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# Supercritical phase process for direct synthesis of middle iso-paraffins from modified Fischer–Tropsch reaction

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## Abstract

A new concept on the direct synthesis of middle iso-paraffins through the modified supercritical Fischer–Tropsch (FT) reaction was proposed and experimentally demonstrated with the combination of $Co/SiO_2$ and palladium-supported β zeolite (Pd/β) catalysts both in one-stage and two-stage fixed-bed reaction systems. Depending on the reaction conditions, the selectivity of $C_4^+$ iso-paraffins mostly in gasoline range was 60–80% due to hydrocracking and hydro-isomerization function of Pd/β. Irrespective of reaction conditions, the hydrocarbons produced from FT reaction were preferentially hydro-converted over Pd/β catalyst while the supercritical solvent of *n*-hexane could only be slightly hydro-converted under severe conditions. The production of iso-paraffin in two-stage process was tested for 100 h without observable deactivation by feeding additional hydrogen in lower reactor, which is ascribed to the inhibition of coke deposition over Pd/β as revealed from TG analysis of the used catalysts.

*Keywords:* Iso-paraffin; Supercritical phase; Fischer–Tropsch synthesis; Hydro-isomerization; Hydrocracking

## 1. Introduction

Due to increasing demand of the limited petroleum reserve and environmental impact, in recent years, there is a significant interest in developing new technologies and processes to produce ultra-clean gasoline from syngas, which is derived from relatively abundant resources such as coal, natural gas and biomass [1]. Being an efficient method to produce fuel and chemicals from syngas, Fischer–Tropsch (FT) synthesis has received significant attentions in recent years. However, because of the limitation of the Anderson–Schulz–Flory (ASF) polymerization kinetics, the FT hydrocarbons, which are composed mainly of normal paraffins and olefins, are nonselective to any specific product and low selectivity to high-octane iso-paraffins [2,3]. Therefore, much effort has been made in the selective synthesis of iso-paraffins by the combination of FT catalysts and (noble metals)/zeolites [4–12]. The two catalytic functions were combined in a variety of ways in gas–solid phase reaction, ranging from a single reactor containing both catalytic functions (taking advantage of a possible synergistic effect between the catalysts) to a dual reactor arrangement in series with the two catalytic functions (so that the operating parameters of the reactors can be optimized individually).

It has been known that supercritical fluid (SCF) has unique characteristics in molecular diffusion and solubility parameter. Fujimoto and co-workers demonstrated both experimentally and theoretically that SCF FT synthesis, comparing with gas-phase and liquid-phase FT reaction, shows several advantages such as quick diffusion of reactants and products, effective removal of reaction heat and in situ extraction of product wax for sustained stability of FT catalyst [13–17]. Utilization of a supercritical media in the FT reaction presents a new challenge to the now 80-year-old FT technology. Recently, industry has also begun to focus on the supercritical FT technology. As an example, Shell (SMDS) revealed its FT

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technology in a new plant (Bintulu, Malaysia) which employs $C_5$ or $C_6$ hydrocarbon injection for cooling, thus improving productivity by reducing heat transfer limitations [18].

In order to promote the direct synthesis of iso-paraffins from syngas, in the present work, a new concept was developed in different configurations by combining the characteristics of SCF and multifunctional hybrid catalyst composed of $Co/SiO_2$ and Pd/β. Namely, in the supercritical media of *n*-hexane, physical mixture of $Co/SiO_2$ and Pd/β was applied in one-reactor process while $Co/SiO_2$ was loaded in the upper reactor for FT reaction and Pd/β was used in the lower reactor for hydro-conversion reactions in two-stage process. The basic idea is to suppress the undesirable methane formation, to enhance the selectivity of $C_4$–$C_{10}$ iso-paraffins and to extend the lifetime of catalysts by utilizing the unique characteristics of supercritical media. It can be expected that in the supercritical FT system, waxy product on the FT catalyst can be extracted easily and transferred to the hydro-conversion catalyst. For these purposes, one-stage and two-stage processes were examined. The effect of temperature and Pd/β to $Co/SiO_2$ ratio on the selectivity of products, the isomerization of *n*-hexane SCF and the stability of catalysts were also reported.

## 2. Experimental

### 2.1. Catalyst preparation

The $Co/SiO_2$ with metallic Co loading of 20 wt% was prepared by the incipient impregnation of $Co(NO_3)_2 \cdot 6H_2O$ solution on commercial $SiO_2$ (Fujisilicia Q-15, specific surface area 200 $m^2/g$, pore volume 1.0 ml/g). The catalyst precursors were dried in air at 120 °C for 12 h and then calcined at 200 °C for 2 h to form the supported metal oxides.

