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A highly active and stable Fe-Mn catalyst for slurry Fischer–Tropsch synthesis

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Abstract

A highly stable and active Fe-Mn catalyst for slurry Fischer–Tropsch synthesis (FTS) was prepared and scaled up for the application in the industrial pilot plant at Institute of Coal Chemistry (ICC), Chinese Academy of Sciences (CAS). One Lab-scale catalyst and one scaled-up catalyst are introduced in the present paper. The particle size of the Lab-scale catalyst is about 5–15 μm, while it is increased to 30–90 μm for the scaled-up catalyst. Simultaneously, the morphology of the catalyst was greatly improved after the catalyst being scaled up. Both the Lab-scale and scale-up catalysts show high FTS activity. CO conversion of the Lab-scale catalyst and the scaled-up one are over 70.0% ($H_2/CO = 0.67$, 275 °C, 1.5 MPa and 3000 h^{-1}) and 55.0% ($H_2/CO = 0.67$, 260 °C, 1.5 MPa and 2000 h^{-1}), respectively. The catalysts also possess excellent stability, no obvious deactivation was observed during stable run of 4200 h and 1200 h on stream for the two catalysts. However, the Lab-scale catalyst produced more methane (about 8–10 wt%) and $C_{2\text{–}4}$ (22–30 wt%) and less $C5^+$ hydrocarbon (55–70 wt%). Meanwhile, the hydrocarbon distribution of the catalyst was greatly improved for after the catalyst being scaled up, and the distribution of hydrocarbon products become much preferable. The selectivity to methane was well controlled at about 5 wt%, and the sum of $C_{2\text{–}4}^{=}$ and C_5^+ was increased to 91–93 wt%. On the whole, the scaled-up catalyst satisfies the requirements of the application for FTS in the industrial pilot plant of slurry bubble column reactor (SBCR) at ICC, CAS.

Keywords: Fischer–Tropsch synthesis; Fe-Mn catalyst; Scale-up; Slurry reactor

1. Introduction

Currently, the transportation fuel and chemical feedstock are predominantly made from petroleum. The presently known reserve of crude oil is insufficient for the near future, however, the reserves of methane and coal is 1.5 and 25 times of that of the crude oil [1]. Production of syngas from methane or coal and conversion of the syngas to a range of fuels and chemicals become increasingly of interest as the reserves of crude oil are depleted and/or the price of the crude oil crazily rises to near US$ 60 bbl^{-1} in recent days.

Fischer–Tropsch synthesis (FTS), i.e. the conversion of syngas ($H_2 + CO$) to hydrocarbons, has been used since the early 20th century to produce liquid fuels and chemicals from coal, natural gas and other C-based materials [2]. It is one of the most feasible routes to make up the deficiency of the crude oil supply. Research and development (R&D) of a high performance catalyst is one of the key technologies for FTS. Presently, although metal Fe, Ni, Co and Ru have the required FTS activity for commercial application [2], under the practical operation, Ni produces too much methane, and besides the very high price of Ru the available amount is insufficient for large-scale industrial application. This leaves only Fe and Co as viable catalysts for industrial FTS. Co-based catalyst is fit for the conversion of syngas with high H_2/CO ratio (2.0) derived from natural gas. Iron-based catalyst is attractive due to their high FTS activity as well as their water–gas shift (WGS) reactivity, which helps to make up the deficit of H_2 in the syngas derived from modern energy-efficient coal gasifiers [1–3]. Typical commercial-grade iron Fischer–Tropsch catalysts consist of iron oxides promoted with copper, potassium and silicon oxides, generally prepared by basic precipitation of the metal salts

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[4]. Attempts has been continued to elucidate factors that affect the catalytic performances (activity, selectivity and stability) of iron-based catalysts and to improve the catalysts potential capability for applications.

