Design and Modification of Zeolite Capsule Catalyst, A Confined Reaction Field, and its Application in One-Step Isoparaffin Synthesis from Syngas

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Four kinds of zeolite capsule catalyst with different crystallization conditions were prepared and utilized for the middle isoparaffin direct synthesis via Fischer–Tropsch synthesis (FTS) reaction. Characterization results exhibited that these capsule catalysts had a compact, integral H-ZSM-5 shell. In FTS reactions on these zeolite capsule catalysts, hydrocarbons of C_{11+} were totally suppressed, accompanied by a sharp anti-Anderson−Schultz−Flory (ASF) law product distribution. The selectivity of light isoparaffin was improved obviously, but with the increase of the olefin's selectivity. Two-stage isoparaffin synthesis reaction, using the combination of zeolite capsule catalyst with hydrogenation catalyst of Pd/SiO_2 in a single reactor as dual-bed catalyst, was also conducted for converting the residual olefins produced by the single zeolite capsule catalyst. Dependent on the palladium role of hydrogenation and hydrogen spillover, almost all the olefins effused from the first stage of zeolite capsule catalyst were hydrogenated, mostly converted to isoparaffin. The selectivity of isoparaffin in the final products was increased markedly as expected.

1. Introduction

Fischer–Tropsch synthesis (FTS) as one option to produce hydrocarbons has been known since 1925.[1] Up to now, FTS reaction had been industrialized for producing clean diesel fuel because FTS products have so many advantages such as sulfur-free, aromatic-free, and nitrogen-free over conventional petroleum-derived products. However, linear paraffins and α-olefins predominated in FTS products, and their distribution follows the Anderson−Schultz−Flory (ASF) law. Therefore, FTS products have high cetane number but low octane number, and can only be used as the diesel fuels. Recently, more attention has been focused on the production of hydrocarbons rich in isoparaffin because of its wide foreground as synthetic gasoline. Several groups had tried to make isoparaffin using FTS-active metal supported on the acidic zeolite.[2–4] But low catalyst activity, very bad metallic reduction degree and high methane selectivity appeared because of the strong interaction between the metal and zeolite.

Zeolites, one of the crystalline aluminosilicate, have special pores, cavities, and regular channels on molecular dimensions.[5] Some zeolites are excellent hydrocracking and isomerization catalysts for the conversion of heavy oil to light hydrocarbons in petroleum industry. The present authors had reported the physical mixture catalyst of zeolite with conventional FTS catalyst Co/SiO_2, showing isoparaffin formation ability.[6,7] Although the formation rate of short-chain isoparaffin was enhanced, the long-chain hydrocarbons were not 100% decomposed there. There were still some heavy hydrocarbons in the final products of physical mixture catalyst. It seems that the hydrocracking and isomerization of the long-chain hydrocarbons occurred on the acidic sites of zeolite at random, and a part of FTS hydrocarbons might have no chances to contact zeolite. Recently, the present authors introduced a novel multiple-functional H-ZSM-5 zeolite capsule catalyst into FTS reaction. In the FTS reactions using these zeolite capsule catalysts, syngas $(CO + H_2)$ passed through the zeolite membrane to reach the Co/SiO_2 catalyst first.[8,9] And then all the formed FTS straight-chain hydrocarbons at the core must enter zeolite channels to receive hydrocracking as well as isomerization in this tailor-made confined reaction field. As a result, the selectivity of middle isoparaffin was increased markedly. However, the olefin content increased with the cracking of long-chain hydrocarbons

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in the zeolite capsule. In order to reduce the olefin content, two-stage isoparaffin synthesis reaction using the zeolite capsule catalyst along with the hydrogenation catalyst Pd/SiO$_2$ was studied. There was zeolite capsule catalyst at the first stage while Pd/SiO$_2$ catalyst at the second stage separately, but loaded inside the same reactor. During the reaction, syngas passing through the first stage reacted similarly to that on the single zeolite capsule catalyst. And then, the effluent products from the first stage entered the second stage.
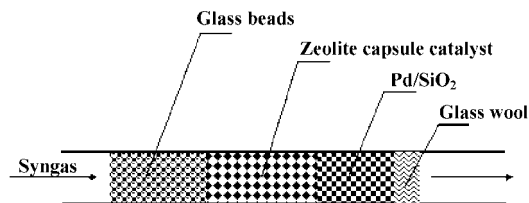

Figure 1. Illustration of two-stage FTS reaction on zeolite capsule catalyst Co/SiO$_2$-Z-7 + Pd/SiO$_2$ in the reactor.

2. Experimental Section

Preparation of the Conventional FTS Catalyst Co/SiO$_2$. The support for preparing the conventional FTS catalyst Co/SiO$_2$ was commercially available Silica (Fuji Silysia Chemical Ltd., Cariact Q-10, specific surface area 323.0 m^2/g, pore volume 1.03 cm^3/g, average diameter of pore 10 nm) with the diameter of 0.85–1.7 mm. Using the incipient wetness impregnation method and Co(NO$_3$)$_2$·6H$_2$O as the cobalt resource, FTS conventional catalyst of Co/SiO$_2$ with 10 wt % cobalt loading was prepared. Then the catalyst precursor was dried at 393 K for 12 h before its calcination in air at 673 K for 2 h.