The 10 wt% $Co/SiO_2$ catalyst was prepared by impregnating cobalt acetate in 4 M $NH_4NO_3$ on silica ID. The catalyst precursors were dried in air at 120 °C for 12 h and calcined at 400 °C for 1 h, then reduced at 400 °C for 12 h, and finally passivated with diluted $O_2$.

The 0.5 wt% Pd/β catalyst was prepared by ion exchange of β zeolite (Tosoh, $SiO_2/Al_2O_3$ molar ratio = 25.6) with an aqueous solution of $[Pd(NH_3)_4]Cl_2$. The ion exchange was carried out at 80 °C for 6 h under stirring. The resulting Pd/β was washed until chloride ion was negative in $AgNO_3$ test. After drying overnight at 120 °C, the catalyst was calcined in air at 450 °C for 2 h.

### 2.2. Experiments and products analysis

Experiments were carried out in a reaction system with consecutively dual fixed-bed reactors. In the case of one-stage process, the hybrid of $Co/SiO_2$ and Pd/β with particle size of 20–40 mesh was loaded in the upper reactor. The desired amounts of $Co/SiO_2$ and Pd/β (20–40 mesh) were loaded in the upper and lower reactors, respectively, for the two-stage reaction. The SCF solvent of *n*-hexane (Kanto Kagaku) was used as received without further purification. Prior to reaction, the catalysts were reduced in situ with pure $H_2$ (100 ml/min) at atmospheric pressure by increasing the temperature at a heating rate of 4 °C/min from ambient to 120 °C, maintaining at this temperature for 30 min, then from 120 °C to 400 °C at a rate of 10 °C/min, and maintaining at 400 °C for 3 h. After reduction, hydrogen and *n*-hexane with desired flow rates were delivered to the reaction system and temperature and pressure of the reaction system were raised simultaneously. Once temperature and pressure reached the desired values, reaction was started with the replacement of hydrogen by syngas. Standard operating conditions were: flow rate of *n*-hexane = 1.42 ml/min, $P_{\text{total}} = 4.5$ MPa, $P_{\text{syngas}}/P_{n\text{-hexane}} = 1.0/3.5$ (or 0.5/3.5), $CO/H_2 = 1/2$, $T_{\text{vaporizer}} = 240$ °C and time-on-stream (TOS) of 6 h. In some cases, 100 ml/min $H_2$ flow was introduced to the lower reactor. To test the stability of the catalysts, experiments with extended TOS of 100 h were carried out.

The effluent gaseous products were analyzed online with two gas chromatographs. One was equipped with a TCD detector for analysis of CO, $CH_4$ and $CO_2$ by using Ar as internal standard. The other was equipped with an FID detector and an $Al_2O_3$–KCl capillary column for analysis of $C_1$–$C_5$ hydrocarbons. The condensed products collected in the ice-cooled trap were analyzed offline for $C_3$–$C_{25}$ hydrocarbons by GC-17A (Shimadzu) equipped with an FID detector and a capillary column (DB-2881). The *n*-hexadecane was added as internal standard.

## 3. Results and discussion

### 3.1. Characteristics of iso-paraffin synthesis in supercritical phase

The reaction conditions and main results of iso-paraffin synthesis by the combination of 20% $Co/SiO_2$ and Pd/β are given in Table 1. For comparison purpose, results of FT reaction without the addition of Pd/β are also provided. As expected, methane selectivity was low for SCF FT reaction, which can be explained as that cracking of longer chain hydrocarbons into smaller ones was significantly inhibited with quick removal of reaction heat by supercritical solvent [9,17,19]. In comparison with the result of SCF FT reaction (No. 1), it is clear that the selectivity of iso-paraffin was significantly increased independent of the addition method of Pd/β into $Co/SiO_2$. From the CO conversion shown in Table 1, it can be reasoned that a certain amount of hydrogen was still available for the reactions over Pd/β catalyst. Therefore, it is reasonable to propose that hydro-conversion reactions significantly occurred over Pd/β catalyst, leading to the sharp increase of iso-paraffin selectivity. This will be

Table 1
Catalytic results over 20 wt% $Co/SiO_2$ and 0.5 wt% Pd/β catalysts[a]

| No. | Catalyst | | $T$ (°C) | | CO conversion (%) | Selectivity (%)[b] | | | | | $n$-$C_6$ SCF converted to $i$-$C_6$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Co/SiO_2$ (g) | Pd/β (g) | $T_1$ | $T_2$ | | $C_1$ | $C_2$ | $C_3$ | α-Olefin | $C_4^+$ iso-para | |
| 1 | 1.0 | 0.0 | 240 | – | 63.9 | 8.5 | 1.1 | 2.9 | 17.6 | 2.6 | 0.00 |
| 2 | 0.5 | 0.5 | 240 | – | 51.5 | 9.4 | 0.9 | 3.2 | 1.8 | 71.4 | 0.05 |
| 3 | 0.5 | 0.8 | 240 | – | 42.9 | 8.9 | 0.7 | 3.5 | 0.5 | 81.4 | 0.26 |
| 4 | 1.0 | 1.0 | 240 | 235 | 60.4 | 9.3 | 1.1 | 4.1 | 0.5 | 58.7 | 0.03 |
| 5 | 1.0 | 1.0 | 240 | 245 | 67.9 | 7.0 | 0.6 | 3.9 | 0.4 | 66.5 | 0.23 |

