



Short communication

Fe-based Fischer Tropsch synthesis of biomass-derived syngas: Effect of synthesis method



Khiet Mai^a, Thomas Elder^b, Leslie H. Groom^b, James J. Spivey^{a,*}

^a Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, USA

^b USDA Forest Service, Southern Research Station, Pineville, LA 71360, USA

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ABSTRACT

Two 100Fe/4Cu/4K/6Zn catalysts were prepared using two different methods: coprecipitation or impregnation methods. The effect of the preparation methods on the catalyst structure, catalytic properties, and the conversion of biomass-derived syngas via Fischer–Tropsch synthesis was investigated. Syngas was derived from gasifying Southern pine woodchips and had the composition of 3.1% CH₄, 11% CO₂, 17% H₂, 22% CO, and 47% N₂. The results show that the coprecipitated Zn-promoted catalyst had higher extent of reduction and carburization, which led to higher carbon conversion and C₅₊ selectivity of this CO₂-rich syngas than the impregnated catalyst.

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1. Introduction

Lignocellulosic biomass is a promising feedstock for producing liquid fuels via gasification and Fischer Tropsch Synthesis (FTS). Gasification produces a biomass-derived syngas that is characterized by a low H₂/CO ratio of ~0.7/1 and concentrations of CO₂ between 10–20% [5]. The water gas shift (WGS) reaction (CO + H₂O → CO₂ + H₂) converts this syngas into one with the required ~2/1H₂/CO ratio for FTS while producing more CO₂. Thus, a key challenge for conversion of biomass-derived syngas to liquid fuels is to develop a catalyst that can promote WGS reaction, and maximize both carbon conversion and C₅₊ selectivity.

Among the most active metals for FTS (Fe, Co, Ru, Ni), Fe-based catalysts are the only catalysts that show significant WGS activity and are widely used for FTS of H₂ deficient syngas [1,2]. Fe-based catalysts for FTS contain several promoters. These include copper (Cu), potassium (K) and zinc (Zn). Cu is used to promote the reduction of Fe₂O₃ to Fe₃O₄ [3]. K enhances the carburization activity of Fe-based catalysts by increasing CO adsorption [4]. Zn is used as structural promoter that prevents iron clusters from sintering, and stabilizes the surface area of iron oxide [5]. Moreover, Zn promoted Fe-based catalyst has higher FTS activity for biomass-derived syngas than Al or Si promoted catalyst [6]. Previous studies show that the optimum mass ratio of Zn/Fe for CO₂-free syngas is 0.1 [7] while it is 0.04 for CO₂-containing syngas [8].

Therefore, 0.07 is chosen to be the mass ratio of Zn/Fe (corresponding to molar ratio of 0.06) for this study.

Even though coprecipitation and impregnation are common methods for synthesizing FT Fe-based catalysts, few studies have directly compared the effect of these two preparation methods on FTS activity; especially for biomass-derived syngas. Sarkari et al. [9] compared the effect of impregnation and coprecipitation methods on the FTS activity and selectivity of Fe-Ni/Al₂O₃. This study shows that the impregnated catalyst has higher selectivity toward C₅₊ than the coprecipitated catalyst [9]. Arsalanfar et al. [10] conducted a comparison between coprecipitation and impregnation methods on Fe/Co/Mn/MgO catalysts and also show that the impregnated catalyst has higher C₅₊ selectivity than the coprecipitated catalyst.

Although these both previous studies compared the two preparation methods, there are differences between earlier works and the present study here. First, the syngas in prior studies was far more concentrated (pure H₂/CO = 2/1) [7,8] compared to the biomass-derived syngas of interest here (H₂/CO = 0.77; diluted to a total of 39% H₂ + CO). This would reduce the total carbon conversion at otherwise similar conditions. Second, Sarkari, et al. [9] prepared his catalysts by impregnating iron and promoter salts onto Al₂O₃ support while Arsalanfar et al. [10] also prepared the catalysts using the same method but on MgO support. Finally, the presence of 11% CO₂ in the biomass-derived syngas may affect the catalyst stability differently for the two Zn-promoted catalysts [1]. Based on these most directly comparable papers, we are aware of no study of the effect of these preparation methods on FTS of biomass-derived syngas using Zn-promoted Fe-based catalysts. The purpose of the present study is to carefully determine the effect of the

* Corresponding author at: Department of Chemical Engineering, Louisiana State University, S. Stadium Drive, Baton Rouge, LA 70803, USA.
E-mail address: jjspivey@lsu.edu (J.J. Spivey).

