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Direct synthesis of middle iso-paraffins from synthesis gas on hybrid catalysts

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Abstract

This paper focuses on the synthesis of iso-paraffin-rich hydrocarbons by Fischer–Tropsch synthesis (FTS) over silica gel supported Co catalyst (Co/SiO_2). The basic concept is to isomerize and/or hydrocrack the primary FTS hydrocarbon products. A physical mixture consisting of a small amount of zeolite or Pd/zeolite mixed with Co/SiO_2 enhanced the formation of C_4–C_{10} iso-paraffins while suppressing the formation of higher molecular hydrocarbons, probably because of the selective cracking of these hydrocarbons on them. In separate experiments, a two-reactor system was used. The first reactor contained a physical mixture of Co/SiO_2 and zeolite, and the second reactor contained zeolites or Pd-supported zeolites. The two-reactor system gave sharp C-number distribution within C_3–C_6 and iso-paraffins-rich products. The hydrocracking of *n*-octane and *n*-decane (model compound simulating products of the FTS reaction) over mixed catalysts composed of various compositions of Pd/SiO_2 and ZSM-5 in the presence of gaseous hydrogen showed high and stable activity, and produced primarily iso-paraffin-rich hydrocarbons. The isomerization was favored for mixtures rich in Pd/SiO_2. The role of Pd was thought to be the inlet of hydrogen spillover to the zeolite surface.

Keywords: Fischer–Tropsch synthesis; Hydrocracking; Isomerization; Iso-paraffin; Hybrid catalysts

1. Introduction

Fischer–Tropsch synthesis (FTS) has recently attracted increasing attention, since high quality diesel fuels without any sulfur or aromatic compounds can be produced directly from syngas derived from natural gas, coal or biomass. It is well known that FTS involves a polymerization reaction beginning with a methylene intermediate to produce a wide distribution of hydrocarbons ranging from methane to wax (C_1–$C_{60}+$) [1,2]. The FTS product is mostly *n*-paraffin or *n*-olefin.

Group VIII metals, such as Fe, Co, Ni and Ru, are the most popular FTS catalysts [3,4]. The product distribution over these catalysts is non-selective and generally governed by the Anderson–Schulz–Flory (ASF) polymerization kinetics. The iron-based catalysts are often used in slurry reactors, but they have a high water-gas shift (WGS) activity. In comparison to iron-based catalysts, cobalt-based catalysts show little WGS activity.

The key to improving the economics of FTS is to get high selectivity of desired products such as diesel or high-octane gasoline. The FTS reaction selectively produces linear hydrocarbons, which are suitable for diesel fuel (whose carbon number distributes from C_{10} to C_{20}). However, since FTS reaction does not produce C_{10}–C_{20} hydrocarbons selectively, the recent efforts on FTS system are concentrated to produce C_5+ (liquid) hydrocarbons selectively while keeping CH_4 selectivity low. High molecular hydrocarbons ($C_{20}+$, wax) produced are subjected to the secondary treatment to be cracked to lower molecular hydrocarbons.

Recently, the production of hydrocarbons rich in iso-paraffins has gained attention because of its excellent gasoline fuel properties. Several groups have tried to synthesize iso-paraffins by utilizing FTS catalyst supported acidic zeolites [5–7]. However, acidic zeolites are not a suitable support for FTS catalysts, and typical results show low

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activity and high methane selectivity. Chen et al. reported light hydrocarbon synthesis at 0.1 MPa from syngas using three kinds of NaY zeolite-supported ruthenium catalyst. Due to low reaction pressure, methane was the main product but isobutene predominated in C_4 fraction [8]. Nijs and Jacobs also reported similar phenomenon on Ru/NaY [9,10]. Kong et al. used a NaOH washed Co/Y zeolite catalyst to carry out FTS. The selectivity to isomers was 20–30% [11,12]. Mesoporous molecular sieves have been used as FTS catalyst supports but their stability under high pressure water vapor during FTS reaction was poor [13,14]. Calejia et al. studied the physical and chemical properties, activity, and selectivity of Co/H-ZSM-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 proportion of aromatics in the liquid hydrocarbon fraction [15]. 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 [16]. The nature of higher molecular 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. Jothimurugesan and Gangwal reported a 50:50 by weight ratio Co–Ni catalyst physically mixed with H-ZSM-5 (5% Co–5% Ni/TiO_2 + H-ZSM-5) gave the highest CO conversion (45.2%) at the conditions tested. Mixing the Co–Ni catalyst with H-ZSM-5 resulted in a significant reduction in methane selectivity and a significant increase in C_4+ selectivity compared to the individual Co or Ni catalyst [17]. Fujimoto et al. have shown that a catalyst composed of a physical mixture of supported Co and zeolite gives excellent catalytic activity and high selectivity to middle iso-paraffins with no aromatics formation [18,19].

