Insights into the promotional roles of palladium in structure and performance of cobalt-based zeolite capsule catalyst for direct synthesis of C₅-C₁₁ iso-paraffins from syngas

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Abstract:

Pd-promoted zeolite capsule catalyst (Co/Pd/SiO₂-HZSM5) was developed by coating H-ZSM-5 zeolite shell over Pd-modified core catalyst (Co/Pd/SiO₂), and employed for direct synthesis of C₅-C₁₁ iso-paraffins from syngas via Fischer-Tropsch synthesis (FTS). The roles of Pd promotion in structure and performance of the capsule catalyst for C₅-C₁₁ iso-paraffins synthesis were deeply studied. Structure characterizations (XRD, FTIR, TPR, and XPS) indicated that the main cobalt species in Pd-promoted capsule catalyst was cobalt silicate, while Co₃O₄ was the predominant cobalt species in un-promoted capsule catalyst (Co/SiO₂-HZSM5). Evolution of cobalt

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species in the synthesis of Pd-promoted capsule catalyst revealed that Pd improved the formation of cobalt silicate in strong basic TPAOH solution during the hydrothermal synthesis of H-ZSM-5 zeolite shell. It was found that Pd not only promoted the reduction of cobalt oxides, but also improved the reduction of cobalt silicate, which could not be reduced under traditional reduction condition for cobalt-based FTS catalysts. Catalytic tests indicated that Pd-promoted capsule catalyst exhibited highly enhanced performance for C₅-C₁₁ iso-paraffins synthesis with molar ratio of iso-paraffins to n-paraffins up to 1.03. Long-chain hydrocarbons were completely eliminated in the capsule catalyst as a consequence of spatial confinement effect of the H-ZSM-5 zeolite shell. The hydrogenation of olefins to paraffins, which was enhanced by Pd promotion, together with the hydrocracking and isomerization of primary hydrocarbons, contributed to the high selectivity of C₅-C₁₁ iso-paraffins in Pd-promoted capsule catalyst.

Keywords: Cobalt, Fischer-Tropsch synthesis, Capsule catalyst, Palladium promotion, H-ZSM-5 zeolite shell, C₅-C₁₁ iso-paraffins

1. Introduction

The direct synthesis of C₅-C₁₁ iso-paraffins (main components of gasoline) from syngas via modified Fischer-Tropsch synthesis (FTS) has received increasing interests due to the dwindling of oil resource and distinctive product advantages of sulphur-free, nitrogen-free, and aromatic-free properties [1-7]. As a result of higher C₅-C₁₁ iso-paraffins selectivities and the complete elimination of the long-chain hydrocarbons (carbon number higher than 12) by the spatial confinement effect, the capsule catalysts with zeolite shells and FTS catalyst cores are more promising [4, 8-11]. Cobalt-based FTS catalysts, which have the advantages of higher activities per gram catalyst and lower selectivities to CO₂ and C₂-C₄ gaseous hydrocarbons compared with the iron-based catalysts [12-16], are primarily selected as the cores of the capsule catalysts. Meanwhile, the H-type zeolites with strong acidic sites, such as H-ZSM-5, H-Beta, and H-MOR are usually employed as the shells of the capsule catalysts [4, 9-11]. For cobalt-based capsule catalysts, the activities and selectivities to iso-paraffins were mainly determined by the reduction levels of cobalt and the hydrocracking/isomerization capability for the primary hydrocarbons formed in the core catalysts.

Pd was widely used to improve the performance of zeolite and FTS hybrid catalysts for C₅-C₁₁ iso-paraffins synthesis [11, 17-18]. It is well accepted that Pd could improve the reduction and dispersion of cobalt-based FTS catalysts [17, 19-21]. Pd and other noble metals, such as Pt and Ru, when supported on or mixed with acidic zeolites, could also enhance the hydrogenation and isomerization of hydrocarbons and consequently increase the selectivity to iso-paraffins [11, 22-23]. The direct impregnation of Pd over zeolite capsule catalyst could result in a difficult reduction of Pd cation due to its strong

interaction with the zeolite surface, which was unfavorable for the activity of the catalyst [17, 24]. Dry sputtering was an ideal method to prepare the catalyst with weak interaction between Pd and zeolite surface [17, 23-24], however, this method is more suitable for preparing the catalysts in a laboratory scale and difficult to be used in a large scale at present. In addition, there is an alternative method to prepare the Pd-promoted capsule catalysts by first introducing Pd into the core catalysts (such as Co/SiO₂) and then synthesizing the zeolite shell of the capsule catalyst. Pd implanted by this method might have a weak interaction with SiO₂ support and zeolite shell, and the prepared catalyst is expected to exhibit excellent performance for C₅-C₁₁ iso-paraffins synthesis.

In this work, Pd-promoted capsule catalyst (Co/Pd/SiO₂-HZSM5) was developed by coating H-ZSM-5 zeolite shell over Pd-modified core catalyst (Co/Pd/SiO₂), and employed for the direct synthesis of C₅-C₁₁ iso-paraffins from syngas. The role of Pd promotion in structure and performance of the capsule catalyst for C₅-C₁₁ iso-paraffins direct synthesis was systematically studied. It is interesting to find that the main cobalt species in the Pd-promoted capsule catalyst was cobalt silicate while Co₃O₄ was the predominant cobalt species in the un-promoted capsule catalyst (Co/SiO₂-HZSM5). Furthermore, it was disclosed that Pd not only improved the reduction of cobalt oxides, but also promoted the reduction of cobalt silicate. Catalytic tests indicated that the Pd-promoted capsule catalyst exhibited excellent C₅-C₁₁ iso-paraffins synthesis performance with molar ratio of iso-paraffins to n-paraffins as high as 1.03.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of the core catalysts

Co(NO₃)₂·6H₂O (Wako Co. Japan) and Pd(NH₃)₂(NO₃)₂ solution (4.59 wt% Pd, Tanaka Noble Metal Co. Japan) were used as the Co and Pd precursors in this work, respectively. Silica pellets (Fuji Silysia Chemical Ltd., Cariact Q-10, BET surface area: 292 m²/g, pore volume: 1.02 cm³/g, and particle size: 0.85-1.70 mm) were used as support of the core catalyst. The core catalyst with 10 wt% cobalt was prepared by incipient-wetness impregnation (IWI) method. A desired amount of cobalt nitrate solution was impregnated into SiO₂ support under the assistance of ultrasonic. The impregnated sample was first dried under vacuum condition at room temperature for 2 h, and then dried at 120 °C for 12 h. The dried sample was calcined in air at 400 °C for 2 h to obtain the core catalyst, which was denoted as Co/SiO₂. Pd-modified core catalyst with 0.5 wt% Pd and 10 wt% Co was prepared by sequence impregnation method. A desired amount of Pd(NO₂)₂(NH₃)₂ solution was first impregnated over SiO₂ pellets, and then dried and further calcined at 400 °C for 2 h. The obtained sample was further impregnated with cobalt nitrate solution. After the following drying at 120 °C for 12 h and calcination at 400 °C for 2 h, the Pd-modified core catalyst was obtained, which was named as Co/Pd/SiO₂.

