution of the two-step reaction. In the two-stage reaction system, the first step catalyst was the Co/SiO_2+ZSM-5 and the second step catalyst was Pd/SiO_2+ZMS-5. Hydrogen was added to the second stage reactor, which resulted

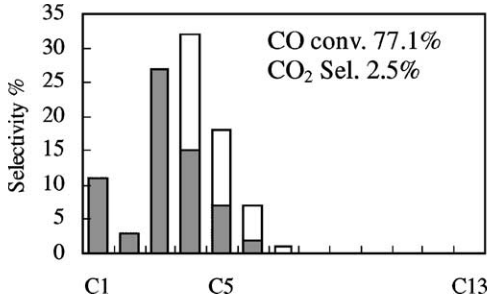


Fig. 4. Product distribution of the 2-stage reactor (1.0 MPa, W/F = 5.1 g h/mol, in first stage reactor: T = 513 K, Co/SiO_2 + ZSM-5 catalyst, H_2/CO = 1.8; in second stage reactor: T = 573 K, ZSM-5 + Pd/SiO_2 catalyst, H_2/CO = 3.0). ▨, paraffin; ☐, *iso*-paraffin; ■, olefin.

in the overall H_2/CO ratio of 3/1 (mole ratio), whereas the H_2/CO ratio at the first reactor was 1.8/1.

It is clear that by passing the effluent from the first reactor through the second reactor, the olefins completely disappear and the product distribution was drastically changed to lower molecular weights. This means that the products of the first reactor were further hydrocracked, giving *iso*-paraffins as the main product. It should be also noted that the methane selectivity was around 10% in spite of the 3/1 H_2/CO ratio because methane was produced in the FTS reaction where the H_2/CO ratio was 1.8/1. Since the reaction conditions can be controlled independently to those of the first reactor, the product pattern of the second reactor can be also controlled.

3.2. Hydrocracking of model hydrocarbons

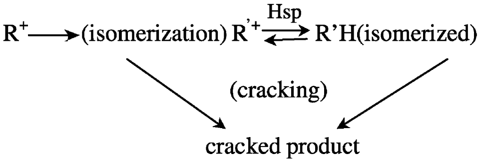
The basic concept of present study is the two-step reaction system, composed of the FTS reaction and the hydrocracking of its products. The hydrocracking of three types of model *n*-paraffins designed to the represent products of FTS reaction was tested.

3.2.1. *n*-Decane ($C_{10}H_{22}$)

Fig. 5(a)–(c) shows the reaction results. The Pd/SiO_2 alone shows no activity and the mordenite alone shows little activity. However, a mixture of the two catalysts shows much higher activity for Pd/SiO_2 contents between 10 and 80%.

The selectivity of the cracking reaction increased with an increase in the mordenite content at the mixture. However, the turnover frequency (TOF, based on the acid sites) of cracking was independent on the mordenite content, while the TOF of hydroisomerization increased with the content of Pd/SiO_2. The role of Pd/SiO_2 has been proved to be the activation of gaseous hydrogen and to transfer to zeolite acid site (hydrogen spillover) [17,18]. The spillover of hydrogen activates paraffinic hydrocarbon as shown below.

$$RH + Hs \longrightarrow R^+ + H_2 \qquad (2)$$



(3)

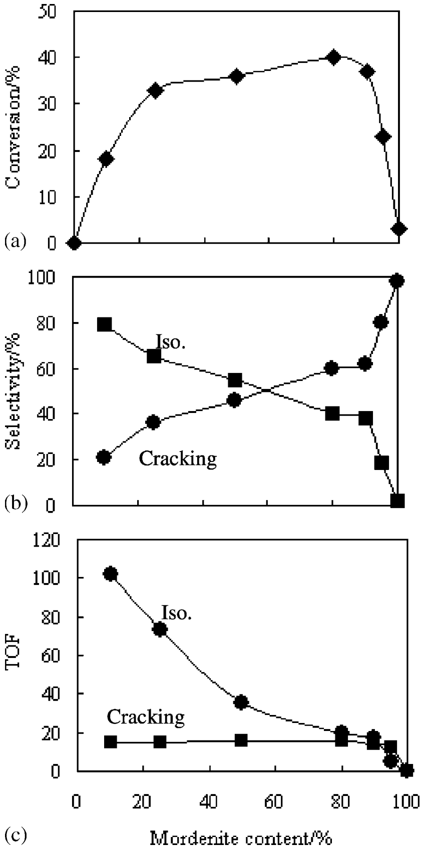


Fig. 5. Results of *n*-decane reaction (1 MPa, $W/F = 1$ g h/mol, H_2/*n*-decane = 9, Pd/SiO_2 + mordenite 0.4 g, 553 K).

