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A Durable Nanocatalyst of Potassium-Doped Iron-Carbide/Alumina for Significant Production of Linear Alpha Olefins via Fischer-Tropsch Synthesis

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Graphical Abstract



A potassium-doped iron-carbide/alumina nanocatalyst shows very high CO conversion (~90%) and significant productivity for C_5-C_{13} linear alpha olefins in Fischer-Tropsch synthesis under high space velocity conditions.

Highlights

• The active iron-carbide nanoparticles (~10 nm) embedded on gamma-alumina with well-dispersed potassium promoters showed high activity and productivity for linear alpha olefins in high-temperature Fischer-Tropsch synthesis.

ABSTRACT

Improvement of activity, selectivity, and stability of the catalyst used in Fischer-Tropsch synthesis (FTS) to produce targeted hydrocarbon products has been a major challenge. In this work, the potassium-doped iron-carbide/alumina (K-Fe₅C₂/Al₂O₃), as a durable nanocatalyst containing small iron-carbide particles (~ 10 nm), was applied to high-temperature Fischer-Tropsch synthesis (HT-FTS) to optimize the

production of linear alpha olefins. The catalyst, suitable under high space velocity reaction conditions $(14-36 \text{ NL} \cdot \text{g}_{cat}^{-1} \cdot \text{h}^{-1})$ based on the well-dispersed potassium as an efficient base promoter on the active iron-carbide surface, shows very high CO conversion (up to ~ 90%) with extremely high activity (1.41 mmol_{CO}·g_{Fe}⁻¹·s⁻¹) and selectivity for C₅-C₁₃ linear alpha olefins.

KEYWORDS

Fischer-Tropsch synthesis, linear alpha olefins, high durability, iron-carbide, alkali promoter

1. INTRODUCTION

The linear alpha olefins (LAOs) obtained by oligomerization of ethylene or by Fischer-Tropsch synthesis (FTS), are very important chemical intermediates used in such as detergents, plasticizers, synthetic lubricants, and polymers (polyethylene) [1, 2]. Because a wide variety of customer demands involve the LAO market, high profits can be expected if LAO production can be increased [3].

The process of oligomerization of ethylene to LAOs is well-known, but the FTS process for effective LAO production is not well studied [4, 5]. Liu et al. reported the use of pretreated CoMn/SiO₂ as a selective catalyst for alpha olefins [6]. Recently, bio-promoted iron-carbide catalysts to convert carbon dioxide to LAOs directly were developed, but the long term stability of the catalysts was not discussed [7].

Commercially, gasoline and lower-olefin products can be obtained efficiently using the high-temperature FTS (HT-FTS) process. This process is conducted at temperatures of 300–350 °C using an iron-based catalyst [8-10]. However, conventional HT-FTS catalysts remain inadequate for production of significant quantities of LAO [11]. Typically, iron-based-support catalysts (e.g., Fe/α-Al₂O₃, Fe/CNT, Fe/SiO₂, Fe@C, and Fe/zeolite) have been used in HT-FTS reactions to produce a variety of hydrocarbon products [12-18]. In recent years, more selective and efficient ways for production of high value-added

hydrocarbons have been developed for FTS. For example, high selectivity (~60%) for C₂–C₄ lower olefins was achieved using Fe/ α -Al₂O₃ and Fe/carbon-nanofiber (CNF) catalysts [19].

Gamma-phase alumina provides a robust support for the high-temperature catalytic reactions. Its use led to high metal dispersion based on strong metal-support interaction, which resulted in more active and stable sites [20, 21]. In addition, alkali metals used as a base-additive donated electrons to active sites. These were also exploited to enhance the FTS catalyst [22-25]. For instance, potassium (K) and cesium (Cs) showed dramatic effects in HT-FTS by facilitating CO dissociation and increasing the growth of carbon chains [26-29]. The doped-K in Fe catalysts also enhanced alkene production [30].

On the other hand, elaborate control of the reaction- conditions could also affect FTS products. For instance, increasing the space velocity in FTS is one effective way to achieve selective formation of the alkene products that result from reduced secondary reactions [31]. The hydrocarbon products spend less time in contact with the catalyst and the probability of re-adsorption and reaction becomes less, thereby reducing alkene hydrogenation.