2.1.2. Preparation of H-ZSM-5 zeolite capsule catalysts

The H-ZSM-5 zeolite precursors with the molar ratio of 1TEOS: 0.25TPAOH: 0.0125Al(NO₃)₃·9H₂O: 4EtOH: 60H₂O was stirred in a Teflon reactor for 6 h to get a homogeneous solution. Then, the un-modified (Co/SiO₂) or Pd-modified core catalyst (Co/Pd/SiO₂) was put into Teflon reactor, and kept in hydrothermal synthesis equipment at 180 °C for 48 h with a rotation rate of 2 rpm (DRM-420DA, Hiro Company, Japan). After the hydrothermal synthesis, the sample was washed with deionized water until neutral pH, and then vacuumed in a desiccator for 1 h, dried at 60 °C for 12 h, and

calcined at 500 °C for 5 h to obtain the capsule catalyst. The as-prepared un-promoted and Pd-promoted zeolite capsule catalysts were assigned as Co/SiO₂-HZSM5 and Co/Pd/SiO₂-HZSM5, respectively. For comparison, the pure H-ZSM-5 zeolite was prepared using the same procedure, except for the absence of core catalyst. The prepared H-ZSM-5 zeolite was named as H-ZSM-5.

2.1.3. Preparation of the physical mixture catalyst

The pure H-ZSM-5 zeolite powder and crashed Co/Pd/SiO₂ catalyst were physically mixed at the weight ratio of 1:5, similar to that in capsule catalyst Co/Pd/SiO₂-HZSM5. Then, the obtained mixture was pressured, and granulated into the size range of 0.85-1.70 mm. The physical mixture catalyst of H-ZSM-5 zeolite and Co/Pd/SiO₂ catalyst was denoted as Co/Pd/SiO₂/HZSM5-M.

2.1.4. Treatment of Co/SiO₂ and Co/Pd/SiO₂ core catalysts by TPAOH solution

To investigate the roles of Pd and TPAOH solution in hydrothermal process of the core catalyst, 0.5 g Co/SiO₂ or Co/Pd/SiO₂ was treated with TPAOH solution under the same condition of H-ZSM-5 zeolite shell synthesis (180 °C, 48 h, and 2 rpm). TEOS, Al(NO₃)₃·9H₂O, or EtOH was not used for the treatment by TPAOH solution. The two treated core catalysts were denoted as Co/SiO₂-TPAOH and Co/Pd/SiO₂-TPAOH, respectively.

2.2. Catalyst Characterization

The scanning electron microscope (SEM, JEOL JSM-6360 LV) equipped with energy dispersive spectroscopy (EDS, JED-2300) was used to collect the morphology and elemental information of the capsule catalysts.

Phase structures of the samples were measured by X-ray diffraction (XRD) using a Rigaku RINT2400 diffractometer with Cu K α radiation (λ =0.154 nm) in the 2 θ angle

range of 2-80°. The operations were performed at 40 kV and 40 mA. In this work, the XRD patterns of reduced core and capsule catalysts were also measured. Before the measurement, the fresh core and capsule catalysts were first reduced by H₂ (40 ml/min) at 400 °C for 10 h, and then passivated by 1% O₂/Ar (15 ml/min) at room temperature for 5 h. The reduced catalyst was named as X-R, where X was the name of the fresh catalyst. For example, Co/Pd/SiO₂-HZSM5-R was the Co/Pd/SiO₂-HZSM5 catalyst after H₂ reduction.

N₂ physisorption and H₂ chemisorption of the prepared catalysts were conducted in the same equipment: Micromeritics 3Flex Surface Characterization Analyzer. For N₂ physisorption, the samples were first degassed at 200 °C for 2 h. N₂ adsorption–desorption isotherms were measured at -196 °C. The specific surface area (S_{BET}) and total pore volume (V_t) were calculated by the Brunauer–Emmett–Teller (BET) and single point methods, respectively. Micropore surface area (S_{micro}) and pore volume (V_{micro}) were obtained by t-plot method. Average pore diameter (D_a) was calculated by $4V_t/S_{BET}$. For H₂ chemisorption, degas was first carried out at 300 °C for 1 h. Then, the sample was reduced at 400°C for 3 h, and evacuated at same temperature for 1 h to remove any chemisorbed H₂. The isotherms were measured at 50 °C. Dispersion of cobalt (D_{Co}) was calculated based on the spherical geometry and adsorption stoichiometry of H/Co=1. The average crystal diameter of cobalt (d_{Co}) was estimated by $96/(D_{Co}\%)$. For Pd-promoted core and capsule catalysts, H₂ could chemisorb on both Pd and Co. Therefore, for the calculation of the Co dispersion, the amount of H₂ chemisorbed on Pd should be subtracted. In this work, we assumed that Pd was totally reduced during the reduction process. According to the literature [25, 26] the Pd dispersions were usually in the region of 20-30% at the loading of about 0.5 wt%. So,

we assumed the dispersion of Pd was 30% to estimate the amount of H₂ chemisorbed on Pd (stoichiometry of H/Pd=1). Based on above assumptions, the amount of H₂ chemisorbed on cobalt and the dispersion of cobalt was calculated.

Infrared transmission spectra of the samples were recorded in the air atmosphere with a Shimadzu Fourier Transform Infrared Spectrophotometer (FTIR-8400). Before the measurement, samples were mixed with KBr and then pressured into tablets. X-ray photoelectron spectra (XPS, Thermo ESCALAB 250 Xi) were used to analyze the Co and Pd states on the crushed catalysts. The binding energy was corrected by taking C1s line at 284.5 eV as an internal standard.

