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Enhanced Production of C_2–C_4 Olefins Directly from Synthesis Gas

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Abstract An attempt made for the selective production of C_2–C_4 olefins directly from the synthesis gas (CO + H_2) has led to the development of a dual catalyst system having a Fischer–Tropsch (K/Fe–Cu/AlOx) catalyst and cracking (H-ZSM-5) catalyst operate in consecutive dual reactors. The flow rate (space velocity) and H_2/CO molar ratio of the feed have been optimized for achieving higher CO conversions and olefin selectivities. The selectivity to C_2–C_4 olefins is further enhanced by optimizing the reaction temperature in the second reactor (cracking), where the product exhibited 51% selectivity to C_2–C_4 hydrocarbons rich in olefins (77%) with a stable time-on-stream performance in a studied period of 100 h.

Keywords FT synthesis · ZSM-5 · Cracking reaction · C_2–C_4 hydrocarbons · Olefins

1 Introduction

The advent of Fischer–Tropsch synthesis (FTS) has opened up new vistas in the frontier areas of catalysis research by facilitating the formation of long chain hydrocarbon molecules that can provide a platform for the production of huge variety of chemicals through secondary reactions [1–3]. Several hydrocarbon materials right from the long chain middle distillate (C_{10}–C_{20}) to medium chain gasoline (C_5–C_{11}) have been produced by the conceptualization of the combination of chain making and selective cracking properties of catalysts [4–6]. Fe based catalysts are generally used for FTS, whereas, solid acid catalysts, especially zeolites are used for the purpose of cracking the long chain hydrocarbons.

Wide number of zeolites has been employed as catalysts for the production of gasoline range hydrocarbons. Fujimoto et al. have studied several zeolites such as ZSM-5, mordenite, Y and BEA to prepare catalysts for the production of isoparaffins in gasoline range [7–9]. A hybrid catalyst containing Co-based catalyst and zeolite is also reported to enhance the selectivity of middle distillates [4]. For the production of aromatics and isoparaffins, a combination of ZSM-5 with FT catalyst is successfully applied [7]. Several catalysts prepared by permutations and combinations of FTS catalyst and cracking catalysts have been used for improving the yields of desired products [5–10]. Most of these studies reveal the superior performance of catalysts when used in consecutive double reactor compared to those (hybrid catalysts) used in a single reactor. The difficulties caused by unmatchable differences in reaction conditions required for the FTS and cracking have successfully been eliminated by applying dual bed reactors for the direct synthesis of isoparaffins from synthesis gas [2, 7, 9, 11]. Recently, Fujimoto et al. have also reported the selective production of Liquified Petroleum Gas (LPG) from synthesis gas [2]. The immediate striking option is for the production of light olefins from synthesis gas, due to their demand as vital raw materials for wide spectrum of petrochemicals. Dupain et al. have processed the wax obtained from FT through Fluid Catalytic Cracking (FCC) route to produce gasoline, where the addition of about 25% of ZSM-5 to an equilibrium catalyst (E-cat) of FCC facilitated the formation of propene and butane (31%) [12]. Subiranas and Schaub used the Pt/ZSM-5 in combination

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with FT catalyst for the selective production of isoparaffins with decreased yields of alkenes and alcohols [13]. Although, olefin appeared as an obvious by product, there is no special focus is given so far for the maximization of light olefin product, especially in the range of C_2–C_4 olefins directly from synthesis gas. The present work is thus aimed to develop the catalyst using two catalyst components, namely, K/Fe–Cu/AlOx and H-ZSM-5, in two reactors arranged consecutively. The concept of maximizing C_2–C_4 olefin yields is realized through the improved concentration of olefins in the first reactor (FTS) followed by their cracking in the second reactor. Here we report the promising results for formation of 51% C_2–C_4 hydrocarbons rich in olefins (77%) directly from the synthesis gas.