In this research, the selective synthesis of C_4–C_6 iso-paraffins from synthesis gas was studied [20,21]. The fundamental concept is the synthesis of hydrocarbon mixtures rich in C_4–C_6 iso-paraffins by hydrocracking and isomerization of the primary hydrocarbons produced by FTS. Catalysts used were physical mixtures of a Co/SiO_2 FTS catalyst, zeolite and Pd/zeolite. In this reaction system product hydrocarbons on the FTS catalyst is expected to diffuse to the hydrocracking catalyst either in the gas phase (volatile products) or on the surface (products such as wax, which does not vaporize under reaction conditions) and are hydrocracked or isomerized to iso-paraffins. It was interesting that higher molecular hydrocarbons, such as wax, were exclusively hydrocracked when the hydrocracking catalyst existed near the FTS catalyst. The hydrocracking catalysts used were zeolite or Pd-supported ones which combine the hydrogen introduction function of Pd and the cracking properties of the zeolite [22–25]. Further, it is hypothesized that hydrogen spilt-over from the Pd plays as the proton or hydride ion for the cracked products [26].

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-15 whose surface area and pore volume were 200 m^2/g, and 1.0 ml/g, respectively) and a aqueous solution of $Co(NO_3)_2$. In certain runs, a small amount of β, H-ZSM-5, USY and H-mordenite powder was physically mixed with the Co/SiO_2 catalyst. All zeolites used were commercially available ones (TOSOH Co., the SiO_2/Al_2O_3 molar ratio was: β 37.1, ZSM-5 40.0, USY 390, mordenite 16.9).

Pd/zeolite (0.5 wt.% loading) was prepared by ion exchange method. The ion exchange was carried out at 353 K for 6 h with $Pd(NH_3)_4Cl_2$ aqueous solution under stirring, the supported Pd/β was washed with water until no chloride ion was detected, then was dried overnight at 393 K, and followed by calcining it in air at 723 K for 2 h. In certain runs, 75% of β zeolite was added to the Pd/β 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.

2.2. Reaction apparatus and procedure

Fig. 1 shows the reaction apparatus [20]. The first (upper) reactor contains the FTS catalyst and the second (lower) reactor contains the hydrocracking/hydroisomerization catalyst.

FTS reaction was conducted under pressures of 0.5–2.0 MPa, 513–573 K using a flow type fixed bed reactor (SS-316 tube, 8 mm ID). The catalyst amount was 1.0 g and the H_2/CO ratio of the feed gas was 2. In some experiments, the hydrocracking catalyst (zeolite or Pd/zeolite) was mixed with the Co/SiO_2 FTS catalyst in first stage. In other experiments, the catalysts were separated. Reaction conditions were: H_2/hydrocarbons mole ratio of 9/1; reaction temperature, 543–553 K. During the reaction, the effluent gas was heated at 453 K and then was introduced to

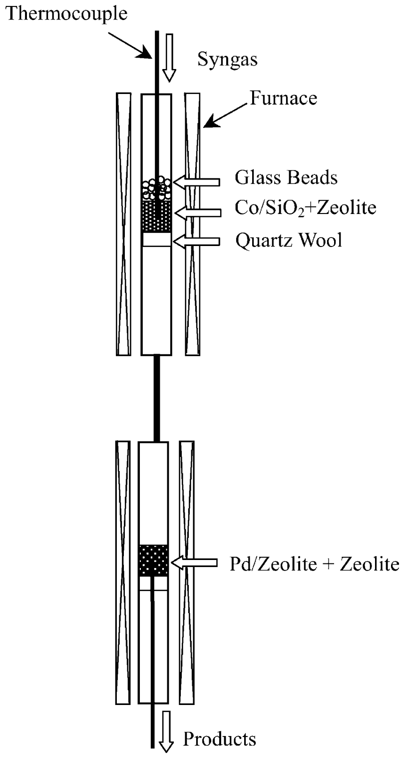


Fig. 1. Illustration of the two-step reaction system (reproduced with permission from Ref. [20]).

gas chromatograph equipped with NB-1 capillary column for C_1–C_{19} (FID) and active carbon column for CO, CH_4, and CO_2 analysis (TCD).