Zn-promoted Fe/Cu/K catalyst synthesis method on carbon conversion and C₅₊ selectivity.

2. Experimental

2.1. Catalyst preparation

For coprecipitated catalyst, desired amounts of Fe(NO₃)₃·9H₂O, Cu(NO₃)₃·2.5H₂O and Zn(NO₃)₂·6H₂O were precipitated together in a continuous stir beaker at temperature of 80 ± 3 °C and pH of 7–7.3 using (NH₄)₂CO₃ solution. The precipitate solution was filtrated and washed with ethanol. The filtrate was then dried at 115 °C for 18 h. Desired amount of KHCO₃ was dissolved in H₂O and impregnated onto the catalyst. The catalyst was calcined in 50 ml/min of flowing air at 360 °C for 6 h.

For impregnated catalyst, iron precursor was prepared by precipitating Fe(NO₃)₃·9H₂O with (NH₄)₂CO₃ solution at 80 ± 3 °C and pH of 7–7.3. Zn(NO₃)₂·6H₂O, Cu(NO₃)₃·2.5H₂O and KHCO₃ were subsequently impregnated onto the iron precursor. The precursor was dried at 115 °C for 1 h after each impregnation step. The catalyst was calcined at 500 °C in 50 ml/min of flowing air for 6 h. The final catalysts have the atomic ratio of 100Fe/4Cu/4K/6Zn and are labeled as ‘Cat_C’ and ‘Cat_I’ for coprecipitated and impregnated catalyst, respectively.

2.2. Catalyst characterization

Powder X-ray diffraction analysis was carried out using Empyrean X-ray diffractometer (PANalytical) equipped with CuKα radiation (λ = 1.5406 Å). The catalyst samples were scan from 2θ = 10° to 80°, step size of 0.026°/s, at 45kV and 40 mA.

Temperature programmed experiments were done on Altamira (AMI 200 HP) instrument. 0.03 g (H₂ TPR) or 0.05 g (CO TPR) of catalyst was first treated with 50 ml/min of He at 150 °C for 30 min. After the catalyst pretreatment, the gas was switched to 10% H₂/Ar (H₂ TPR) or 5% CO/He (CO TPR) at the flow rate of 50 ml/min, and the temperature was ramped to 950 °C at 5 °C/min. Thermal Conductivity Detector (TCD) was used to measure H₂ TPR signal while AMETEC Mass Spectrometer (MS) was used to measure the amount of CO₂ produced. The amount of H₂ consumed in H₂ TPR is calculated using silver oxide (Ag₂O) as standard. Known amounts of Ag₂O were reduced in H₂ in the same conditions as the studied catalysts, and area calibration was used to calculate the amount of H₂ consumed by the iron catalysts. The amount

of CO₂ produced was calculated by flowing a known amount of CO₂ for 10 min; the area under the CO₂ curve was used to calculate the amount of CO₂ produced.

For temperature programmed hydrogenation (TPH) experiment, 0.1 g of catalyst was pretreated with syngas (H₂/CO = 0.7) at 280 °C for 16 h. He was then flowed through the reactor bed to cool the reactor to room temperature. TPH was carried out by flowing 15 ml/min of pure H₂ over the catalyst bed, the bed temperature was raised to 950 °C at 5 °C/min. MS (mass signal 15) was used to measure the amount of CH₄ leaving the reactor [11].