The reduction behaviors of the samples were measured by H₂ temperature-programmed reduction (TPR, BELCAT-B). 30 mg sample was first dried at 150 °C in argon flow for 2 h, and then cooled down to 50 °C. Next, the sample was heated from 50 to 800 °C at a rate of 5.0 °C/min in 5 % H₂/Ar flow (30 ml/min). In order to verify the promotion effect of Pd for different cobalt species reduction, TPR of Co/Pd/SiO₂-HZSM5 was first measured at 400 °C for 10 h, and then at 800 °C for 40 min. Heating rate of the sample was set at a constant of 5.0 °C/min (from 50 to 400 °C or from 400 to 800 °C). H₂ consumption during the reduction was detected by a thermal conductivity detector (TCD). Thermal gravimetry (TG) analysis of the used catalysts was carried out on a NETZSCH TG-DTA2010SA-TD23 thermogravimetric analyzer from room temperature to 1000 °C with the rate of 10 °C /min under air flow (50 ml/min).

2.3. Catalytic tests for C₅-C₁₁ iso-paraffins synthesis

The C₅-C₁₁ iso-paraffins synthesis was conducted in a fixed-bed reactor (i.d. 8 mm) at 260 °C and 1.0 MPa. Prior to the reaction, the catalyst was reduced in-situ by pure H₂

(40 ml/min) at 400 °C for 10 h. After the reactor was cooled to 150 °C, the syngas with H₂/CO mole ratio of 2 was introduced. Then, the pressure was regulated to 1.0 MPa. The reaction was started by raising the temperature to 260 °C. In order to achieve relative low CO conversions, a low W/F ratio of 2.5 gh/mol was used, where W was the weight of bare core catalyst or the weight of core catalyst in the capsule and physical mixture catalysts and F was the flow rate of syngas. The reaction time was set as 6 h. After the reactions, the catalysts were treated at 300 °C for 1 h by Ar flow. The used catalyst was named as X-U, where X was the name of the fresh catalyst. For example, Co/Pd/SiO₂-HZSM5-U was the Co/Pd/SiO₂-HZSM5 catalyst after catalytic test. The effluents (Ar, CO, CH₄, and CO₂) of the reaction were analyzed with online gas chromatograph with a TCD detector (Shimadzu, GC-320, active charcoal column). Light hydrocarbons (C1-C6) were analyzed with online gas chromatograph with a flame ionization detector (FID) (Shimadzu, GC-390B, J&W Scientific GS-Alumina capillary column). Liquid products collected in the ice trap with n-dodecane (0.1 g) being added as internal standard were analyzed by gas chromatograph with a FID detector (Shimadzu, GC-2014) equipped with a capillary column (silicone SE-30 column). Mass balances (MB) of the reactions were obtained by the ratio of the total carbon species produced and the amount of CO consumed. The selectivities of the products were calculated on a carbon basis. After repeat catalytic tests, we got the error value of $\pm 2\%$ in CO conversion and product selectivities in our system.

3. Results and discussion

3.1 Preparation and identification of the Pd-promoted and un-promoted capsule catalysts

3.1.1. SEM-EDS analysis of the capsule catalysts

In this work, the Co/SiO₂ and Co/Pd/SiO₂ catalysts were used as cores to prepare the capsule catalysts Co/SiO₂-HZSM5 and Co/Pd/SiO₂-HZSM5, respectively. The SEM images and EDS results of the external surface of the prepared capsule catalysts are shown in Fig. 1. H-ZSM-5 zeolite crystallites with sizes of about 1.5 μm were observed in both the un-promoted (Fig. 1a) and Pd-promoted (Fig. 1b) capsule catalysts. This result indicated that the H-ZSM-5 zeolite shells were successfully synthesized over the core catalysts. The EDS results showed that Al and Si were the major elements in the external surface of the capsule catalysts. No Co or Pd signal was detected in the external surfaces of the capsule catalysts, indicating that the core catalysts Co/SiO₂ or Co/Pd/SiO₂ were completely covered by H-ZSM-5 zeolite shells. It is interesting to find the Si/Al ratio in external surface of Co/Pd/SiO₂-HZSM5 (66.1) was much higher than that in external surface of Co/SiO₂-HZSM5 (24.1). For the two capsule catalysts, the recipe and procedure for the H-ZSM-5 zeolite shell synthesis were same. The different Si/Al ratios on external surfaces of the two capsule catalysts were mainly caused by the modification of Pd.

Fig. 1. SEM images and EDS results of the external surfaces of the capsule catalysts:

a,c, Co/SiO₂-HZSM5; b, d, Co/Pd/SiO₂-HZSM5.

The SEM images and EDS line scanning results along the cross-section of the capsule catalysts are displayed in Fig. 2. An obvious interface between core catalyst and H-ZSM-5 zeolite shell was found in the capsule catalyst Co/SiO₂-HZSM5, where the Al and Si signals abruptly changed. The thickness of the H-ZSM-5 zeolite shell in Co/SiO₂-HZSM5 was approximately 5.5 μm. For Co/Pd/SiO₂-HZSM5 (Fig. 2b), it is clear to see that a shell with thickness of 14.6 μm was formed, which was much thicker than that of Co/SiO₂-HZSM5. During the synthesis of the zeolite shell, part of the silica

in the core catalyst could be dissolved (or etched) in the strong basic solution under the hydrothermal condition [9, 27]. In Pd-promoted catalyst, Pd might act as a catalyst for improving the etching of silica support, which meant that more silica was dissolved and the etching of the core catalyst was deeper [28]. During the synthesis of the zeolite shells, a same amount of Al precursor was employed. Since more silica was dissolved (or etched) and employed for the synthesis of H-ZSM-5 zeolite shell over the Pd-promoted core catalyst, a higher of Si/Al ratio and thicker shell were achieved in the Pd-promoted capsule catalyst. Nevertheless, Pd signal was not detected in the core catalyst or the zeolite shell by EDS (Fig. 2b), which might be attributed to the small amount of Pd loading (0.5 wt%) in the core catalyst.

Fig. 2. SEM images and EDS line scanning results along the cross-section of the capsule catalysts: a, Co/SiO₂-HZSM5; b, Co/Pd/SiO₂-HZSM5.