Herein, we introduce for the first time an extremely active K-Fe₅C₂/Al₂O₃ nanocatalyst with high durability. It is prepared through melt-infiltration of an iron salt and sequential impregnation of a potassium solution, for the efficient production of high value-added alkene hydrocarbons. The catalyst shows extremely high activity and productivity for C₅–C₁₃ LAOs. The high stability of the catalyst was monitored as it was recycled two times under harsh reaction conditions (340 °C and 15 bar).

2. EXPERIMENTAL SECTION

2.1. Synthesis of potassium doped iron-carbide/alumina nanocatalyst

Details for the preparation of iron-carbide/alumina were reported in our previous publication [20]. Typically, 1.57 mmol Fe(NO₃)₃·9H₂O (Aldrich, \geq 98%) was physically ground with 1.0 g of alumina

powder (Strem Chemicals, Inc.) in a mortar for 5 min under ambient conditions. Next, the mixed powder was placed in a polypropylene bottle and aged at 50 °C in a tumbling oven. After aging for 24 h, the sample was allowed to cool to room temperature, and then it was transferred to an alumina boat in a tubetype furnace. The powder mixture was slowly heated at the rate of 2.7 °C ·min⁻¹ up to 350 °C under a flow of CO (0.2 L·min⁻¹); then was thermally treated at the same temperature for 8 h. After that, the resulting black powder was cooled to room temperature, and then submerged into 30 mL of ethanol under an N₂ flow of 1.0 L·min⁻¹. The powder immersed in ethanol was separated simply using a magnet and dried in a vacuum oven at 60 °C. A portion (0.376 mmol) of K₂CO₃ (Aldrich, ReagentPlus, 99%) dissolved in distilled water (0.5 mL) was impregnated on the dried iron-carbide/alumina powder. The K-incorporated sample was thermally treated again at 350 °C for 8 h under a continuous CO flow at 0.2 mL·min⁻¹. Then, the resulting powder was cooled to room temperature and submerged again in anhydrous ethanol under flowing nitrogen. Finally, the potassium doped iron-carbide/alumina was separated and dried in a vacuum oven.

2.2. High-temperature Fischer-Tropsch synthesis reaction

Fischer-Tropsch (F-T) reactions were performed in a fixed-bed stainless steel reactor tube (inner diameter: 5 mm). The catalyst sample (0.3 g) was diluted with glass beads ($425-600 \mu m$, 3.5 g) for prevention of hot-spot generation by the severe exothermic reaction. Before reaction, the catalyst was reduced in situ at atmospheric pressure by passing a flow of CO ($40 \text{ mL} \cdot \text{min}^{-1}$) over it at 350 °C for 8 h. After reduction, the reaction was carried out at 340 °C and 15 bar for 90 h using reactant gas ($H_2/CO = 1.0$, GHSV = 14 NL·g_{cat}⁻¹·h⁻¹). After reaction for 90 h, the cooled iron-carbide/alumina catalyst was recycled two times at 340 °C and 15 bar for an additional 48 h using the same reactant gas ($H_2/CO = 1.0$, GHSV = 20 and 36 NL·g_{cat}⁻¹·h⁻¹) with no pre-treatment. The composition of the outlet gases was analyzed using a gas chromatograph (Agilent, 3000 Micro GC) equipped with TCD and FID. The flow rates of the outlet gases were measured using a wet-gas flow meter (Shinagawa Co.). After reaction, the solid-phase hydrocarbons were collected in a hot trap (240 °C) and the liquid-phase hydrocarbons and water were collected in a cold

trap (-2 °C), respectively. The isolated solid (wax) and liquid (oil) products were analyzed using an offline gas chromatograph (Agilent, 6890 N) and the simulated distillation method (ASTM D2887). Detailed hydrocarbon analysis (DHA) of the LAO component and mass percent in the liquid oils was determined using ultra-high resolution capillary gas chromatography and ASTM D6730.