2 Experimental

2.1 Catalyst Preparation

A 6K/100Fe–6Cu–16AlOx (number indicates the molar composition) was selected as an FTS catalyst of first reactor. Preparation of the catalyst was conducted in two steps: co-fprecipitation of 100Fe–6Cu–16AlOx precursor, followed by potassium impregnation. The 100Fe–6Cu–16AlOx precursor was prepared by using aqueous solutions of $Fe(NO_3)_3$, $Cu(NO_3)_2$ and $Al(NO_3)$ that are precipitated using $(NH_4)_2CO_3$ as a precipitator. The solution was heated to 70 °C for 2 h. After cooling to room temperature, the resulting mixtures were collected after repeated washing with water. The precipitated catalysts were dried at110 °C for 12 h and then calcined at 500 °C for 5 h in static air. After impregnation with potassium carbonate by the incipient wetness technique, the catalyst was dried at 110 °C for 12 h, and then calcined at 500 °C for 5 h. Details of structural and chemical properties of FT catalyst have been reported in our previous work [14, 15]. A ZSM-5 (Zeolyst, CBV 28014, $SiO_2/Al_2O_3 = 280$) sample calcined at 600 °C for 5 h was selected as cracking catalyst of second reactor.

2.2 Reaction Studies

The reaction was carried out in a fixed-bed consecutive dual reactor system. In the first reactor, 0.5 g of palletized and sized (0.85–1.18 mm particles) FT catalyst (6K/100Fe–6Cu–16AlOx) was loaded and was reduced in a flow of 5%H_2/Ar (200 cc/min) mixture at 450 °C for 12 h. The FTS activity tests were conducted under the following reaction conditions; Reaction Temperature = 300 °C; Pressure = 10 bar and GHSV = 6,000 h^{-1} with feed composition of (H_2/CO/Ar; mol.%) = 31.3/63.19/5.51. In the second reactor, 0.15 g of ZSM-5 catalyst (sized to 0.85–1.18 mm particles) was loaded for hydrocracking of C_{5+} hydrocarbons obtained from the first-bed reactor, where the reaction temperature is varied from 300 °C to 600 °C. CO conversion and hydrocarbon selectivity were calculated according to the following equations:

$$\text{CO conversion } (\%\ ) = \frac{(\text{moles of CO introduced}) - (\text{moles of CO unreacted})}{(\text{moles of CO introduced})} \tag{1}$$

$$\text{Hydrocarbon selectivity } (\text{mol\% C}) = \frac{(\text{moles of C in specific hydrocarbon produced})}{(\text{moles of C in total hydrocarbon produced, including } CO_2)} \tag{2}$$

3 Results and Discussion

Selective production C_2–C_4 olefins can be achieved through controlled chain making of hydrocarbons in FTS in first reactor followed by its selective cracking to C_2–C_4 fragments in the second reactor. The FT catalyst developed in the laboratory by optimization of the composition of the metal oxides has exhibited promising catalytic activity in the conversion of bio-mass derived synthesis gas into long chain hydrocarbons and olefins [14]. In continuation to that, the present study focused on the three important factors that can influence the production of smaller olefins, namely, (1) cracking reaction temperature of olefins, (2) space velocity of the reactants and (3) relative composition of H_2 and CO in the reactant mixture that have been discussed in this session.

3.1 Effect of Cracking Reaction Temperature

In order to understand the role of cracking catalyst, the product obtained after FTS is analyzed and compared with the products obtained after cracking at various reaction temperatures. In FTS alone condition, about 96% conversion of CO was observed with about 65% conversion to hydrocarbons (Table 1). FTS reaction is then coupled with cracking reaction over H-ZSM-5 ($SiO_2/Al_2O_3 = 280$). The ZSM-5 catalyst with particular SiO_2/Al_2O_3 is selected based on the activity and product