The selectivity of hydrocarbon is defined as follows:

$$\text{selectivity} = \frac{M}{C_{CO}\alpha_{CO}}$$

where C_{CO} is the CO flow rate in reaction gas, α_{CO} the CO conversion and M the carbon-flow rate in iso-paraffin, *n*-paraffin or olefin.

$$\text{Hydrocarbon recovery (\%)} = \left(\frac{\text{carbon flow rate in hydrocarbon}}{\text{carbon flow rate in reacted CO}}\right) \times 100$$

3. Results and discussion

3.1. FTS reaction

3.1.1. Single-step reaction

Fig. 2 shows the CO conversion and product selectivity in FTS reaction on hybrid catalysts with a variety of catalysts composed of the Co/SiO_2 and different zeolites or Pd/zeolites. For FTS reaction on Co/SiO_2 catalyst, only *n*-paraffins and *n*-olefins were formed, and little iso-paraffin was detected. However, on the hybrid catalysts, $Co/SiO_2 + \beta$, Co/SiO_2 + H-ZSM-5 and Co/SiO_2 + mordenite, iso-paraffins were formed, the selectivity was 17.0, 9.7 and 1.82%, respectively. On Co/SiO_2 + USY and Co/SiO_2 + mordenite, only a little amount of iso-paraffin and no detectable aromatic hydrocarbons were formed. When β and ZSM-5 were added to Co/SiO_2 catalyst, the recovery (the sum of C_1–C_{19} selectivity and CO_2 selectivity) increased, indicating that the heavy product from the conventional FTS reaction was subjected to the secondary hydrocracking effectively to form lighter hydrocarbons. This is in good agreement with the reported finding that hydrocarbons with longer chain were easier to be hydrocracked [27].

Other important characters of the hybrid catalyst are that when Pd/β or Pd/ZSM-5 was used as one of the component

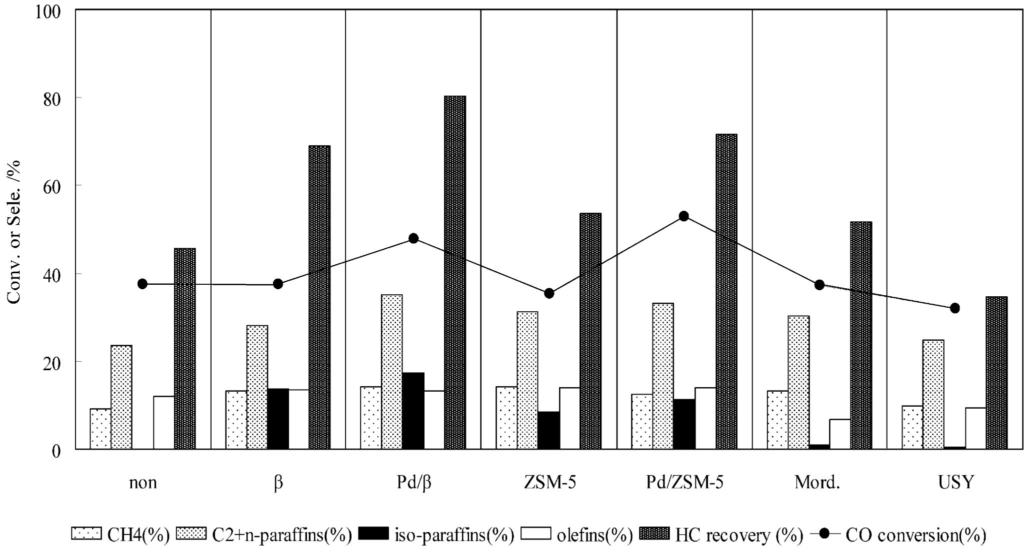


Fig. 2. CO conversion and product selectivity in a single-step FTS reaction on hybrid catalysts containing Co/SiO_2 and a variety of zeolite: H_2/CO ratio = 2; W/F = 5.1 g h/mol; 1.0 MPa; 513 K; reaction time, 4 h; (Co/SiO_2)/zeolite ratio, 4:1 by weight.