2.3. Characterization

The catalyst samples were characterized using a Tecnai TF30 ST and a Titan Double Cs corrected TEM instrument (Titan cubed G2 60-300). Energy-dispersive X-ray spectroscopy (EDS) elemental mapping data were obtained using a higher-efficiency detection system (Super-X detector) and high power powder XRD (Rigaku, D/MAX-2500, 18 kW). The TEM samples were prepared by putting a few drops of the corresponding colloidal solutions on carbon-coated copper grids (Ted Pellar, Inc). XPS studies were carried out using a Sigma Probe (Thermo VG Scientific, Inc.) with a micro-focused monochromator X-ray source. The XPS sample was prepared by placing a few drops of the colloidal solution on small pieces of gold wafer. A Mössbauer spectrometer of the electromechanical type, with a 50 mCi 57 Co source in a rhodium matrix, was used in constant-acceleration mode. Nitrogen sorption isotherms were measured at -196 °C with a Tristar II 3020 surface area analyser. Before measurements, the samples were degassed in a vacuum at 300 °C for 4 h.

3. RESULTS AND DISCUSSION

3.1. Synthesis of potassium doped iron-carbide/alumina nanocatalyst

Scheme 1 illustrates the overall procedure for synthesis of the K-Fe₅C₂/Al₂O₃ nanocatalyst. The active iron-carbide nanoparticles promoted by potassium were obtained through a melt-infiltration process and the impregnation method [28, 32]. First, an iron nitrate hydrate salt was melt-infiltrated into mesopores of the alumina support by aging at 50 °C. By a thermal treatment at 350 °C under a CO condition, small iron-carbide nanoparticles in alumina pores could be generated. K-Fe₅C₂/Al₂O₃ nanocatalyst was obtained using a wetness impregnation method with aqueous K₂CO₃ solution as a K source.

The transmission electron microscopy (TEM) image shows well-dispersed iron-carbide nanoparticles around 10 nm (Fig. 1a and b). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image also presents bright dots, indicating Fe-rich regions within the porous alumina support (Fig. 1c). The elemental mapping of iron (red) and aluminum (green) demonstrates small and uniform nanoparticles (Fig. 1d). Elemental potassium (cyan) is also well-dispersed in the K-Fe₅C₂/Al₂O₃ sample. The high-resolution TEM (HR-TEM) image and the corresponding Fourier-transform (FT) pattern indicated the formation of iron-carbide crystals with a distance of 0.21 nm between adjacent fringes that match with the (510) planes of Hägg iron-carbide (Fig. 1e–f).

In the X-ray diffraction (XRD) patterns of pristine alumina and K-Fe₅C₂/Al₂O₃ nanocatalyst, alumina peaks were mainly observed at $2\theta = 37.6^{\circ}$, 45.9° , and 67.0° ; corresponding to the reflections of the (311), (400), and (440) planes of gamma-phase alumina (Fig. 2a, JCPDS no. 10-0425). From the XRD data, the exact crystal phase of the incorporated nanoparticles was difficult to be assigned due to the broad peaks of the alumina, but the shoulder ($2\theta = 41^{\circ}-45^{\circ}$) of the main peak showed a relatively increased intensity compared to that of pristine alumina, indicating the presence of iron-carbide phases.

To investigate the surface states of K-Fe₅C₂/Al₂O₃ nanocatalyst, core-level X-ray photoelectron spectra (XPS) of iron and potassium (K) were recorded (Fig. 2b and c). The XPS spectra of the energy region of the Fe band exhibited peaks assigned to iron-carbide (Fe(0)) at 707 eV and iron-oxide (Fe(3+)) at 711 eV (Fig. 2b). The surfaces of the iron-carbide nanoparticles were mainly observed as oxidized forms, because oxidation of the fresh catalyst powders occurs readily. In the K 2p core-level XPS spectrum, a peak around 293 eV was observed, which is low binding energy compared to the peak (294.4 eV) of metallic K (Fig. 2c).

