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Iso-paraffins synthesis from modified Fischer–Tropsch reaction—Insights into Pd/beta and Pt/beta catalysts

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Abstract

The direct iso-paraffin synthesis from synthesis gas (CO + H_2, syngas) via Fischer–Tropsch (FT) route was investigated in a consecutive dual reactor system, in which FT reaction was carried out over Co/SiO_2 catalyst in the upper reactor and hydroconversion of the FT hydrocarbons occurred over Pt/beta or Pd/beta catalyst in the lower reactor. The products with very high iso-paraffin selectivity were composed mainly of hydrocarbons with carbon number less than 10, indicating that both hydrocracking and hydroisomerization reactions significantly occurred. Under the present operating conditions, time-on-steam results indicate that Pt/beta catalyst containing 0.5 wt.% Pt deactivated quickly while 0.5 wt.% Pd/beta catalyst showed stable performance in the case of iso-paraffin selectivity. Either the increase in Pt loading to 1 wt.% Pt or the increase of hydrogen partial pressure in the lower reactor can alleviate the deactivation of the catalyst for the titled reaction. This was mainly ascribed to the different effect of the adsorbed CO molecule on the metallic function of Pt and Pd.

Keywords: Iso-paraffin synthesis; Syngas; Fischer–Tropsch; Beta zeolite; Platinum; Palladium; Bifunctional catalyst

1. Introduction

In recent years, the production of clean fuels for transportation has received significant attentions as a result of the implementation of more and more stringent environmental legislations on gasoline [1–3]. In particular, comparing with technologies such as blending with oxygenates and aromatics, it is environmentally more acceptable to boost the octane quality of gasoline by increasing the branched alkanes [3]. Alternatively, it is more attractive to produce iso-paraffins from coal, natural gas, and biomass, which are abundant in the world, rather than petroleum because of the very limited reservoir.

The FT synthesis is an effective process to produce liquid fuels and high-value added fine chemicals from syngas derived from coal, natural gas and biomass [4]. However, the FT products, which are controlled by the so-called Anderson–Schulz–Flory (ASF) polymerization kinetics, are non-selective to any specific hydrocarbons and low selective to iso-paraffins. To circumvent the ASF distribution of FT products, Dalai et al. have demonstrated to selectively synthesize C_4 hydrocarbons by the combination of Co-Fe/ZrO_2 and SO_4^{2-}/ZrO_2 in a consecutive dual reactor system [5]. However, the super acid catalyst quickly deactivated even at a CO conversion of 5%. In addition, several groups have tried to make iso-paraffins by directly loading FT active components on acidic zeolites [6–8]. As zeolites are not suitable support for FT active components, typical results showed low activity and high methane selectivity. On the contrary, a physical mixture of supported Co and zeolite catalysts gave improved catalytic activity and selectivity to middle iso-paraffins [9,10]. In previous works [11,12], a fundamental concept by using physical mixture of FT catalyst and Pd/zeolite catalysts or Pd/SiO_2 + zeolite was proposed for direct production of iso-paraffins. Here, the function of FT catalyst is to synthesize long-chain hydrocarbons while Pd/zeolite or Pd/SiO_2 + zeolite catalyst is to hydroconvert the FT products. Results of the preliminary experiments both in one reactor and a consecutive dual reactor system indicate that high selectivity to iso-paraffins of $C_4 \sim C_8$ can be more efficiently and easily

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achieved in a dual reactor system by loading Pd/beta catalyst in the downstream reactor [12]. In this investigation, the time on stream (TOS) performance of Pt/beta and Pd/beta catalysts was comparatively investigated in a consecutive dual reactor system. The TOS carbon number distribution, iso-paraffin selectivities and iso-alkane to *n*-alkane ratio obtained over different catalysts were compared quantitatively. The possible reasons why the Pd/beta and Pt/beta catalysts behaved differently for the titled reaction were discussed based on the characteristics of the reaction system.

2. Experimental

The Co/SiO_2 catalyst (20 wt.% Co) was prepared by incipient wetness impregnation of aqueous solution of cobalt nitrate on silica gel (Fujisilicia Q-15). The beta zeolite (Sud Chemie, $SiO_2/Al_2O_3 = 25$) was ion-exchanged at 353 K for 6 h in the solution of $Pt(NH_3)_4Cl_2$ and $Pd(NH_3)_4Cl_2$, respectively, for the preparation of 0.5 wt.% Pd/beta and Pt/beta catalysts containing 0.5 wt.% Pt and 1 wt.% Pt. After filtration and washing with distilled water, the final catalysts were dried overnight at 393 K and then calcined at 723 K for 2 h.