Advanced reactor is the other key one of the process. FTS is a highly exothermic reaction and the bubble column slurry reactor is the ideal reactor choice to this purpose, due to the possibility of achieving near isothermal conditions and also because of the relatively high heat transfer coefficients to cooling tubes. The slurry reactor also possesses the advantage of lower operating and reactor construction costs. SASOL has introduced this technology in 1993 in a unit with a capacity of 2500 bbl/day at Bintulu, Malaysia [5]. In this system, synthesis gas is bubbled through slurry of heavy liquid products and catalyst particles. Unreacted synthesis gas and light products leave the reactor in the gas phase, while the liquid products are removed as a part of the slurry. Heat is removed by cooling coils mounted inside the reactor. Thirty to ninety millimeters spherical catalyst particles are generally employed in slurry FTS. However, a serious issues in slurry phase operation, catalyst attrition and separation from the waxy liquid product appeared by comparing with that used in the fixed-bed reactor and circulating fluidized bed reactor [6,7]. To meet the requirements for the application of the catalyst in slurry reactor, many efforts have been performed to improve the structural strength, morphology and attrition resistance of the catalyst used in slurry FTS.

Although precipitated Fe-Cu-K/SiO_2 catalyst, is often used for slurry FTS to produce high quality diesel, has high FTS activity and can be operated at lower temperature, it produces too much heavy hydrocarbon which make it is difficult to separate the catalyst particles from the mixture. It has also been reported that a moderate amount of manganese incorporated into Fe-based catalyst could improve the selectivity to both light olefins and middle distillate cut and FTS activity [8–11].

There may be great predominance, for example, the enhancement in the selectivity to light olefins and middle distillate can greatly decrease the load of catalyst separation, if Fe-Mn catalyst is applied in slurry FTS. However, a variety of efforts on Fe-Mn catalyst were performed for its elemental investigation in fixed-bed reactor. The studies on the scale up, spray-drying and application of Fe-Mn catalyst for the slurry FTS are seriously lacking. Our group in Institute of Coal Chemistry (ICC), Chinese Academy of Sciences (CAS), has performed some efforts on optimizing composition and scaling up of the Fe-Mn catalyst [12,13] and tried to apply it in the slurry FTS. Some interest results (high activity and stability, optimized hydrocarbon distribution and preferable attrition resistance) have been obtained.

The objective of this study is to develop a highly active and stable, attrition resistant and spherical Fe-Mn FTS catalyst which is suitable for the applications in slurry reactor in laboratory and finally for its first application in the industrial pilot plant of slurry bubble column reactor (SBCR) in ICC, CAS. A highly active and stable and attrition resistant Fe-Mn catalyst for the slurry FTS was obtained. The Fe-Mn catalyst was prepared by the combination of continuous co-precipitation and spray-drying technologies at different scales (Lab-scale and industrial-scale). The activity, selectivity, stability and attrition resistance of the catalysts prepared by the different scales were tested in 1 L continuous stirring tank reactor (CSTR). The results of the present tests show some potentials of the Fe-Mn catalyst for the application in industrial slurry bubble column reactors (SBCR).

2. Experimental

2.1. Catalyst preparation

The catalysts mentioned in the present paper, mainly comprised Fe, Mn, SiO_2 and K, were prepared by the combination of co-precipitation and spray-drying methods at different scales. The Lab-scale catalyst was prepared in 1.0 kg quantity, and the scaled-up catalyst was prepared in 200 kg quantity. For optimizing the distribution of hydrocarbon products, shortening the period of induction, decreasing the operation temperature and improving the spherical morphology of the Lab-scale catalyst, the contents of SiO_2 and K in the catalyst were increased and optimized. The detailed description of catalyst was given elsewhere [12–14]. In brief, the mixed solution of Fe and Mn nitrates was precipitated with ammonium solution. After precipitation, the precipitate was filtered and washed completely. The required amount of silica sol, potassium salt solution and de-ioned water were mixed with the filtered cake. The mixture was then re-slurred and spray-dried in the spray-drier with different scales and under the optimized conditions. The spray-dried samples were calcined at 500 °C for 5 h.