The quantitative analysis of iron-carbides and iron-oxides could be accessed by Mössbauer spectroscopy (Fig. 3). The Mössbauer spectrum at 295 K could be fitted with the superposition of the 3 sextets for Fe sites corresponding to Fe_5C_2 crystallography (Fig. 3a). In the spectrum, the deconvoluted peaks (1 doublet and 1 singlet) are analyzed to be Fe_2O_3 and Fe_3O_4 phase. The Mossbauer spectrum at 4.2

K was fitted with 3 sextets for Fe₅C₂, 1 sextet for Fe₂O₃, and 1 singlet for Fe₃O₄ with different hyperfine parameters (Fig. 3b). From the fitted Mössbauer parameters, the relative areas of χ -Fe₅C₂, Fe₂O₃, and Fe₃O₄ were calculated to be approximately 38%, 48% and 14% (Table S1 in the Electronic Supplementary Material: ESI).

 N_2 sorption experiments for the K-Fe₅C₂/Al₂O₃ catalyst exhibited type IV adsorption-desorption hysteresis (Fig. 4a). The Brunauer-Emmett-Teller (BET) surface area and total pore volume calculated was 176 m²·g⁻¹ and 0.28 cm³·g⁻¹, respectively. The pore size of the catalyst was found to be ca. 8.5 nm on the adsorption branch by the Barrett-Joyner-Halenda (BJH) method (Fig. 4b). The Fe content in the K-Fe₅C₂/Al₂O₃ catalyst was calculated to be ~ 8 wt% on the basis of Fe converted from the used Fe salt after the thermal treatment.

3.2. Fischer-Tropsch Synthesis reaction

To investigate the performance of the catalyst for high-temperature Fischer-Tropsch synthesis, reaction tests with K-Fe₅C₂/Al₂O₃ were performed at 15 bar, 340 °C, and a H₂/CO ratio of '1'. The CO conversion and selectivity of the catalysts were measured over time-on-stream (TOS) by gas chromatography (GC) of the outlet gases containing the unreacted CO, H₂, CH₄, C₂–C₄ hydrocarbons, and CO₂. Liquid oil and solid wax recovered in a cold trap and a hot trap, respectively, were further analyzed using simulated distillation (SIMDIS).

During FTS, multiple reactions can proceed as indicated below:

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$
 (paraffins)

 $nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \qquad (olefins)$

Significant amounts of CO₂ are generated by the accompanying water-gas shift (WGS) reaction as follows:

 $CO + H_2O \leftrightarrow CO_2 + H_2$

The K-Fe₅C₂/Al₂O₃ nanocatalyst exhibited very high CO conversions even under very high gas hourly space velocity (GHSV) conditions in the range 14–30 NL·g_{cat}⁻¹·h⁻¹. The total CO conversion rates of the K-Fe₅C₂/Al₂O₃ nanocatalyst were observed to be 94.1% at GHSV = 14 NL·g_{cat}⁻¹·h⁻¹, 92.9% at 20 NL·g_{cat}⁻¹·h⁻¹, and 89.8% at 36 NL·g_{cat}⁻¹·h⁻¹ (Fig. 5a, c, and e, respectively). The data for the K- Fe₅C₂/Al₂O₃ nanocatalyst showed selectivity for CO₂ (41.5%), CH₄ (7.6%), C₂–C₄ (15.6%), and C₅₊ (35.3%) at GHSV = 14 NL·g_{cat}⁻¹·h⁻¹ (Fig. 5b). At GHSV = 20 NL·g_{cat}⁻¹·h⁻¹, selectivity for CO₂ (43.4%), CH₄ (7.8%), C₂–C₄ (15.8%) and C₅₊ (33.0%) was observed (Fig. 5d). With increase of GHSV, the selectivity for CH₄ and C₂–C₄ slightly increased. The C₅₊ selectivity with GHSV at 20 and 36 NL·g_{cat}⁻¹·h⁻¹ was observed to be 33.0% in both cases (Fig. 5d and e).