[a] $T_1$ and $T_2$ designate for temperature in the upper and lower reactors. Reaction conditions: SCF = $n$-hexane, $P_{total}$ = 4.5 MPa, $P_{syngas}/P_{n\text{-hexane}}$ = 1.0/3.5, syngas = 81 ml/min, $H_2/CO$ = 2.

[b] Selectivity was based on carbon number for $C_1$–$C_{25}$ hydrocarbons, $C_6$ was calculated from the average of $C_5$ and $C_7$.

further discussed in the following section combining the results of product distribution. Moreover, as shown in Table 1, selectivities of $C_1$–$C_3$ hydrocarbons under different conditions with or without the addition of Pd/β catalyst were basically the same in considering the experimental errors, indicating that $C_1$–$C_3$ hydrocarbons were predominantly produced from FT reaction and the contribution of hydro-conversion reactions over Pd/β catalyst was negligible.

In order to investigate the effect of FT catalyst on iso-paraffin synthesis, 10 wt% $Co/SiO_2$ prepared by using different impregnation solution and silica support was applied for the titled reaction. Table 2 shows the reaction conditions and the main results. In comparison with the results over 20 wt% $Co/SiO_2$ (No. 1, Table 1), SCF FT reaction over 10 wt% $Co/SiO_2$ showed much higher activity for CO hydrogenation in considering the lower reaction temperature and significantly higher selectivity of α-olefins. This may be caused by differences of cobalt dispersion and pore structure of the catalysts because impregnation solution and silica support for the preparation of 10 wt% $Co/SiO_2$ catalyst were different from those of 20 wt% $Co/SiO_2$. To confirm this explanation, characterization of the catalysts is going on. With the addition of Pd/β catalyst, by comparing the data in Tables 1 and 2, the same characteristics for iso-paraffin synthesis could be found irrespective of the different FT catalyst applied.

From the above preliminary results and discussion, in considering of the undesired light products of $C_1$–$C_3$ hydrocarbons and the selectivity of iso-paraffins, one can see that the newly proposed concept for the production of iso-paraffins in supercritical media is practically viable.

### 3.2. Iso-paraffin production in one-stage process over 20 wt% $Co/SiO_2$ and Pd/β

The product distributions of the titled reaction over $Co/SiO_2$ and physical mixture of $Co/SiO_2$ and Pd/β catalysts are shown in Figs. 1 and 2, respectively. By comparing Figs. 1 and 2, it is clear that long-chain FT hydrocarbons were exclusively hydrocracked when hybrid catalyst composed of $Co/SiO_2$ and Pd/β was used, leading to high selectivities of $C_4$–$C_{13}$, especially $C_4$–$C_{10}$ hydrocarbons. Moreover, irrespective of carbon numbers, iso-paraffin selectivity was very high and olefin selectivity was extremely low. Because a considerable amount of olefin was formed during supercritical FT reactions as shown in Fig. 1, the olefins were significantly hydro-converted to paraffins over bifunctional Pd/β catalyst during iso-paraffin synthesis over the hybrid catalyst. Comparing Fig. 2(A and B) obtained over hybrid catalyst with the same amount of $Co/SiO_2$ catalyst, one can see that products were shifted to relatively lighter hydrocarbons, iso-paraffins selectivity was increased and the selectivity of normal paraffins was decreased when the amount of Pd/β increased from 0.5 g to 0.8 g. This can also be clearly observed from Nos. 2 and 3 of Table 1, i.e., the selectivity of $C_4^+$ iso-paraffins increased from 71.4% to 81.4% by increasing the amount of Pd/β from 0.5 g to 0.8 g. This can be reasonably explained as the enhancement of hydrocracking and hydro-isomerization reactions over Pd/β with the increase of the amount of Pd/β catalyst.

