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Direct synthesis of isoparaffin from synthesis gas under supercritical conditions

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ABSTRACT

To produce isoparaffins from synthesis gas directly, modified Fischer–Tropsch (FT) synthesis was carried out under supercritical conditions using n-butane as a medium. One-step FT synthesis using a hybrid catalyst consisting of Co/SiO_2, HZSM-5 and Pd/SiO_2 was carried out. Introduction of supercritical-phase n-butane increased light isoparaffins significantly and suppressed the formation of the by-product, methane. Under supercritical-phase butane, hydrogenolysis and isomerization reactions were promoted. Due to the fact that the optimum temperatures for FT and HZSM-5 catalysts are different, 513 K and over 573 K, respectively, two-step FT synthesis was also carried out to optimize the reaction temperatures. The first-step reaction used Co/SiO_2 catalyst containing small amount of HZSM-5 for FT synthesis at 513 K, and the second-step reaction used a hybrid catalyst containing Pd/SiO_2 and zeolite for hydrogenolysis and isomerization of hydrocarbons at 573 K. Introduction of supercritical n-butane increased the isoparaffin selectivity, and decreased the methane selectivity significantly. The production of heavy hydrocarbons C_9+ was inhibited in both gas and supercritical phase. The isoparaffin selectivity in the gas phase decreased with time-on-stream, but very stable for the supercritical-phase reaction. Because water and heavy hydrocarbons were removed from active sites on zeolite and the zeolite acidity was promoted in the supercritical medium, the selectivity of isoparaffin was considered stable. Among zeolites added to the hybrid catalyst in the second-step reactor, HZSM-5 and H-beta zeolite were suitable for producing light isoparaffins. These results indicated that two-step FT synthesis under supercritical n-butane was superior for producing light isoparaffins from synthesis gas directly.

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1. Introduction

Fischer–Tropsch (FT) synthesis is well known as a method of producing alternative clean fuels, other than petroleum, from synthesis gas (CO + H_2). Synthesis gas can be effectively produced from various organic resources such as natural gas, biomass as well as coal. FT oil, which is a liquid-phase hydrocarbon mixture, is extensively expected as petroleum substituted fuels [1,2]. FT oil contains normal-paraffins, which have high cetane number but low octane number, being used as synthetic diesel only. To produce synthetic gasoline (isoparaffins, alkylates) from FT synthesis, FT oil must be further hydrocracked and isomerized with solid acid catalyst at a separate reactor after removal of water formed from FT reaction, which can deactivate solid acid catalysts [1,3,4].

The SMDS process by Shell in Malaysia is using this two-step method to produce gasoline from natural gas. Besides the complexity of the two-step process, another problem of this process is that the FT reaction is operated at gas phase, where wax formed will cover the catalyst surface and deactivate catalyst quickly. Conducting FT synthesis in the slurry phase can extend FT catalyst lifetime effectively, as liquid medium can dissolve wax and absorb reaction heat. But slurry phase FT reaction is not suitable for isoparaffin synthesis here as zeolite catalyst component employed here will decompose liquid reaction medium.

The present authors reported that using the physical mixture of FT catalyst such as supported cobalt catalyst or iron-based catalyst with solid acid catalyst, isoparaffin was produced directly from synthesis gas in a single reactor [1,5,6]. The formed normal-paraffins at the surface of FT catalyst could migrate to the adjacent zeolite catalyst to start hydrogenolysis and isomerization of the

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normal-paraffins in situ. Besides the simplicity of this one-step process, one merit of this kind of reaction was that waxy FT hydrocarbon can be in situ hydrocracked to light isoparaffins, protecting FT catalyst lifetime from deactivation by wax accumulation. Another merit was that FT reaction heat was in situ absorbed by endothermic hydrocracking reaction, avoiding local overheating of the FT catalyst bed which happens very often in the conventional FT reaction, especially in gas phase FT reaction. But a drawback of this new method is that formed water in the FT reaction will contact zeolite directly in the same reactor, deactivating zeolite acidic sites as water is a typical Lewis base [7]. Furthermore, water steam under high pressure and high temperature inside the reactor might damage the zeolite framework structure. To overcome these problems, one approach is introducing expensive noble metal into zeolite, to strengthen the zeolite acid site stability against water via the hydrogen spillover effect [8]. But this method is not effective for keeping the zeolite framework from the surrounding pressurized steam.