On the other hand, the CO conversion rates were significantly lower (58.0% at GHSV = 20 NL· g_{cat}^{-1} · h^{-1} ¹ and 41.9% at 36 NL· g_{cat}^{-1} · h^{-1}) with the K-free Fe₅C₂/Al₂O₃ catalyst than with the K-Fe₅C₂/Al₂O₃ catalyst under the same GHSV conditions (Fig. 6a and c). The selectivity data for K-free Fe₅C₂/Al₂O₃ catalyst at GHSV = 20 NL· g_{cat}^{-1} · h^{-1} showed selectivity for CO₂ (42.9%), CH₄ (8.3%), C₂–C₄ (20.5%), and C₅₊ (28.3%) (Fig. 6b).

The FT activity can be represented by iron-time-yield (FTY) indicating the number of CO moles converted to hydrocarbons per gram of iron per second. At GHSV = 20 NL· g_{cat}^{-1} ·h⁻¹, the K-Fe₅C₂/Al₂O₃ nanocatalyst showed a higher FTY value (8.3×10⁻⁴ mol_{CO}· g_{Fe}^{-1} ·s⁻¹) than did the K-free Fe₅C₂/Al₂O₃ catalyst (5.3×10⁻⁴ mol_{CO}· g_{Fe}^{-1} ·s⁻¹) (Fig. 7a). With Fe₅C₂/Al₂O₃ catalyst, increasing the space velocity to GHSV = 36 NL· g_{cat}^{-1} ·h⁻¹ resulted in the highest FTY value (14.1×10⁻⁴ mol_{CO}· g_{Fe}^{-1} ·s⁻¹) (Fig. 7b). This value is extremely high, comparable to the data for the recently reported Fe catalysts for FTS (Table S2). In particular, the K-Fe₅C₂/Al₂O₃ nanocatalyst at GHSV = 36 NL· g_{cat}^{-1} ·h⁻¹ showed a very high liquid oil productivity of 2.15 g_{liq} · g_{cat}^{-1} ·h⁻¹ after the FTS reaction for 48 h (Table S3). This is a very high value compared to those of other catalysts such as Fe₅C₂ nanoparticles on porous carbon and silica [20, 33].

To determine the hydrocarbon product distributions and specific hydrocarbon productivity, the detailed composition of the liquid and solid hydrocarbons was analyzed by the simulated distillation method. For the hydrocarbon products recovered after the FTS reactions using the K-Fe₅C₂/Al₂O₃ nanocatalyst, higher

GHSV conditions led to more narrower carbon distributions in the C_5-C_{13} range (Fig. 8). The measured C_5-C_{13} portions in all the syncrude and liquid oils was 78.9% (Fig. 8a), 85.1% (Fig. 8b), 80.6% (Fig 8c), 86.6% (Fig. 8d), 82.0% (Fig. 8e), and 86.6% (Fig. 8f).

With increase of space velocity, heavy hydrocarbons (C₁₉₊) were slightly decreased from 4.47% at GHSV = 14 NL· g_{cat}^{-1} · h^{-1} to 3.27% at GHSV= 36 NL· g_{cat}^{-1} · h^{-1} (Fig. 9). On the other hand, the portion of C₂–C₄ olefins was increased from 15.7% at GHSV = 14 NL· g_{cat}^{-1} · h^{-1} to 17.4% at GHSV = 36 NL· g_{cat}^{-1} · h^{-1} . These trends were supported by the carbon chain growth probability (α) of the hydrocarbons, using the Anderson-Schulz-Flory (ASF) chain growth mechanism [34]. The equation used is as follows:

 $\log(W_n/n) = \log(\ln^2 \alpha) + n \cdot \log \alpha$

where W_n is the weight fraction of hydrocarbons with carbon number n. The α value of the K-Fe₅C₂/Al₂O₃ nanocatalyst under the different reaction conditions was 0.816 at GHSV = 14 NL·g_{cat}⁻¹·h⁻¹, 0.804 at GHSV = 20 NL·g_{cat}⁻¹·h⁻¹, and 0.799 at GHSV = 36 NL·g_{cat}⁻¹·h⁻¹.