3.1.2 Pore structure and H_2 chemisorption analysis of the core and capsule catalysts

Table 1. The structure characteristics of the fresh and used catalysts

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	V_{t} (cm^3/g)	V_{micro} (cm^3/g)	D_{a} (nm)	D_{Co} (%)	d_{Co} (nm)
Co/SiO ₂	268	13	0.90	0.01	13.4	3.1	31
Co/Pd/SiO ₂	265	11	0.85	0	12.8	4.3	22
Co/SiO ₂ -HZSM5	245	106	0.71	0.05	11.6	2.6	37
Co/Pd/SiO ₂ -HZSM5	217	88	0.65	0.04	12.0	2.2	43
Co/SiO ₂ -U	249	21	0.80	0.01	12.9	-	-
Co/Pd/SiO ₂ -U	249	7	0.80	0	12.9	-	-
Co/SiO ₂ -HZSM5-U	180	101	0.70	0.05	15.6	-	-
Co/Pd/SiO ₂ -HZSM- 5-U	210	86	0.65	0.04	12.4	-	-

Pore structures of the core and capsule catalysts were characterized by N_2 physisorption, and the results are presented in Table 1. The core catalysts Co/SiO₂ and Co/Pd/SiO₂ exhibited typical mesoporous structures with very small micropore surface areas and volumes. As a result of Pd promotion, the surface area and total pore volume of Co/Pd/SiO₂ were slightly smaller than those of Co/SiO₂. After the growth of the H-ZSM-5 zeolite shell, the micropore surface area and volume increased significantly. This result indicated that microporous zeolite was formed in the capsule catalysts. Co dispersion (D_{Co}) and crystal size (d_{Co}) in the core and capsule catalysts were estimated by H_2 chemisorption, which are also listed in Table 1. The Co dispersion in Co/Pd/SiO₂ (4.3%) was higher than that in Co/SiO₂ (3.1%). This result indicated that Pd promoted

the dispersion of cobalt in the core catalyst. The Pd existing in close proximity to Co could promote the reduction and dispersion of cobalt [20, 21]. It is worth noting that dispersions of cobalt in capsule catalysts were lower than those in the bare core catalysts. The possible reason is that the structures of the core catalysts changed during the synthesis of H-ZSM-5 zeolite shell, which resulted in the in-complete reduction of cobalt. Meanwhile, the crystalline sizes of cobalt were also overestimated for the capsule catalysts.

3.1.3. X-ray diffraction (XRD) analysis of the core and capsule catalysts

Fig. 3. XRD patterns of the core and capsule catalysts.

XRD patterns of the core and capsule catalysts are presented in Fig. 3. The diffraction peaks of the core catalyst Co/SiO_2 can be assigned to Co_3O_4 , indicating that the major phase of cobalt was Co_3O_4 . Pd-promoted core catalyst Co/Pd/SiO_2 showed similar diffraction peaks to Co/SiO_2 . The crystallite size of the Co_3O_4 calculated by the Scherrer equation was 12 nm in Co/SiO_2 , which was slightly larger than that in Co/Pd/SiO_2 (11 nm). This result indicated that Pd slightly improved the dispersion of

cobalt in the core catalyst. For capsule catalysts Co/SiO₂-HZSM5 and Co/Pd/SiO₂-HZSM5, the diffraction peaks for H-ZSM-5 zeolite crystallite were identified, demonstrating that H-ZSM-5 zeolite was formed in the capsule catalyst. Combined with the SEM-EDS and N₂ physisorption results (Fig. 1, Fig. 2, and Table 1), it can be concluded that Pd-promoted and un-promoted H-ZSM-5 zeolite capsule catalysts were successfully synthesized in this work. No diffraction peaks for Pd species were identified in Co/Pd/SiO₂ and Co/Pd/SiO₂-HZSM5 catalysts because of the small amount of Pd loading. It is noted that the diffraction peaks of Co₃O₄ were observed in capsule catalyst Co/SiO₂-HZSM5, but they disappeared in Pd-promoted capsule catalyst Co/Pd/SiO₂-HZSM5. This result suggested that the major phase Co₃O₄ in the core catalyst changed during the hydrothermal synthesis of H-ZSM-5 shell in Pd-promoted capsule catalyst.

Fig. 4. XRD patterns of the reduced core and capsule catalysts

XRD patterns of the reduced core and capsule catalysts are given in Fig. 4. After H₂ reduction at 400 °C for 10 h, diffraction peaks for Co₃O₄ disappeared and new peaks

for metallic cobalt were observed in the core catalysts (Co/SiO₂-R and Co/Pd/SiO₂-R). However, no diffraction peaks for metallic cobalt could be identified on the reduced capsule catalysts (Co/SiO₂-HZSM5-R and Co/Pd/SiO₂-HZSM5-R). The possible reason was that the reduced metallic cobalt had small crystalline sizes and was well dispersed in the capsule catalysts. Since XRD could not supply further information about the cobalt species in the capsule catalyst, other characterizations were required to identify the state of cobalt species in the Pd-promoted capsule catalyst.

3.2. Identification of cobalt species in Pd-promoted capsule catalyst

3.2.1. Fourier Transform infrared spectroscopy (FTIR) analysis

FTIR is one of the most conventional analysis tools for distinguishing the cobalt species, such as Co₃O₄ and cobalt silicate [13,29-30]. FTIR absorption spectra of the core and capsule catalysts were shown in Fig. 5. In the range of 400-1400 cm⁻¹, the bands at around 570 and 664 cm⁻¹ were related to BOB₃ and AOB₃ vibration modes of Co-O bonds in Co₃O₄, where B represented for Co ion in an octahedral position and A stood for the metal ions in a tetrahedral position. In addition, the band at approximately 913 cm⁻¹ could be assigned to cobalt silicate [29-30]. For the core catalysts and capsule catalyst Co/SiO₂-HZSM5, strong absorption peaks were observed at the wavenumbers of 570 and 664 cm⁻¹. This result indicated that the main cobalt species in these catalysts was Co₃O₄, which was in agreement with the XRD results (Fig. 3). In the case of Pd-promoted capsule catalyst Co/Pd/SiO₂-HZSM5, strong absorption peak at about 913 cm⁻¹ was found, while no obvious absorption peaks were observed at the wavenumber of 570 and 664 cm⁻¹. This result meant that the predominant cobalt species in the Co/Pd/SiO₂-HZSM5 was cobalt silicate. It was inferred that Co₃O₄ could be transformed

to cobalt silicate during the hydrothermal synthesis of zeolite shell on the core catalyst in the presence of Pd. Since cobalt silicate mostly had high dispersions and very small sizes, it was not detected by XRD in Fig. 3.

Fig. 5. FTIR spectra of the core and capsule catalysts.

3.2.2. X-ray photoelectron spectroscopy (XPS) analysis

Fig. 6. The Co 2p XPS spectra the core and capsule catalysts.