2.2. Catalyst characterization

The BET surface area, pore volume and pore size distribution of fresh catalysts were determined via N_2 physisorption at the normal boiling point of N_2 (-196 °C), using a Micromeritics ASAP 2500 instruments. The catalyst samples were degassed under vacuum at 150 °C for 6 h prior to the measurement.

Mössbauer spectroscopy was measured with a CANBERRA Series 40 MCA constant-acceleration Mössbauer spectrometer (CANBERRA, USA) at room temperature, using a 25 mCi ^{57}Co in Pd matrix. The spectrometer was operated in the symmetric constant acceleration mode. The spectra were collected over 512 channels in the mirror image format. Data analysis was performed using a non-linear least square fitting routine that models the spectra as a combination of singlets, quadruple doublets and magnetic sextuplets based on a Lorentzian line shape profile.

Table 1
The detailed description and textural properties of the catalysts

Catalysts	Particle size (μm)	Description	Textural properties		
			BET area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
Cat 1	5–15	Laboratory-scale sample	173	0.29	6.73
Cat 2	30–90	Scale-up sample	231	0.42	7.23

The spectral components were identified on the basis of their isomeric shift (δ), quadruple splitting (Δ) and magnetic hyperfine field (Hhf). All isomer shift values were reported with respect to metallic iron (α-Fe). Magnetic hyperfine fields were calibrated with the 330 kOe field of a-Fe at room temperature.

The morphology of samples was obtained using an ESEM XL30 (FEI, USA) scanning electron microscopy (SEM). The samples were coated with gold/palladium for 80 s in 20 s intervals before the measurements to avoid charging problems.

2.3. Reaction apparatus

The catalysts were tested in a 1 dm^3 continuous slurry tank reactor unit (CSTR). Detailed description of the reactor and product analysis systems has been provided elsewhere [15]. In brief, the syngas feed passes through a series of alumina de-oxygen, activated charcoal, and 5 Å molecular sieve traps to remove tiny impurities in feed-gas. The flow-rates of H_2 and CO were adjusted with two mass flow controllers, respectively. Products and un-reacted gas passed through a hot and a cold trap to condense products (oil and water). The flow-rate of incondensable gas (tail gas) was measured by a wet-gas flow meter. High molecular-weight hydrocarbon (wax) was withdrawn from the slurry reactor through a porous cylindrical sintered metal filter.

For each FTS test, about 320 g liquid wax and 20 g fresh catalyst were loaded in the reactor. After reduction, the reactor system was adjusted to the required reaction conditions.

The amount of CO_2 in tail gas was analyzed periodically with a packed column (Hayesep N 2.44 mm × 3.175 mm i.d., H_2 carrier) attached to a thermal conductivity (TCD). H_2, CO, CH_4 and tiny of N_2 and O_2 in both feed gas and tail gas were analyzed by using a 5A molecular sieve packed column (30 m × 0.53 mm i.d. (Ar carrier, TCD)). C_1–C_8 hydrocarbons (*n*-paraffins, *n*-olefins and branched isomers) were analyzed by using the same GC equipped with an alumina packed column (50 m × 0.53 mm i.d., N_2 carrier, TCD). The analysis of the oil product was carried out with a 60 m × 0.25 mm i.d. DB-1 capillary column (N_2 carrier, FID). A 30 m × 0.32 mm i.d., DB-WAX capillary column (N_2 carrier, FID) was used to analyze oxygenates in the water phase. High molecular weight product (wax) was analyzed on an UA^+-(HT) capillary column (15 m × 0.53 mm i.d., N_2 carrier and FID).