As an alternative method, we apply supercritical fluid here to extract water or steam from the catalyst bed as quickly as possible, protecting zeolite acidity as well as zeolite framework structure. Considering the limitation of pressure and temperature of the FT reaction, hydrocarbon is selected as the supercritical medium. More importantly, supercritical-phase hydrocarbon, n-butane has enough affinity with hydrocarbon product from FT reaction and it is also expected that the hydrocarbon at the supercritical state has strong extraction ability on water. Furthermore, the quick removal of reaction heat is expected in supercritical n-butane, because the removal of reaction heat in supercritical medium occurs efficiently, similarly to that in liquid.

In this study, to synthesize branched paraffin (mainly C_4–C_8) from synthesis gas selectively, both one-step and two-step reactions were examined under supercritical conditions. The supercritical medium has both characteristics of liquid and gas phase [8,9]. Quick heat removal was expected in the supercritical phase, and thus the methane selectivity would decrease in supercritical n-butane, as local overheating of the catalyst bed due to FT reaction heat will accelerate the formation of methane. In addition, linear and branched olefins formed during FT synthesis and hydrocracking were expected to be extracted from zeolite surface by supercritical butane, to avoid the deactivation from olefin adsorptions to Lewis acidic sites of zeolite. Olefin is a typical Lewis base with electron pair, to readily attack and deactivate the zeolite acidic sites. For the one-step reaction, a new hybrid catalyst containing FT catalyst, HZSM-5 and Pd/SiO_2 were employed. Normal butane ($n\text{-}C_4H_{10}$) was utilized as the supercritical medium. The separation of FT products from the mixture of supercritical n-butane is not so difficult, because of low boiling point of n-butane at ambient temperature. Since HZSM-5 catalyzes hydrogenolysis and isomerization of linear paraffins, addition of HZSM-5 to FT catalyst can produce isoparaffin from synthesis gas. Addition of Pd/SiO_2 was expected to extend the lifetime of the hybrid catalyst by means of supposed hydrogen spillover [4,10,11].

On the other hand, there is a difference of the optimum temperature between FT catalyst (Co/SiO_2) and hydrogenolysis and isomerization on HZSM-5. Under the conditions we used, the optimum temperatures of Co/SiO_2 catalyst and HZSM-5 are around 513 K and over 573 K, respectively. Too high reaction temperature will increase methane selectivity in FT synthesis and low reaction temperature is not effective for hydrogenolysis and isomerization of hydrocarbons. Furthermore, with high conversion of synthesis gas in FT synthesis, hydrogen in synthesis gas is almost consumed and cannot be provided for hydrogenolysis of hydrocarbons. Therefore, to optimize the reaction temperatures for both reactions, the two-step reaction using a sequential two-stage reactor was also examined. The first-step reaction used Co/SiO_2 catalyst containing small amount of HZSM-5 for FT synthesis. A small amount of HZSM-5 was added for limiting the formation of heavy hydrocarbons by cracking of primary FT products. The second-step reaction adopted a hybrid catalyst containing Pd/SiO_2 and zeolite for successive hydrogenolysis and isomerization of the first-step reaction products with H_2 addition.

2. Experimental

2.1. Catalyst preparation

The Co/SiO_2 FT catalyst was prepared by incipient wetness method of $Co(NO_3)_2 \cdot 6H_2O$ (Kanto Chem. Co.) solution on commercially available SiO_2 (Fuji Silysia, ID Type, BET surface area: 120 m^2/g; pore volume: 1.2 ml/g). Pd/SiO_2 (1 wt% or 2.5 wt%) was prepared by a similar method to that of Co/SiO_2, with a $Pd(NH_3)_2(NO_2)_2$ nitric acid solution (Tanaka Co.). The catalyst precursors were dried in air at 393 K overnight, and then calcinated at 673 K for 1–2 h. The hybrid catalysts for the one-step reaction was prepared by physical mixture with FT catalyst, HZSM-5 (Süd Chemie Inc.; SiO_2/Al_2O_3 = 83.7) and Pd/SiO_2. And the catalysts for first-step or second-step reaction of two-step reaction were prepared by a similar method with mixing FT catalyst and HZSM-5 (Süd Chemie Inc.; SiO_2/Al_2O_3 = 83.7), as well as HZSM-5 and Pd/SiO_2, respectively. After pressurization under 60.0 MPa, all the mixed catalysts were crushed to 20–40 mesh, and used for the reactions.

