HYDROCARBONS SYNTHESIS FROM A SIMULATED BIOSYNGAS FEED OVER Fe/SiO₂ CATALYSTSP. UBILLA¹, R. GARCÍA¹, J.L.G. FIERRO², N. ESCALONA^{1*}.¹Universidad de Concepción, Facultad de Ciencias Químicas, Casilla 160C, Concepción, Chile²Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, 28049, Madrid, Spain

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ABSTRACT

The Fischer Tropsch reaction, using a simulated gas mixture similar to that obtained from biomass transformation (biosyngas), was studied over Fe/SiO₂ catalysts. The reaction was carried out in a stainless steel fixed bed reactor at 300 °C and 1 MPa. Excess solvent impregnation was used to prepare the catalysts. Nitrogen adsorption at -196 °C, thermal programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) were used as characterization methods. The highest CO conversion was obtained for the catalyst with Fe-loading of 15wt% whereas it decreased at higher Fe loadings. The decrease of the activity is explained in terms of the drop of the active sites due to the formation of large Fe metallic aggregates. The Fe/SiO₂ catalysts presented a wide distribution of liquid hydrocarbons (C₆ to C₁₈₊) and high methane formation. The liquid product distribution was related to the average size of iron particles. The increase of iron particle size favours the formation of hydrocarbons centred in C₁₁₋₁₄ chain length.

Keywords: Fischer Tropsch synthesis, biosyngas; Fe/SiO₂ catalysts, biomass

INTRODUCTION

The Fischer Tropsch synthesis (FTS) is the most important catalytic process in the synthesis of gasoline and/or diesel from syngas (CO/H₂) mixture [1]. While the first commercial FTS plants operated with syngas mixtures produced from coal gasification, modern FTS units use CO/H₂ mixtures mainly obtained from the methane steam reforming, where the molar H₂/CO ratio is around of 2 [1]. The metals used as catalysts in the FTS are mainly Fe and Co promoted by K, Re, Cu or Zn [2, 3]. On the other hand, the environmental regulations and the depletion of oil reserves have motivated the search of new technologies for the synthesis of environmentally friendly fuels. In this context, the production of synthetic hydrocarbons using the biomass gasification streams as source of CO and H₂ appears highly attractive. The biomass can be gasified in a gas mixture consisting mainly in CO₂, CO, CH₄, H₂ and N₂. This mixture is called "biosyngas" and the H₂/CO ratio is close to 1. The hydrocarbons produced according to the FT synthesis using biosyngas mixtures are free of S and N, and in principle can be considered neutral in the CO₂ greenhouse effect. The body of work related to hydrocarbon synthesis using syngas mixtures produced according to the steam methane reforming technology is enormous [1,2,3,4,5,6], however the literature describing the production of hydrocarbons from biosyngas is much more limited [7,8,9,10,11]. In the line Jun et al. [7] reported the synthesis of liquid hydrocarbons over Fe/Cu/Al/K (100/6/16/4) catalysts using biosyngas mixtures. These authors found that this catalyst produces high fuel yield and selectivity to olefins. Recently, Escalona et al. [8] have studied the synthesis of hydrocarbons from biosyngas over Co/SiO₂ catalysts promoted by Cu, Re, Ru and Cu [9]. They found that the CO conversion over these catalysts is mainly determined by the dispersion of Co species. In addition, they observed that the higher metal particles result in a decrease of the production of long hydrocarbon chain (C₁₄₊) and promote the synthesis of smaller hydrocarbon chain lengths (C₈-C₉). Also, Re and Ru increases significantly both the activity and the selectivity to long chain hydrocarbons, whereas in those Cu- and Zn-promoted the effect is strongly affected by the amount of promoter. On the other hand, the Fe supported catalysts have not been reported in the FT synthesis using the biosyngas as feed. Therefore, the focus of this work was to study the effect of Re content in the hydrocarbon synthesis over Fe/SiO₂ catalysts using the biosyngas as feed.