The reaction was carried out in consecutive dual fixed-bed reactors (SUS tube, 8 mm I.D.), in which 0.4 g Co/SiO_2 mixed with 0.1 g beta zeolite (Tosoh, $SiO_2/Al_2O_3 = 39$), diluted with 0.5 g quartz sands, was loaded in the upper reactor and 0.5 g metal/beta catalyst diluted with the same amount of quartz sands was in the lower reactor. Before reaction, the catalysts were pre-treated at 673 K for 3 h in a flow of hydrogen. The operating conditions were $P = 1.0$ MPa, $H_2/CO = 2.0$, W/F(syngas) = 4.95 g h mol^{-1}. To prove the effect of hydrogen partial pressure on the performance of the Pt/beta catalyst, in one experiment, hydrogen in a separate line was fed to the lower reactor with the same flow rate of H_2 in the syngas. The effluent hydrocarbons, which were cooled at 453 K, were analyzed by an on-line GC equipped with NB-1 capillary column and flame ionization detector (FID). The CO, CH_4, and CO_2 in the effluent after cooling in an ice-water trap were analyzed on-line by a GC with a packed active carbon column and thermal conductivity detector (TCD). The selectivity of hydrocarbons was calculated on the basis of carbon number.

3. Results

3.1. Effect of the admixed beta zeolite on the product distribution

To comparatively study the effect of catalyst loaded in the lower reactor on the iso-paraffin synthesis, the catalyst and operating conditions in the upper reactor were kept the same for all the experiments. The typical carbon number distribution over Co/SiO_2 + beta zeolite is given in Fig. 1(B). For the purpose of comparison, the carbon number distribution of FT synthesis over Co/SiO_2 catalyst at the same reaction conditions is also provided in Fig. 1(A). As expected and stated in many literatures, the products of FT synthesis over Co/SiO_2 showed a wide carbon number distribution and were mainly composed of normal paraffins and olefins together with a very small amount of iso-paraffins. Our basic idea to mix a certain amount of beta zeolite with Co/SiO_2 catalyst in the upper reactor is to primarily crack the very heavy hydrocarbons produced from FT reaction. Comparing Fig. 1(A) and (B), one can see that the addition of 20 wt.% beta zeolite into Co/SiO_2 increased the selectivity of iso-paraffins and olefins and the products shifted to lower hydrocarbons, suggesting that simple cracking and isomerization of the FT hydrocarbons occurred over the acidic sites of beta zeolite. Furthermore, there was no obvious increase in the selectivity of C_1 to C_3 hydrocarbons, indicating that no additional C_1–C_3 hydrocarbons were produced during the cracking reactions. At the present conditions, CO conversion was around 55% and the CO_2 selectivity was low (less than 5%) due to the low activity of Co for water-gas shift (WGS) reaction. For clarity, only metal/beta catalyst loaded in the lower reactor will be mentioned in the following if it is not specified.