Tailor-Made Co/SiO$_2$-Z-X (X = 1, 2, 2S, and 7) Zeolite Capsule Catalysts. Using H-ZSM-5 zeolite membrane as the capsule shell and 10 wt % Co/SiO$_2$ pellets (0.85–1.7 mm) mentioned above as the core, H-ZSM-5 zeolite capsule catalysts were prepared successfully. In the constructing of H-ZSM-5 membrane coated on the Co/SiO$_2$pellets, hydrothermal synthesis was employed. Tetra-propylammonium hydroxide (TPAOH) was selected as the structure directed agent. Tetratethylortho silicate (TEOS) and Al(NO$_3$)$_3$·9H$_2$O were the Si and Al resources respectively. The synthesis solution was prepared based on the molar ratio of 0.25TPAOH:0.025Al(NO$_3$)$_3$:1TEOS:4EtOH:60H$_2$O. Mixing these reagents in a Teflon container, the precursor solution was stirred at room temperature for 2 h. Before hydrothermal synthesis, Co/SiO$_2$ pellet and precursor sol were sealed in a stainless steel autoclave with a Teflon inner tank, and then, the autoclave was fixed in the hydrothermal synthesis apparatus (DRM-420DA, Hiro Company, Japan). Hydrothermal synthesis was performed at 453 K for varied crystallization times of 1, 2, or 7 d in order to get different zeolite loading amounts and varied membrane thicknesses. The final H-ZSM-5 capsule catalysts were calcined at 773 K in air for 5 h to remove the organic template.[8] In the following discussion, the capsule catalysts will be noted as Co/SiO$_2$-Z-X (X = 1, 2, 7) where X stands for the number of hydrothermal synthesis days. For Co/SiO$_2$-Z-2S catalysts, the "2S" means a twice-repeated synthesis.

Preparation of 2.5 wt % Pd/SiO$_2$ Hydrogenation Catalyst. Silica gel (Fuji Silysia Chemical Ltd., ID type, specific surface area 120 m^2/g, pore volume 1.24 cm^3/g, pellet size 0.38–0.85 mm) was used as the catalyst support. Pd/SiO$_2$ catalyst with 2.5 wt % palladium loading was prepared by incipient wetness impregnation of the silica support with Pd(NH$_3$)$_2$(NO$_3$)$_2$ solution. The impregnated samples were dried first by slow evaporation at room temperature for 2 h and then drying in a 393 K oven for 12 h. The final calcination process was performed in air from room temperature to 673 K with a ramping rate of 2 K/min and kept at 673 K for 1 h.

Catalyst Characterization. Measurements of the surface area and pore volume of catalysts were performed in an automatic gas adsorption system (Quantachrome, Autosorb-1, Yuasa Co.) by N$_2$ adsorption. Before analysis, the samples were degassed at 573 K and 3.0 Pa for 3 h. The physical structures of the catalysts, as well as compositional analysis and surface morphology observation, were measured by scanning electron microscopy (SEM) (JEOL, JSM-6360LV) with energy-diffusive X-ray spectroscopy (EDS) (JEOL, JED-2300). The samples for this analysis were first coated with a platinum layer on the surface by an auto fine coater (JEOL, JFC-1600). An X-ray diffractometer (RINT 2400, Rigaku. Co) equipped with Cu Kα radiation was used to determine the chemical structure and collect the data of the particle size of the cobalt oxide.
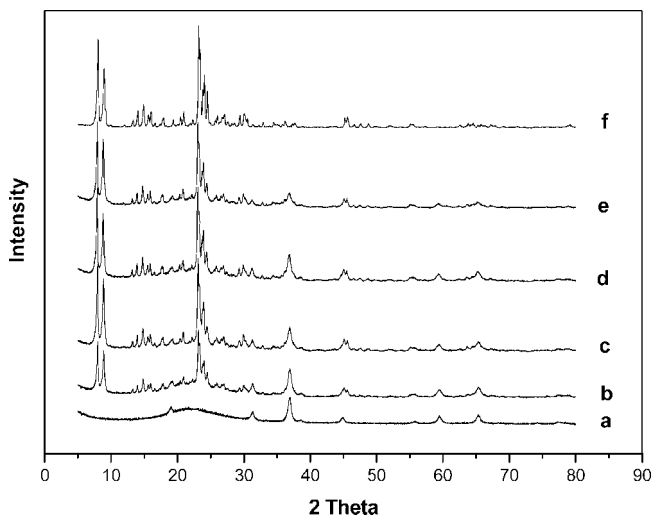
Figure 2. XRD patterns of (a) Co/SiO$_2$, (b) Co/SiO$_2$-Z-1, (c) Co/SiO$_2$-Z-2S, (d) Co/SiO$_2$-Z-2, (e) Co/SiO$_2$-Z-7, and (f) H-ZSM-5.