Table 1 Effect of olefin cracking temperature in the dual bed reactor

Cracking temperature (°C)	Nil (FT only)	300	400	500	600
CO conversion	96.1	96.2	96.1	95.8	86.9
Conversion to CO_2	31.4	31.8	32.3	32.0	28.9
Conversion to hydrocarbons	64.7	64.4	63.8	63.8	58.0
Hydrocarbon distribution (Selectivity, C-mol.%)					
(I) C_1	7.6	7.9	7.9	8.3	14.6
(II) C_2–C_4 ($C_2^{=}$–$C_4^{=}$)	24.1(17.6)	29.0(18.4)	39.8(28.2)	51.0(39.2)	58.7(42.5)
C_2 ($C_2^{=}$)	7.4(4.9)	8.0(6.2)	9.9(8.2)	14.7(12.7)	25.6(18.8)
C_3 ($C_3^{=}$)	8.8(6.8)	7.3(5.4)	14.7(12.4)	21.8(19.3)	23.1(19.1)
C_4 ($C_4^{=}$)	8.0(5.9)	13.8(6.8)	15.3(7.7)	14.5(7.2)	10.0(4.7)
(III) C_5–C_7 ($C_5^{=}$–$C_7^{=}$)	20.5(4.0)	21.0 (3.6)	13.3(1.9)	8.5(1.5)	2.4(0.4)
C_5 ($C_5^{=}$)	8.2(2.0)	12.7(1.9)	9.0(1.5)	6.1(1.2)	1.8(0.3)
C_6 ($C_6^{=}$)	7.7(2.0)	6.7(1.7)	3.4(0.4)	2.1(0.3)	0.6(0.1)
C_7	4.6	1.6	0.8	0.3	0.1
(IV) C_{8+}	47.8	42.1	39.0	32.2	24.3
Total	100.0	100.0	100.0	100.0	100.0

Catalysts: F-T = 6K/100Fe–6Cu–16AlOx; Cracking = ZSM-5 ($SiO_2/Al_2O_3 = 280$)

Reaction conditions: F-T synthesis (0.5 g cat.): $T = 300$ °C; $P = 10$ atm; GHSV = 6000 (syn gas: 35 cc/min), Cracking reaction (0.15 g cat.): $T = 300$–600 °C

selectivities. At lower SiO_2/Al_2O_3 the product exhibited higher selectivity to CO_2, methane and C_{8+} hydrocarbons, where as at higher SiO_2/Al_2O_3 the olefine yields are very low. At the $SiO_2/Al_2O_3 = 280$, the ZSM-5 could exhibit the superior performance with respect to conversions and product selectivities for light olefins. This observation envisions the higher cracking and olefin oligomerization activity of low SiO_2/Al_2O_3 of ZSM-5 on one hand and the lower cracking activity of ZSM-5 at higher SiO_2/Al_2O_3 ratios on the other. The ZSM-5 with optimum SiO_2/Al_2O_3 (280) is thus selected as cracking catalyst and its performance is evaluated at four different reaction temperatures from 300 °C to 600 °C (Table 1). These values of CO conversion and conversion to hydrocarbons are not much changed even after the cracking reaction up to 500 °C, but decreased at 600 °C. The observed decrease in CO conversion at higher reaction temperatures may be due to the additional formation of CO from the reaction of hydrocarbons with water, which is produced during FTS, through the reforming route at 600 °C cracking temperature.

The hydrocarbon distribution with C-mol.% selectivity given in Table 1 indicates the formation of several hydrocarbon products. The entire product has been classified into four main groups, namely, (I) C_1, (II) C_2–C_4, (III) C_5–C_7 and (IV) C_{8+}. The selectivity to C_1 is around 8% in FTS as well as FTS followed by cracking up to 500 °C and then significantly increased at 600 °C. The selectivity to C_2–C_4 hydrocarbons is continuously increased while that of C_5–C_7 and C_{8+} is decreased with increasing cracking reaction temperature. The olefin content in C_2–C_4 hydrocarbon (values given in parenthesis in Table 1) is also increased with the reaction temperature. However, the percent of olefins in C_2–C_4 fragments is almost constant (about 75%) at all the cracking temperatures, which is advantageous for obtaining enhanced C_2–C_4 olefin yields at higher reaction temperatures. The product pattern suggests that higher reaction temperatures are favorable for C_2–C_4 formation up to 500 °C, and above this temperature the severity in cracking caused the increased formation of C_1. This situation suggests 500 °C as optimum cracking reaction temperature to minimize the formation of CO and CH_4 on one hand and increasing the formation of C_2–C_4 hydrocarbons on the other.