2.2. Reaction procedure

2.2.1. One-step reaction

Synthesis gas ($H_2/CO = 2$) with helium or n-butane (Tc = 425 K, Pc = 3.8 MPa) was used for gas phase or supercritical phase, respectively. After the hybrid catalyst consisted of Co/SiO_2, HZSM-5 and Pd/SiO_2 was reduced in situ with hydrogen at 673 K for 10 h, FT synthesis was carried out using catalyst of 0.5 g (Co/SiO_2 base), under synthesis gas partial pressure of 1.0 MPa by using a flow-type fixed reactor. The total pressure was 5.0 MPa, and the partial pressure of helium or n-butane was 4.0 MPa, higher than Pc of n-butane. During the reaction, product gases were on-line analyzed by two gas chromatographs with TCD (Shimadzu GC-8A, active carbon) and FID (Shimadzu GC-14B, J&W alumina) detectors. The liquid products collected in an ice-trap were analyzed off-line on a gas chromatograph (Shimadzu GC-14B, SE-30) with FID detector [5]. The separation method of isoparaffin, normal-paraffin and olefin was described in detail elsewhere [12].

2.2.2. Two-step reaction

The schematic two-step reactor for FT synthesis is illustrated in Fig. 1. Both the first-step and second-step reactors were flow-type fixed-bed pressurized reactors. The first-step reactor contained the hybrid catalyst composed of 20 wt% Co/SiO_2 and HZSM-5 of 0.5 g (Co/SiO_2 base). The second-step reactor was loaded with the hybrid catalyst composed of HZSM-5 and 2.5 wt% Pd/SiO_2. Synthesis gas ($H_2/CO = 2$) with helium or n-butane (Tc = 425 K, Pc = 3.8 MPa) was used for gas phase or supercritical phase, respectively. Additional hydrogen was introduced just at the entrance of the second-step reactor. Prior to reaction, the catalysts were reduced in situ with H_2 at 673 K for 10 h. After reduction, FT synthesis was carried out under synthesis gas ($H_2/CO = 2$) partial pressure of 1.0 MPa and total pressure was 5.0 MPa while the partial pressure of helium or n-butane was 4.0 MPa. When an additional H_2 was introduced into the inlet of the second-stage reactor, H_2/CO was adjusted and reached 3. Analysis of the products was carried out similar to that of one-step reaction.

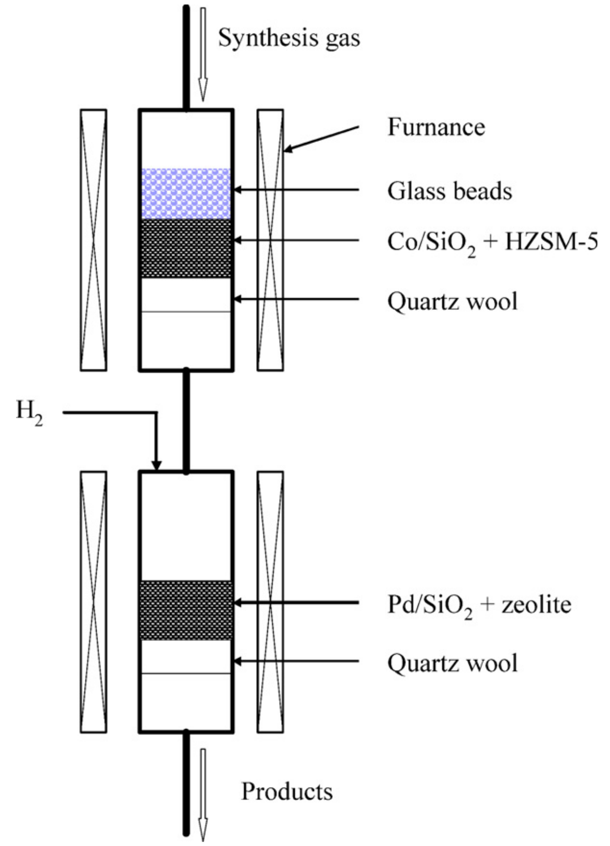

Fig. 1. Illustration of two-step reactor for isoparaffins under supercritical conditions.