All the samples were scanned at 40 KV and 40 mA within the range of 5° < 2θ < 80°. The mean crystallite size (D) of cobalt oxide in the passivated catalysts was calculated using the Scherrer equation. Experiments on temperature programmed NH$_3$ desorption (TPD) were adopted to determine the quantity and strength of the acid sites of the catalysts. The sample was first pretreated in flowing helium at 473 K for 1 h. After cooling down to 423 K in helium, it was then kept in ammonia flow for 30 min until no signal variation in the effluent could be detected by the downstream gas chromatograph (Shimadzu, TCD, GC-8A). The temperature programmed desorption was performed by ramping the sample temperature by the heating rate of 5 K/min from 300 to 800 K. TCD gas chromatography monitored the state of desorption.

Isoparaffin Synthesis by Single- and Two-Step Reaction. Isoparaffin synthesis via FTS reaction using these zeolite capsule catalysts was carried out in a high-pressure flow-type fixed bed reactor. Before the FTS reaction, the mixture of 3.0 g quartz sand and zeolite capsule catalyst, containing 0.5 g Co/SiO$_2$, was loaded in the center of the stainless steel reactor (i.d. Eight mm). Then the catalysts reduction was carried out in situ at 673 K for 10 h in H$_2$ flow. For this isoparaffin direct synthesis via FTS reaction, the reaction temperature and pressure were 533 K and 1.0 MPa respectively. The ratio of H$_2$ to CO in the syngas was 2. In the reaction system, one ice trap set before the back pressure regulator was used to capture the effluent heavy products from the reactor. The solvent and internal standard inside the trap were n-octane and n-heptane, respectively, for the zeolite capsule catalysts, but they were n-heptadecane and tridecane, respectively, while doing the conventional FTS reaction on Co/SiO$_2$ catalyst without zeolite. Other light components through the ice trap were online heated at 398 K and finally analyzed by an online gas chromatography (Shimadzu, FID, GC-14B) equipped with a capillary column (J&W Scientific GS-Alumina, i.d. 0.53 mm × 30 m). Another gas chromatography (Shimadzu, TCD, GC-8A) was used to determine the catalysts activity using 3% argon in syngas as the internal standard. Another trap with concentrated sulfuric acid was set behind the back pressure regulator to identify the olefins contained in the light components. Liquid oil collected by ice trap was

Table 1. Physical and Chemical Properties of Support and Different Zeolite Capsule Catalysts

| samples	specific surface area (m²/g)	pore volume (cm³/g)	weight increment of zeolite capsule (%)	thickness of zeolite capsule (μm)	NH₃ uptake (μmol/g cat)	size of Co₃O₄ (nm)
SiO₂	323	1.142	0		5.5	
Co/SiO₂	269.8	1.100	0		9.3	12
Co/SiO₂-Z-1	275.3	0.529	11.5	2.3	47.0	11
Co/SiO₂-Z-2	286.1	0.406	17.2	7.6	56.8	12
Co/SiO₂-Z-2S	306.3	0.310	25.1	23.6	79.2	14
Co/SiO₂-Z-7	310.9	0.282	24.3	23.1	76.4	13

separated into two parts to be analyzed by the same FID mentioned above, because comparing one part which was treated by sulfuric acid with another one could identify the olefins content.[9] For the conventional FTS catalyst Co/SiO₂, the oil products were further analyzed by a high-temperature gas chromatography (HP6890) in detail besides the FID gas chromatography mentioned above.

Experiment on two-stage reaction using the catalyst of Co/SiO₂-Z-7 + Pd/SiO₂ was performed in the same reactor, as shown in Figure 1. The catalyst loading sequence from the reactor inlet to exit was glass beads, Co/SiO₂-Z-7 catalyst, Pd/SiO₂ catalyst, and then glass wool. Experiment manipulation and products analysis method were the same to the FTS reaction on single zeolite capsule catalyst.

3. Results and Discussion

Catalyst Characterization. Figure 2 showed the XRD patterns of Co/SiO₂, zeolite capsule catalysts Co/SiO₂-Z-X (X = 1, 2, 2S, and 7) and pure zeolite powder H-ZSM-5 prepared by the same method but without Co/SiO₂ pellet. Peaks