The specific hydrocarbon (HC) productivity data (gram of generated hydrocarbons per gram of iron per second) for reactions with the K-Fe₅C₂/Al₂O₃ and K-free Fe₅C₂/Al₂O₃ nanocatalysts were obtained (Fig. 10). The K-Fe₅C₂/Al₂O₃ nanocatalyst at GHSV = 36 NL·g_{cat}⁻¹·h⁻¹ showed the highest total HC productivity, calculated to be 17.1×10^{-3} g_{HC}·g_{Fe}⁻¹·s⁻¹. In particular, regarding the production of C₅-C₁₂, the K-Fe₅C₂/Al₂O₃ catalyst at GHSV = 36 NL·g_{cat}⁻¹·h⁻¹ showed a 6.2×10^{-3} g_{HC}·g_{Fe}⁻¹·s⁻¹ product yield, which is 3.4 times higher than the yield (1.8×10^{-3} g_{HC}·g_{Fe}⁻¹·s⁻¹) of the K-free Fe₅C₂ catalyst at GHSV= 20 NL·g_{cat}⁻¹·h⁻¹.

The specific C_5-C_{13} LAO contents in the liquid oils recovered after the HT-FTS reactions were obtained by detailed hydrocarbon analysis (Table S4-8). The K-doped catalyst showed a higher C_5-C_{13} LAOs/C₅- C_{13} n-paraffin ratio than did the K-free catalyst under the same space velocity conditions (Table S5-8). As expected, with increase of the space velocity in the FTS reaction using K-Fe₅C₂/Al₂O₃ catalyst, the

ratio of C₅–C₁₃ LAOs/C₅–C₁₃ n-paraffins was much increased. These ratios were measured and found to be 0.59 at GHSV = 14 NL·g_{cat}⁻¹·h⁻¹, 0.62 at GHSV = 20 NL·g_{cat}⁻¹·h⁻¹, and 0.72 at GHSV = 36 NL·g_{cat}⁻¹·h⁻¹, ¹, calculated by the contents of C₅-C₁₃ LAOs and n-paraffins in isolated liquid products after reaction using the K-Fe₅C₂/Al₂O₃ catalyst (Table S4, S5, S7). The maximum C₅–C₁₃ LAOs content (17.46 wt%) in the recovered liquid oil was obtained with the K-Fe₅C₂/Al₂O₃ nanocatalyst at GHSV= 36 NL·g_{cat}⁻¹·h⁻¹ (Table S7).

The C₅–C₁₃ LAO productivity data (the number of CH₂ micromoles assigned to LAOs per gram of catalyst per second) of reactions with K-Fe₅C₂/Al₂O₃ and K-free Fe₅C₂/Al₂O₃ nanocatalysts were also calculated, based on the obtained C₅–C₁₃ LAO contents (Fig. 11). Figure 11a, b, and c show the detailed productivity values of each catalyst for C₅–C₇, C₈–C₁₀, and C₁₁–C₁₃ LAOs, respectively. The K-Fe₅C₂/Al₂O₃ nanocatalyst at GHSV = 36 NL·g_{cat}⁻¹·h⁻¹ showed the highest total C₅–C₁₃ LAO productivity (7.45 CH₂ µmol·g_{cat}⁻¹·s⁻¹, Fig. 11d). This value is five times higher than the 1.45 CH₂ µmol·g_{cat}⁻¹·s⁻¹ of K-free Fe₅C₂/Al₂O₃ nanocatalyst at GHSV = 20 NL·g_{cat}⁻¹·h⁻¹. In particular, 1-octene (a valuable chemical intermediate) was effectively obtained (0.87 CH₂ µmol·g_{cat}⁻¹·s⁻¹) using the K-Fe₅C₂/Al₂O₃ nanocatalyst at GHSV = 36 NL·g_{cat}⁻¹·h⁻¹. In particular, 1-octene (a valuable chemical intermediate) was effectively obtained (0.87 CH₂ µmol·g_{cat}⁻¹·s⁻¹) using the K-Fe₅C₂/Al₂O₃ nanocatalyst at GHSV = 36 NL·g_{cat}⁻¹·s⁻¹) using the K-Fe₅C₂/Al₂O₃ nanocatalyst at GHSV = 36 NL·g_{cat}⁻¹·h⁻¹ (Fig. 11b). The high productivity for LAOs mainly originated from the less H* around the methylene monomer (CH₂*) on the active surfaces, and from high catalytic conversion of the adsorbed carbon monoxide under the increased high space velocity conditions (Fig. 12).