2.1 Catalyst preparation

Iron-based catalysts containing metal loading of 10–25 wt.% Fe were prepared by wet impregnation of commercial silica support (BASF D11-11, S_{BET} = 136 m² g⁻¹) with appropriate amounts of aqueous solution of Fe(NO₃)₃ (Aldrich, p.a.), in a rotary evaporator. After impregnation, the samples were dried at 110 °C for 12 h and then calcined at 450 °C for 5 h. Prior to characterization and testing, the catalysts were activated in flowing hydrogen at 500 °C for 12 h. The catalysts and the nomenclature used are listed in Table 1.

2.2 Catalyst characterization

The BET specific surface area (S_{BET}) was evaluated from nitrogen adsorption isotherms recorded at -196 °C in an automatic Micromeritics system Model ASAP 2010. Temperature programmed reduction (TPR) studies were carried out in a conventional system having a thermal conductivity detector and a quartz cell. In each experiment 500 mg of the sample was used, with a heating rate of 10 °C min⁻¹ and the temperature range from 25 to 1000 °C. The mixture used in the reduction experiments was a 5% H₂/Ar with a flow of 50 cm³/min. TEM micrographs (methanol dispersion method) were obtained in a transmission electron microscopy (TEM) taken with a Jeol Model JEM-1200 EXII System. In order to obtain the Fe particle size, a histogram study, using software Image Tool 3.0 from TEM, using over 400 particles of each catalyst was carried out.

X-ray photoelectron spectra (XPS) was acquired with a Escalab 200R spectrometer equipped with a hemispherical electron analyzer and an AlK_α (hν = 1486.6 eV, 1 eV = 1.602 × 10⁻¹⁹ J) 120 W X-ray source. Prior to the analysis, the samples were reduced *in situ* in H₂ flow at 500 °C for 12 h. All binding energies (BE) were referenced to the Si 2p line at 103.4 eV. This reference gave BE values within an accuracy of ± 0.2 eV. Atomic ratios were calculated from the intensity ratios normalized by atomic sensitivity factors.

2.3 Catalytic reaction

Activity tests were carried out in a fixed bed stainless steel reactor. The reaction conditions were: space velocity (GHSV) of 1800 ml g⁻¹ h⁻¹, pressure of 1 MPa and reaction temperature of 300 °C. The feed was a representative mixture obtained from biomass gasification having H₂/CO/CO₂/CH₄/N₂ in the molar proportion 32/32/12/18/6, respectively [12]. Prior to the reaction, the catalysts were reduced *in situ* at 500 °C during 12 h under hydrogen flow. Activity data were taken at steady-state conditions, approximately after 96 h on-stream. The analysis of products were performed by gas chromatography using a Perkin Elmer 3920B system provided with a thermal conductivity detector, using a n-octane Porasil-C column for liquids and a Carbosieve II column for the gaseous products.

RESULTS AND DISCUSSION

3.1. Catalyst characterization

The S_{BET} and total pore volume (obtained at a relative pressure P/P° = 0.95) of calcined Fe/SiO₂ catalysts are shown in Table 1. The S_{BET} values decrease slightly with the Fe loading. This result suggests that Fe species were highly dispersed into the pores of the silica substrate and that pore blockage was negligible.

Table 1. Iron content (wt %), specific surface area (S_{BET}), total pore volume (Vp) and Iron particle size (Fe-PS) estimated from TEM of Fe/SiO₂ catalysts.

Catalysts	Fe (%)	Vp (cm ³ g ⁻¹)	S_{BET} (m ² g ⁻¹)	Fe-PS (nm)
Fe (10)	10	0.39	117	29
Fe (15)	15	0.38	86	32
Fe (20)	20	---	---	37
Fe (25)	25	0.37	78	40

The Figure 1 shows the TEM micrograph recorded from the Fe(x)/SiO₂ catalyst. The EDX analysis showed the presence of Fe particles (not shown here). The Fe metal displays a black colour, such as is shown in the Figure 1. The histogram studies shown a broad particle size distribution and the maximum of each histogram is summarized in the Table 1. In general, the Fe/SiO₂ catalysts present a broad particle size distribution upon increasing Fe-loading and the average particle size was found to increase gradually with Fe loading from 29 to 40 nm (Table 1). This trend is similar to that found with Co/SiO₂ catalysts [9]. However, the average particle size obtained for Co/SiO₂ is higher than for Fe/SiO₂ catalysts.