Table 2
Catalytic results over 10 wt% $Co/SiO_2$ and 0.5 wt% Pd/β catalysts[a]

| No. | Catalyst | | $T$ (°C) | | CO conversion (%) | Selectivity (%)[b] | | | | | $n$-$C_6$ SCF converted to $i$-$C_6$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Co/SiO_2$ (g) | Pd/β (g) | $T_1$ | $T_2$ | | $C_1$ | $C_2$ | $C_3$ | α-Olefin | $C_4^+$ iso-para | |
| 1 | 1.0 | 0 | 230 | – | 64.2 | 7.4 | 1.1 | 3.8 | 34.9 | 3.5 | 0.00 |
| 2 | 1.0 | 3.0 | 230 | 230 | 63.0 | 9.8 | 1.2 | 5.3 | 0.2 | 59.6 | 0.19 |
| 3 | 1.0 | 3.0 | 230 | 245 | 63.3 | 9.7 | 1.3 | 5.7 | 0.1 | 64.8 | 0.64 |
| 4 | 1.0 | 3.0 | 230 | 260 | 68.3 | 8.6 | 0.9 | 6.1 | 0.2 | 71.3 | 3.06 |

[a] $T_1$ and $T_2$ designate for temperature in the upper and lower reactors. Reaction conditions: SCF = $n$-hexane, $P_{total}$ = 4.5 MPa, $P_{syngas}/P_{n\text{-hexane}}$ = 0.5/3.5, syngas = 41 ml/min, $H_2/CO$ = 2, 100 ml/min $H_2$ fed to the lower reactor.

[b] Selectivity was based on carbon number for $C_1$–$C_{25}$ hydrocarbons, $C_6$ was calculated from the average of $C_5$ and $C_7$.

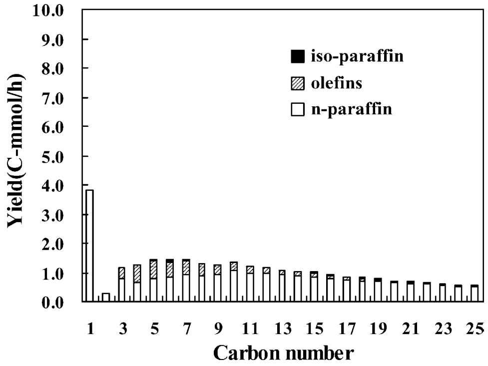

Fig. 1. Product distribution of SCF FT reaction over 20 wt% $Co/SiO_2$ (reaction conditions: 1.0 g 20 wt% $Co/SiO_2$, $T = 240$ °C, $P_{total} = 4.5$ MPa, $P_{syngas}/P_{n\text{-hexane}} = 1.0/3.5$, syngas = 81 ml/min, $H_2/CO = 2$, TOS = 6 h).

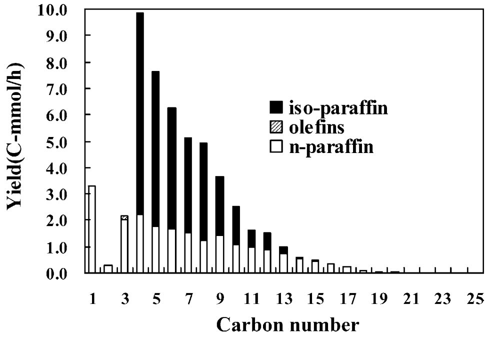

Fig. 3. Product distribution over 20 wt% $Co/SiO_2$ and Pd/β in two-stage reaction system (reaction conditions: upper reactor—1.0 g $Co/SiO_2$, $T = 240$ °C; lower reactor—1.0 g Pd/β, $T = 245$ °C; $P_{total} = 4.5$ MPa, $P_{syngas}/P_{n\text{-hexane}} = 1.0/3.5$, syngas = 81 ml/min, $H_2/CO = 2$, TOS = 6 h).

### 3.3. Two-stage process for iso-paraffin synthesis

Fig. 3 shows the product distribution of two-stage iso-paraffin synthesis over 20 wt% $Co/SiO_2$ and Pd/β catalysts. Although the comparison of iso-paraffin synthesis in one-stage and two-stage processes cannot be conclusively made due to the difference of the reaction conditions, it is clear that quite similar product distributions were observed by comparing the data in Figs. 2 and 3.

In order to study the effect of lower-reactor temperature on the synthesis of iso-paraffins, 10 wt% $Co/SiO_2$ was applied for FT reaction together with Pd/β catalyst for hydro-conversion reactions. The result of product distribution at different temperatures is given in Fig. 4. For comparison, the product distribution of SCF FT reaction over 10 wt% $Co/SiO_2$ is also given, as shown in Fig. 5. As expected, with the increase of reaction temperature in the