3. Results and discussion

3.1. Textural and structural properties of the catalysts

Table 1 presents the BET surface areas, pore volumes and average pore sizes measured using N_2 physisorption for the catalysts as-prepared. The surface area and pore volume of the Lab-scale sample are relatively lower, about 173 m^2/g and 0.29 cm^3/g, respectively. However, both the surface area and pore volume of the scale-up sample greatly increased to 231 m^2/g and 0.42 cm^3/g, respectively. The increments in the surface area and pore volume of the catalyst may be due to the increase of SiO_2 amount and the different preparation parameters during spray-drying [13,16,17]. The high BET surface areas imply that the active phase is well dispersed.

The bulk compositions of the active metal (Fe) of the catalysts were measure by Mössbauer spectroscopy. The Mössbauer spectra of the two catalysts used in this paper are presented in Fig. 1, and the parameters derived from the analysis of these spectra are given in Table 2. The spectra of two catalysts are mainly composed of a doublet, which can

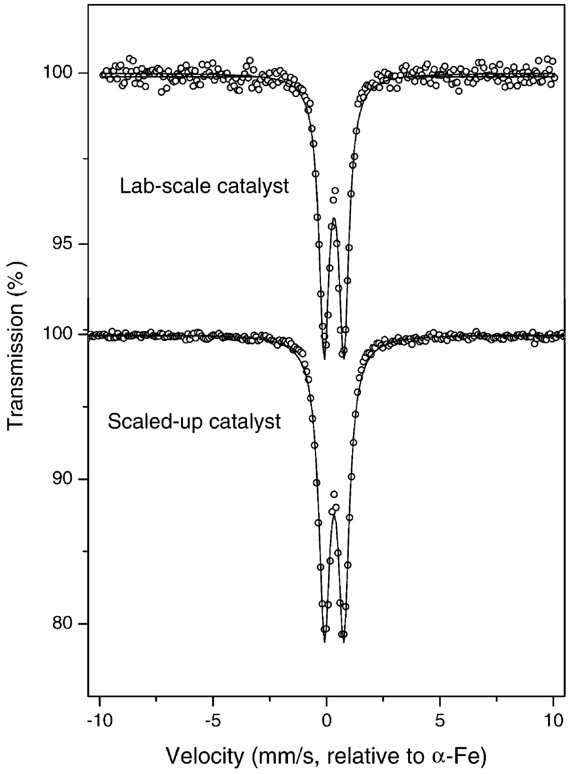

Fig. 1. Mössbauer spectra of catalyst samples as-prepared.

Table 2
Mössbauer parameters of the catalysts as-prepared

Catalyst	IS (mm/s)	QS (mm/s)	Area (%)	Phase
Lab-scale catalyst	0.33	0.85	100	Fe^{3+}(spm)
Scaled-up catalyst	0.33	0.87	100	Fe^{3+}(spm)

be assigned to the superparamagnetic Fe^{3+} ions on the non-cubic sites of α-Fe_2O_3 with the crystallite diameters smaller than 13.5 nm [18,19]. The result implies that α-Fe_2O_3 is well dispersed with SiO_2. It is also found that the quadruple splitting values of the scaled-up sample is larger than that of the Lab-scale one, which means the extents of the metal–support interaction are strengthened [17]. These results are well consistent with the results of N_2 physisorption analysis.

3.2. Catalyst morphology

The SEM images of the fresh catalyst sample are illustrated in Fig. 2. The Lab-scale one (left) possesses roughly spherical morphology and particle size of 5–15 μm, and the surface of the catalyst is highly accidented. The morphology of the scaled-up sample was greatly improved, and its particle size was magnified to 30–90 μm (right). The catalyst particles present perfect sphericity, and there is no any defect on the surface of the catalyst particle.

Since the particle size of the Lab-scale catalyst is too small to be employed for the industrial slurry FTS, only the SEM images of the scaled-up catalyst after FTS reaction were measured and presented in Fig. 3. As shown in Fig. 3, although the catalyst has been used in slurry FTS for about 1200 h, the catalyst still possesses the perfect spherical morphology as the fresh catalyst. There are no any breakages and attrition on the surface of the catalyst particles. It indicates that the scaled-up catalyst has excellent attrition resistance.