of H-ZSM-5 and Co₃O₄ of the capsule catalysts can be distinguished clearly. The XRD peaks intensity of zeolite on capsule catalysts increased from the Co/SiO₂-Z-1 to Co/SiO₂-Z-7, suggesting the increasing of zeolite loading amount on the capsule catalysts by controlling the hydrothermal synthesis duration. The weight increment of zeolite capsule catalysts after the hydrothermal synthesis had been exhibited in Table 1. This result accorded with one general rule of zeolite membrane synthesis that the crystallization time and hydrothermal synthesis repeated times decided zeolite coating amount. It is interesting to find that the catalyst of Co/SiO₂-Z-2S with twice synthesis had the similar weight increase and membrane thickness to those of Co/SiO₂-Z-7 with the crystallization time of 7 days. Perhaps it was easier for zeolite membrane growth on the zeolite layer than on the naked Co/SiO₂ substrate. Moreover, similar Co₃O₄ size of zeolite capsule catalysts to conventional Co/SiO₂ catalyst, as also listed in Table 1, indicated that this hydrothermal synthesis had no obvious effect on the cluster size or distribution
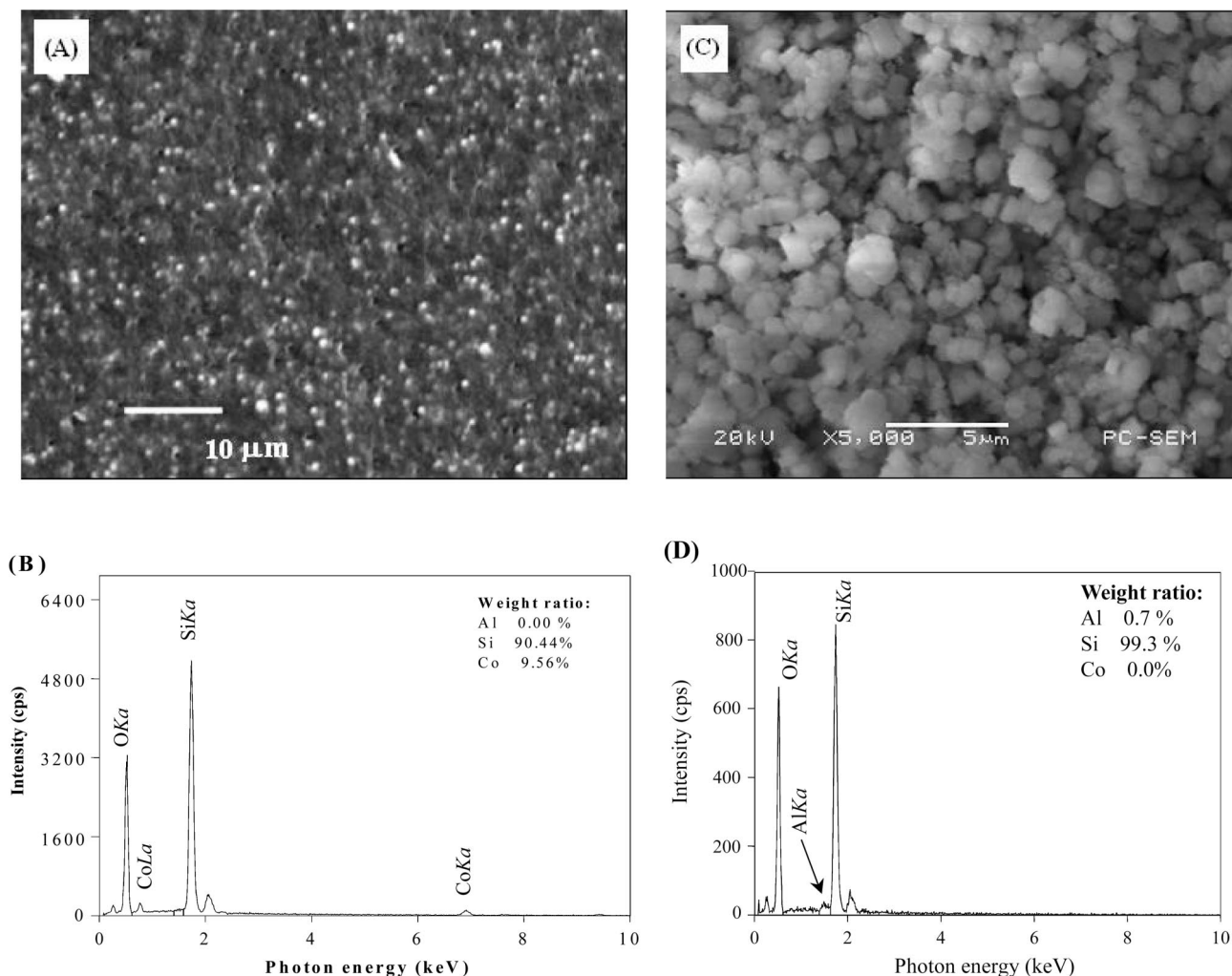
Figure 3. Surface SEM image and EDS analysis of the Co/SiO₂ and zeolite capsule catalyst. (A and B) Co/SiO₂. (C and D) Co/SiO₂-Z-1.

of Co_3O_4 on SiO_2 surface, suggesting this zeolite capsule catalyst preparation was successful.