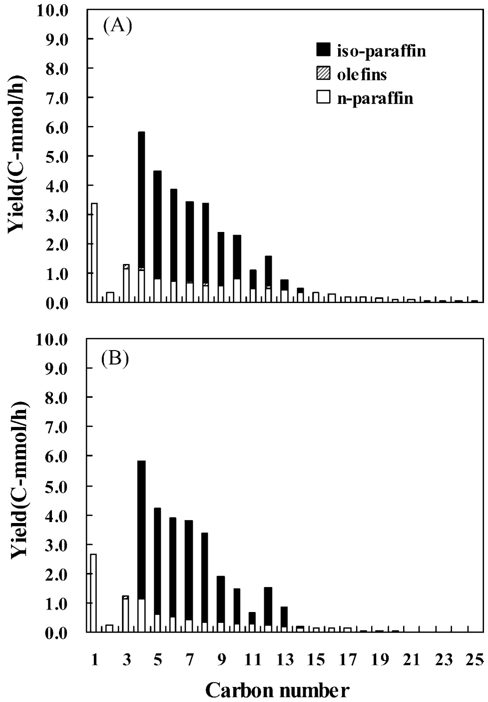

Fig. 2. Product distribution over hybrid catalyst with weight ratios of 20 wt% $Co/SiO_2$ to Pd/β of: (A) 0.5/0.5 and (B) 0.5/0.8 (reaction conditions: $T = 240$ °C, $P_{total} = 4.5$ MPa, $P_{syngas}/P_{n\text{-hexane}} = 1.0/3.5$, syngas = 81 ml/min, $H_2/CO = 2$, TOS = 6 h).

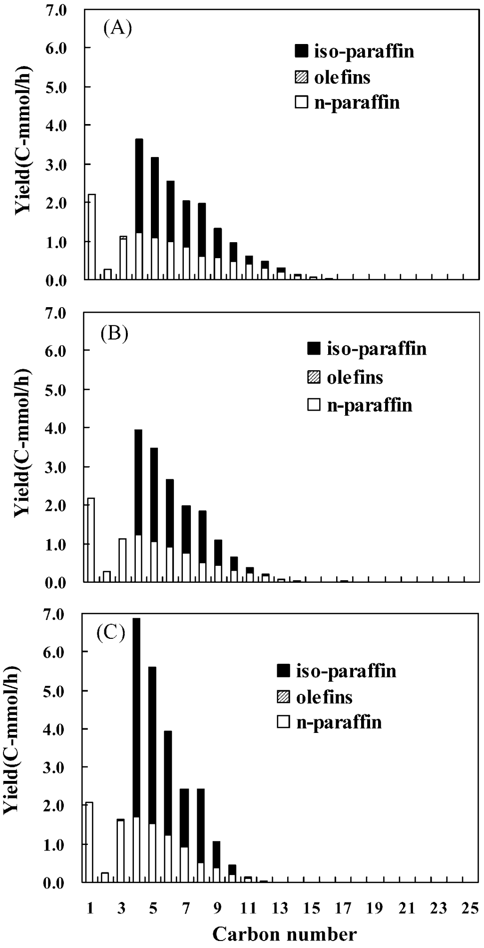

Fig. 4. Product distribution over 10 wt% $Co/SiO_2$ and Pd/β in two-stage reaction system at lower-reactor temperatures of: (A) 230 °C, (B) 245 °C and (C) 260 °C (reaction conditions: upper reactor—1.0 g $Co/SiO_2$, $T = 230$ °C; lower reactor—3.0 g Pd/β; $P_{total} = 4.5$ MPa, $P_{syngas}/P_{n\text{-hexane}} = 0.5/3.5$, syngas = 41 ml/min, $H_2/CO = 2$, TOS = 6 h).

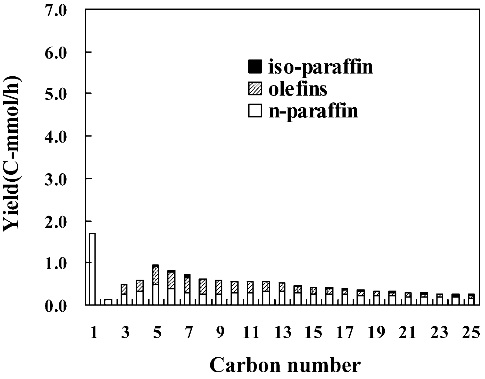

Fig. 5. Product distribution of SCF FT reaction over 10 wt% Co/$SiO_2$ (reaction conditions: 1.0 g Co/$SiO_2$, $T = 230$ °C, $P_{total} = 4.5$ MPa, $P_{syngas}/P_{n\text{-hexane}} = 0.5/3.5$, syngas = 41 ml/min, $H_2/CO = 2$, TOS = 6 h).

lower reactor from 230 °C to 260 °C, the longer-chain FT hydrocarbons with carbon number above 11 were basically disappeared and the products were obviously shifted to lighter ends. Moreover, the selectivity of iso-paraffins was also increased with the increase of reaction temperature in lower reactor, as clearly reflected from Table 2. This can be reasonably ascribed to the increased activity of the Pd/β catalyst for hydrocracking and hydro-isomerization reactions at higher temperature. Even if a large amount of olefins was produced during FT reaction as shown in Fig. 5, olefin selectivity in the two-stage process was still extremely low irrespective of the reaction temperatures in the lower reactor, which can be explained as that ability of Pd/β catalyst for hydro-conversion of olefins to paraffins was enhanced when more Pd/β catalyst (3 g) was loaded and additional hydrogen was fed to the lower reactor.