3.2 Effect of Space Velocity

Table 2 contains the data on effect of Gas Hourly Space Velocity (GHSV) of the feed on CO conversion and product selectivity. The change in CO conversion is not significant but a general trend of continuous decrease in conversion is observed with space velocity.

Among the products, the selectivity to methane is almost constant (7.7–8.6%). The selectivity to C_{8+} is increased, whereas that of C_5–C_7 goes through a maximum at 4,000 h^{-1}. Above this value of space velocity, a sudden decrease in C_5–C_7 selectivity is observed. The selectivity to C_2–C_4 hydrocarbons including the olefin content in C_2–C_4 has gone through a maximum at 6,000 h^{-1}. The apparently different trends in selectivity of heavier (C_{8+}), medium (C_5–C_7) and lighter (C_2–C_4) products are basically connected through the two fundamental reaction steps, namely,

Table 2 Effect of space velocity of the feed

FT GHSV (h^{-1})	CO conv. (%)	Conv. to CO_2 (%)	Selectivity (C-mol.%)			
			CH_4	C_2–C_4 ($C_2^=$–$C_4^=$)	C_5–C_7	C_{8+}
2000	96.9	30.0	8.6	41.7 (27.8)	11.9	37.8
4000	97.0	29.5	7.7	43.3 (31.3)	12.9	36.1
6000	95.8	32.0	8.3	51.0 (39.2))	8.5	32.2
8000	92.3	26.3	7.9	43.1 (33.5)	6.4	42.6
10000	92.8	27.7	8.1	41.5 (32.3)	7.4	43.0
12000	92.5	28.2	8.3	38.7 (30.0)	7.4	45.7

Catalysts: F-T = 6K/100Fe–6Cu–16AlOx; Cracking = ZSM-5 (SiO_2/Al_2O_3 = 280)

Reaction conditions: F-T synthesis (0.5 g cat.): $T = 300$ °C; $P = 10$ atm; GHSV = 2,000–12,000 h^{-1} (syn gas: 35 cc/min), Cracking reaction (0.15 g cat.): $T = 500$ °C

(1) formation of C_{8+} in FT and (2) cracking of C_{8+} through the following route.

$$C_{8+} \rightarrow C_5{-}C_7 \rightarrow C_2{-}C_4$$

At lower space velocity conditions, cracking of C_{8+} to form C_5–C_7 followed by its further cracking to C_2–C_4 is proceeded. With increase in space velocity, the concentration of C_{8+} is increased either due to the increased formation of C_{8+} in the first reactor or due to the decreased conversion of C_{8+} to C_5–C_7 and C_2–C_4. But, the decreased CO conversion observed with space velocity rules out the former case. Hence, the decrease in cracking of C_{8+} in the second reactor only is responsible for increase in C_{8+} at higher space velocity. The selectivity to C_2–C_4 hydrocarbons including olefins is increased up to 6,000 h^{-1}. At this space velocity, the selectivity to C_5–C_7 is decreased significantly and supports the decreased formation of C_5–C_7 from C_{8+}. Above the value of 6,000 h^{-1}, C_2–C_4 selectivity is decreased with simultaneous increase of C_{8+} indicating the lower severity for cracking reaction. The severity in operation seems to be optimum for the conversion of CO and for the selective production of C_2–C_4 hydrocarbons at 6,000 h^{-1} space velocity.