Figure 1. TEM of reduced catalysts of: a) Fe(10), b) Fe(15), c) Fe(20) and d) Fe(25).

TPR profiles of the oxide precursors are shown in Figure 2. It can be observed that the reduction process of the catalysts occurs according the three characteristic steps of the reduction of Fe₂O₃ species. The first peak centred at 420 °C is related to the transformation of Fe₂O₃ to Fe₃O₄, the second stage centred to 615 °C represents the transformation of Fe₃O₄ to FeO and the third stage centred around 720 °C corresponds to the transformation of FeO to metallic Fe [13,14]. The intensity of the three peaks increases gradually with the Fe loading. Figure 2 also shows that the position of the maximum reduction of three peaks does not change significantly with increasing iron loading. This observation suggests that iron species are homogeneously dispersed on the surface of the silica substrate.

Figure 2. Temperature programmed reduction profiles of Fe/SiO₂ catalysts.

Photoelectron spectroscopy has been used to determine the chemical state and relative concentration of the reduced Fe/SiO₂ catalysts. The binding energies of core-level electrons and the Fe/Si surface atomic ratios are compiled in Table 2. The Fe 2p core-level spectra (not shown) of all catalysts show the characteristic doublet (Fe 2p_{3/2}-Fe 2p_{1/2}) of iron species, whose splitting is about 13.6 eV. On looking at the most intense Fe2p_{3/2} component, a minor peak placed at 707.3 eV belonging to metallic iron is observed for all samples [15], whereas a major peak whose maximum intensity is located at 710.5 eV is usually assigned to iron oxide [16]. As no satellite line is observed somewhere around 719.0 eV indicative of the presence of Fe³⁺ ions, it is inferred that the iron oxides responsible for the peak around 710.5 eV in the reduced catalysts comes from partially reduced iron oxides such as Fe₃O₄ (magnetite) species. The relative intensity of the two Fe 2p components (peaks at 707.3 and 710.5 eV) is also included in Table 2 (in parentheses). It can be seen, that the fraction of metallic iron determined on the surface region of these catalysts is much lower than the fraction of Fe oxides. In addition, the fraction of reduced iron to metallic state (peak at 707.3 eV) increases upon increasing the iron loading in the catalysts. This behaviour suggests that at low Fe content, the ionic iron species interact strongly with the SiO₂ surface and therefore are difficult to reduce to the metal state under the experimental conditions employed in this work. On the contrary, in the catalysts with higher Fe loadings a higher proportion of tridimensional iron oxide structures are developed and therefore they can be easily reduced to metal state.

Table 2. Binding energies (eV) and atomic surface ratios of Fe/SiO₂ reduced catalysts.

Catalysts	Si 2p (eV)	Fe 2p _{3/2} (eV)	Fe/Si (at/at)
Fe(10)	103.4	707.3 (12) 710.5 (88)	0.006
Fe(15)	103.4	707.3 (14) 710.5 (88)	0.009
Fe(20)	103.4	707.3 (20) 710.5 (80)	0.014
Fe(25)	103.4	707.3 (24) 710.5 (76)	0.029

In order to get an estimate of the extent of dispersion of the active phase over the silica surface, the Fe/Si atomic ratios were calculated (see Table 2). The variation of the Fe/Si atomic surface ratio as a function of Fe-loading of the Fe(x)/SiO₂ catalysts is shown in Figure 3. Clearly, the Fe phase appears as rather large crystallites (around 32 nm) up to 15 % of Fe. This trend is similar to that found with Co/SiO₂ catalysts previously [9], where the activity increased almost linearly with increasing Co-loading, reaching the maximum at about 20 wt% Co and then levelled off. The observed deviation from linearity above 15 % of Fe suggests the formation of large segregated crystalline particles (over 37 nm) mainly on the external surface of the silica particles. The higher Fe/Si ratios observed at higher Fe loading, especially for Fe(20)/SiO₂ and Fe(25)/SiO₂ catalysts, results likely from the presence of a high density of iron oxide particles and therefore keep less exposed silica surface. This is in good agreement with TEM results.