From the above results, one can see that the product distribution in two-stage process was significantly regulated by independently changing of the reaction parameters in the two reactors such as reaction temperature and hydrogen partial pressure in the lower reactor.

### 3.4. Long-term stability and coke deposition

In order to investigate the stability of both Co/$SiO_2$ and Pd/β catalysts for the production of iso-paraffins, long-term experiments for one-stage and two-stage processes were carried out. Generally, for the hydro-conversion of normal paraffins over bifunctional catalysts, higher molar ratio of hydrogen to paraffin is required for suppressing the coke formation to keep the lifetime of the catalyst longer. Under the present conditions, CO conversion at the initial stage of the reaction was about 60%. Therefore, majority of hydrogen was consumed for FT reaction and the ratio of hydrogen to hydrocarbon for hydro-conversion reactions may not be high enough for inhibiting the coke accumulation over Pd/β catalyst. Therefore, in the case of two-stage process, additional hydrogen with a flow rate of 100 ml/min was fed to lower reactor. The time-on-stream CO conversion and selectivity of $C_4^+$ iso-paraffins, accounting for the stability of Co/$SiO_2$ and Pd/β catalyst, are given in Fig. 6. After reaching a steady state, CO conversion was very stable during the 100 h test either in one-stage or two-stage processes and longer lifetime stability of the FT catalyst can be reasonably expected.

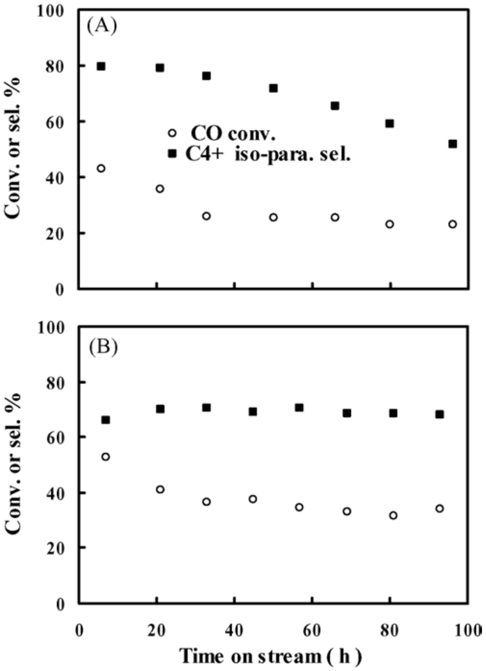

Fig. 6. Time-on-stream CO conversion and iso-paraffin selectivity in: (A) one-stage process (0.5 g 20 wt% Co/$SiO_2$ + 0.8 g 0.5% Pd/β, $T = 240$ °C, syngas = 81 ml/min, $P = 4.5$ MPa, $P_{syngas}/P_{n\text{-hexane}} = 1.0/3.5$) and (B) two-stage process (upper reactor: $T = 240$ °C, 1.0 g 20 wt% Co/$SiO_2$; lower reactor: $T = 245$ °C, 3.0 g 0.5 wt% Pd/β; syngas = 81 ml/min, $P = 4.5$ MPa, $P_{syngas}/P_{n\text{-hexane}} = 1.0/3.5$, 100 ml/min $H_2$ fed to lower reactor).

When the Pd/β catalyst was considered, in the case of one-stage process as shown in Fig. 6(A), gradual deactivation with TOS as reflected from the continuously decrease of $C_4^+$ iso-paraffins selectivity was clearly observed. On the contrary, for two-stage process, the Pd/β catalytic activity was sustained without observable decrease during 100 h run.

Coke deposition always accompanied with the conversion of hydrocarbons over solid acid or metal/solid acid catalysts. Moreover, it is commonly known that olefin is one of the precursors for coke formation during the hydro-conversion of hydrocarbons over bifunctional metal/zeolite catalysts. Thus, if $H_2$ was not sufficient or the hydrogenation function of the catalyst was low, olefins would be formed and consumed for coke accumulation on the catalyst, which caused the deactivation of the catalyst. To confirm this reasoning, coke accumulated on the used catalysts after long-term reaction was characterized by TG analysis and the results are shown in Fig. 7. For comparison, TG result of fresh Pd/β catalyst is also given in Fig. 7. The weight loss from room temperature to 250 °C was reasonably ascribed to water desorption as reflected