The spiltover hydrogen activates saturated hydrocarbons and also stabilizes the carbenium ion which leads to isomerized products. Therefore, if the amount of spillover hydrogen is insufficient, the cracking reaction of carbenium ion is preferred over isomerization. This is consistent with the effect of Pd/SiO_2 catalyst.

Fig. 6 shows the isomerization selectivity as a function of *n*-decane conversion on two types of Pd/SiO_2 + mordenite mixed catalysts with different compositions. It is clear that the isomerization selectivity decreases with increasing *n*-decane conversion (secondary cracking) for both catalysts, but the isomerization selectivity is always higher for the catalyst with high Pd/SiO_2 content.

3.2.2. *n*-Hexane (C_6H_{14})

Fig. 7 shows the results of the *n*-hexane reaction on mixtures of Pd/SiO_2 + mordenite. Similar to that of

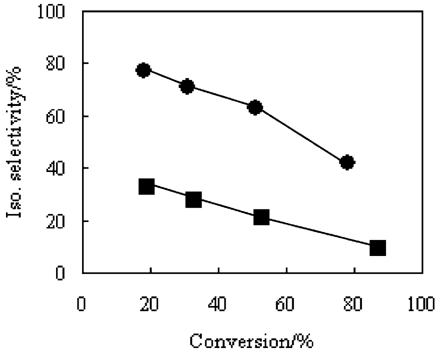


Fig. 6. Results of *n*-decane reaction (1 MPa, $W/F = 0.5$–4 g h/mol, H_2/*n*-decane = 9, Pd/SiO_2 + mordenite 0.4 g, 553 K). ●, Pd:mordenite = 3:1; ■, Pd:mordenite = 1:4.

n-decane, this mixed catalyst showed high and stable catalytic activity. The characteristic features of the *n*-hexane reaction is that little cracking reaction proceeded under these reaction conditions, which means that the cracking reactivity of *n*-paraffin decreases drastically with a decrease in the chain length.

3.2.3. *n*-Octane (C_8H_{18})

Figs. 8 and 9 show the product distribution of the *n*-octane conversion on the Pd/SiO_2-mordenite mixed catalyst. It is clear from the data in Fig. 8, that the product is the mixture of isomerized octane and almost equi-molar amount of C_3, C_4 and C_5 paraffins. This phenomenon suggests that the cracking is the result of simple splitting of the *n*-C_8 skeleton into stable products. Also, it is clear from Fig. 9 that the cracked product is rich in *iso*-paraffins, which might be due isomerization followed by cracking.

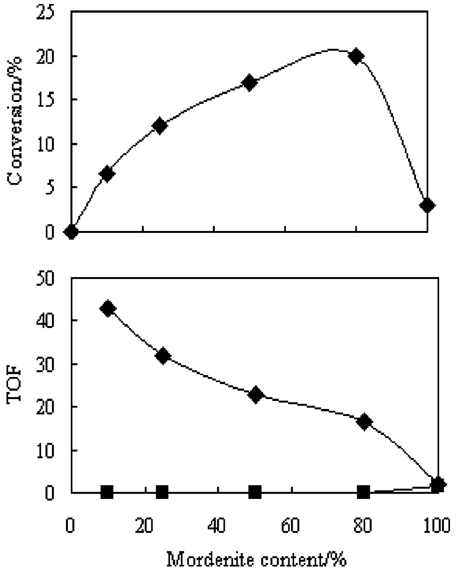


Fig. 7. Results of *n*-hexane reaction (1 MPa, H_2/*n*-hexane = 9, Pd/SiO_2 + mordenite 0.4 g, $W/F = 1$ g h/mol, 553 K).