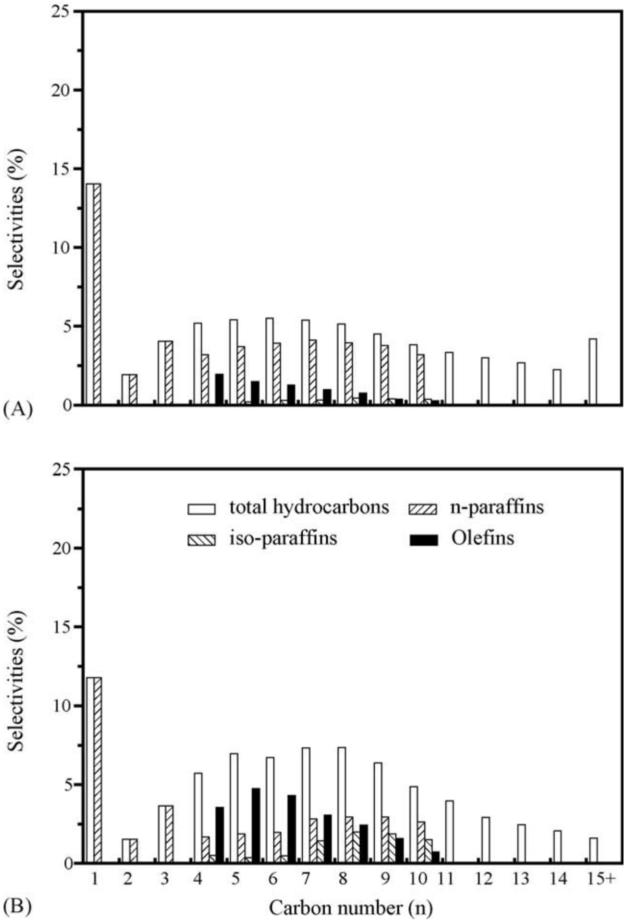

Fig. 1. Carbon number distribution of FT synthesis at time on stream of 4 h over Co/SiO_2 catalyst (A) and Co/SiO_2 + beta zeolite (4:1, weight ratio) (B) at the conditions of $T = 510$ K, $P = 1.0$ MPa, $W/F = 4.95$ g h mol^{-1}.

3.2. Product distribution over 0.5 wt.% Pd/beta catalyst

The product distribution over 0.5 wt.% Pd/beta catalyst is given in Fig. 2. In comparison with Fig. 1, it is clear that long-chain hydrocarbons produced in the upper reactor was cracked dominantly and very high selectivities towards C_4–C_7 hydrocarbons were achieved. Moreover, the selectivity to propane increased slightly in comparison with the results shown in Fig. 1, indicating that more propane was formed in the lower reactor during the hydrocracking reactions. As mentioned above, CO conversion was about 55%, indicating that an appreciable amount of un-reacted hydrogen from the upper reactor was available in the lower reactor. Therefore, it is rational to propose that the main reactions occurred over Pd/beta catalyst were hydrocracking and hydroisomerization. Only a slight difference was observed for the carbon number distribution at different TOS.

3.3. Product distribution over 0.5 wt.% Pt/beta catalyst

Comparing the carbon number distribution over 0.5 wt.% Pt/beta at TOS of 2 and 7 h shown in Fig. 3, almost the same changing trend as that over 0.5 wt.% Pd/beta catalyst could be recognized. Moreover, irrespective of the carbon number, olefin selectivity increased while iso-paraffin selectivity decreased obviously as time passed. It should be emphasized that an appreciable amount of hydrocarbons with carbon number higher than 11 was still observed, especially at the later stage of the reaction, suggesting that heavy hydrocarbons produced in the upper reactor was less hydrocracked over 0.5 wt.% Pt/beta than that over 0.5 wt.% Pd/beta catalyst. In addition, olefin selectivities over 0.5 wt.% Pt/beta were obviously higher than those over 0.5 wt.% Pd/beta catalyst. These results indicate that 0.5 wt.% Pt/beta is less efficient to produce iso-paraffins than 0.5 wt.% Pd/beta catalyst. As shown in the product distribution, the selectivities of *n*-alkanes and iso-paraffins were varied significantly with carbon numbers.

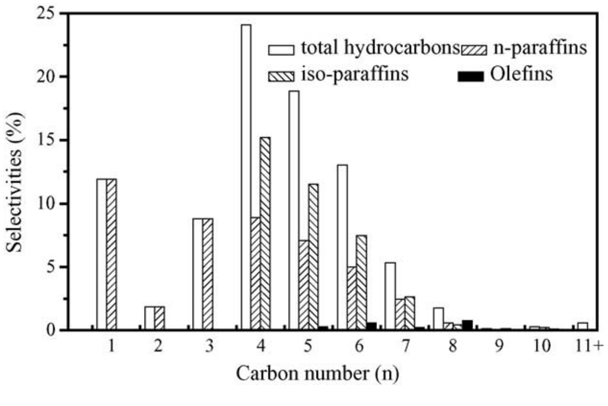

Fig. 2. Carbon number distribution at time on stream of 7 h in consecutive dual reactor system. Reaction conditions: $T = 508$ K (upper reactor) and 573 K (lower reactor), $P = 1.0$ MPa, $W/F = 4.95$ g h mol^{-1}, catalyst: Co/SiO_2 + beta zeolite (4:1 weight ratio) in upper reactor, 0.5 wt.% Pd/beta in lower reactor.