2.3. Catalytic FTS test

Fischer Tropsch synthesis was carried out in a PID MA 1000 Microactivity Reactor. 1 g of catalyst was diluted with 5 g of sand and loaded into the fix bed reactor. The catalyst was activated with pure syngas (H₂/CO = 0.7) at 280 °C, 0.1 MPa and 3600 h⁻¹ for 24 h. After the activation step, biomass-derived syngas consisting of 3.1% CH₄, 11% CO₂, 17% H₂, 22% CO, and 47% N₂ (H₂/CO = 0.77) was introduced to the reactor at the space velocity of 1500 h⁻¹. The reactor was slowly pressurized to 2.5 MPa, and the reaction was run for 144 h at 280 °C.

The total carbon (CO + CO₂) conversions and hydrocarbon distribution are calculated using Eqs. (1) and (2), respectively.

$$\% \text{ C conversion} = \frac{n(\text{CO} + \text{CO}_2)_{\text{in}} - n(\text{CO} - \text{CO}_2)_{\text{out}}}{n(\text{CO} + \text{CO}_2)_{\text{in}}} * 100\% \quad (1)$$

$$\% \text{ C selectivity} = \frac{n_{\text{product}} * \text{no. of C atoms present}}{n(\text{CO} + \text{CO}_2)_{\text{consumed}}} * 100\% \quad (2)$$

3. Results and discussions

3.1. X-ray diffraction powder (XRD)

X-ray powder diffraction patterns of the freshly calcined catalysts are showed in Fig. 1. The XRD pattern of Cat_C shows that the catalyst contains poorly crystalline cubic magnetite Fe₃O₄ and rhombohedral hematite α-Fe₂O₃. Sharma et al. [6] showed that the coprecipitated catalyst with Zn as structural promoter was XRD amorphous, which is consistent with Fig. 1. The XRD pattern of Cat_I shows that the catalyst is comprised of rhombohedral hematite (α-Fe₂O₃) and magnetite

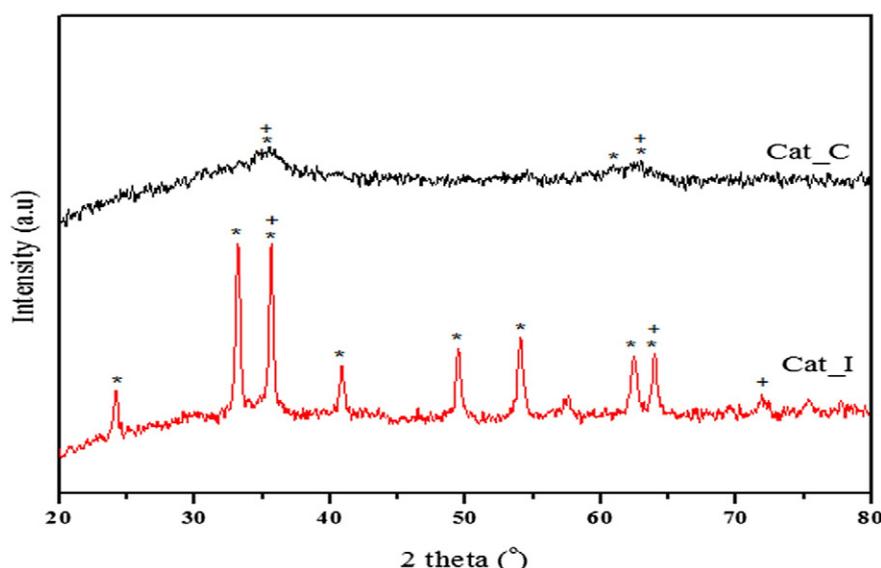


Fig. 1. XRD patterns of the freshly calcined catalysts + Fe₃O₄, *Fe₂O₃.