The pore properties and suface acidic sites data of zeolite capsule catalysts were also listed in Table 1. The specific surface area of Co/SiO_2-Z-X ($X = 1, 2, 7$) increased from 275.3 to 310.9 m^2/g, and the pore volume decreased from 0.529 to 0.282 cm^3/g, also indicating the linear increase of zeolite coating amount of zeolite capsule catalysts. Co/SiO_2-Z-2S had the similar specific surface area and pore volume to those of Co/SiO_2-Z-7. All these data, such as XRD, NH_3-TPD and BET, accorded with the weight increment of zeolite capsule exhibited in Table 1, indicating the zeolite loading amount on the capsule catalysts can be adjusted easily only by controlling the hydrothermal synthesis conditions. Furthermore, the fact that catalyst acidity changed with increasing the zeolite coating amount, had been reported in our previous paper.[9] A linear relationship between the catalyst acidity and the zeolite coating amount was obtained, indicating that the property of the acidic sites was the same, despite of hydrothermal synthesis conditions. But, the amount of the acidic sites increased with increasing crystallization time and hydrothermal synthesis times.

SEM and EDS were employed to analyze the catalyst surface structure and chemical composition. Figure 3A and C showed the surface SEM images of Co/SiO_2 and Co/SiO_2-Z-1 zeolite capsule catalyst respectively. In Figure 3C, H-ZSM-5 crystallites constructing the zeolite capsule on the surface of Co/SiO_2 substrates could be observed clearly, while there was no crystal on the Co/SiO_2 pellet as shown in Figure 3A. Surface EDS analysis of the uncovered catalyst Co/SiO_2 was shown in Figure 3B. The signals could be detected, and the cobalt weight ratio 9.34% was close to the original catalyst preparation content. For the zeolite capsule catalyst, Co/SiO_2-Z-1, EDS analysis result in Figure 3D gave no signals of cobalt, confirming the integrality of the zeolite membrane enwrapped Co/SiO_2 pellet, suggesting that there was no submicrometer pinhole or crack of the zeolite capsule.

In order to reveal the information on the interface connection of capsule catalyst core with its capsule shell, SEM and linear EDS analysis on catalyst cross-section were conducted. Cross-sectioned SEM analysis on Co/SiO_2-Z-7, the first stage catalsyt in two-stage FTS reaction, was shown in Figure 4. A compact zeolite membrane can be observed at the outside of Co/SiO_2 substrate. The thickness of zeolite membrane was about 23.1 μm. Moreover, there was no gap or submicrometer pinhole on the membrane, suggesting that it was defect-free. From its linear EDS analysis, at the interface of the Co/SiO_2 substrate with zeolite capsule, the radial distribution of Si dropped suddenly while that of Al increased a little, indicating the phase change from SiO_2 to H-ZSM-5, proving the complete coverage of zeolite membrane onto Co/SiO_2 core. Similar findings were also obtained on other zeolite capsule catalysts with the crystallization time of 1 or 2 d. The difference was that they had thinner zeolite membrane. For zeolite capsule catalyst Co/SiO_2-Z-1, or 2, thickness of zeolite membrane was 2.3 and 7.6 μm, respectively. Twice-synthesized catalyst Co/SiO_2-Z-2S had the larger membrane thickness than Co/SiO_2-Z-1 or 2, but similar to Co/SiO_2-Z-7. Different zeolite membrane thickness, namely different zeolite loading amounts, also suggested that it is feasible to control the zeolite capsule properties only by adjusting the hydrothermal synthesis conditions.

Zeolite capsule catalyst had two parts: one was the Co/SiO_2 core and another was the H-ZSM-5 zeolite shell. During the hydrothermal synthesis, some mother liquid entered the pore of Co/SiO_2 and, then, settled in the core as the silica oxide solid
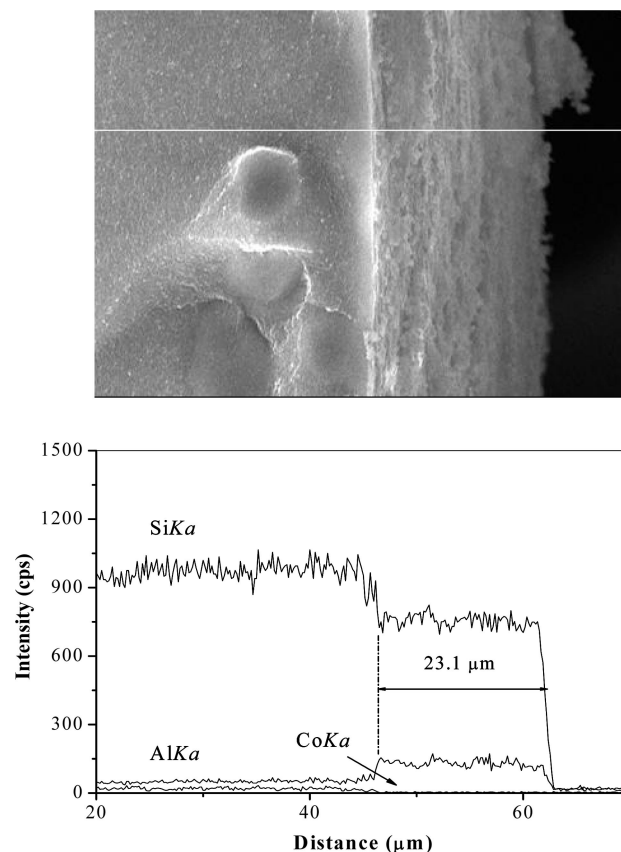
**Figure 4.** Cross-sectional SEM image and line EDS analysis of zeolite capsule catalyst Co/SiO_2-Z-7.

after the zeolite capsule catalyst calcination, reducing the real pore volume of original Co/SiO_2. This "anchor" phenomenon is very important for the formation of stable capsule catalyst. We used the weight increment between naked Co/SiO_2 catalyst and the obtained calcined capsule catalyst to determine the pure weight of the zeolite membrane. This calculation method was reliable no matter where the anchor part of the membrane was. There was no any loss in filtration of the samples and Co/SiO_2 was very stable during zeolite synthesis.