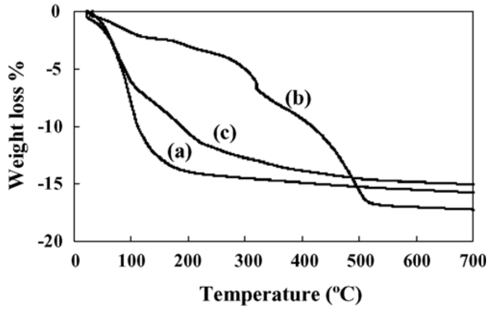

Fig. 7. TG pattern of 0.5 wt% Pd/β catalyst: (a) fresh catalyst, (b) used catalyst after 100 h reaction in one-stage process and (c) used catalyst after reaction test of 100 h in two-stage process.

from the TG curve of the fresh catalyst and the DTA curves (not shown). Moreover, all the TG curves were levelled off at temperature of 500 °C, indicating that all the coke was essentially burned off below this temperature. Therefore, the weight loss in TG analysis from 250 °C to 500 °C was defined as coke. Comparing curves (b) and (c) in Fig. 7, the amount of coke deposited over Pd/β catalyst in two-stage process was much less than that in one-stage process, which is consistent with the long-time stability results. Therefore, it can be concluded that the decrease of iso-paraffin selectivity with TOS was mainly caused by coke accumulation on the Pd/β catalyst. However, it is necessary to point out that other factors such as Pd sintering and poisoning of acidic functions by water produced in FT reaction may also, in a less degree, contribute to the deactivation of Pd/β catalyst, which cannot be ruled out from the present results.

Therefore, in considering the long-term stability of the catalyst for the production of iso-paraffins, two-stage process with more flexible operating conditions was advantageous to one-stage process.

### 3.5. Hydro-conversion of the SCF solvent

From the above results, question may be arisen from the hydro-conversion of supercritical solvent over Pd/β during iso-paraffin synthesis under supercritical conditions. Based on composition of the received and after-reaction *n*-hexane and material balance of experiments, the conversion of *n*-hexane to *iso*-hexane was estimated for each experiment and the results are given in Tables 1 and 2. As shown in Table 1, with the addition of Pd/β catalyst, the selectivity of $C_4^+$ iso-paraffins sharply increased from 2.6% to 70–80% while the hydro-isomerization of *n*-hexane solvent was only about 0.03–0.23% depending on the reaction conditions. Furthermore, as shown in Table 2, the hydro-isomerization of *n*-hexane solvent was slightly increased with increasing lower-reactor temperature from 230 °C to 260 °C and increasing Pd/β to $Co/SiO_2$ ratio of 3. The interesting observation of the above facts is that the addition of supercritical solvent had almost no observable effect on the hydro-conversion of FT products even though the amount of solvent was about 100–200 times higher than that of FT products. In order to confirm the above calculations, experiments for hydro-conversion of *n*-hexane solvent under similar conditions with those of the titled reaction were carried out and the results are shown in Table 3. From Table 3, irrespective of the reaction conditions, hydrocracking of *n*-hexane solvent was negligible as reflected from the very low content of the cracked products. Moreover, an apparent increase in conversion of *n*-hexane to *iso*-hexane was observed in comparison with the calculated results under similar conditions.

As expected, reactivity of normal paraffins increases rapidly with increasing chain length. It was reported that a 10-fold increase in the initial reaction rate was observed

Table 3
Product distribution of hydroisomerization and hydrocracking of *n*-hexane

| Species | Composition (wt.%) | | | | |
|---|---|---|---|---|---|
| | Feedstock (*n*-hexane) | R1 | R2 | R3 | R4 |
| $C_1$–$C_3$ | 0.00 | 0.01 | 0.03 | 0.04 | 0.12 |
| *i*-$C_4$ | 0.00 | 0.02 | 0.02 | 0.03 | 0.04 |
| *n*-$C_4$ | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 |
| *i*-$C_5$ | 0.00 | 0.01 | 0.01 | 0.01 | 0.03 |
| *n*-$C_5$ | 0.02 | 0.02 | 0.02 | 0.03 | 0.03 |
| *i*-$C_6$ | 1.38 | 1.67 | 2.52 | 3.87 | 6.95 |
| *n*-Hexane | 97.58 | 97.28 | 96.42 | 95.06 | 91.92 |
| $C_6^{2-}$ | 1.01 | 0.98 | 1.00 | 0.97 | 0.96 |
| *i*-$C_7$ | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 |
| *n*-$C_7$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| *i*-$C_8$ | 0.00 | 0.01 | 0.01 | 0.01 | 0.02 |
| *n*-$C_8$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| *i*-$C_9$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| *n*-$C_{12}$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| *n*-Hexane converted to *i*-hexane (%) | – | 0.30 | 1.17 | 2.55 | 5.71 |

Reaction conditions: catalyst = 0.5% Pd/β, $P$ = 4.5 MPa, *n*-hexane = 1.42 ml/min, TOS = 6 h; R1: $T$ = 240 °C, catalyst = 0.5 g, syngas = 41 ml/min; R2 − R4: catalyst = 3.0 g, syngas = 18 ml/min, $H_2$ = 100 ml/min, $H_2$/*n*-hexane (mole) = 6.17, $T$(R2) = 230 °C, $T$(R3) = 245 °C, $T$(R4) = 260 °C.

from *n*-hexane to *n*-undecane [20]. Based on these facts and the above results, it seems that the system was strongly governed by competitive chemisorption of different hydrocarbons and the hydro-isomerization and hydrocracking of FTS products were predominantly preferred rather than the hydro-isomerization and hydrocracking of *n*-hexane solvent.