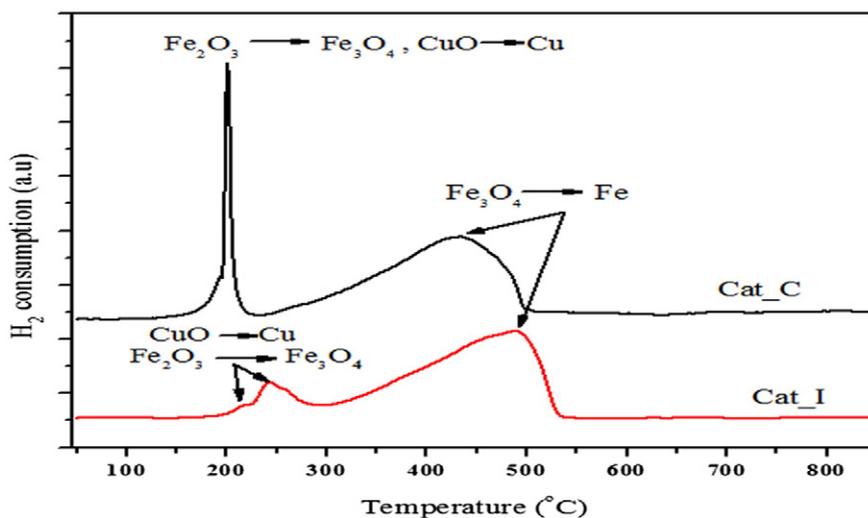


Fig. 2. H₂ temperature programmed reduction for Cat_C and Cat_I.

(Fe₃O₄). These results show that coprecipitation produces a poorly crystalline catalyst while impregnation produces a more crystalline catalyst.

3.2. H₂ temperature programmed reduction (H₂ TPR)

Fig. 2 shows the H₂ TPR results. For Cat_C, the first peak at 200 °C corresponds to the reduction of Fe₂O₃ to Fe₃O₄ and CuO to Cu. The second peak at 434 °C corresponds to the reduction of Fe₃O₄ to Fe⁰. The presence of Cu in both catalysts facilitates the reduction of Fe₂O₃ to Fe₃O₄. When CuO is reduced to Cu at the temperature range of 100 °C–220 °C, Cu crystallites nucleate and provide active sites for H₂ dissociative adsorption. As a result, the reactive hydrogen atoms can reduce Fe₂O₃ at lower temperature than a catalyst without a Cu reduction promoter [7].

For Cat_I, the shoulder peak at 217 °C is attributed to the reduction of CuO to Cu while the peak at 241 °C is the reduction peak for Fe₂O₃ to Fe₃O₄. The second peak at 491 °C corresponds to the reduction of Fe₃O₄ to Fe⁰. The TPR profiles for Cat_C has a well-defined first peak than that of Cat_I. This is because Cu is more dispersed on Cat_C than on Cat_I which leads to higher rate of reduction. Moreover, for Cat_C, the experimental amount of H₂ consumed (16.7 ± 0.3 mmol H₂/gcat) is consistent with the theoretical value (16.4 mmol H₂/gcat),

corresponding to complete reduction of Fe and Cu. For Cat_I, however, the measured amount of H₂ (13.3 ± 0.6 mmol H₂/gcat) is less than the theoretical value (15.6 mmol H₂/gcat). Based on H₂ TPR results, Cat_C is reduced more completely than Cat_I, which is also in agreement with literature [10].

3.3. CO temperature programmed reduction (CO TPR)

CO TPR is used to study the carburization behavior of the catalysts. The CO TPR profiles (Fig. 3) show that Fe₂O₃ is reduced to Fe₃O₄ at 180 °C for both catalysts. For Cat_C, the second peak at 300 °C is attributed to the reduction of Fe₃O₄ to ε-Fe₂C, ε-Fe_{2.2}C, γ-Fe_{2.5}C [7]. The third peak at 460 °C corresponds to the transformation of active iron carbides to a more stable phase θ-Fe₃C [7]. The CO TPR profile of Cat_C also shows a shoulder peak at 520 °C which is ascribed to carbon disproportionation via the Boudouard reaction [7]. For Cat_I, the shoulder peak at 280 °C is probably due to the reduction of the less reducible and more crystalline Fe₂O₃ to Fe₃O₄. Above 300 °C, the CO TPR profile of Cat_I shows a multi-peak curve with the maximum peak at 375 °C. This peak temperature is higher than the reduction peak of Fe₃O₄ to active iron carbides of Cat_C. The total amount of CO₂ produced during CO reduction for Cat_C (155 μmol CO₂/gcat) is higher than that