3.3 Effect of H_2/CO Ratio

The significance of hydrogen in the reaction mixture implies to its importance in chain termination reaction to control the carbon number of hydrocarbon in FTS and its influence on hydrocracking reaction in the second reactor. Attaining a balance between these two reactions is an obvious condition for the selective production of C_2–C_4 hydrocarbons rich in olefins. In order to study this aspect, the H_2/CO molar ratio of the feed was varied from 1 to 2. Figure 1a shows the changes in CO conversion and product selectivities in FTS alone condition. The conversion of CO has continuously increased with hydrogen flow and maximum conversion of 95% is observed at $H_2/CO = 2$. This is in accordance with the empirical equation of FTS synthesis shown below, where two moles of H_2 is required for complete reaction with one mole of CO and a H_2/CO molar ratio of 2 is an ideal feed composition for effective FTS reaction.

$$nCO + 2n\,H_2 \rightarrow [CH_2]_n + nH_2O$$

Among the various hydrocarbons, the selectivity to C_{8+} is continuously decreased, while that of smaller hydrocarbon, i.e., C_2–C_4 and C_5–C_7 is increased with hydrogen concentration (Fig. 1a). The oppositely following trends in selectivity of longer and smaller hydrocarbons envisions the shift in formation of longer hydrocarbons to shorter hydrocarbons that can be possible only through the enhanced chain termination reactions facilitated at increased hydrogen flow.

The influence of increased hydrogen flow on the product pattern of second reactor is shown in Fig. 1b. The trends in product pattern are similar to that of FTS only condition except a noticeable increase in C_2–C_4 hydrocarbons, which is significant at the H_2/CO mol. ratio of 2. The selectivity to C_5–C_7 is decreased but that of C_1 is almost constant with hydrogen flow. Thus the selective cracking of long chain hydrocarbons (C_{8+}, C_5–C_7) seems to be responsible for the production of C_2–C_4 hydrocarbons but not C_1 in the second reactor by mildly acidic silicious ZSM-5 (SiO_2/Al_2O_3 = 280) employed in the reaction.

In order to estimate the relative contribution of individual reactions to the product quality, the three main aspects of products obtained after FTS and cracking reactions, namely, changes in CO conversion (Fig. 2a), selectivity to C_2–C_4 hydrocarbons (Fig. 2b) and C_2–C_4 olefins (Fig. 2c) have been compared at all the H_2/CO values. The CO conversions after both the reactions are almost comparable with a common trend of increased conversion with hydrogen flow. While that of C_2–C_4 hydrocarbons as well as C_2–C_4 olefins are remarkably increased after cracking reaction. This trend is continued at all the H_2/CO values revealing the absence of any negative

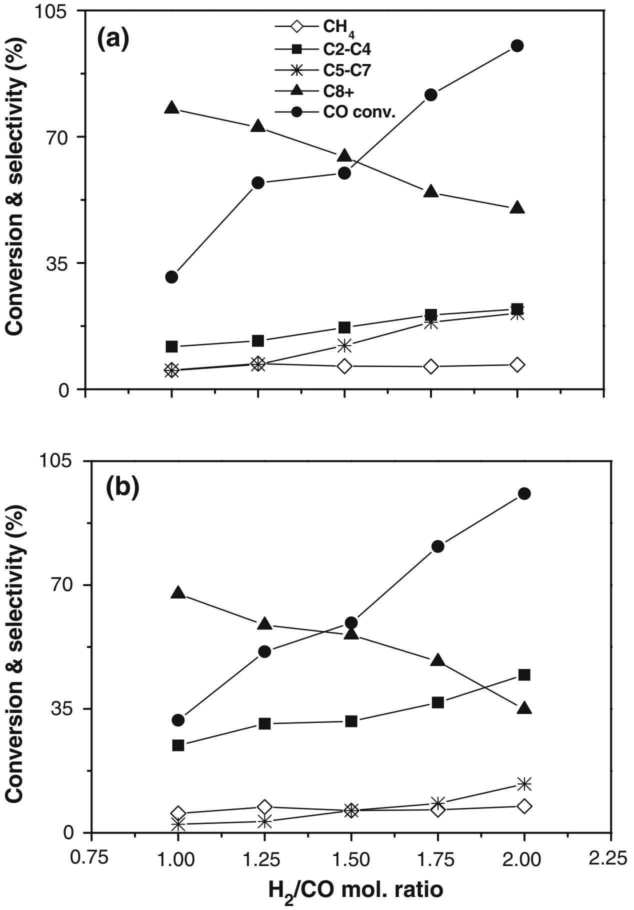

Fig. 1 Effect of H_2/CO molar ratio on (**a**) FTS product and (**b**) cracking product. Catalysts: F-T = 6K/100Fe–6Cu–16AlOx; Cracking = ZSM-5 (SiO_2/Al_2O_3 = 280). Reaction conditions: F-T synthesis (0.5 g cat.): $T = 300$ °C; $P = 10$ atm; GHSV = 6,000 h^{-1} (syn gas: 35 cc/min), Cracking reaction (0.15 g cat.): $T = 500$ °C