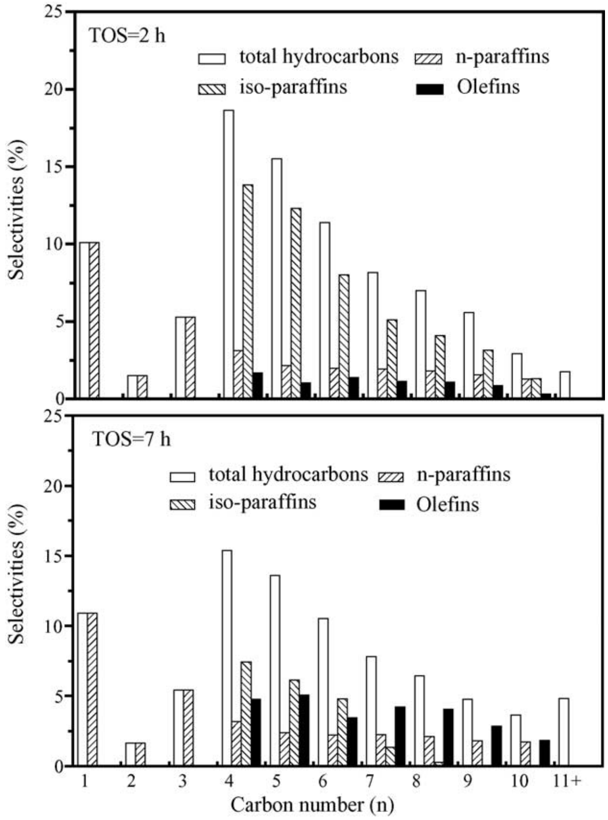

Fig. 3. Carbon number distribution at different time on stream in a dual reactor system. Reaction conditions: $T = 508$ K (upper reactor) and 573 K (lower reactor), $P = 1.0$ MPa, $W/F = 4.95$ g h mol^{-1}, catalyst: Co/SiO_2 + beta zeolite (4:1 weight ratio) in upper reactor, 0.5 wt.% Pt/beta in lower reactor.

3.4. TOS iso-paraffin selectivities over different catalysts

As shown above, the products in a dual reactor system were still a mixture of hydrocarbons with varied carbon numbers. Therefore, to characterize and to compare the performance of the catalyst for iso-paraffin production at different TOS, molar ratio of the total iso-paraffins to all C_4+ hydrocarbons (I/C_4+) was defined and calculated as shown in Fig. 4. At the initial reaction stage of 2 h, the I/C_4+ over 0.5 wt.% Pt/beta catalyst was slightly higher than that over 0.5 wt.% Pd/beta catalyst, indicating that the 0.5 wt.% Pt/beta catalyst has a higher activity toward the iso-paraffin synthesis. However, it decreased sharply with TOS and reached about 30% at TOS of 7 h. In the case of 0.5 wt.% Pd/beta catalyst, a different trend was observed. The I/C_4+ ratio was stable during the reaction although its initial value was slightly lower than that over 0.5 wt.% Pt/beta catalyst.

3.5. TOS composition of C_4 hydrocarbons over different catalysts

It was found that the formation of butenes was closely related to the iso-paraffin selectivity. To demonstrate this, the molar percentage of iso-butane, *n*-butane and butenes in

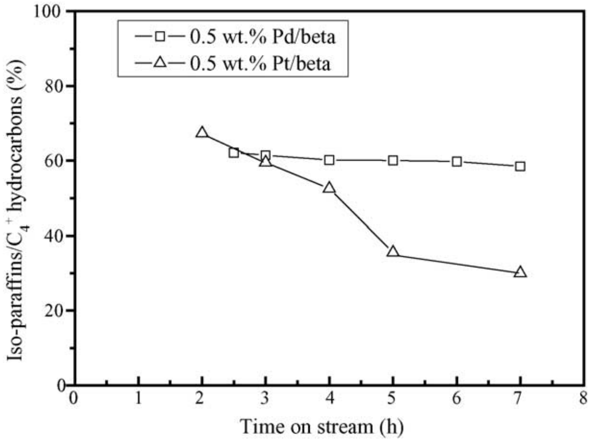

Fig. 4. Time-on-stream molar ratio of iso-paraffins to C_4+ hydrocarbons in a dual reactor system. Reaction conditions: $T = 508$ K (upper reactor) and 573 K (lower reactor), $P = 1.0$ MPa, $W/F = 4.95$ g h mol^{-1}, catalyst: Co/SiO_2 + beta zeolite (4:1 weight ratio) in upper reactor.