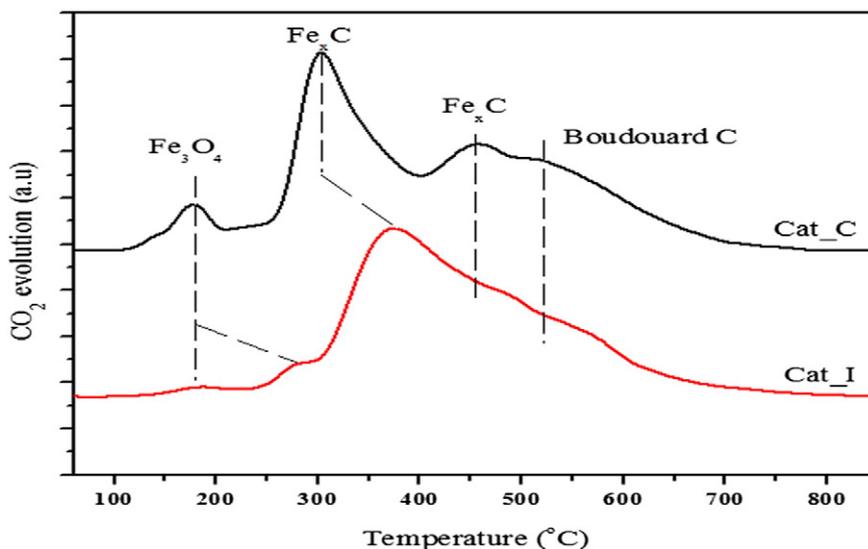


Fig. 3. CO TPR profiles of the calcined catalysts prepared using different methods.