Figure 3. Relationship between the Co/Si atomic surface ratio and the nominal surface density of Fe for Fe/SiO₂ catalysts.

3.2 Catalytic activity

The conversion of CO over Fe(x)/SiO₂ catalysts as a function of Fe-loading at 300 °C is shown in Figure 4. The activity, expressed as percent of CO conversion, increases linearly with increasing Fe-loading up to about 15 wt%, and then slightly decreases. Similar behaviour has been found for Co/SiO₂ catalysts, where the maximum activity is reached at 20 wt% Co-loading [9]. The initial increase of CO conversion is associated with the increase in the amount of well-dispersed Fe species. Such increase in performance for catalysts with Fe-loadings up to 15 wt% is consistent with the observation that Fe species are deposited relatively uniformly in both the external and internal surface of silica pores in the catalysts as it was revealed by the Fe/Si ratios derived from XPS analysis (cf. Fig. 3). However, a different picture emerges for higher Fe-loadings. Above 15wt% Fe-loading, some segregation of iron species toward the external surface of SiO₂ particles occurs; this phenomenon being more marked for the catalysts with the highest (25wt%) Fe-loading. Thus, for the 20 and 25 wt% Fe catalysts the lower CO conversion achieved can be related to segregation of an important fraction of the iron species from the pores of the substrate toward the external surface (cf. Fig. 3) where they develop larger iron oxide crystallites (Table 1). Indeed, the lowest CO conversion achieved on the catalyst containing 25 wt% Fe is achieved whose average crystallite size is the highest (over 37 nm) and for which a strong increase in the Fe/Si atomic ratio is observed.

Figure 4. CO conversion over Fe/SiO₂ catalysts as function of Fe loading.

The morphology of the iron phase in these catalysts plays a major role on their performance. This is illustrated by comparing the highest CO conversion of the Fe(15)/SiO₂ catalyst, whose metal fraction in the reduced state is the lowest (14% metal by XPS), with the lowest CO conversion achieved on the Fe(15)/SiO₂ catalyst for which the fraction of metal area increased up to 24%. Therefore, the absence of direct correlation between the fraction of Fe metal and CO conversion indicate that factors other than metal dispersion must be considered to explain catalytic performance. To explain this trend, it is suggested that the highest CO conversion achieved on the 15 wt% Fe catalyst is the result of two consecutive reactions:

Thus it is likely that the highly dispersed iron species within the pores of the substrate catalyse both the synthesis of hydrocarbons and WGS reactions with the subsequent increase in CO conversion. Notwithstanding CO₂ selectivity data summarized in Table 3 indicate that CO₂ proportion decreases markedly upon increasing Fe-loading. Thus, it can be inferred that reactivity is basically associated to the dispersed iron species within the pores of the substrate.

Table 3. Selectivity under steady state conditions in the Fischer Tropsch reaction over Fe(x)/SiO₂ catalysts at 300°C and 1 MPa.