total C_4 hydrocarbons was calculated. The results are illustrated in Fig. 5. The interesting observation in the case of C_4 hydrocarbons at different TOS is that the percentage of butenes was 0 over 0.5 wt.% Pd/beta catalyst during the 7 h reaction while a significant percentage of butenes was observed over Pt/beta catalyst even at the beginning of the reaction. Moreover, the percentage of butenes over 0.5 wt.% Pt/beta catalyst obviously increased with TOS. As an appreciable amount of butenes was produced in the upper reactor as seen from Fig. 1, therefore, hydrogenation of butenes over 0.5 wt.% Pd/beta catalyst in the lower reactor occurred sufficiently such that there were no detectable butenes in the products. However, when 0.5 wt.% Pt/beta catalyst was considered, the inhibition for hydrogenation of butenes coming from the upper reactor and/or the formation of extra butenes during the cracking reactions cannot be ruled out.

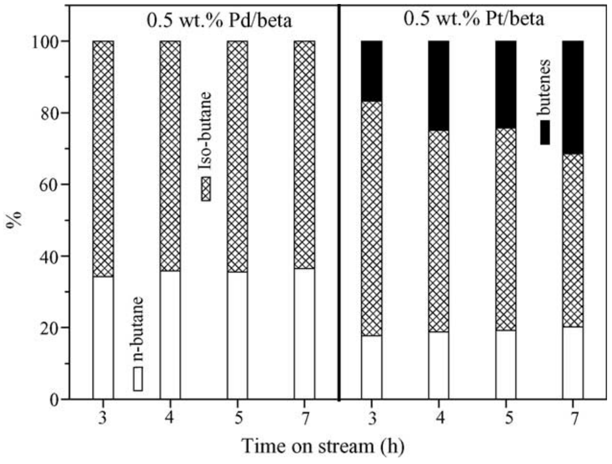

Fig. 5. Molar composition of C_4 hydrocarbons obtained in a dual reactor system at different time on streams. Reaction conditions are the same as indicated in Fig. 4.

3.6. Effect of catalyst composition on molar ratios of iso-alkane to n-alkane

From the carbon number distribution, it is a fact that the selectivities of *n*-alkanes were varied significantly with carbon number. To examine the isomerization extent of *n*-alkanes with different carbon numbers, C_4, C_5 and C_6 paraffins, which are abundant in the products, were selected. The molar ratios of iso-C_4–C_6 alkanes to the corresponding *n*-C_4–C_6 alkanes at different TOS were calculated, respectively and compared in Fig. 6. Over 0.5 wt.% Pd/beta catalyst, the ratio of iso-butane to *n*-butane was kept almost constant around 1.8 during the test. When pentane and hexane were considered, almost same values and changing trends with TOS were observed. In the case of 0.5 wt.% Pt/beta catalyst, it was seen from Fig. 6 that much higher molar *i*/*n* ratios of C_4–C_6 paraffins were obtained at TOS of 3 h, and then decreased sharply with the increase of reaction time. Moreover, the ratio of iso-pentane to *n*-pentane was obviously higher than those of iso-butane to *n*-butane and iso-hexanes to *n*-hexane at TOS of 3 h, and this difference decreased apparently with TOS. At TOS of 7 h, almost same values in the case of *i*/*n* ratios of C_4–C_6 alkanes were obtained. It is worthy to note that, during the test, the *i*/*n* ratios of C_4–C_6 alkanes were always higher over 0.5 wt.% Pt/beta catalyst than those over 0.5 wt.% Pd/beta catalyst, indicating that 0.5 wt.% Pt/beta catalyst is prone to give higher *i*/*n* ratios of C_4–C_6 alkanes. However, the I/C_4+ for 0.5 wt.% Pt/beta was still lower than that for 0.5 wt.% Pd/beta catalyst after an initial reaction time of 2 h. This was caused by the significantly higher selectivities of olefins over 0.5 wt.% Pt/beta catalyst.