role of hydrogen on suppressing the formation of C_2–C_4 olefins at higher hydrogen concentrations. How is it possible? It is important to remember that the formation of short chain hydrocarbons is favored at higher H_2 concentrations in FTS, and the nature of product obtained in FTS is source for the hydrocracking reactions in the second reactor. Hence, the high concentration of H_2 can have the following two effects that operate in opposite way, namely, (1) the light hydrocarbon-rich FTS product can cause increased formation of C_2–C_4 olefins in the second reactor and (2) the higher H_2 concentrations in the feed can cause increased hydrogenation to yield lower C_2–C_4 olefins. The product obtained in the studied H_2/CO range of 2 strongly supports the dominance of the former factor to produce enhanced C_2–C_4 olefins at higher hydrogen flow. At these conditions, the enormous increase of hydrocarbon formation in FTS followed by its fragmentation in the second reactor makes the hydrogenation reactions insignificant for determining the product quality.

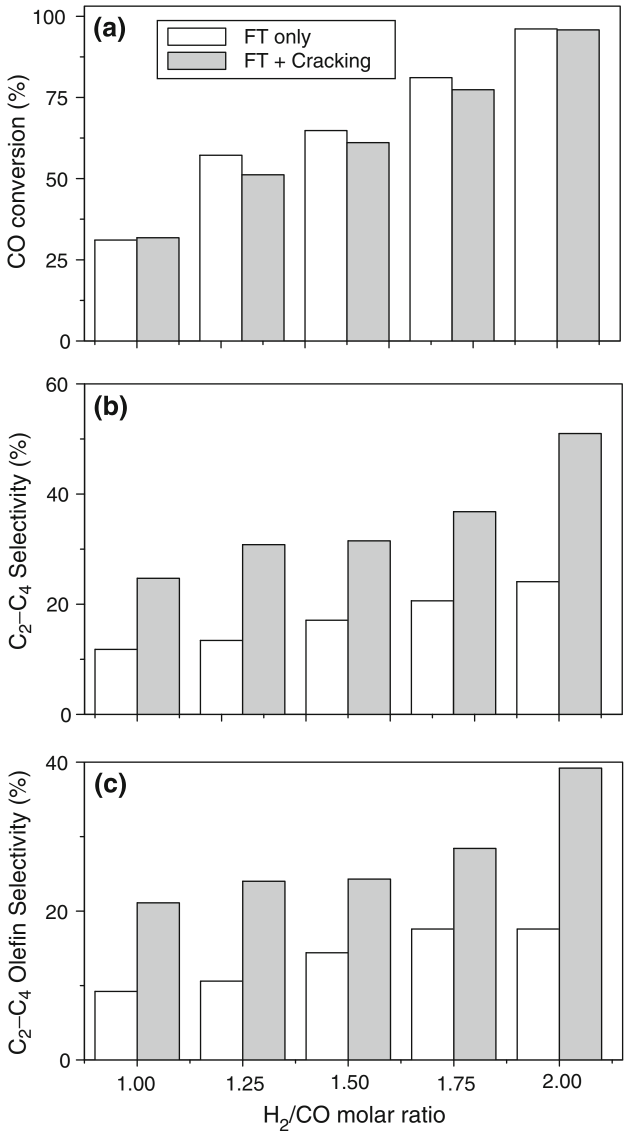

Fig. 2 Effect of H_2/CO molar ratio on (**a**) CO conversion and (**b**) C_2–C_4 selectivity and (**c**) C_2–C_4 olefin selectivity. Catalysts: F-T = 6K/100Fe–6Cu–16AlOx; Cracking = ZSM-5 (SiO_2/Al_2O_3 = 280). Reaction conditions: F-T synthesis (0.5 g cat.): $T = 300$ °C; $P = 10$ atm; GHSV = 6,000 h^{-1} (syn gas: 35 cc/min), Cracking reaction (0.15 g cat.): $T = 500$ °C