Catalyst	Selectivity (mol % C)		
	CH ₄	CO ₂	C _s +
Fe(10)	25.7	62.4	11.8
Fe(15)	20.5	31.6	47.8
Fe(20)	37.5	21.6	40.9
Fe(25)	75.0	19.0	5.9

3.3 Selectivity

Table 3 shows the selectivity to CH₄, CO₂ and C_s hydrocarbons for the Fe/SiO₂ catalysts as a function of Fe-loading. These results indicate that Fe/SiO₂ catalysts present a high selectivity to CH₄ which also increases with Fe-loading. However, these values are lower than those recorded for Co/SiO₂ catalysts (95 %) [9]. On the other hand, the Fe(10)/SiO₂ catalyst presents a high formation rate of CO₂, which decreases with the increase of Fe content. In addition, the Fe/SiO₂ catalysts show higher formation rates of CO₂ than the Co/SiO₂ catalysts, reported previously [9]. This behaviour is expected because it is well known that iron catalysts perform the WGS reaction. The participation of other CO₂ forming reactions to CO₂ selectivity cannot be precluded. For instance, a fraction of the CO₂ formed might well arise from recombination of the oxygen fragment coming from CO dissociation with other CO molecules as

proposed by Krishnamoorthy et al. [17].

The decrease of the CO_2 formation as the increase in the CH_4 formation with the Fe content in the Fe/SiO_2 catalysts is not clear yet. Tentatively, this change in selectivity is associated to changes in morphology of iron species when increasing Fe-loading, i.e. increase in metal particle size and segregation of iron phase toward the particle surface.

Table 3 also shows the highest formation rate of C_{5+} hydrocarbons on Fe(15)/SiO_2 catalyst. In general, Fe/SiO_2 catalysts record values of selectivity of C_{5+} much larger than on Co/SiO_2 catalysts (around of 5 %) [9]. This result suggests that Fe/SiO_2 catalysts are more selective than Co/SiO_2 ones for the production of liquid hydrocarbon from biosyngas. However, in the classic FT where the H_2/CO ratio equals 2, Co/SiO_2 catalysts are more active than Fe/SiO_2 counterparts [1]. This different behaviour may result from the feed mixture employed. The feed mixture (biosyngas) employed here is deficient in H_2 (H_2/CO ratio equal 1) and Fe/SiO_2 catalyst may increase the formations of H_2 “*in situ*” via WGS reaction and therefore may improve the selectivity to C_{5+} .

Figure 5 shows the distribution of condensable products over Fe(x)/SiO_2 catalysts as function of Fe-loading. An increase in Fe-loading produces a shift in the distribution of condensable products. Thus, the $\text{C}_9\text{--C}_{10}$ production of hydrocarbon chain increases with a decrease of Fe-loading. Similarly, the production of $\text{C}_{11\text{--}12}$ hydrocarbons increases with Fe-loading. This behaviour cannot be due to changes in the acidity of the catalysts upon increasing the reduction of Fe_2O_3 species with the raise of Fe content. Wan et al. [18] reported that surface basicity suppresses the chemisorption of CO and facilitates the chemisorption of H_2 , so it favours the production of low molecular weight products and enhances the hydrogenation capability. Therefore, the variation in the yield to hydrocarbon chain also may be related to metal particle size. The increase of iron particle size could favour the formation of hydrocarbons centred in $\text{C}_{11\text{--}14}$ chain length. In general, this variation in the hydrocarbon selectivity on larger Fe particles can be attributed to the rate of secondary reactions such as olefin readsorption, as has been proposed earlier [19].

Figure 5. Product distribution in the liquid extract produced in the Fischer-Tropsch reaction over Fe/SiO_2 catalysts as function of Fe loading.

4. Conclusions

The results reported in this contribution show that Fe/SiO_2 catalysts are active in the Fischer-Tropsch synthesis from a simulated biosyngas feed. The maximum conversion of CO is reached for metal loading of 15 wt%, and then decreases at higher metal loadings. The activity drop is associated to the loss of active sites by formation of large metallic Fe aggregates, mainly on the external surface of silica particles. The selectivity to methane increases with Fe-loading. The distribution of condensable products shifts to longer-chain hydrocarbons with the increase of iron content. These behaviours may be due to changes in the distribution of average particle size of Fe. Fe/SiO_2 catalysts with a large average iron particle size, favours the formation of longer chain hydrocarbons.

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