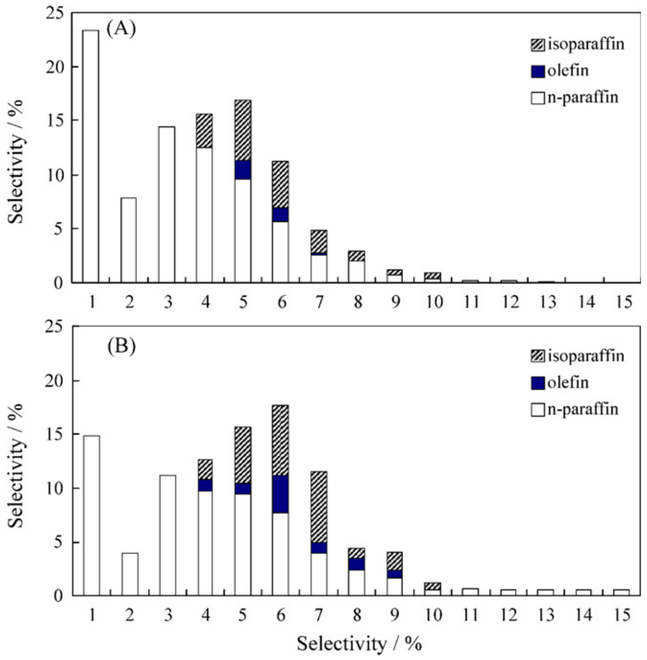

Fig. 2. Effect of supercritical butane on product selectivity of FT synthesis by one-step (A) helium and (B) supercritical butane. Conditions: 533 K; 5.0 MPa (synthesis gas:helium or butane = 1:4); *W*/*F* (synthesis gas) = 10 g h/mol; *W* = 0.5 g (Co/SiO$_2$ weight); H$_2$/CO = 2; 10 wt% Co/SiO$_2$:HZSM-5:1 wt% Pd/SiO$_2$ = 2:1:1.

3. Results and discussion

3.1. One-step reaction

In order to determine the effect of supercritical butane on FT synthesis, one-step reaction was carried out. In this study, to extend the lifetime of the hybrid catalyst and reducing olefin selectivity, 1 wt% Pd/SiO$_2$ was added to the hybrid catalyst. CO conversion and the product selectivity of FT synthesis using FT catalyst only or hybrid catalyst (10 wt% Co/SiO$_2$:HZSM-5:1 wt% Pd/SiO$_2$ = 2:1:1) are summarized in Table 1 and Fig. 2. When the reaction conditions changed from gas phase to supercritical phase, CO conversion did not change significantly, indicating that n-butane was only an inert reaction medium, not influencing reaction mechanism. Supercritical butane increased the isoparaffin selectivity from 16.8% to 23.3%, significantly.

The produced hydrocarbon distribution was compared in Fig. 2. Zeolite addition sharply enhanced C$_5$–C$_9$ isoparaffins. The ratio of H$_2$ to CO was 2 here, and if more H$_2$ is utilized, olefins can be completely hydrogenated to paraffins, especially isoparaffins. But at the same time, CH$_4$ selectivity might be increased. Supercritical n-butane was effective for increasing isoparaffins selectivity. Because the isomerization of paraffin occurred on the acidic sites of HZSM-5, it was considered that supercritical n-butane kept and protected the acidity of the zeolite. As described above, water produced in FT synthesis might deactivate the acidic site of HZSM-5. But water might be dissolved in supercritical n-butane, and was removed from the acidic site of zeolite. Therefore acidic sites of HZSM-5 were still active during supercritical-phase FT synthesis; and the isoparaffin selectivity by hybrid catalyst in supercritical phase was enhanced dramatically. On the other hand, it is found that olefin selectivity on the hybrid catalyst in the supercritical phase was still very high because the olefins formed in FT synthesis or hydrocracking reaction were effectively extracted by supercritical n-butane and transported outside catalyst bed. This quick removal was also important to suppress the zeolite catalyst deactivation as olefins might deactivate Lewis acidic sites on the zeolite.

The methane selectivity in the supercritical phase decreased dramatically from 23.6% in gas phase to 15.3%. Supercritical fluid is superior for removing reaction heat from the catalyst and effective for mass transfer, and thus methane selectivity was suppressed. The olefin selectivity increased from 3.4% in gas phase to 8.4% in the supercritical condition. Because the hybrid catalyst contained Pd/SiO$_2$, the olefin selectivity was lower than that of the catalyst without Pd/SiO$_2$ [13]. Supercritical butane dissolved heavy hydrocarbons including olefins formed from FT synthesis as well

Table 1
Effect of supercritical butane on FT synthesis by one-step reaction.

Reaction medium	CO conv. (%)	Hydrocarbon selectivity (%)					CO$_2$^{a} Sel.
		CH$_4$	C$_2$–C$_3$	C$_4$–C$_{15}$			
				Normal-paraffin	Olefin	Isoparaffin	
He	61.4	23.6	22.1	34.1	3.4	16.8	0.0
Supercritical butane	68.2	15.3	14.9	38.1	8.4	23.3	2.1

[a] CO$_2$ selectivity was calculated based on the reacted CO. Conditions: 533 K; 5.0 MPa (syngas:He or butane = 1:4), *W*/*F* (syngas) = 10 g h/mol; *W* = 0.5 g (Co/SiO$_2$ weight); H$_2$/CO = 2; 10 wt% Co/SiO$_2$:HZSM-5:1 wt% Pd/SiO$_2$ = 2:1:1.

Table 2
Effect of supercritical butane on FT synthesis by two-step reaction.