XPS is an effective surface chemical analysis technique that can help us to understand the state of cobalt species in the catalysts. The Co 2p spectra of the core and capsule catalysts were presented in Fig. 6. The binding energies of Co 2p_{3/2} peaks in core catalysts Co/SiO₂ and Co/Pd/SiO₂ were 780.3 and 780.7 eV, respectively. The spin-orbit splitting energies of these two catalysts ($\Delta E_{\text{Co } 2p_{1/2}-\text{Co } 2p_{3/2}}$) were about 15.1 eV, accompanying with weak shake-up satellites of 788.2 eV. These results indicated that the main cobalt species in Co/SiO₂ and Co/Pd/SiO₂ was Co₃O₄. The binding energy of Co 2p_{3/2} peak in Co/SiO₂-HZSM5 catalyst was 780.4 eV, but its spin-orbit splitting energy (16.0 eV) and shake-up satellite of Co/SiO₂-HZSM5 were higher than those of Co/SiO₂ catalyst. These results suggested that Co/SiO₂-HZSM5 exhibited more property of Co²⁺ species. In the case of Co/Pd/SiO₂-HZSM5 catalyst, the binding energy of Co

$2p_{3/2}$ was 781.7 eV and its spin-orbit splitting energy was 16.0 eV. The higher Co $2p_{3/2}$ binding energy and spin-orbit splitting energy combined with the FTIR result indicated that the predominant cobalt species in Co/Pd/SiO₂-HZSM5 was cobalt silicate [31-35].

Fig. 7. The Pd 3d XPS spectra of Co/Pd/SiO₂ and Co/Pd/SiO₂-HZSM5 catalysts.

In this work, Pd 3d XPS spectra of Pd-promoted core and capsule catalysts were also recorded, and presented in Fig. 7. The binding energies of Pd $3d_{5/2}$ in Co/Pd/SiO₂ and Co/Pd/SiO₂-HZSM5 catalysts were 336.8 and 336.3 eV, which could be assigned to PdO [36-38]. The slight decrease of Pd $3d_{5/2}$ binding energy after hydrothermal synthesis indicated that Pd species in the Co/Pd/SiO₂-HZSM5 was also PdO, but it trended to reduction state compared to that of Co/Pd/SiO₂.

3.3. Causes for cobalt silicate formation in Pd-promoted capsule catalyst

Fig. 8. XRD patterns of Co/SiO₂ and Co/Pd/SiO₂ catalysts after treatment with TPAOH solution.

XRD results have proved that the main cobalt species in Pd-promoted core catalyst Co/Pd/SiO₂ was Co₃O₄, but it changed into cobalt silicate in Pd-promoted capsule catalyst as demonstrated by XRD, FTIR, and XPS results. It can be inferred that cobalt silicate was formed during the hydrothermal synthesis of H-ZSM-5 zeolite shell and the following calcination. In the hydrothermal process, Pd and the strong basic template agent TPAOH might play important roles in the formation of cobalt silicate. To investigate the influence of Pd and TPAOH solution during hydrothermal process, the Pd-promoted and un-promoted core catalysts were treated by the TPAOH solution under the same condition as the hydrothermal synthesis of the zeolite shell. The XRD profiles of the Co/SiO₂ and Co/Pd/SiO₂ catalysts after treatment with the TPAOH solution are shown in Fig. 8. It is clear to see that the main phase of the TPAOH treated Co/SiO₂ was Co₃O₄, which was similar to the original core catalyst Co/SiO₂. It is noted that very weak diffraction peaks that can be assigned to MFI-typed zeolite were identified at a

magnified XRD signals. These results suggested that very small amount of SiO_2 was etched and MFI-typed zeolite was formed in the presence of the template agent TPAOH during the hydrothermal treatment [9,27]. For Pd-promoted core catalyst, the diffraction peaks of Co_3O_4 crystallite disappeared, and strong diffraction peaks of MFI-typed zeolite appeared after the treatment with TPAOH solution. It meant that Pd played important roles in the synthesis of the MFI-typed zeolite and the transformation of Co_3O_4 to cobalt silicate during the hydrothermal process [9, 28, 33].

3.4. Reduction behavior of Pd-promoted capsule catalyst

Fig. 9. H_2 -TPR profiles of the core and capsule catalysts.

H_2 -TPR was employed to study the reduction behavior of the Pd-promoted and un-promoted capsule catalysts. H_2 -TPR profiles of the core and capsule catalysts were presented in Fig. 9. The Co/SiO_2 core catalyst exhibited two reduction peaks at 260 and 330 °C, indicating the reduction of Co_3O_4 to Co via the intermediate CoO [13, 39-40]. The wide reduction range of Co/SiO_2 indicated different interactions between cobalt and silica. After Pd promotion, the reduction curve was clearly divided into two parts. H_2

reduction peaks markedly shifted from 260 °C to 150 °C and from 330 °C to 300 °C, which indicated that Pd improved the reduction of cobalt in the core catalyst [21]. For the capsule catalysts, except for the reduction peaks for Co₃O₄ in the temperature range of 150-500 °C, the reduction peaks at higher temperature (>500 °C) were ascribed to the cobalt species that have strong interaction with support, such as cobalt silicate [33]. The contents of cobalt in the forms of Co₃O₄ and CoSiO₃ in the core and capsule catalysts were estimated by the H₂ consumptions below and above 500 °C in the TPR profiles. The results are listed in Table 2. It is clear to see the main cobalt species in the core catalysts and capsule catalyst Co/SiO₂-HZSM5 was Co₃O₄. However, cobalt silicate was the main cobalt species in Co/Pd/SiO₂-HZSM5. This result further confirmed that more cobalt silicate was formed in the Pd-promoted capsule catalyst. From Fig. 9, it is also noted that the reduction temperature of cobalt silicate in Co/Pd/SiO₂-HZSM5 (about 730 °C) was lower than that in Co/SiO₂-HZSM5 (about 800 °C). This result suggested that Pd also promoted the reduction of cobalt silicate.

Table 2. H₂ consumptions and contents of cobalt species calculated from Fig.9

Sample	H ₂ consumption (peak area)		Cobalt content in the form of Co ₃ O ₄ (%)	Cobalt content in the form of CoSiO ₃ (%)
	<500 °C	>500 °C		
Co/SiO ₂	2.9E+06	0.3E+06	90.6	9.4
Co/Pd/SiO ₂	4.4E+06	0.3E+06	93.6	6.4
Co/SiO ₂ -HZSM5	2.5E+06	2.3E+06	52.0	48.0
Co/Pd/SiO ₂ -HZSM5	0.5E+06	1.7E+06	22.7	77.3

Fig. 10. H₂-TPR profiles of Co/Pd/SiO₂-HZSM5 catalyst under different reduction condition.