3.3. FTS performances

3.3.1. Lab-scale catalyst

The FTS activity and selectivity results for the Lab-scale catalysts are shown in Fig. 4. Following a long induction period (ca. 500 h), during which steady-state was achieved

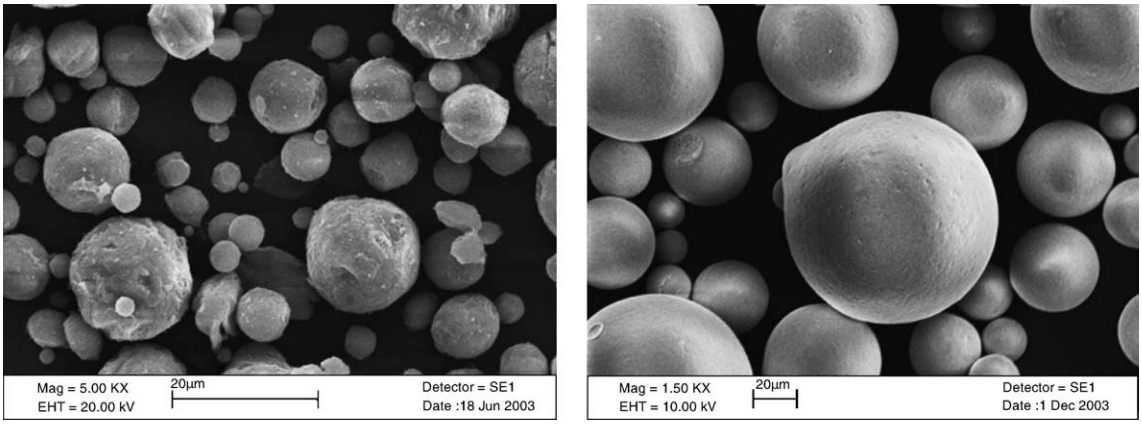

Fig. 2. SEM images of Cat 1 and Cat 2 (left: Cat 1 and right: Cat 2).

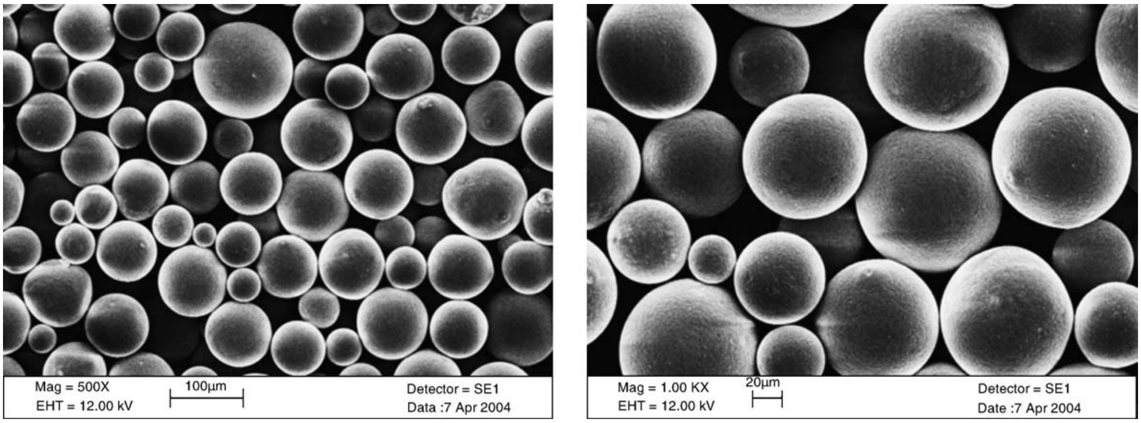

Fig. 3. SEM images of the scaled-up sample after FTS for 1200 h (left: ×500 and right: ×1000).