Isoparaffin Synthesis Performance by Single- and Two-Stage FTS Reaction. In single catalyst FTS reaction, the isoparaffin synthesis performance was tested on the catalyst of Co/SiO_2 and four zeolite capsule catalysts Co/SiO_2-Z-1, 2, 2S, and 7. The reaction performances were presented in Table 2. Under $W_{Co/SiO2}/F_{CO+H2} = 10$ g·h/mol, all the capsule catalysts gave the similar CO conversions, which were slightly lower than that of the conventional FTS catalyst Co/SiO_2, probably because of the partial coverage of Co active sites on the core by zeolite membrane during the hydrothermal synthesis process. From Co/SiO_2-Z-1 to Co/SiO_2-Z-7, the activity did not decrease with the enhanced capsule thickness, indicating that the rate-controlling step was not the diffusion inside the zeolite membrane. These should be attributed to the higher diffusion efficiency of H_2 to CO through zeolite capsule. In the capsule catalyst core, there was a higher H_2/CO ratio than the syngas especially with the increase of capsule thickness, accelerating the conversion of CO. This is supported by the CH_4 selectivity change trend in Table 2 where CH_4 selectivity was higher for the capsule catalyst with larger thickness because CH_4 forms quicker under higher H_2/CO ratio. For the isoparaffin direct synthesis, although conventional FTS catalyst Co/SiO_2 exhibited the highest catalytic activity, it had the lowest isoparaffin synthesis selectivity of 0.3%.

Table 2. Reaction Performance of Conventional and Zeolite Capsule Catalysts[a]

| catalyst | $W_{Co/SiO2}/F_{CO+H2}$ (g·h/mol) | conv % CO | selectivity (%) | | C_n (%) | C_{iso} (%) | $C^=$ (%) | $C_{iso}/C_n{}^b$ ($n \geq 4$) | $C^=/C_n{}^c$ ($n \geq 2$) |
			CH$_4$	CO$_2$					
Co/SiO$_2$	10	98.4	15.7	10.6	81.3	0.3	18.4	0	0.28
Co/SiO$_2$-Z-1	10	83.6	22.7	10.0	78.2	14.2	7.6	0.37	0.14
Co/SiO$_2$-Z-2	10	85.5	31.3	10.2	66.5	15.9	17.6	0.73	0.51
Co/SiO$_2$-Z-2S	10	86.5	31.9	13.9	66.3	12.7	21.0	0.68	0.66
Co/SiO$_2$-Z-7	10	86.1	37.4	7.0	59.3	13.4	27.3	1.88	1.35
	5	52.1	38.7	3.1	59.0	12.5	28.5	1.11	1.35
Co/SiO$_2$-Z-7 + Pd/SiO$_2$	10	86.4	35.2	5.8	68.0	27.8	4.2	1.17	0.13
	5	53.2	36.1	2.6	76.2	20.2	3.6	0.97	0.1

[a] Reaction conditions: 533 K, 1.0 MPa, 6 h, H$_2$/CO = 2. [b] C_{iso}/C_n is the ratio of isoparaffin to n-paraffin of C$_{4+}$. [c] $C^=/C_n$ is the ratio of olefin to n-paraffin of C$_{2+}$.
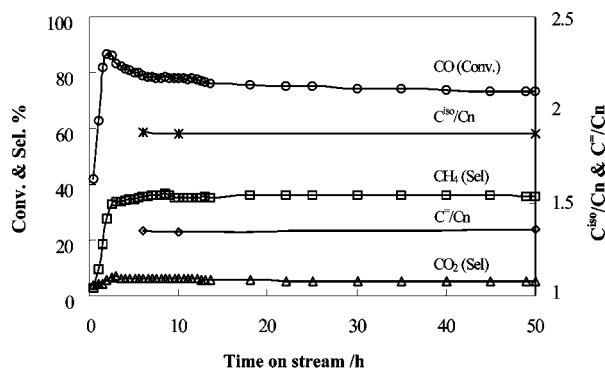
Figure 5. Reaction performance of 50 h of continuous FTS using Co/SiO$_2$-Z-7. The reaction conditions were as follows: 533 K, 1.0 MPa, H$_2$/CO = 2; (○) CO conversion, (□) CH$_4$ selectivity, (△) CO$_2$ selectivity, (*) C_{iso}/C_n, (◇) $C^=/C_n$.