Reaction medium	CO conv. (%)	Selectivity (%)						CO$_2$[a] Sel.
		CH$_4$	C$_2$–C$_3$	C$_4$–C$_8$		C$_9$+		
				Normal-paraffin	Isoparaffin	Normal-paraffin	Isoparaffin	
He	76.7	45.0	19.3	23.3	12.4	0.0	0.0	6.0
Supercritical butane	80.3	21.4	10.4	31.3	34.0	1.1	1.9	3.4

[a] CO$_2$ selectivity was calculated based on the reacted CO. Conditions: 5.0 MPa (synthesis gas:He or butane = 1:4), W/F (synthesis gas) = 10 g h/mol; W = 0.5 g (Co/SiO$_2$ weight); first-step: 513 K, 1 g, 20 wt% Co/SiO$_2$:HZSM-5 = 1:1; H$_2$/CO = 2; second-step: 573 K; 1.25 g; 2.5 wt% Pd/SiO$_2$:H-ZSM-5 = 1:4; H$_2$/CO = 3.

as from hydrocracking and scavenged them from the catalyst fast. However, the heavy hydrocarbons remained on the catalyst surface under helium gas. Furthermore, under the supercritical phase, mass transfer of the FT products became fast; thus the heavy hydrocarbons were removed from the FT catalyst before being subjected to secondary hydrogenolysis on cobalt sites.

3.2. Two-step reaction

3.2.1. Effect of supercritical conditions on isoparaffin selectivity

As described above, for one-step isoparaffin production from synthesis gas, FT synthesis, hydrogenolysis and isomerization of the products must occur simultaneously in one reactor. However, the optimum temperature for FT synthesis, and hydrogenolysis and isomerization of the FT products is different. To optimize the reaction temperature for the reactions, two-step reaction was examined. The first reaction-step used a hybrid catalyst composed of Co/SiO$_2$ and HZSM-5 for FT synthesis, and the second-step adopted Pd/SiO$_2$ and H-zeolite for hydrogenolysis and isomerization of the hydrocarbons from the first-step reaction. The results of two-step reaction under gas and supercritical phase were summarized in Table 2. Similar to the one-step reaction, although the reaction conditions changed from gas phase to supercritical phase, CO conversion did not change significantly, 76.7–80.3%. But methane selectivity decreased sharply from 45.0% to 21.4%. Production of heavy hydrocarbon C$_9$+ inhibited for both gas and supercritical conditions. In the one-step reaction under supercritical conditions, the selectivity of heavy hydrocarbons C$_9$–C$_{30}$ was 12.1%. It was found that hydrogenolysis of heavy hydrocarbons occurred effectively on the hybrid catalyst in the second-step reactor at higher temperature. Isoparaffin selectivity (C$_4$–C$_8$) increased from 12.4% to 34.0%, about three times, when reaction medium was changed from gas phase to supercritical phase. In gas phase, water produced by FT synthesis deactivated the acidic sites on HZSM-5 in the second-step reactor, and decreased isomerization activities of the second-step catalyst. On the other hand, in supercritical phase, water could be removed from the acidic sites of HZSM-5 by supercritical butane, and the acidic sites in the second-step catalyst were still active. The olefins did not appear for both conditions, because olefins produced from FT synthesis in the first-step reactor were hydrogenated and isomerized in the second-step reactor to produce light normal-paraffins and isoparaffins.

As described above, water produced from FT synthesis in the first-step reaction might deactivate the acidic sites of HZSM-5 in the second-step catalyst and seemed to decrease the catalyst life. But, because water might be dissolved in supercritical n-butane and was removed from the acidic site of HZSM-5, it was expected that the catalyst life was longer in supercritical phase than in gas phase. As indicated in Fig. 3, isoparaffin selectivity in gas phase decreased with time-on-stream, but very stable and high for supercritical-phase reaction. Therefore acidic sites of HZSM-5 in the second-step catalyst were still active during supercritical FT synthesis, and the isoparaffin selectivity under supercritical conditions did not change with time-on-stream. In addition, because hybrid catalyst used in the second-step contained Pd/SiO$_2$, the hydrogen spillover from Pd/SiO$_2$ to the acidic sites on the zeolite enhanced the acidity of the zeolite [4,10,11]. Thus the acidic sites on the zeolite were still active for isomerization of hydrocarbons, especially for supercritical conditions. Under supercritical conditions, both the hydrogen spillover and water removal activated and stabilized the acidic sites on HZSM-5 in the second-step catalyst. On the other hand, CO conversions in both conditions did not change with time-on-stream. In the first-step reaction, a small amount of the zeolite was included in the hybrid catalyst to decompose too heavy hydrocarbons and extended the life of the hybrid catalyst in the first-step reactor. Therefore it was found that heavy hydrocarbons might be decomposed in the first-step reaction and CO conversions did not change for either reaction conditions.