3.7. Effect of Pt loading and hydrogen partial pressure

Because the deactivation of 0.5 wt.% Pt/beta catalyst was unexpectedly fast, to find out the reasons, the other

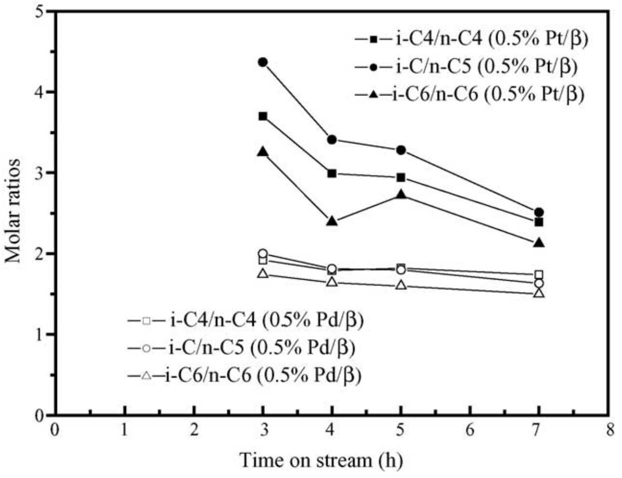

Fig. 6. Molar ratios of iso-C_4–C_6 alkanes to the corresponding *n*-C_4–C_6 alkanes obtained in a dual reactor system at different time on streams. Reaction conditions are the same as indicated in Fig. 4.

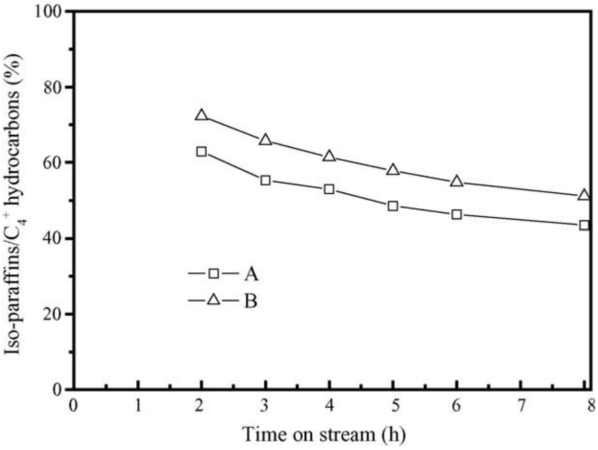

Fig. 7. Time-on-stream molar ratio of iso-paraffins to C_4+ hydrocarbons in a dual reactor system over 1 wt.% Pt/beta (A) and 0.5 wt.% Pt/beta with additional H_2 fed to the lower reactor (B). Reaction conditions: $T = 508$ K (upper reactor) and 573 K (lower reactor), $P = 1.0$ MPa, $W/F = 4.95$ g h mol^{-1}, catalyst: Co/SiO_2 + beta zeolite (4:1 weight ratio) in upper reactor.

experiments were designed and carried out. One is to increase the Pt loading, 1 wt.% Pt/beta catalyst was prepared and tested at the same operating conditions. The other is to increase the molar ratio of hydrogen to hydrocarbons by feeding additional hydrogen to the lower reactor while all of the other operating parameters including catalyst were kept the same. At the CO conversion of about 55%, the molar ratio of hydrogen to hydrocarbons can be increased to be about 2 times higher than the case without feeding additional hydrogen. The results are given in Figs. 7 and 8. In comparison with the results over 0.5 wt.% Pt/beta catalyst shown in Fig. 4, 1 wt.% Pt/beta catalyst produced almost the same value of I/C_4+ at TOS of 2 h (Fig. 7). However, the I/C_4+ ratios became more stable when Pt loading over the catalyst was increased from 0.5 to 1 wt.%, indicating that higher Pt loading can improve the stability of Pt/beta catalyst. From the carbon number distribution (not shown), the selectivity of olefins decreased when Pt loading increased. This can also be clearly illustrated by comparing the results in Figs. 5 and 8, which were the composition of C_4 hydrocarbons at different TOS. It was evident that the percentage of butenes decreased significantly when Pt/beta catalyst containing 1 wt.% Pt was used. Therefore, the improved stability of the catalyst by increasing Pt loading can be ascribed to the decrease of olefin selectivities. In the case of the experiment by feeding additional hydrogen to the lower reactor, more pronounced effect than increasing Pt loading to 1 wt.% could be found by comparing the results in Figs. 4, 5, 7 and 8, i.e., obvious higher I/C_4+ ratios and lower percentage of butenes.