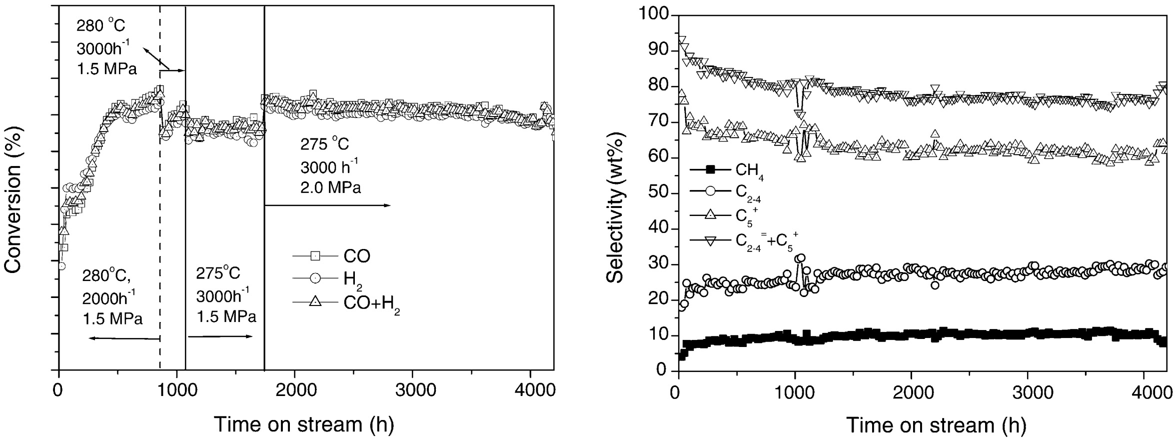

Fig. 4. FTS performances of the Lab-scale catalyst in slurry reactor; left: conversion (%) and right: hydrocarbon selectivity (wt%). *Reaction conditions*: 275–280 °C, 2000–3000 h^{-1}, $H_2/CO = 0.7$ and 1.5–2.0 MPa.

(500–4200 h), there was no significant variations with time on stream in CO, H_2 and $H_2 + CO$ conversions or hydrocarbon selectivities. CO conversion is over 70% during the steady-state period at the conditions of 275 °C, 3000 h^{-1}, $H_2/CO = 0.7$ and 1.5–2.0 MPa. After steady-state run, the condition tests were performed for about 550 h, and the activity decreased subsequently. The condition tests include the variations of temperature, space velocity, H_2/CO ration of feed gas and pressure finally were carried out, which are not listed in the present study. Although the catalyst show attractive activity and stability, the distribution of hydrocarbon is not very suitable. Too much methane and C_{2-4} produced, small amount of valuable hydrocarbon ($C_{2-4}^{=} + C_5^{+}$) formed. The selectivities to methane, C_{2-4}, C_5^{+} and $C_{2-4}^{=} + C_5^{+}$ are about 8–10, 22–30, 55–70 and 75–85 wt%, respectively. The reaction results indicate that the composition of the catalyst is required to be optimized to improve the distribution of hydrocarbon products, to shorten the period of induction and to decrease the temperature of operation.

3.3.2. Scaled-up catalyst

The catalyst was optimized during its stage of scale up to make up its defects in FTS performances. Fig. 5 shows FTS performances (activity, stability and selectivity) of the scaled-up catalyst in the slurry reactor. It is found that the initial activity (0–200 h) is high and that there is no apparent induction period. After the adjustment of H_2/CO from 1.1 to 0.7, there is unstable period (200–600 h). The reaction is subsequently in steady-state, during which CO conversion is about 60% at the condition of 260 °C, 2000 h^{-1}, $H_2/CO = 0.7$ and 1.5 MPa. Compared with the Lab-scale catalyst, the distribution of hydrocarbon of the scaled-up catalyst was greatly improved. The selectivities to methane and C_{2-4} were controlled to 5 and 20 wt%, respectively. At the same time, the selectivities to C_5^{+} and $C_{2-4}^{=} + C_5^{+}$ were increased to 75 and 91–93 wt%, respectively. The decrease of the selectivity to methane and the shifting of product to heavy hydrocarbon may be caused by the lower operation temperature and the increase of K amount in the catalyst, since K often acts as a promoter to restrain the formation of