In order to verify the promotion effect of Pd for the reduction of cobalt silicate, the TPR of Co/Pd/SiO₂-HZSM5 was first measured at 400 °C for 10 h and then at 800 °C for 40 min, where the first step is the traditional reduction procedure for cobalt catalysts before FTS reaction [41-43]. The TPR profiles of the catalyst under different reduction condition are shown in Fig. 10. The H₂ consumption at 400 °C for 10 h (peak area: 3.16×10^6) is 4.3 times higher than that in the region of 400 to 800 °C and at 800 °C for 40 min (peak area: 7.29×10^5). This result indicated that approximately 81.1 % Co species could be reduced under the traditional reduction condition. Since the main cobalt species in the Co/Pd/SiO₂-HZSM5 was cobalt silicate, a large proportion of cobalt silicate must be reduced to metallic cobalt under the promotion of Pd. The Pd

located on the Co surface or in close proximity to Co could improve the reduction of cobalt silica [21,44]. There was also some cobalt silicate that could not be reduced at 400 °C for 10 h. This might be attributed to the low loading of Pd and a long distance between some cobalt silicate and Pd, where Pd could not improve the reduction of cobalt silicate.

3.5. Performance of Pd-promoted capsule catalyst for C₅-C₁₁ iso-paraffins synthesis

The catalytic tests of the bare core and capsule catalysts for the direct synthesis of C₅-C₁₁ iso-paraffins from syngas were carried out in a fixed bed reactor under the condition of 260 °C, 1.0 MPa, and H₂/CO=2. In order to achieve relative low CO conversions, a low W/F of 2.5 g·h/mol was employed for the catalytic tests. The activities and selectivities of the catalysts are summarized in Table 3. The bare core catalyst Co/SiO₂ exhibited a high CO conversion of 61.2%, but had a very low C₅-C₁₁ iso-paraffins (C_{iso}) selectivity of 1.3%. High turnover frequency (TOF) of 0.43 s⁻¹ and olefins selectivity of 14.4% were achieved in Co/SiO₂ due to the much higher reaction temperature (260 °C) compared to those (200-220°C) for traditional cobalt-based FTS catalysts [45-47]. Pd promotion, although improved the dispersion of Co, decreased the activity of the core catalyst significantly as shown in Table 3. In particular, the TOF decreased from 0.43 to 0.16 S⁻¹ after Pd modification. The possible reason for the decline of activity was that Pd blocked the Co active sites and limited the CO adsorption. Similar results were also reported by other researchers [21, 44]. In addition, Pd improved the hydrogenation activity of the catalyst, which resulted in enhanced CH₄ selectivity and reduced olefin selectivity. However, the C₅-C₁₁ iso-paraffins selectivity of Co/Pd/SiO₂ was also very low (1.9%). Furthermore, considerable amount of

long-chain hydrocarbons (C_{12+}) were produced in these two core catalysts. Thus, the individual core catalysts could not be used for the direct synthesis of C_5 - C_{11} iso-paraffins from syngas.

Table 3. The catalytic performance of catalysts for C_5 - C_{11} iso-paraffins synthesis.^a

Catalyst	Conv. CO (%)	FTY (10^{-4} mol CO/(g Co s))	TOF (s^{-1})	Sel. CO ₂ (%)	Hydrocarbon selectivity (%) ^b					C_{ole} / C_n	$C_{iso}/$ C_n^{*f}	MB (%)
					CH ₄	C_n^c	C_{ole}^d	C_{iso}^e	C_{12+}			
Co/SiO ₂	61.2	2.3	0.43	1.6	21.3	62.8	14.4	1.3	25.6	0.23	0.05	0.98
Co/Pd/SiO ₂	32.0	1.2	0.16	1.0	22.6	66.9	8.0	1.9	14.4	0.12	0.06	0.97
Co/SiO ₂ -HZSM 5	48.9	1.8	0.41	2.9	32.1	35.5	13.7	18.2	0	0.39	0.97	0.95
Co/Pd/SiO ₂ -HZ SM5	15.1	0.6	0.15	0	29.9	39.8	7.6	22.0	0	0.19	1.03	0.96
Co/Pd/SiO ₂ /HZ SM5-M	30.9	1.1	0.16	0.6	23.4	45.9	10.9	17.8	3.2	0.24	0.88	0.96

^a Reaction condition: 260 °C, 1.0 MPa, W/F=2.5 g·h/mol, H₂/CO=2, TOS=6 h.

^b Carbon molar selectivity, calculated on the basis of all the hydrocarbons.

^c n-paraffins with carbon number $n \geq 2$.

^d Olefins selectivity with carbon number $n \geq 2$.

^e Iso-paraffins selectivity in the range of C_5 - C_{11} .

^f Molar ratio of iso-paraffins to n-paraffins in the range of C_5 - C_{11} (C_n^*).

The capsule catalysts exhibited lower activities than those of bare core catalysts.

The un-promoted capsule catalyst Co/SiO₂-HZSM5 had a little lower Co-specific

activity (FTY) compared to that of Co/SiO₂. This was mainly because small amount of cobalt silicate was not reduced in Co/SiO₂-HZSM5. The Pd-promoted capsule catalyst Co/Pd/SiO₂-HZSM5 exhibited much lower FTY than that of Co/Pd/SiO₂. This result suggested that except for the incomplete reduction of cobalt silicate, some small cobalt crystallites (< 6 nm) might be formed during the reduction, which also resulted in the relatively lower activity [48-50].

The capsule catalysts showed completely different product selectivities compared to bare core catalysts, and the formation of heavy hydrocarbons (C₁₂₊) was completely suppressed due to the spatial confinement effect of H-ZSM-5 zeolite shell. For Co/SiO₂-HZSM5, a high C₅-C₁₁ iso-paraffins selectivity of 18.2% was obtained, accompanied by a relative high methane selectivity (32.1%). The high C₅-C₁₁ iso-paraffins selectivity was mainly contributed by the hydrocracking and isomerization of the primary hydrocarbons at the strong acidic sites of the H-ZSM-5 zeolite shell. It is noted that a high olefin selectivity (13.7%) was obtained in Co/SiO₂-HZSM5, which is detrimental for the direct use of the products as gasoline. In the case of Co/Pd/SiO₂-HZSM5, the highest C₅-C₁₁ iso-paraffins selectivity of 22.0% was achieved. Moreover, the olefins selectivity decreased significantly compared with that of the un-promoted capsule catalyst. The introduction of Pd enhanced hydrogenation of olefins to paraffins on the core catalysts and decreased the selectivity of olefins. It is noted that some Pd might migrate to the pores of H-ZSM-5 zeolite shell during the hydrothermal synthesis of the capsule catalyst. Pd in the H-ZSM-5 zeolite shell could also improve the hydrocracking and isomerization reactions of primary hydrocarbons. The total elimination of long-chain hydrocarbons, together with the enhanced hydrogenation and the isomerization by Pd, contributed to the high mole ratio of iso-paraffins to

n-paraffins in the range of C₅-C₁₁ (C_{iso}/C_n) in Co/Pd/SiO₂-HZSM5 (1.03).