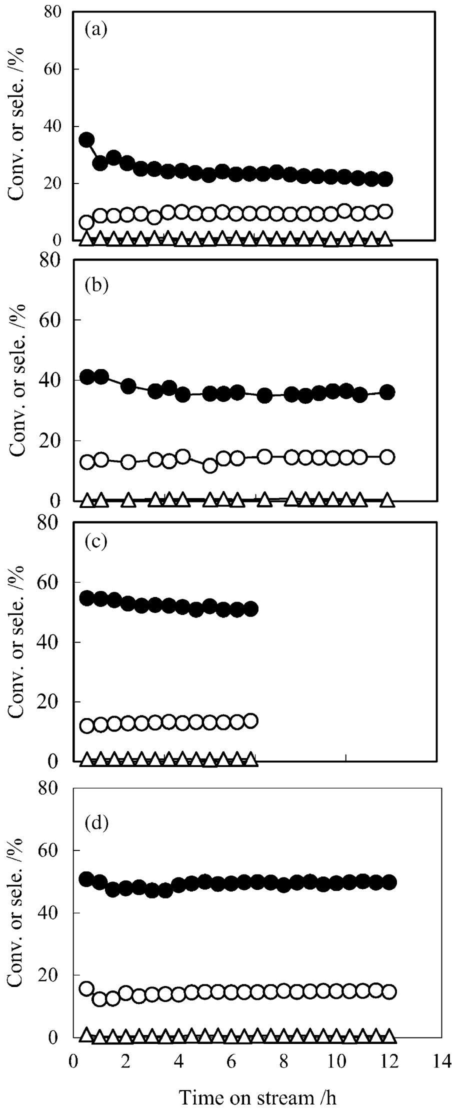


Fig. 3. Time course of a single-step FTS on (a) Co/SiO_2, (b) $Co/SiO_2 + ZSM\text{-}5$, (c) $Co/SiO_2 + Pd/ZSM\text{-}5$, and (d) $Co/SiO_2 + Pd/\beta$: H_2/CO ratio = 2; $W/F = 5.1\,g\,h/mol$; 1.0 MPa; 513 K; (Co/SiO_2)/zeolite ratio, 4:1 by weight. (●) CO conversion, (○) CH_4 selectivity, (△) CO_2 selectivity.

both the CO conversion and the selectivity of iso-paraffins was high. Fig. 3 shows the time-on-stream dependencies of FTS reactions on various catalysts, showing that for the Co/SiO_2 catalyst alone, the FTS activity deactivated rather quickly. On the other hand, for the hybrid catalyst containing ZSM-5 or Pd/ZSM-5 or Pd/β, little deactivation was observed during the reaction. It is claimed that hydrogen spillover from Pd to zeolite and Co/SiO_2 would promote the hydrocracking reaction and FTS reaction as well.

Fig. 4 shows the concept of reaction mechanism of FTS on Co/SiO_2 and Co/SiO_2+zeolite. When only Co/SiO_2 catalyst was used, heavy hydrocarbons (such as wax) were formed on the catalyst, and did not evaporate under reaction conditions, to accumulate and to retard the syngas access. Interestingly, when the hydrocracking catalyst (zeolite or Pd/zeolite) existed near the Co/SiO_2 catalyst, higher hydrocarbons (such as wax) diffused to the hydrocracking catalyst on which they were exclusively cracked to light hydrocarbons to vaporize from the catalyst into gas phase, which reduce the accumulated wax to prevent the catalyst deactivation.

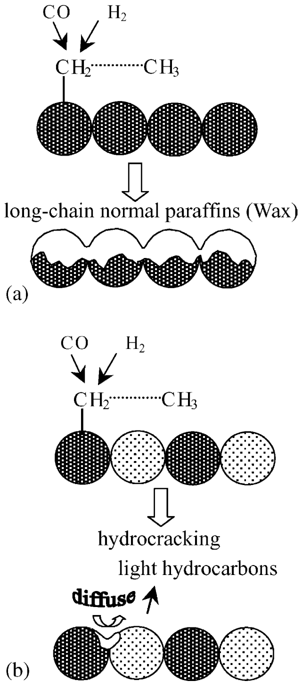


Fig. 4. The concept of reaction mechanisms on hybrid catalysts: (a) Co/SiO_2; (b) $Co/SiO_2 + $ zeolite.

Figs. 5 and 6 show the effect of Pd/β content on the activity and the selectivity to CH_4 and CO_2 on the one stage reactor system as well as the product distribution [21]. The composition of three catalysts were Co/SiO_2 (0.8 g) + SiO_2 (0.8 g), Co/SiO_2 (0.8 g) + Pd/β (0.4 g) + SiO_2 (0.4 g), and Co/SiO_2 (0.8 g) + Pd/β (0.8 g), respectively. When the content of Pd/β increased, CO conversion and selectivity to

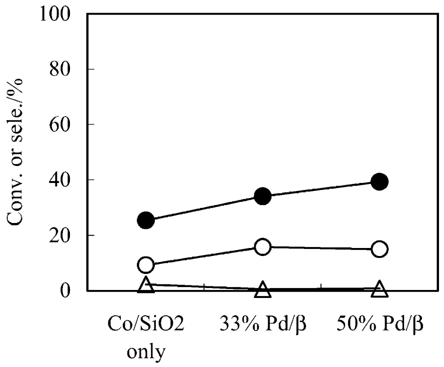


Fig. 5. Effect of Pd/β content on CO conversion, CH_4 and CO_2 selectivity: H_2/CO ratio = 2; $W/F = 5.1\,g\,h/mol$; 1.0 MPa; 513 K; reaction time, 4 h; catalyst compositions were Co/SiO_2 (0.8 g) + SiO_2 (0.8 g) for Co/SiO_2 only, Co/SiO_2 (0.8 g) + Pd/β (0.4 g) + SiO_2 (0.4 g) for 33% Pd/β, and Co/SiO_2 (0.8 g) + Pd/β (0.8 g) for 50% Pd/β. (●) CO conversion, (○) CH_4 selectivity, (△) CO_2 selectivity.