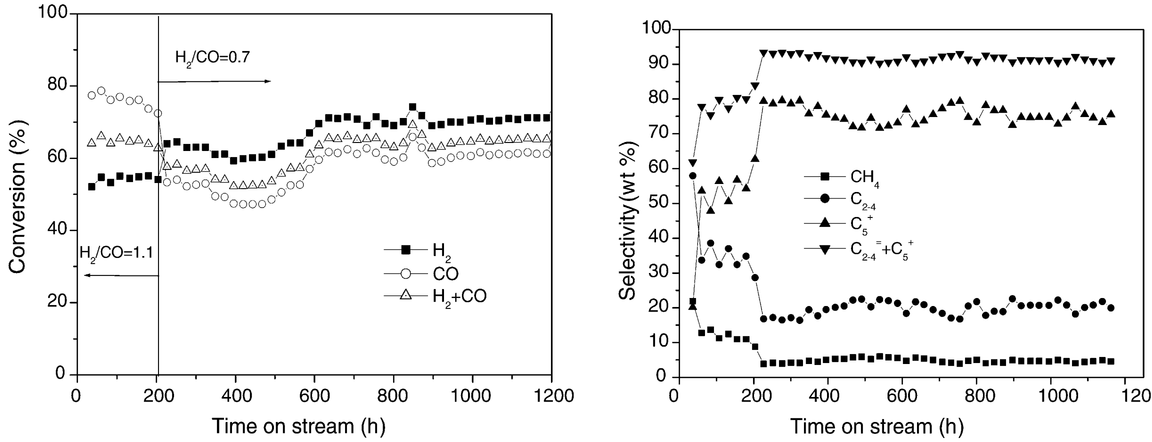

Fig. 5. FTS performances of the scaled-up catalyst in slurry reactor; left: conversion (%) and right: hydrocarbon selectivity (wt%). *Reaction conditions*: 260 °C, 2000 h^{-1}, $H_2/CO = 0.7$–1.1 and 1.5 MPa.

methane and shift the selectivity to higher molecular weight products [12,20].

4. Conclusion

A highly active and stable Fe-Mn catalyst for slurry FTS was prepared by the combination of co-precipitation and spray-drying methods at different scales. CO conversion of the Lab-scale catalyst with average size of 5–15 μm was over 70.0% during its steady-state run ($H_2/CO = 0.67$, 275 °C, 3000 h^{-1}). The Lab-scale catalyst also possessed preferable stability, no obvious deactivation occurred during stable run of 4200 h on stream. However, the Lab-scale catalyst produced too much methane (about 8–10 wt%) and C_{2-4} (15–18 wt%) and less C_5^+ (>60 wt%) hydrocarbon. Due to its high activity and stability, the Lab-scale Fe-Mn catalysts are therefore considered to have a strong potential for the further optimizing and scaling up.

Based on the experience gained, the catalyst (Cat 2) has been successfully scaled up and spray-dried in 200 kg quantity. The scaled catalyst particles have perfect spherical morphology with average size of 30–90 μm. There were no any attrition and breakage after slurry FTS for 1200 h on stream. It implies that the catalyst possessed high attrition resistance. The scaled catalyst also showed perfect FTS performances, the conversion was over 55.0% under the conditions of $H_2/CO = 0.67–1.2$, 250–260 °C and 2000–3000 h^{-1}. The selectivities to methane and C_{2-4} were controlled to 5 and 20 wt%, respectively. At the same time, the selectivity $C_{2-4}^{=} + C_5^+$ were increased to 91–93 wt%. Although there was some faultiness for the present catalyst, the scaled-up catalyst satisfies the requirements for its first application on the industrial pilot plant in ICC, CAS.

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