For comparison, the physical mixture catalyst Co/Pd/SiO₂/HZSM5-M was tested under the same reaction condition and the results are also shown in Table 3. It is clear to see that Co/Pd/SiO₂/HZSM5-M had a similar activity to that of bare core catalyst Co/Pd/SiO₂. The C₅-C₁₁ iso-paraffins selectivity of Co/Pd/SiO₂/HZSM5-M was 17.8%, a little lower than that of Co/Pd/SiO₂-HZSM5. Besides, some long-chain hydrocarbons (3.2%) were observed in this catalyst. The random diffusion of long-chain hydrocarbons in catalyst bed resulted in the incomplete hydrocracking and isomerization of long-chain hydrocarbons in catalyst bed of Co/Pd/SiO₂/HZSM5-M. Brønsted acid sites are the active centers for the isomerization reaction [51], which played important roles in the selectivity of the C₅-C₁₁ iso-paraffins. In this work, the physical mixture catalyst had a same amount of H-ZSM-5 zeolite to that of the capsule catalyst. Theoretically, the Brønsted acid site density should be same in the two catalysts. However, during the hydrothermal synthesis of the capsule catalyst, some core catalyst could be etched and some cobalt ion might be trapped in the acidic zeolite, which could decrease the Brønsted acid site density of the capsule catalyst [52-54]. Therefore, a lower Brønsted acid site density should be obtained in the capsule catalyst. However, the iso-paraffins selectivity of the capsule catalyst was higher than that of the physical mixture catalyst. These results indicated that the selectivity of the C₅-C₁₁ iso-paraffins was not solely decided by the Brønsted acid site density. The spatial structure of the catalyst also played important roles in the selectivity of C₅-C₁₁ iso-paraffins. In the capsule catalyst, although the Brønsted acid site density was a little lower, the formed long-chain hydrocarbons in the core catalyst was forced to contact Brønsted acid sites in the zeolite shell during their diffusion to outside of the catalyst, and thus a higher iso-paraffins

selectivity was achieved. In the case of physical mixture catalyst, Brønsted acid site density was higher, but due to the free diffusion of the long-chain hydrocarbons in the catalyst bed, part of the Brønsted acid sites were not used for the isomerization reaction. Therefore, a lower C₅-C₁₁ iso-paraffins selectivity was obtained in the physical mixture catalyst.

From Table 3, we can also see that the methane selectivity (29.9%) of Pd-promoted capsule catalyst Co/Pd/SiO₂-HZSM5 was higher than that of bare core (22.6%) and physical mixture catalyst (23.4%). Although H₂ was consumed in the hydrocracking reactions of primary hydrocarbons, the high diffusion rate of H₂ compared to CO in microporous zeolite shell might result in a higher H₂/CO ratio than 2 in the core catalyst [17,46]. The higher H₂/CO ratio in the core of Co/Pd/SiO₂-HZSM5 caused the higher methane selectivity.

3.6 Carbon deposition analysis of the used catalysts

Catalytic tests indicated that long-chain hydrocarbons (C₁₂₊) were totally eliminated in the capsule catalysts. In section 3.5, our explanation on the disappearance of long-chain hydrocarbons was their hydrocracking and isomerization into short-chain hydrocarbons. However, there was another possibility that the long-chain hydrocarbons were trapped in the H-ZSM-5 zeolite shell in the form of coking or heavy wax. In order to clarify if the carbon deposition (coking or heavy wax) resulted in the elimination of the long-chain hydrocarbons, TG of the used catalysts were measured in air flow. The TG profiles of the catalysts are shown in Figure 11. For core catalysts and Pd-promoted capsule catalyst, the weight first decreased from room temperature to about 150 °C, then increased until about 360 °C, and after that decreased with the temperature. In the case

of Co/SiO₂-HZSM5, no weight increase was found in the temperature region of 150-360 °C. The weight loss below 150 °C was attributed to the desorption of water or gases adsorbed on the catalysts. The weight increase above 150 °C was caused by the oxidation of metallic cobalt in the catalysts. Meanwhile, deposited carbon on the catalysts was removed by oxidation or combustion. Therefore, for the calculation of carbon deposition, the weight increase caused by the cobalt oxidation must be subtracted. Here, the weight at 150 °C ($W_{T=150\text{ }^{\circ}\text{C}}$) was supposed as total weight of the deposited carbon, metallic cobalt, SiO₂ support and/or H-ZSM-5 zeolite, while the weight at 600 °C ($W_{T=600\text{ }^{\circ}\text{C}}$) was denoted as the weight of “fresh” catalyst because all the carbon could be oxidized and removed below this temperature [11, 55]. Combined with the cobalt loading of 10 wt % in the core catalysts, the carbon deposition can be calculated and the results were presented in Table 4. It is noted that the surface cobalt atoms of the used catalysts were oxidized in air before TG measurement, and only the oxidation of inner part of metallic cobalt could result in the weight increase in the temperature of 150-600 °C in Fig. 11. Thus, the amount of carbon deposition calculated here was overestimated and the actual carbon amount was lower than those shown in Table 4.

Fig. 11. TG curves of the used catalysts measured in air atmosphere.

Table 4. Amount of carbon deposition calculated by TG curves

Sample	$W_{T=150}^{\circ C}$ (%)	$W_{T=600}^{\circ C}$ (%)	Carbon deposition ^a (g C /g Catalyst)
Co/SiO ₂ -U	98.31	98.67	0.033
Co/SiO ₂ /HZSM5-U	98.19	97.25	0.040
Co/Pd/SiO ₂ -U	98.10	98.42	0.033
Co/Pd/SiO ₂ -HZSM5-U	97.63	97.07	0.036
Co/Pd/SiO ₂ /HZSM5-M-U	96.94	97.30	0.026

^a total amount of carbon deposition in 6 h on stream.

It is clear to see that the amount of carbon deposition was very low for every catalyst. The core catalysts Co/SiO₂ and Co/Pd/SiO₂ had a same amount of carbon deposition (0.033 g C /g Catalyst). Capsule catalysts exhibited a little higher carbon deposition compared with the bare core catalysts. The increased carbon deposition could be thought as the coking or wax trapped by the H-ZSM-5 zeolite shell of the capsule

catalyst. Taking the Pd-promoted capsule catalyst as an example, the carbon deposition caused by H-ZSM-5 zeolite shell was 0.003 g C/g Catalyst. Meanwhile, the estimated long-chain hydrocarbons formed in the core catalyst was about 0.017 g C/g Catalyst according to the results of catalytic tests (Table 3). The carbon deposition caused by H-ZSM-5 zeolite shell was only about 18 % of the formed long-chain hydrocarbons. In addition, due to carbon deposition was overestimated in our current calculation method, the long-chain hydrocarbons that caused the carbon formation were much lower than 18%. Therefore, most of the long-chain hydrocarbons produced in the core catalyst were hydrocracked and isomerized into short-chain hydrocarbons. It is interesting to see that Pd-promoted capsule catalyst caused lower carbon deposition than un-promoted capsule catalyst. Pd at the interface of core catalyst and H-ZSM-5 zeolite shell might promote the carbon elimination by the enhanced hydrogenation, which resulted in a relatively low carbon deposition.