After the long-term FTS reaction, the recovered K-Fe₅C₂/Al₂O₃ nanocatalyst showed slightly increased particle sizes, but any significant agglomeration or sintering from the original one was not observed (Fig. S1).

To compare the catalytic performance of the K-Fe₅C₂/Al₂O₃ nanocatalyst with other supported nanocatalysts for high-temperature Fischer-Tropsch synthesis, Fe₅C₂/SBA-15 and Fe₅C₂/activated carbon (AC) were employed. The catalysts could be obtained via melt infiltration of hydrated iron nitrate salt with the same iron loading (8 wt%) of the K-Fe₅C₂/Al₂O₃ nanocatalyst. Under the same reaction condition at GHSV = 14 NL·g_{cat}⁻¹·h⁻¹, 15 bar, and a H₂:CO ratio of '1', the K-Fe₅C₂/Al₂O₃ nanocatalyst showed a much higher FTY value ($6.0 \times 10^{-4} \text{ mol}_{CO} \cdot g_{Fe}^{-1} \cdot s^{-1}$) at TOS = 90 h than those of Fe₅C₂/SBA-15 and

Fe₅C₂/activated carbon (Table S9). The C₅–C₁₃ LAOs contents in the recovered liquid oil were measured to be 15.70% at K-Fe₅C₂/Al₂O₃, 13.93% at Fe₅C₂/SBA-15, and 12.43% at Fe₅C₂/activated carbon, respectively (Table S10). In the C₅–C₁₃ LAO productivity data, the K-Fe₅C₂/Al₂O₃ catalyst showed much a higher value (2.63 CH₂ µmol·g_{cat}⁻¹·s⁻¹) than those of Fe₅C₂/SBA-15 (0.41 CH₂ µmol·g_{cat}⁻¹·s⁻¹) and Fe₅C₂/activated carbon (0.48 CH₂ µmol·g_{cat}⁻¹·s⁻¹) under the same space velocity condition (Fig. S2). At the K-Fe₅C₂/Al₂O₃ nanocatalyst among the hydrocarbon distribution data of the catalysts, the highest C₅–C₁₂ selectivity (36.5%) was observed due to the appropriate hydrogenation reactions based on the suitable surface electronic state, apt for the selective C₅–C₁₃ LAO production (Fig. S3).

Conclusions

The K-Fe₅C₂/Al₂O₃ nanocatalyst was prepared simply through a melt-infiltration of hydrated iron salt and subsequent impregnation of aqueous potassium solution. The catalyst showed high catalytic performance (FT activity = 1.41 mmol_{CO}·g_{Fe}⁻¹·s⁻¹, liquid oil productivity = 2.15 g_{liq}·g_{cat}⁻¹·h⁻¹, and C₅–C₁₃ LAO productivity = 7.45 CH₂ µmol·g_{cat}⁻¹·s⁻¹) under the optimum FTS reaction condition (GHSV condition = 36 NL·g_{cat}⁻¹·h⁻¹), based on the well-dispersed Fe₅C₂ nanoparticles with potassium promoter. The doped-K on the active Fe₅C₂ surface under the higher space velocity conditions suppressed the hydrogenation of alkenes and led to greater production of alkenes. It is anticipated that the optimum reaction condition and active iron-carbide nanoparticles promoted by potassium could be effectively applied to commercial FTS to produce high value-added LAO products.

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FIGURE CAPTIONS

Fig. 1. (a, b) TEM images, (c) HADDF-STEM image, (d) Elemental mapping image, (e) HRTEM image of a single particle with (f) corresponding FT pattern of K-Fe₅C₂/Al₂O₃ nanocatalyst. The bars indicate 200 nm (a), 40 nm (b-d) and 2 nm (e).