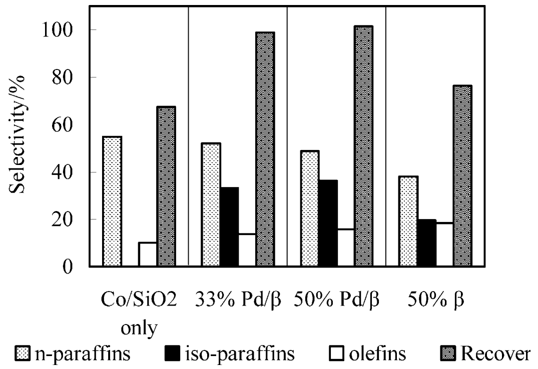


Fig. 6. Effect of Pd/β content on selectivity to *n*-paraffins, iso-paraffins and olefins and hydrocarbon recovery with a single-step reaction system: H_2/CO ratio = 2; $W/F = 5.1$ g h/mol; 1.0 MPa; 513 K; reaction time, 4 h; the same catalyst compositions as in Fig. 5.

CH_4 increased, while the selectivity to CO_2 decreased. This indicates that hydrocracking/hydroisomerization catalyst, Pd/β, promotes the FTS reaction on the Co/SiO_2 catalyst and the formation of CH_4, while suppressing the formation of CO_2. Also, when hydrocracking/hydroisomerization catalyst (Pd/β) is added, the recovery increase to about 100%, the iso-paraffins selectivity increases obviously. If a hydrocracking/hydroisomerization catalyst, such as Pd/β, exists in FTS system the initial product of FTS reaction such as wax transfers to the surface of Pd/β catalyst to form lighter hydrocarbons containing iso-paraffins by the hydrocracking and hydroisomerization. The selectivity of iso-paraffins on the $Co/SiO_2 + Pd/\beta$ is much higher than that on $Co/SiO_2 + \beta$ catalyst, indicating that the activity of hydrocracking/hydroisomerization of zeolite is markedly promoted by added Pd. The increase in the catalytic activity and the methane selectivity should be attributed the hydrogen spillover from Pd/β to Co/SiO_2 to increase in the hydrogen concentration on the Co/SiO_2 catalyst. The preliminary experiment has shown that Pd/β shows no activity of making CH_4 from either $CO + H_2$ or hydrocarbons (olefins or paraffins).

Fig. 7 shows the effect of contact condition on FTS reaction results for $Co/SiO_2 + Pd/\beta$ catalyst [21]. The condition of granular mixture catalyst is much poorer than that of powder hybrid catalyst. Although CO conversion on powder hybrid catalyst is slightly higher than that on granular mixture catalyst, which indicates that the contact condition on CO conversion is not effective, the selectivity of iso-paraffins on granular mixture catalyst is much higher than that on powder hybrid catalyst (from 39 to 65%), while the selectivity to CH_4 is much lower for the granular mixed catalyst (from 15 to 8%). This phenomena indicates that granular mixture catalyst is much more selective for isomerization than the powder hybrid catalyst. The formation of iso-paraffins is much easier on granular mixture catalyst which might be attributed to the suppressed hydrogen (H-atom) transfer from Pd/β to Co/SiO_2. This phenomenon causes the suppressed CO conversion and CH_4 selectivity.