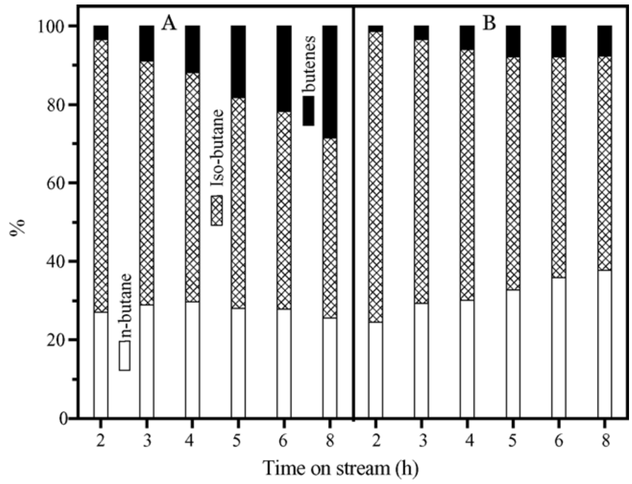

Fig. 8. The molar composition of C_4 hydrocarbons obtained in a dual reactor system at different time on streams over 1 wt.% Pt/beta (A) and 0.5 wt.% Pt/beta with additional H_2 fed to the lower reactor (B). Reaction conditions are the same as indicated in Fig. 7.

4. Discussion

4.1. Examination on characteristics of the reaction system

Blank tests showed that CO conversion was less than 2% at the same operating conditions when only either Pt/beta or Pd/beta catalyst was loaded in the reactor. As mentioned above, the catalyst and operating conditions in the upper reactor were kept the same for all of the experiments. Within the test error, almost the same CO conversion and CH_4 selectivity were obtained irrespective the catalyst used in the lower reactor. Therefore, the above phenomena must only be related to the hydroconversion function of the metal/beta catalyst.

To our knowledge, there is no report on the application of Pt/beta catalyst for hydroconversion reactions in FT conditions although the hydroisomerization of pure short-chain *n*-alkanes such as butane, pentane, hexane and heptane have intensively been investigated over different solid acids (zeolites, zirconia-based super acids, heteropolyacids, etc.) supported Pt or Pd catalysts [13–17]. Unfortunately, those kinds of reference results cannot be directly compared with the present data because of the complexity of the reaction atmosphere. It is well known that the FT product is a very complex mixture, which is composed mainly of alkanes, olefins and a small amount of oxygen-containing species with varied carbon numbers (Fig. 1). Moreover, due to the low activity of Co for WGS reaction, water produced from FT reaction was always present in the reaction system, in which its profound effect on acid sites has been reported [18]. In addition to those, the un-reacted CO from the upper reactor may have influence on the hydroconversion reactions. Even if it is so, one cannot deny the fact that acidic sites are responsible for the cracking or isomerization reactions irrespective of the kind of solid acids although the action mechanism of metal is still debatable [19]. Therefore, the possible explanation on the different performance of Pd/beta and Pt/beta catalysts in the titled reaction must mainly be from the effect of the above-mentioned factors on Pt and

Pd because that the beta zeolite used in this study was the same for both Pd/beta and Pt/beta catalysts.