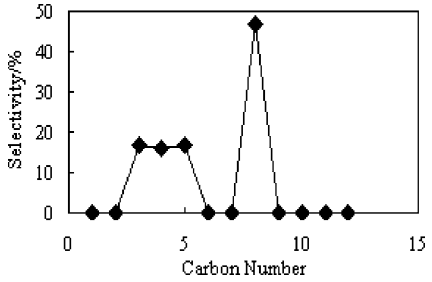


Fig. 8. Results of *n*-octane reaction (1 MPa, H_2/*n*-octane = 9, Pd/SiO_2 + mordenite 0.4 g, $W/F = 2.4$ g h/mol, 503 K).

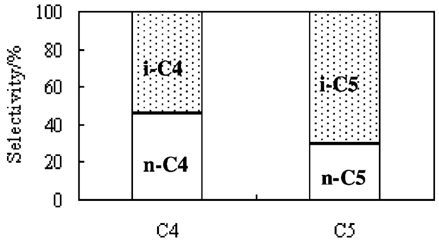


Fig. 9. Results of *n*-octane reaction (1 MPa, H_2/*n*-octane = 9, Pd/SiO_2 + mordenite 0.4 g, $W/F = 2.4$ g h/mol, 503 K).

4. Conclusion

The direct production of *iso*-paraffins from syngas can be accomplished by the conventional FTS reaction and the subsequent hydrocracking/hydroisomerization of the products, either in one stage or two stages. The addition of small amount of physically mixed H-ZSM-5 to a Co/SiO_2 FTS catalyst changes the hydrocarbon distribution drastically by the selective cracking of higher hydrocarbons (wax).

The hydrocracking of *n*-C_6, *n*-C_8 and *n*-C_{10} (simulates for FTS products) as individual compounds in three separate experiments over a physical mixture of Pd/SiO_2 and mordenite in different proportions, showed high and stable activity. The isomerization was favored for Pd rich mixture while the TOF of cracking reaction was independent on the catalyst composition. The hydrocracking was the simple splitting of hydrocarbon skeleton, yielding a product rich in *iso*-paraffins.

Acknowledgements

This research was supported by Research for the Future Program of Japan Society for the Promotion of Science (JSPS) under the project “Synthesis of ecological high quality transportation fuels” (JSPS-RFTF98P01001).

References

[1] D. Fraenkel, B.C. Gates, J. Am. Chem. Soc. 102 (1980) 2480.
[2] D.B. Tkachenko, G. Coudrier, H. Mozzarnda, J. Mol. Catal. 6 (1979) 293.
[3] H.H. Nijs, P.A. Jacobs, J.B. Uytterhoeven, J. Chem. Soc., Chem. Commun. (1979) 180.
[4] K. Fjimoto, M. Adachi, H. Tominaga, Chem. Lett. (1985) 783.
[5] Y.W. Chen, H.T. Tang, J.G. Goodwin Jr., J. Catal. 83 (1983) 415.
[6] H.H. Nijs, P.A. Jacobs, J. Catal. 66 (1980) 401.
[7] P.A. Jacobs, in: B. Imelik, C. Naccache, J.C. Vedrine (Eds.), Catalysis by Zeolites, Elsevier, Amsterdam, 1980, p. 293.
[8] D. Kong, J. Chung, Y. Kim, Ind. Eng. Chem. Res. 34 (1995) 1969.
[9] D. Kong, J. Chung, Y. Kim, J. Chem. Soc. Chem. Commun. (1991) 849.
[10] D. Yin, W. Li, H. Xiang, Y. Sun, B. Zhong, S. Peng, Micropor. Mesopor. Mater. 47 (2001) 15.
[11] L. Guczi, I. Kiricsi, Appl. Catal. A 186 (1999) 375.
[12] G. Calejia, A. De Lucas, R. Van Grieken, Appl. Catal. 68 (1991) 11.
[13] S. Bessell, Appl. Catal. A 96 (1993) 253.
[14] K. Jothimurugesan, S.K. Gangwal, Ind. Eng. Chem. Res. 37 (1998) 1181.
[15] N. Tubaki, K. Michiki, Y. Yoneyama, K. Fujimoto, J. Petro. Inst. Jpn. 44 (5) (2001) 338.
[16] G. Leclercq, L. Leclercq, R. Maurel, J. Catal. 44 (1976) 68.
[17] I. Nakamura, K. Sunada, K. Fujimoto, Stud. Surf. Sci. Catal. 105 (1997) 1005.
[18] A. Zhang, I. Nakamura, K. Aimoto, K. Fujimoto, Ind. Eng. Chem. Res. 34 (4) (1995) 1074.