The pore structures of the used catalysts were characterized by N₂ physisorption and the results were shown in Table 1. The micropore volumes and surface areas of the capsule catalysts were almost kept constant after the catalytic tests, suggesting that there was no obvious pore plugging caused by carbon deposition in the H-ZSM-5 zeolite shell. This result further confirmed that the elimination of long-chain hydrocarbons was mainly caused by their hydrocracking and isomerization into short-chain hydrocarbons, but not by the carbon deposition in the H-ZSM-5 zeolite shell.

3.7. Roles of Pd promotion in structure and performance of the capsule catalyst for C₅-C₁₁ iso-paraffins synthesis

Fig. 12. Mechanism schemes of the roles of Pd promotion in structure (a) and performance (b) of the capsule catalyst for C₅-C₁₁ iso-paraffins synthesis.

The structure characterizations indicated the Pd-promoted and un-promoted zeolite capsule catalysts were successfully synthesized in this work. Different from the un-promoted capsule catalyst, the main cobalt species in the Pd-promoted capsule catalyst was cobalt silicate, which was formed during the hydrothermal synthesis of H-ZSM-5 zeolite shell. Pd promoted the dissolution (or etching) of silica and the transformation of Co_3O_4 to cobalt silicate during the hydrothermal synthesis in the strong basic solution (TPAOH) [9,27,28]. Pd played essential roles in the formation of cobalt silicate in the capsule catalyst and its reduction during the following reduction process. The mechanism scheme of Pd promotion in the structure evolution of the capsule catalyst is shown in Fig. 12 (a).

Pd-promoted capsule catalyst exhibited high performance for C₅-C₁₁ iso-paraffins direct synthesis from syngas. First, syngas ($\text{H}_2 + \text{CO}$) reached readily the core part of the capsule catalyst due to their small molecular volumes, and produced primary

hydrocarbons including considerable long-chain hydrocarbons and olefins at the Co active sites via FTS reactions. Then, the primary hydrocarbons were forced to diffuse in the zeolite channels, where they could be hydrocracked and isomerized to the C₅-C₁₁ iso-paraffins at the acidic sites of the H-ZSM-5 zeolite shell. Due to the spatial confinement of the H-ZSM-5 zeolite shell, all the long-chain hydrocarbons formed in the core catalyst could be eliminated. Moreover, Pd promoted the hydrogenation of olefins in the core catalyst, which decreased the selectivity of olefins and further improved the selectivity of iso-paraffins. The scheme of C₅-C₁₁ iso-paraffins direct synthesis over Pd-promoted capsule catalyst is shown in Fig. 12 (b).

4. Conclusions

Pd-promoted zeolite capsule catalyst (Co/Pd/SiO₂-HZSM5) was developed by coating H-ZSM-5 zeolite shell over the Pd-modified Co/SiO₂ core catalyst (Co/Pd/SiO₂), and employed for C₅-C₁₁ iso-paraffins direct synthesis from syngas via Fischer-Tropsch synthesis (FTS). The roles of Pd promotion in structure and performance of the capsule catalyst for C₅-C₁₁ iso-paraffins direct synthesis was deeply studied. Structure characterizations indicated that the main cobalt species in the Pd-promoted capsule catalyst was cobalt silicate, while Co₃O₄ was the main cobalt species in the un-promoted capsule catalyst (Co/SiO₂/HZSM5). Evolution of cobalt species in the synthesis of Pd-promoted capsule catalyst revealed that Pd improved the formation of cobalt silicate in strong basic TPAOH solution during the hydrothermal synthesis of H-ZSM-5 zeolite shell. It was found that Pd not only promoted the reduction of cobalt oxides, but also improved the reduction of cobalt silicate, which could not be reduced under traditional reduction condition for cobalt-based FTS

catalysts. Catalytic tests indicated that the Pd-promoted capsule catalyst exhibited highly enhanced performance for C₅-C₁₁ iso-paraffins synthesis with molar ratio of iso-paraffins to n-paraffins up to 1.03. The long-chain hydrocarbons were completely eliminated in the capsule catalyst as a consequence of spatial confinement effect of the H-ZSM-5 zeolite shell. TG and N₂ physisorption analysis of the used catalysts confirmed that the elimination of long-chain hydrocarbons was mainly caused by their hydrocracking and isomerization into short-chain hydrocarbons, but not by the carbon deposition in the H-ZSM-5 zeolite shell. The hydrogenation of olefins to paraffins, which was enhanced by Pd promotion, together with the hydrocracking and isomerization of primary hydrocarbons, contributed to the high selectivity of C₅-C₁₁ iso-paraffins.

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Figure captions:

Fig. 1. SEM images and EDS results of the external surface of the capsule catalysts: a,c, Co/SiO₂-HZSM5; b, d, Co/Pd/SiO₂-HZSM5.

Fig. 2. SEM images and EDS line scanning results along the cross-section of the capsule catalysts: a, Co/SiO₂-HZSM5; b, Co/Pd/SiO₂-HZSM5.

Fig. 3. XRD profiles of the core and capsule catalysts.

Fig. 4. XRD patterns of the reduced core and capsule catalysts

Fig. 5. FTIR spectra of the core and capsule catalysts.

Fig. 6. Co 2p XPS spectra the core and capsule catalysts.

Fig. 7. Pd 3d XPS spectra of Co/Pd/SiO₂ and Co/Pd/SiO₂-HZSM5.

Fig. 8. XRD profiles of Co/SiO₂ and Co/Pd/SiO₂ catalysts after treating with TPAOH solution.

Fig. 9. H₂-TPR profiles of the core and capsule catalysts.

Fig. 10. H₂-TPR profiles of Co/Pd/SiO₂-HZSM5 catalyst under different reduction condition.

Fig. 11. TG curves of the used catalysts in air atmosphere.

Fig. 12. Mechanism scheme of the roles of Pd promotion in structure (a) and performance (b) of the capsule catalyst for C₅-C₁₁ iso-paraffins synthesis.