4.2. Effect of CO on the metallic function of Pt and Pd

It is surprising that the 0.5 wt.% Pt/beta catalyst deactivated quickly for the titled reaction. At the present operating conditions, an appreciably high partial pressure of CO could be anticipated based on the CO conversion of 55%. According to the common knowledge, CO adsorbs dissociatively on metals such as Ni, Co, Ru and Rh while molecular adsorption of CO prevails on the late 4d and 5d metals like Pt, Pd, and Ir although abnormal behavior from this has recently been reported [20]. Over Pt (1 1 1) model catalyst, CO in mTorr range or above formed an incommensurate hexagonal overlayer, in which the adsorbed CO poisoned the catalytic activity for ethylene hydrogenation reaction [21]. Although the above reference results were obtained over model catalyst under ultra high vacuum conditions, it cannot be denied that the molecularly adsorbed CO interrupted the function of Pt. In fact, in a study on the hydroisomerization of *n*-butane over Pt/SO_4^{2-}/ZrO_2 [22], it was found that *n*-butane conversion decreased sharply when hydrogen was switched to a mixture of CO and H_2 with a molar ratio of 0.5. Our present results over Pt/beta catalysts are agreeable with these reported results. Due to the competitive adsorption of CO with H_2 over Pt sites, the metallic function of Pt for the activation of H_2 decreased, which can be demonstrated clearly by the high olefin selectivity over 0.5 wt.% Pt/beta catalyst. Increasing in Pt loading, the quantity of Pt active sites will be increased correspondingly such that the amount of H_2 adsorbed on Pt can be reasonably expected. The improved performance of 1% Pt/beta catalyst for the titled reaction supports this idea. Similarly, the increase of hydrogen partial pressure by feeding additional hydrogen in the lower reactor will favor the adsorption of H_2 relative to CO, which diminishes the deteriorative effect of CO on the activation of H_2 over Pt. To explain why the Pt/beta catalyst deactivated quickly, the function of acidic sites must be considered together with the CO effects. For the hydroisomerization of *n*-alkanes over metal/acid catalysts, it is commonly recognized that the balance of metal function and acidic function of the catalyst plays key role for achieving high selectivity and stability. It is reasonably expected that the acidic function of Pt/beta will be declined easily when the metal function of Pt was reduced as a result of the CO adsorption. The reciprocal influence of the declined metal function and acidic function in Pt/beta catalyst caused its quick deactivation for the iso-paraffin synthesis.

To explain why Pd/beta catalyst showed stable performance during the reaction, other reasons different from the above-mentioned aspects must be found out because Pd also adsorbs CO in a molecular form [23]. It was reported that separate islands of adsorbed CO and H over Pd (1 1 1) were formed during the co-adsorption of mixed gases of CO and H_2 [24]. Furthermore, bulk H in Pd can be formed easily with the presence of CO [24]. If these results are applied for the explanation of our present data, nothing will be surprised about the stable performance of Pd/beta catalyst. The metallic function of Pd was not damaged by the co-adsorption of CO as both H islands and H in bulk Pd, which can be a reservoir for H due to its high mobility, were still present on the catalyst.

4.3. Effect of water and coke deposition

In addition to those, water produced in FT synthesis may also impart some influences on the performance of the catalysts. The slight decrease of iso-paraffin selectivity over Pd/beta catalyst may be ascribed partly to the deteriorative effect of steam on the acid sites over beta zeolite. The fast deactivation of Pt/beta catalyst may also be contributed, in a less extent, from this aspect. Another possible reason may be from the accumulation of coke on the catalyst as coke formation always accompanied with the conversion of hydrocarbons over acidic sites. In fact, the used catalyst showed a dark grey color, indicating that carbon was deposited on the catalyst, although it was not subject to carbon analysis. Presently, anyone of the above reasons cannot be ruled out.

5. Conclusion

Based on the above results and discussion, the conclusions are summarized as follows.

1. The direct synthesis of iso-paraffin with carbon number less than 10 can be effectively achieved in a dual reactor system with the combination of Co/SiO_2 catalyst for FT synthesis and Pd/Beta catalyst for hydroconversion of FT hydrocarbons.
2. By physically mixing a small amount of beta zeolite with Co/SiO_2 catalyst, the products were shifted to lower hydrocarbons without increasing selectivities of C_1–C_3 hydrocarbons.
3. Under the same operating conditions, 0.5% Pt/beta catalyst deactivated quickly while 0.5 wt.% Pd/beta catalyst was quite stable. The deactivation of the catalyst can be apparently alleviated by either increasing Pt loading in Pt/beta catalyst and/or increasing hydrogen partial pressure in the lower reactor.
4. The adsorbed CO in the molecular form poisoned the metallic function of Pt. Consequently, the balance of metal and acid over 0.5 wt.% Pt/beta catalyst was destroyed, which is composed of the main reasons for the fast deactivation of the catalyst.
5. The slight decrease of I/C_4+ over Pd/beta catalyst may be caused by either carbon deposition and/or the effect H_2O on acidic sites.

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