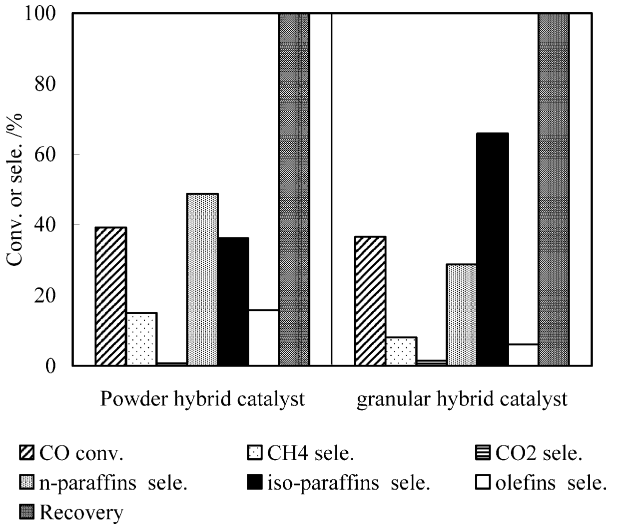


Fig. 7. Effect of contact conditions of hybrid catalysts on FTS reaction results: H_2/CO ratio = 2; $W/F = 5.1$ g h/mol; 1.0 MPa; 513 K; reaction time, 4 h. (◍) Powder mixture (pressure molded, 20–40 mesh); (●) Co/SiO_2 (pressure molded, 20–40 mesh), (○) Pd/β (pressure molded, 20–40 mesh).

3.1.2. Two-step reaction

Table 1 shows the effect of the kind of catalyst used in the second reactor on CO conversion and product dis-

Table 1
Effect of the kind of a second reactor catalyst on CO conversion and hydrocarbon selectivity for the two-step reaction system[a]

Catalyst	CO conversion (%)	CO_2 selectivity (%)	Hydrocarbon selectivity (%)				Iso-paraffin selectivity (%) in C_4+ hydrocarbons
			C_1	C_2–C_3	C_4–C_9	C_{10}+	
No catalyst	37.5	0.45	13.5	5.17	45.7	35.18	14.4
Pd/Pd	43.7	0.84	13.4	14.4	72.1	0.27	74.2
Pd/mordenite	42.8	1.10	11.2	19.0	73.4	0.44	67.0
Pd/ZSM-5	44.1	0.80	12.0	26.7	56.8	0.35	56.7
Pd/USY	41.6	1.10	13.5	6.29	56.1	17.8	39.1
Pd/NaY	43.0	0.74	12.9	6.71	57.5	20.0	37.0

[a] In the first reactor, 1.0 g of $Co/SiO_2 + \beta$ (4:1 by weight) is used at 513 K. In the second reactor, 1.0 g of Pd/zeolite is used at 573 K. Time on stream, 4 h; syngas flow rate, 73 ml/min (NTP).

tribution. As seen in Table 1, CO conversion and CH_4 selectivity were similar when the different catalyst was used. However, the distribution of hydrocarbon products depended on the catalyst type in the second reactor. The order of iso-paraffin selectivity in C_4–C_9 was Pd/β > Pd/mordenite > Pd/ZSM-5 > Pd/USY > Pd/NaY. On the Pd/β and Pd/mordenite catalysts, the olefin completely disappeared and the product pattern was drastically changed to lower molecular hydrocarbon, while the selectivity of methane was unchanged. It means that the products in the first reactor were further hydrocracked, giving iso-paraffins as the main product in the second reactor.

Fig. 8 shows the effect of temperature of the second reactor on product distribution. It was clear that, with increasing reaction temperature, the carbon number distribution of the product shifted to lower side and the iso-paraffin selectivity became lower, while CO conversion and CH_4 selectivity were kept almost constant, which indicates that syngas conversion and CH_4 selectivity are determined in the first reactor, and product distribution can be controlled mostly by the temperature of the second reactor. The products from the first reactor contained water vapor, which may be the poison of the zeolite catalyst. However, Fig. 8 shows clearly that the hydrocracking reaction proceeds quite smoothly at 498 K even in the presence of water vapor to produce light hydrocarbons rich in iso-paraffin.

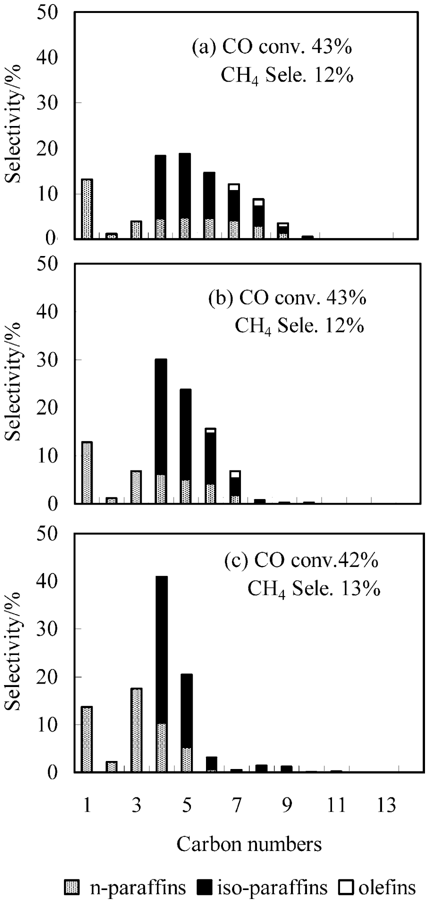


Fig. 8. Effect of temperature of the second reactor on hydrocarbon distribution—in the first reactor: H_2/CO ratio = 2; $W/F = 5.1$ g h/mol; 1.0 MPa; 513 K; $(Co/SiO_2)/\beta$ ratio, 4:1 by weight; in the second reactor: (Pd/β)/β, 1:4 by weight; 1.0 MPa; temperature (a) 498 K, (b) 513 K and (c) 623 K.