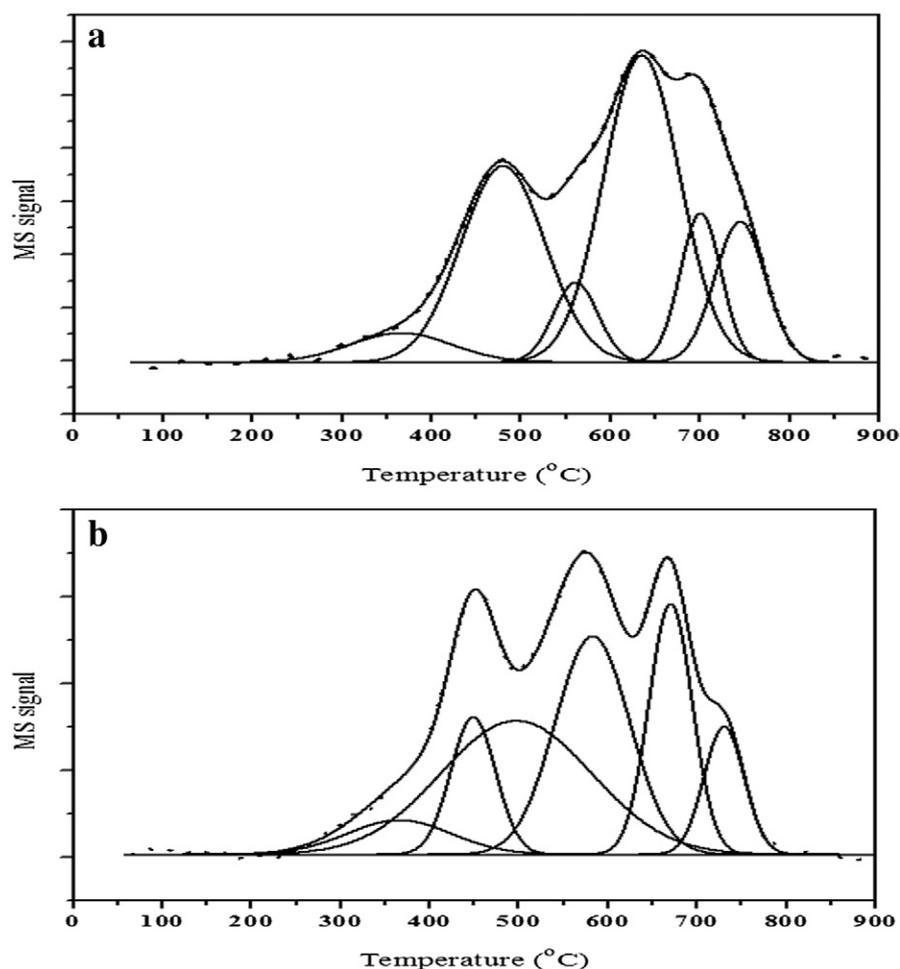


Fig. 4. TPH curves of a) Cat_C, b) Cat_I and their corresponding peak deconvolutions.

(134 $\mu\text{mol CO}_2/\text{gcat}$) for Cat_I. Thus, Cat_C has greater extent of carburization than Cat_I, probably due to better interaction between Fe and K in Cat_C.

3.4. Temperature programmed hydrogenation (TPH)

TPH is used to identify different types of surface and bulk carbonaceous species on iron catalyst after 16 h in syngas ($\text{H}_2/\text{CO} = 0.7$) at 280 °C. Each of these carbon species has different reactivity and peak temperature when reacts with H_2 to form CH_4 . The amount of various carbonaceous species formed on the catalyst can be qualitative and quantitative calculated using a method suggested by Eliason and Bartholomew [12]. In this method, the overlapping TPH spectra are fitted with Gaussian curves to yield up to 7 peaks: i) adsorbed, atomic carbon (270–390 °C); ii) amorphous, lightly polymerized hydrocarbon or carbon surface species (420–455 °C); iii) bulk carbide $\epsilon\text{-Fe}_{2.2}\text{C}$

(480–597 °C) and $\chi\text{-Fe}_{2.5}\text{C}$ (517–688 °C); and iv) semi-order sheets (600–700 °C) and moderately ordered graphitic surface carbon (650–750 °C) [11].

Here, the TPH spectra are analyzed using the same deconvolution method (Fig. 4). Peak temperatures, amount of carbon formed equivalent of peak area are tabulated in Table 1. Table 1B shows that Cat_C has higher α -carbon (the most reactive carbon form) content than Cat_I which results in higher initial FTS activity for Cat_C (see also Section 3.5 below) [11,12]. The total amount of carbides ($\gamma_1 + \gamma_2$) is higher for Cat_C than Cat_I which is in agreement with previous results that Cat_C has higher extent of carburization (Section 3.3). Cat_C also

Table 1

Peak temperature, carbon content of TPH profiles.

Catalyst	Carbide		Amorphous		Graphitic	
	α	B	γ_1	γ_2	δ_1	δ_2
A. TPH peak temperature (°C)						
Cat_C	362	475	563	634	696	742
Cat_I	366	450	501	586	666	726
B. Carbon content ($\mu\text{gm/gcat}$)						
Cat_C	5.10	28.5	6.17	40.8	10.6	11.9
Cat_I	3.88	6.72	21.9	17.8	11.9	5.3

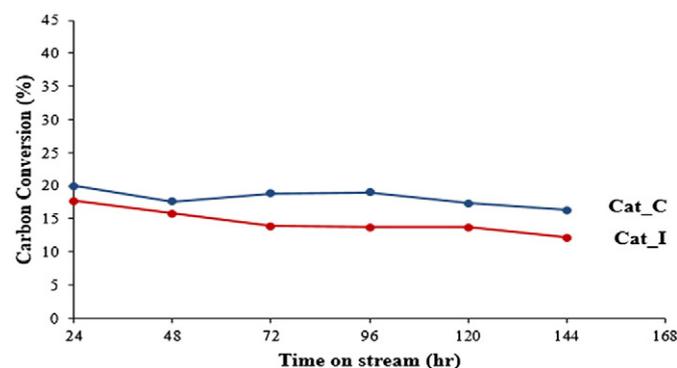


Fig. 5. FTS activity of the studied catalysts. Reaction condition: 280 °C, 2.5 MPa, $\text{H}_2/\text{CO} = 0.77$ and GHSV = 1500 h^{-1} .