Zeolite capsule catalysts were very effective for the direct synthesis of isoparaffin via FTS. With increasing zeolite membrane amounts, the ratio of isoparaffin to n-paraffin ($\geq$C$_4$) increased dramatically for the catalysts of Co/SiO$_2$-Z-X (X = 1, 2, and 7). But, it is interesting that Co/SiO$_2$-Z-2S had the lower isoparaffin selectivity than Co/SiO$_2$-Z-7, even though it had a similar zeolite coating amount. These findings might be attributable to the different zeolite membrane properties caused by the (twice) repeated hydrothermal synthesis. The mother liquid capability of offering nurture for zeolite membrane growth weakened during the single hydrothermal synthesis to prepare Co/SiO$_2$-Z-X (X = 1, 2, and 7). Whereas, twice-repeated hydrothermal synthesis could keep a stable nurture supply, resulting in a thicker zeolite membrane in shorter time with the possible microstructural change such as grain size or orientation and dissimilar acidic sites amounts and/or intensity.

Therefore, the yield of isoparaffin depended on not only the zeolite membrane coating amount but also the capsule catalyst preparation method. Furthermore, methane selectivity increased with increasing the zeolite coating amount, which should be attributed to the higher H$_2$/CO ratio in the core part of the capsule catalyst, which is decided by the higher diffusion efficiency of H$_2$ over that of CO inside the zeolite membrane. To confirm the reaction stability and characteristics of zeolite capsule catalysts, the 50 h continuous reaction test on Co/SiO$_2$-Z-7 was presented in Figure 5. The CO conversion, CH$_4$ selectivity, CO$_2$ selectivity, ratio of isoparaffin to n-paraffin, and ratio of olefin to n-paraffin were stable during the entire experimental duration. And, the zeolite capsule catalyst had a quick arrival at steady state compared to other conventional FTS catalysts, because of the special consecutive reaction model (one FTS, another cracking and isomerization) realized by its novel shell–core catalyst structure. The reaction heat of FTS was in situ consumed here by the endothermal cracking reaction of FTS hydrocarbons, avoiding overheating the FTS catalyst bed,
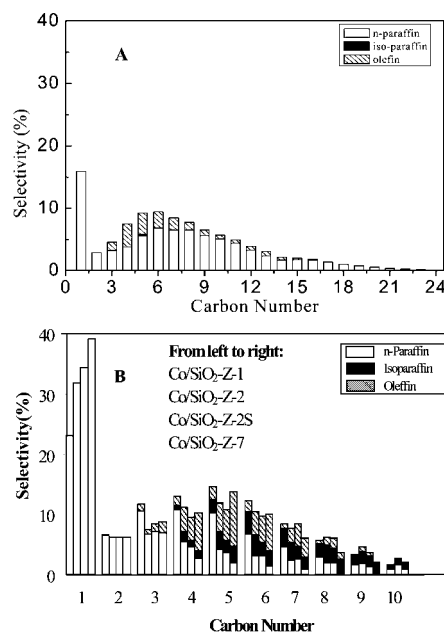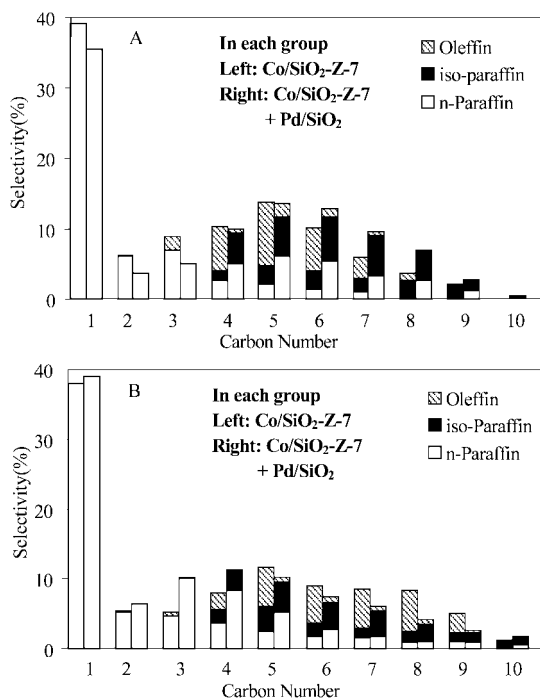

Figure 6. Product distribution of FTS reaction on the catalyst (A) Co/SiO$_2$ and zeolite capsule catalysts (B) Co/SiO$_2$-Z-X (X = 1, 2, and 7). The reaction conditions were as follows: 533 K, 1.0 MPa, 6 h, $W_{Co/SiO2}/F_{CO+H2}$ = 10 g·h/mol, H$_2$/CO = 2.

which was a troublesome problem in other conventional gas-phase FTS reactions.