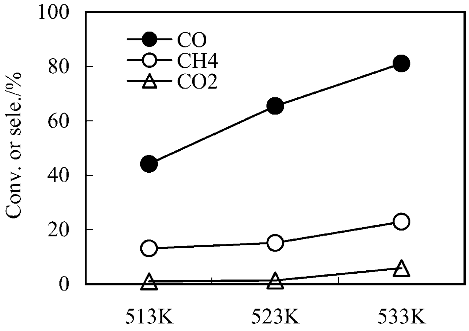


Fig. 9. Effect of temperature of the first reactor on CO conversion, CH_4 and CO_2 selectivity—in the first reactor: H_2/CO ratio = 2; $W/F = 5.1$ g h/mol; 1.0 MPa; $(Co/SiO_2)/\beta$ ratio, 4:1 by weight; in the second reactor: (Pd/β)/β, 1:4 by weight; 1.0 MPa; 573 K.

Fig. 9 shows the effect of temperature of the first reactor on CO conversion, CH_4 and CO_2 selectivity. The conversion and the selectivity increased with increasing reaction temperature. Fig. 9 also indicates that the syngas reaction depends on the first reactor. On the other hand, the carbon number distribution (except CH_4) and selectivity of iso-paraffin were almost unchanged by the temperature of the first reactor. The results in the two-step reaction system show that the best conditions for FTS reaction and for hydrocracking/hydroisomerization can be selected independently to maximize the syngas conversion and the favorable product distribution.

3.1.3. Discussions on the single-step and two-step reaction system

Since the iso-paraffin synthesis from syngas aims at producing gasoline, the requirement of the product pattern is severe. For example, the carbon number should distribute from C_4 to C_{10}, and the production of C_1–C_3 hydrocarbons (especially CH_4) should be minimized. However, the AFS distribution observed with FTS products predicts that high selectivity of C_4–C_{10} hydrocarbon is inevitably accompanied by high selectivity of C_1–C_3 hydrocarbons. The in situ hydrocracking of FTS products or their secondary hydrocracking is one of the reasonable methods to realize the product distribution suitable for gasoline fraction and the favorable molecular structure (high-octane number).

3.2. Hydrocracking of model hydrocarbons

The basic concept of the present study is to clarify secondary reactions of FTS products. The hydrocracking of two types of *n*-paraffin, such as *n*-C_8H_{18} and *n*-$C_{10}H_{22}$, were thus selected as the product models.

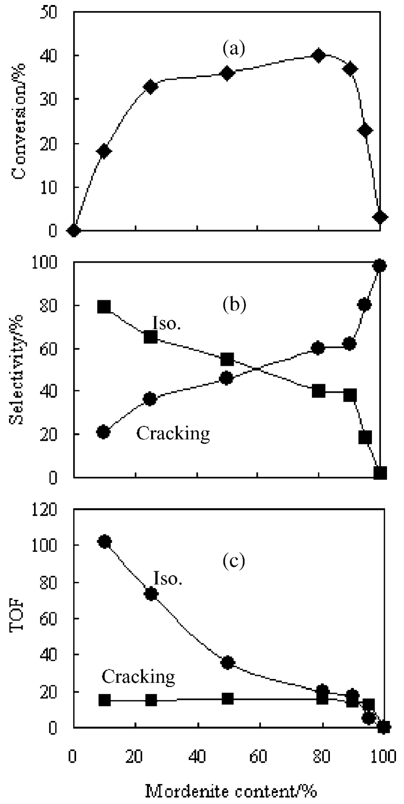


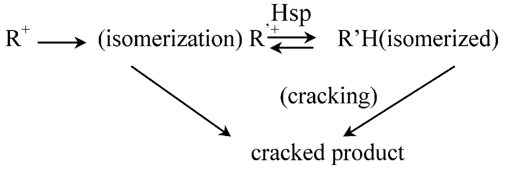
Fig. 10. Hydrocracking results of *n*-decane (reproduced with permission from Ref. [20]): $W/F = 1.0\,g\,h/mol$; 1.0 MPa; 553 K; H_2/*n*-decane = 9; Pd/SiO_2 + mordenite, 0.4 g.