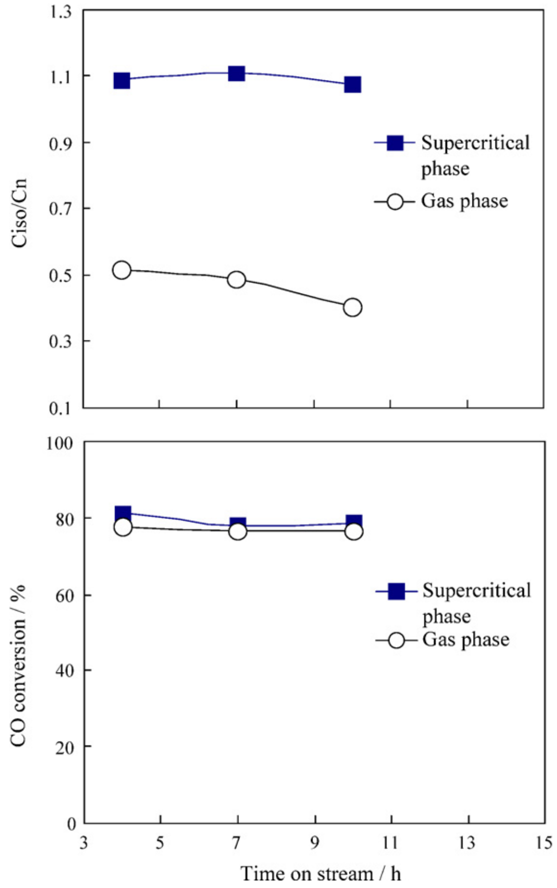

Fig. 3. Change of hydrocarbon selectivity with time-on-stream. Ciso/Cn was the ratio of isoparaffin to normal-paraffin and obtained for C$_4$+ hydrocarbons. Conditions: 5.0 MPa (synthesis gas:He or butane = 1:4), W/F (synthesis gas) = 10 g h/mol; W = 0.5 g (Co/SiO$_2$ weight); first-step: 513 K, 1 g 20 wt% Co/SiO$_2$/HZSM-5 (1:1); H$_2$/CO = 2; second-step: 573 K; 1.25 g 2.5 wt% Pd/SiO$_2$/HZSM-5 (1/4); H$_2$/CO = 3.

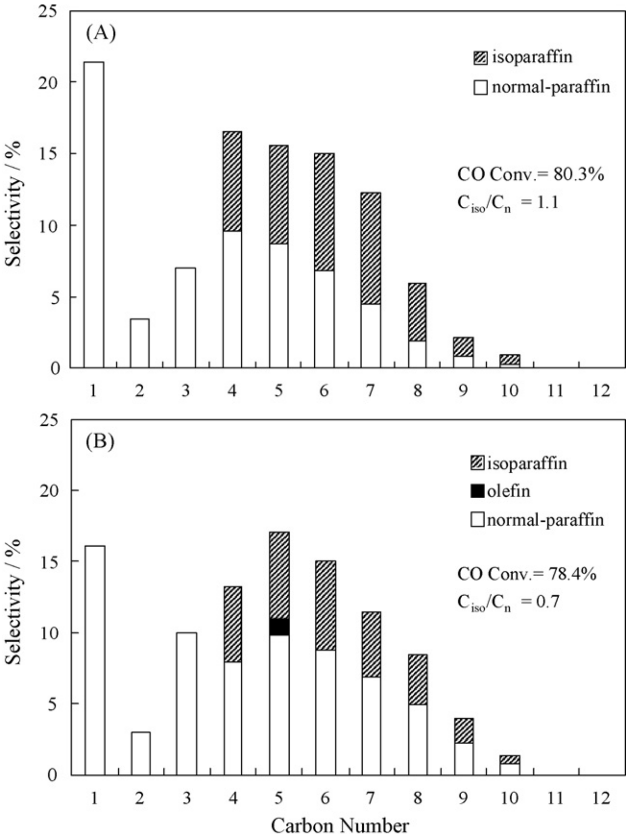

Fig. 4. Effect of H_2 addition to second-step reaction on hydrocarbon selectivity: (A) with H_2 addition; (B) without H_2 addition; Ciso/Cn: ratio of isoparaffin to normal-paraffin(C_4+). Conditions: 5.0 MPa (synthesis gas:He or butane = 1:4), *W*/*F* (synthesis gas) = 10 g h/mol; *W* = 0.5 g (Co/SiO_2 weight); first-step: 513 K, 1 g 20 wt% $Co/SiO_2/HZSM$-5 (1:1); $H_2/CO = 2$; second-step: 573 K; 1.25 g 2.5 wt% $Pd/SiO_2/HZSM$-5 (1/4); $H_2/CO = 3$ (with H_2 addition).