Figure 6 showed the product distribution of Co/SiO$_2$ catalysts and four zeolite capsule catalysts under the $W_{Co/SiO2}/F_{CO+H2}$ = 10 g·h/mol. Different from the hydrocarbon distribution of conventional Co/SiO$_2$ catalyst, zeolite capsule catalysts gave a very sharp product distribution. To all capsule catalysts, the hydrocarbons with carbon number more than 11 were suppressed totally, which should be attributed to the role of the zeolite capsule reaction field. The FTS products produced by the core catalyst must pass through the H-ZSM-5 zeolite capsule to escape. Consequently, long-chain hydrocarbons stayed in the zeolite membrane longer, leading to the fact that all long-chain hydrocarbons were cracked and isomerized, suppressing the selectivity of long-chain paraffin and enhancing the selectivity of light isoparaffin remarkably.[10]

Although single FTS reaction using the zeolite capsule catalysts, especially that using Co/SiO$_2$-Z-7, had achieved high selectivity of the isoparaffin via direct synthesis method, the olefins content increased synchronously due to the cracking of long-chain hydrocarbons by the zeolite capsule. In order to lower the olefin selectivity, a two-stage reaction using the zeolite capsule catalyst Co/SiO$_2$-Z-7 + Pd/SiO$_2$ was investigated. The first-stage catalyst in the reactor was Co/SiO$_2$-Z-7, and that of the second-stage was Pd/SiO$_2$ in

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Figure 7. Product distribution of single FTS reaction on the catalyst Co/SiO$_2$-Z-7 and two-stage reaction on the Co/SiO$_2$-Z-7 + Pd/SiO$_2$. (A) $W_{Co/SiO2}/F_{CO+H2}$ = 10 g·h/mol. (B) $W_{Co/SiO2}/F_{CO+H2}$ = 5 g·h/mol. The reaction conditions were as follows: 533 K, 1.0 MPa, 6 h, H$_2$/CO = 2.

the same reactor, as exhibited in Figure 1. During the reaction, syngas passing through the first stage reacted similarly to the reaction on a single zeolite capsule catalyst. And then, the effluent products from first stage entered the second stage inside the same reactor. The olefins in the products were hydrogenated immediately by the hydrogenation on Pd/SiO$_2$. As a result, the selectivity of isoparaffin was increased obviously compared with that on the single zeolite capsule catalyst Co/SiO$_2$-Z-7, even if the W/F value was varied as listed in Table 2. The selectivity of olefins was markedly decreased from 27.3% to 4.2% for $W_{Co/SiO2}/F_{CO+H2}$ = 10 g·h/mol, and it was also lowered from 28.5% to 3.6% when $W_{Co/SiO2}/F_{CO+H2}$ = 5 g·h/mol, while the syngas conversion and methane selectivity were kept almost constant.

The product distributions of FTS reaction on the single zeolite capsule catalyst Co/SiO$_2$-Z-7 and that of the two-stage reaction

on the catalyst Co/SiO$_2$-Z-7 + Pd/SiO$_2$ were compared in Figure 7. From Figure 7A and B, it could also be found that two-stage FTS reaction on Co/SiO$_2$-Z-7 + Pd/SiO$_2$ had a similar methane selectivity to that with single Co/SiO$_2$-Z-7, indicating that the second-stage reaction had no obvious effects on the methane selectivity and CO conversion of first-stage reaction, except for the olefin selectivity, compared with the single FTS reaction on the zeolite capsule catalyst. But, the selectivity of isoparaffin was markedly enhanced, which was contributed by the olefin hydrogenation happening on Pd/SiO$_2$ catalyst.

In order to depress the formation of olefin, we also tried to directly load the palladium onto the membrane surface of capsule catalyst using incipient wetness impregnation method. But, the result was not good and an improvement effect from Pd on the decreasing olefin content was not observed, possibly due to the fact that Pd could not be reduced with the strong interaction from the zeolite surface.

4. Summary and Conclusions

Four kinds of zeolite capsule catalysts were prepared successfully by coating H-ZSM-5 zeolite membrane onto the conventional FTS catalyst Co/SiO$_2$. Different hydrothermal synthesis conditions controlling the membrane thickness and zeolite coating amount were realized. Although these zeolite capsule catalysts showed slightly lower CO conversion than the conventional FTS Co/SiO$_2$ catalyst, they exhibited excellent selectivity on the light isoparaffin synthesis directly from syngas. Membrane thickness increased along with the extended crystallization time or repeated synthesis times, but the yield of isoparaffin was decided by not only the zeolite loading amount but also by the catalyst preparation method. Zeolite capsule catalyst Co/SiO$_2$-Z-7 gave high selectivity of isoparaffin comparing with Co/SiO$_2$-Z-1, 2, or 2S, but the olefin content increased at the same time. In two-stage FTS reactions, the effluent olefins from the fist stage of zeolite capsule catalyst received hydrogenation further on the Pd/SiO$_2$ catalyst, increasing sharply the selectivity of middle isoparaffins keeping the CO conversion and methane selectivity constant. The design of a zeolite capsule catalyst offered a novel concept in syngas-to-gasoline conversion. The combination of a zeolite capsule catalyst with a hydrogenantion catalyst possibly opened a new way to produce isoparaffin selectively and constantly.