3.2.1. Hydrocracking of n-decane ($C_{10}H_{22}$)

Fig. 10a–c shows the results [20]. The Pd/SiO_2 alone showed no activity, and the mordenite alone showed little activity. However, a mixture of the two catalysts showed much higher activity at Pd/SiO_2 content of 10–80%.

The selectivity of the cracking reaction increased with an increase in the mordenite content in 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 Pd/SiO_2 content. The role of Pd/SiO_2 has been shown to be the activation of gaseous hydrogen and its transfer to acid sites of the zeolite (hydrogen spillover) [28,29]. The spillover of hydrogen activates paraffinic hydrocarbons as shown below:

$$RH + Hsp \rightarrow R^+ + H_2 \qquad (1)$$



(2)

where Hsp is the spilt-over hydrogen.

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

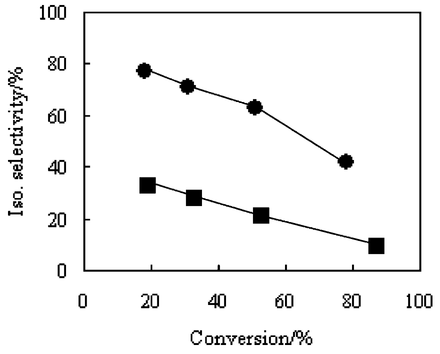


Fig. 11. Hydrocracking results of *n*-decane (reproduced with permission from Ref. [20]): $W/F = 0.5–4\,g\,h/mol$; 1.0 MPa; 553 K; H_2/*n*-decane = 9; Pd/SiO_2 + mordenite, 0.4 g. (●) Pd:mordenite = 3:1, (■) Pd:mordenite = 1:4.

Fig. 11 shows the isomerization selectivity as a function of *n*-decane conversion on two types of Pd/SiO_2+mordenite mixed catalysts with different compositions [20]. 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. Hydrocracking of n-octane (C_8H_{18})

Figs. 12 and 13 show product distribution of *n*-octane conversion on the Pd/SiO_2–mordenite hybrid catalyst [20]. It is

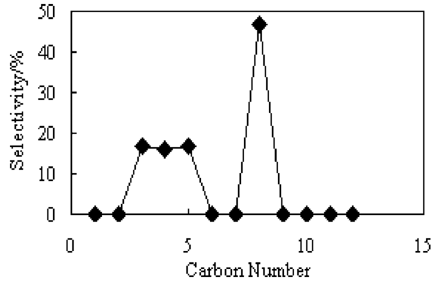


Fig. 12. Hydrocracking results of *n*-octane (reproduced with permission from Ref. [20]): $W/F = 2.4\,g\,h/mol$; 1.0 MPa; 503 K; H_2/*n*-octane = 9; Pd/SiO_2 + mordenite, 0.4 g.

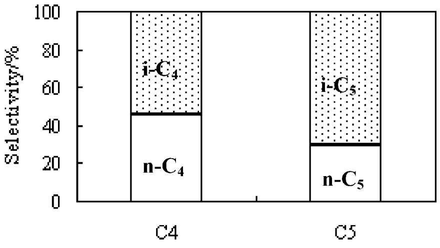


Fig. 13. Product selectivity in *n*-octane reaction (reproduced with permission from Ref. [20]): the same conditions as in Fig. 12.

clear in Fig. 13 that the product is the mixture of isomerized octane and almost equimolar amounts 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. Fig. 13 also shows that the cracked product is rich in iso-paraffins, which might be formed by isomerization followed by cracking.

4. Conclusion

1. The addition of a small amount of zeolite to the Co/SiO_2 FTS catalyst changed drastically the distribution of hydrocarbon products by the selective cracking of higher molecular hydrocarbons (wax).
2. The direct synthesis of iso-paraffins from syngas can be achieved by combining the conventional FTS reaction with in situ hydrocracking/hydroisomerization in one step (CH_4 selectivity $<10\%$, iso-paraffin selectivity $>60\%$).
3. The two-step reaction system gave sharp C-number distribution and iso-paraffins-rich products (CH_4 selectivity $<10\%$, iso-paraffin in C_4+ $>75\%$).
4. The hydrocracking of n-C_8 and n-C_{10} (simulants of FTS products) over physical mixtures of Pd/SiO_2 and mordenite with different proportions showed that these catalysts had high and stable activity. Isomerization was favored for the Pd/SiO_2-rich mixture, while the TOF of the cracking reaction was independent of the catalyst composition. In the hydrocracking, the simple splitting of hydrocarbon skeleton took place, yielding a product rich in lower molecular iso-paraffins.

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