Fig. 2. (a) XRD spectra of the pristine Al_2O_3 and K-Fe₅C₂/Al₂O₃ nanocatalyst and (b, c) XPS spectra of K-Fe₅C₂/Al₂O₃ nanocatalyst.

Fig. 3. Mössbauer spectra at (a) 295 K and (b) 4.2 K of K-Fe₅C₂/Al₂O₃ nanocatalyst.

Fig. 4. (a) N_2 adsorption/desorption isotherms, (b) Pore size distribution diagram of K-Fe₅C₂/Al₂O₃ nanocatalyst.

Fig. 5. CO conversion (a, c, e) and hydrocarbon product selectivity (b, d, f) graphs of K-Fe₅C₂/Al₂O₃ nanocatalyst by GHSV variation (a–b: GHSV = 14 NL·g_{cat}⁻¹·h⁻¹, c-d: GHSV = 20 NL·g_{cat}⁻¹·h⁻¹, e-f: GHSV = 36 NL·g_{cat}⁻¹·h⁻¹). The total CO conversion is the sum of the CO conversion to hydrocarbons (CO to HC) and the CO conversion to CO₂ (CO to CO₂). All reaction tests were conducted at 340 °C, 15 bar, and H₂ : CO ratio of '1'.

Fig. 6. CO conversion (a, c) and hydrocarbon product selectivity (b, d) graphs of K-free Fe_5C_2/Al_2O_3 nanocatalyst by GHSV variation (a–b: GHSV = 20 NL· $g_{cat}^{-1}\cdot h^{-1}$, c–d: GHSV = 36 NL· $g_{cat}^{-1}\cdot h^{-1}$). All reaction tests were conducted at 340 °C, 15 bar, and H₂ : CO ratio of '1'.

Fig. 7. Catalytic performance for K-doped and K-free Fe_5C_2/Al_2O_3 catalysts by GHSV conditions. (a: GHSV=20 NL·g_{cat}⁻¹·h⁻¹, b: GHSV=36 NL·g_{cat}⁻¹·h⁻¹). All reaction tests were conducted at 340 °C, 15 bar, and '1' in the H₂ : CO ratio.

Fig. 8. Hydrocarbon product distribution graphs of total syncrude (a,c,e) and liquid oil products (b,d,f) obtained using the K-Fe₅C₂/Al₂O₃ catalyst. The samples were recovered after FTS reactions conducted at three different GHSV conditions of (a,b) 14 NL·g_{cat}⁻¹·h⁻¹; (c,d) 20 NL·g_{cat}⁻¹·h⁻¹; and (e,f) 36 NL·g_{cat}⁻¹·h⁻¹. The total syncrude means the sum of recovered liquid oil and solid wax.

Fig. 9. The hydrocarbon distribution graphs of the K-Fe₅C₂/Al₂O₃ catalyst. The samples were recovered after FTS reactions conducted at three different GHSV conditions.

Fig. 10. Specific hydrocarbon productivity data for K-Fe₅C₂/Al₂O₃ and K-free Fe₅C₂/Al₂O₃ nanocatalysts in relation to GHSV variation.

Fig. 11. Productivity data of (a) C_5 - C_7 LAOs, (b) C_8 - C_{10} LAOs, (c) C_{11} - C_{13} LAOs, and (d) total C_5 - C_{13} LAOs for the catalysts by GHSV variation.

Fig. 12. Brief scheme for LAO formation over K-Fe₅C₂/Al₂O₃ and K-free Fe₅C₂Al₂O₃ nanocatalysts: The combination of high space velocity condition and potassium as an alkali promoter on iron-carbide leads to decreased secondary hydrogenation of olefins and increased carbon coupling reaction.

Scheme 1. Synthetic scheme of K-Fe₅C₂/Al₂O₃ nanocatalyst.







Fig. 2











Fig. 5



Fig. 6



Fig. 7



Fig. 8







Fig. 10



Fig. 11



Fig. 12



porous alumina

hydrated iron salt

1) melt infiltration& thermal treatment under CO

2) K solution impregnation& thermal treatment under CO



 $K-Fe_5C_2/Al_2O_3$

Scheme 1