Under the conditions for iso-paraffin synthesis in supercritical media by the combination of $Co/SiO_2$ and Pd/β catalysts, it can be summarized that hydro-conversion of *n*-hexane solvent was negligible and the FT products were favorably hydro-converted.

## 4. Conclusion

Based on the above results and discussion, the following conclusions can be drawn from the present investigation:

1. By combining the characteristics of SCF and multi-functional hybrid catalyst of $Co/SiO_2$ and Pd/β, a new concept on the direct synthesis of middle iso-paraffins through the modified supercritical FT reaction was proposed and experimentally demonstrated both in one-stage and two-stage fixed-bed reaction system.
2. In comparison with supercritical FT reactions, the addition of Pd/β catalyst in the newly developed process gave very high selectivity of middle iso-paraffins without apparent increase of the undesirable $C_1$–$C_3$ hydrocarbons. In considering the long-term stability of the catalyst for the production of iso-paraffins, two-stage process with more flexible operating conditions was advantageous to one-stage process.
3. Irrespective of reaction conditions, due to the competitive adsorption of different hydrocarbons over Pd/β catalyst, the FT hydrocarbons were preferentially hydro-converted over Pd/β catalyst and the hydro-conversion of *n*-hexane solvent was negligible.
4. In one-stage and two-stage processes, CO conversion was very stable during 100 h run. However, the selectivity of iso-paraffins decreased continuously with TOS in one-stage process while quite stable iso-paraffin selectivity was obtained in two-stage process by feeding additional hydrogen in the lower reactor. Coke deposition over Pd/β catalyst was explained as the main reason for the deactivation of Pd/β catalyst for the production of iso-paraffins.

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## References

[1] W. Keim, Catalysis in C1 Chemistry, D. Reidel Publishing Co., Dordrecht, Holland, 1983.
[2] H.G. Olive, S. Olive, The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide, Springer-Verlag, Tokyo, 1984, p. 144.
[3] M.E. Dry, in: J.R. Anderson, M. Boudart (Eds.), Catalysis Science and Technology, vol. I, Springer, Berlin, 1981 (Chapter 4).
[4] F.G. Botes, Appl. Catal. A 284 (2005) 21.
[5] J.J. He, B.L. Xu, Y. Yoneyama, N. Nishiyama, N. Tsubaki, Chem. Lett. 34 (2005) 148.
[6] X.H. Li, K. Asami, M.F. Luo, K. Fujimoto, Stud. Surf. Sci. Catal. 367 (2004) 147.
[7] N. Tsubaki, Y. Yoneyama, K. Michiki, K. Fujimoto, Catal. Commun. 4 (2003) 108.
[8] F.G. Botes, W. Böhringer, Appl. Catal. A 267 (2004) 217.
[9] T.-S. Zhao, J. Chang, Y. Yoneyama, N. Tsubaki, Ind. Eng. Chem. Res. 44 (2005) 769.
[10] X.H. Li, M.F. Luo, K. Asami, Catal. Today 89 (2004) 439.
[11] X.H. Li, K. Asami, M.F. Luo, K. Michiki, N. Tsubaki, K. Fujimoto, Catal. Today 84 (2003) 59.
[12] Z.-W. Liu, X.H. Li, K. Asami, K. Fujimoto, Catal. Today 104 (2005) 41.
[13] K. Yokota, Y. Hanakata, K. Fujimoto, Chem. Eng. Sci. 45 (1990) 2743.
[14] L. Fan, K. Yokota, K. Fujimoto, Top. Catal. 2 (1995) 267.
[15] K. Yokota, K. Fujimoto, Ind. Eng. Chem. Res. 30 (1991) 95.
[16] L. Fan, K. Yokota, K. Fujimoto, AIChE J. 38 (1992) 1639.
[17] L. Fan, K. Fujimoto, Appl. Catal. A 186 (1999) 343.
[18] Editor, World Fuels Today, July 3, 2003, pp. P1, P5.
[19] P. Chaumette, C. Verdon, P. Boucot, Top. Catal. 2 (1995) 301.
[20] J.W. Ward, S.A. Qader, Hydrocracking and Hydrotreating, American Chemical Society, Washington, DC, 1975.