The reaction condition of 6,000 h^{-1} GHSV, H_2/CO of 2 molar ratio, and cracking temperature of 500 °C in the second reactor could give the highest selectivity towards C_2–C_4 hydrocarbons as well as C_2–C_4 olefins in the present study. It is important to remember that water is an unavoidable by product of this reaction that can affect the hydrothermal stability and catalytic activity of the ZSM-5 catalyst. However, at the above-mentioned reaction conditions the catalyst exhibited almost constant activity for CO conversion and C_2–C_4 olefin selectivity in the studied period of 100 h without the apparent deactivation on both the catalysts (Fig. 3). The results reveal the hydrothermal

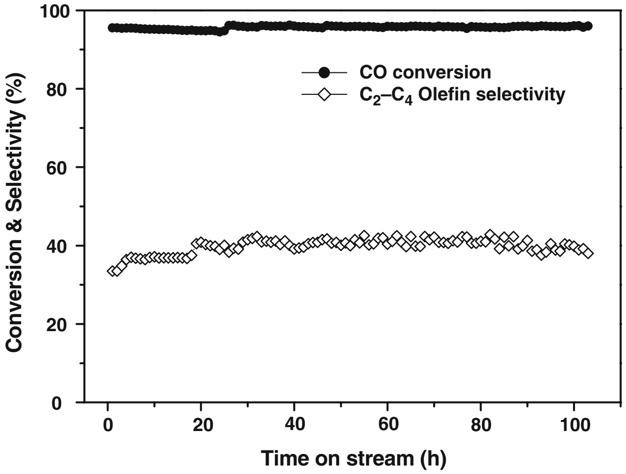

Fig. 3 Time-on-stream performance of the catalysts. Catalysts: F-T = 6K/100Fe–6Cu–16AlOx; Cracking = ZSM-5 (SiO_2/Al_2O_3 = 280). Reaction conditions: F-T synthesis (0.5 g cat.): $T = 300$ °C; $P = 10$ atm; GHSV = 6,000 h^{-1} (syn gas: 35 cc/min), Cracking reaction (0.15 g cat.): $T = 500$ °C

stability of the ZSM-5 against the water produced in the reaction. This may be due to the formation of small amount water that may not be effective for framework dealumination of ZSM-5 at the reaction conditions operated. Detailed studies are in progress for estimating the amount of water and coke and their relative contribution to the long time catalytic activity. On the behalf of comparison of this process with other processes in light olefins production, the UOP/Hydro process employs SAPO-34 catalyst for the production of as high as 90% olefins from methanol, but the catalyst suffers from a fast deactivation. The ZSM-5 based Lurgi process also produces about 70% of propylene from methanol via recycling of by-products. Unlike the above-mentioned processes, the present process utilizes syngas directly for the production of 51% olefins and suggests a scope for tailoring of ZSM-5 properties for the industrial applications.

4 Conclusion

Effective formation of C_2–C_4 olefins from synthesis gas can be achieved by combination of K/Fe–Cu/AlOx and H-ZSM-5 catalysts in a consecutive dual reactor system. Cracking reaction temperature and H_2/CO molar ratios have played a significant role in determining CO conversion and product selectivity, where the selective cracking of hydrocarbons to C_2–C_4 fragments rich in olefins is obtained on a silicious ZSM-5 (medium acidity) catalyst at 500 °C. Increased H_2/CO mol. ratio has enriched the formation of C_2–C_4 hydrocarbons rich in olefins. At optimized reaction conditions, the catalyst exhibited improved formation of lighter hydrocarbons, minimum selectivity to methane with stable performance in CO conversion and olefin selectivity for 100 h.

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