3.2.2. Effect of addition of hydrogen to second-step

In the two-step reaction, the hybrid catalyst composed of Pd/SiO_2 and HZSM-5 was used for the second-step hybrid catalyst. When the CO conversion at first-step reaction was very high, the amount of H_2 might be insufficient for hydrogenolysis of hydrocarbons and hydrogenation of olefins in the second-step reaction. Thus, additional H_2 was provided to the second-step reactor. The effect of H_2 addition on hydrocarbon selectivity was investigated. Fig. 4 shows the effect of H_2 addition on the hydrocarbon selectivity. H_2 addition did not change the CO conversions. However, H_2 addition increased the ratio of isoparaffin to normal-paraffin (Ciso/Cn) from 0.7 to 1.1 and decreased C_9–C_{10} hydrocarbon selectivity from 5.4% to 3.1%. These findings indicated that H_2 addition promoted the isomerization and hydrogenolysis of hydrocarbons. Because the hybrid catalyst contained Pd/SiO_2, hydrogen spillovered from Pd/SiO_2 to acidic site of HZSM-5 was available, which strengthened zeolite acidity. Addition of H_2 initiated hydrogen spillover from Pd/SiO_2 to acidic sites on HZSM-5, and enhanced the isomerization and hydrogenolysis of normal-paraffins. A small amount of C_4 olefin was contained in the produced hydrocarbons without H_2 addition; but H_2 addition erased olefins completely.

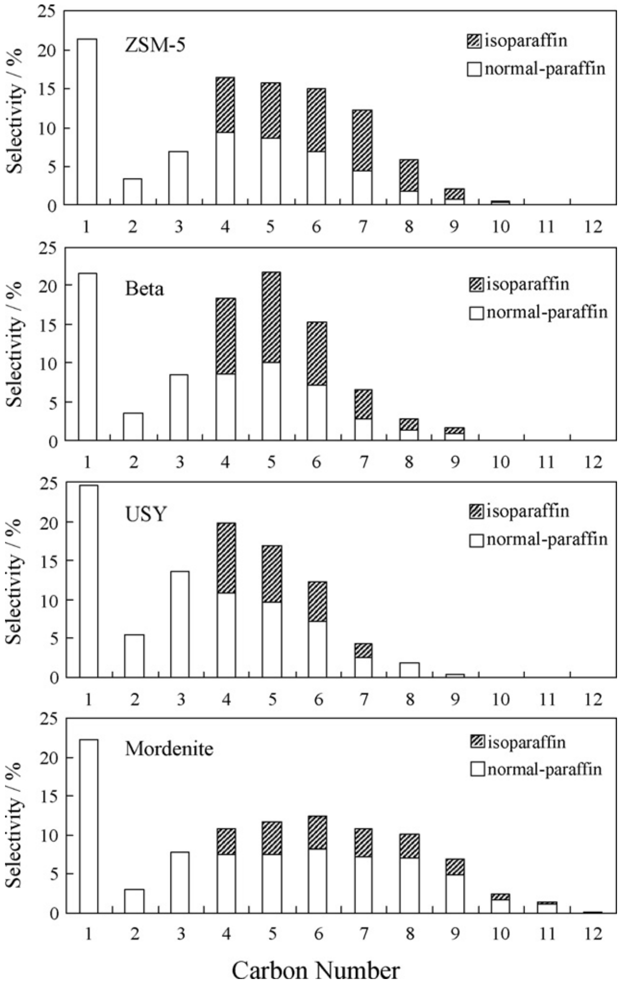

Fig. 5. Effect of various zeolite in second-step catalyst on hydrocarbon selectivity. Conditions: 5.0 MPa (synthesis gas:He or butane = 1:4), *W*/*F* (synthesis gas) = 10 g h/mol; *W* = 0.5 g(Co/SiO_2 weight); first-step: 513 K, 1 g 20 wt% $Co/SiO_2/HZSM$-5 (1:1); $H_2/CO = 2$; second-step: 573 K; 1.25 g 2.5 wt% Pd/SiO_2/ zeolite (1/4); $H_2/CO = 3$.

3.2.3. Effect of various zeolite in the second-step catalyst on hydrocarbon selectivity

To understand the effect of zeolite type on hydrogenolysis and isomerization performance of hydrocarbons, four kinds of H-zeolite were examined as the main component of the second-step catalyst.

Table 3
Effect of zeolites on FT synthesis by two-step reaction.