Table 2
The activity and selectivity of the catalysts.

	Cat_C	Cat_I
Carbon conversion (%)	18.2	14.4
<i>HC distribution (C%)</i>		
CH ₄	8.81	12.7
C ₂ –C ₄	23.5	27.3
C ₅ –C ₁₁	15.6	13.8
C ₁₂ –C ₁₈	6.26	2.13
Wax	37.9	39.7
Oxygenates	8.40	4.48
<i>Olefins/n-paraffins</i>		
C ₅ [≡] –C ₁₁ [≡] /n-C ₅ –C ₁₁	3.69	3.30
C ₁₂ [≡] –C ₁₈ [≡] /n-C ₁₂ –C ₁₈	3.50	2.44

Reaction condition: 280 °C, 2.5 MPa, GHSV = 1500 h⁻¹; carbon conversion after 144 TOS.

contains more active carbide (γ_2 , Fe_{2.5}C) than Cat_I, consistent with greater FTS for Cat_C than Cat_I.

3.5. Fischer Tropsch synthesis

The carbon conversion of Cat_C and Cat_I versus time on stream is presented in Fig. 5 while the activity and product selectivity of the catalysts are showed in Table 2.

Fig. 5 and Table 2 show that the carbon conversions are relative low compared to those reported in literature in which pure H₂/CO is used as the reactant [7,9,10]. This is expected due to the dilute concentrations of H₂ and CO that are typical of air-blown biomass-derived syngas. The concentrations of H₂ and CO here are 17 and 22%, respectively compared to 67 and 33% in the most directly comparable studies [7,9,10]. The carbon conversions in the present study are comparable to those obtained from previous studies that used similar biomass-derived syngas. For example, Jun et al. [1] shows a carbon conversion of 21.2% for Fe/Cu/K/Al catalyst in synthetic biomass-derived syngas at different reaction conditions to those in Table 2. Another study by Sharma et al. [3] shows a carbon conversion of 33.7% for Fe/Cu/K/Zn in biomass-derived syngas at reaction conditions similar to those in Table 2 but different in Fe/Zn ratio and activation conditions.

Cat_I has lower carbon conversion than Cat_C (14.4 vs. 18.2%). These activity results are in agreement with TPH results. TPH profiles of the carbided catalysts show that Cat_I formed less atomic carbon and iron carbide than Cat_C which results in lower initial and overall carbon conversion. Table 2 shows that Cat_C has slightly higher (C₅₊) selectivity than Cat_I due to the higher amount of CO adsorbed on Cat_C. The olefin-to-paraffin ratio is also higher for Cat_C than Cat_I which suggests that Cat_I has slightly higher hydrogenation activity, which also corresponds to its higher CH₄ selectivity.

The overall results obtained from the present study differ from those reported in literature, which we attribute to the differences in the preparation steps for the impregnated catalyst. Specifically, Sarkari et al. [9] impregnated iron and promoter salts onto Al₂O₃ support, and Arsalanfar, et al. [10] used the same method but on MgO support. Here, the iron precursor was made by the coprecipitation method; Zn, Cu, K salt solutions were then impregnated onto the iron precursor.

4. Conclusion

The results obtained from this study show that the coprecipitated catalyst has the following.

- Smaller cluster particles (XRD)
- Slightly higher extent of reduction (H₂ TPR) and carburization (CO TPR)
- More Hagg carbide (χ -Fe_{2.5}C) formation (TPH).

These differences resulted in slightly higher carbon conversion (18.2 versus 14.4%), C₅₊ selectivity (60 versus 56%), and lower CH₄ selectivity (8.8 versus 13%) for coprecipitated catalyst.

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