Zeolite	SiO_2/Al_2O_3 ratio	CO conv. (%)	Selectivity (%)						CO_2[a] Sel.
			CH_4	C_2–C_3	C_4–C_8		C_9+		
					Normal-paraffin	Isoparaffin	Normal-paraffin	Isoparaffin	
HZSM-5	83.7	80.3	21.4	10.4	31.3	34.0	1.1	1.9	3.4
H-Beta	27.0	82.5	21.7	12.1	29.8	34.8	0.9	0.7	1.4
H-USY	7.0	84.5	24.5	19.2	32.3	22.8	0.5	0.0	2.8
H-Mordenite	18.0	80.8	22.3	11.0	37.9	17.6	8.3	3.0	3.4

[a] CO_2 selectivity was calculated based on the reacted CO. Conditions: 5.0 MPa (syngas:butane = 1:4), *W*/*F* (syngas) = 10 g h/mol; *W* = 0.5 g (Co/SiO_2 weight); first-step: 513 K, 1 g, 20 wt% Co/SiO_2:HZSM-5 = 1:1; $H_2/CO = 2$; second-step: 1.25 g, 2.5 wt% Pd/SiO2:zeolite = 1:4; $H_2/CO = 3$.

The CO conversion and the products selectivity are given in Table 3, and the hydrocarbon distribution is shown in Fig. 5. The CO conversions were between 80.3% and 84.5%, which was attributed to the same FT catalyst in the first-step reaction at 513 K. The CO_2 selectivity was below 3.4%. The selectivity of C_4–C_8 isoparaffins was large for HZSM-5 and H-beta zeolite, 34.0% and 34.8%, respectively. The hydrocarbons from H-beta zeolite were lighter than those from HZSM-5. This means that hydrogenolysis of hydrocarbons occurred more intensively on H-Beta than on HZSM-5, and isomerization reaction occurred significantly for both zeolites. For H-USY zeolite, the isoparaffin selectivity was not so high, but the light hydrocarbon selectivity was high, indicating that hydrogenolysis of hydrocarbons occurred significantly, but isomerization not. For H-Mordenite, the hydrocarbons contained much amount of C_9+ hydrocarbons, and less amount of isoparaffins. These results showed that the products from the first-step reaction were further converted to isoparaffins on the zeolite at second-step reactions. The activity sequence can be attributed to the difference in acidity and the microporous structure of the zeolite. H-Beta, H-USY and H-Mordenite have large microporous structures, and H-ZSM-5 has a medium microporous one. It can be inferred that the second-step reactions were simultaneously affected by the acidity and microporous structures of the H-zeolites. The results obtained here suggested that H-ZSM-5 and H-Beta zeolites were more suitable as components of the second-step catalyst. The selectivity C_4–C_8 isoparaffins was controlled by the acidity strength, acidity amount, and microporous structure of zeolite.

4. Conclusions

To produce isoparaffins from synthesis gas directly, a modified Fischer–Tropsch (FT) synthesis was carried out by either one-step or two-step reaction under supercritical conditions using n-butane as a medium. For one-step reaction, a hybrid catalyst composed of Co/SiO_2, zeolite and Pd/SiO_2 was used. Introduction of supercritical n-butane into the one-step reaction increased the isoparaffin selectivity, and decreased the methane selectivity significantly. It was found that supercritical n-butane promoted FT synthesis as well as hydrogenolysis and isomerization of hydrocarbons. To optimize reaction temperature for FT synthesis, hydrogenolysis and isomerization, two-step reactions were also carried out. The first-step reaction used the hybrid catalyst composed of Co/SiO_2 and HZSM-5 for FT synthesis while the second-step reaction used a hybrid catalyst containing Pd/SiO_2 and H-zeolite for hydrogenolysis and isomerization of hydrocarbons from first-step reactions. Introduction of supercritical n-butane increased the isoparaffin selectivity, and decreased the methane selectivity in the second-step reaction as well. The production of heavy hydrocarbons C_{11}+ was inhibited, because of accelerated hydrogenolysis at the second-step reaction. The isoparaffin selectivity in the gas phase decreased with time-on-stream, but it was high and very stable in the supercritical-phase reaction. Because water and heavy hydrocarbons were removed from active sites on zeolite and its acidity was kept in the supercritical medium, the selectivity of isoparaffin was stable. In addition, additional H_2 to second-step reaction further promoted hydrogenolysis and isomerization of hydrocarbons, because of enhanced acidity by the hydrogen spillover from Pd/SiO_2 to acidic sites on zeolite. As zeolite added to the hybrid catalyst in the second-step reactor, HZSM-5 and H-beta were more suitable for producing light isoparaffins.

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