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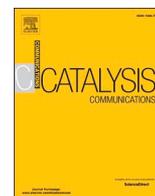
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Short communication

New mechanism insight for the hydrogenation of CO/CO₂ gas mixtures to hydrocarbons over iron-based catalyst

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ABSTRACT

Iron-based catalysts are the most suitable candidates for converting CO₂ or CO₂-rich syngas to hydrocarbons. However, several issues about the mechanism of CO₂ hydrogenation are still unclear. In this work, we investigated the performance of an iron-based catalyst with H₂/CO₂, H₂/CO/N₂ and H₂/CO/¹³CO₂/N₂ gas mixtures at the same process conditions ($T = 270^\circ\text{C}$, $P = 175$ psi and $SV = 3$ NL/h/g_{cat}). The CO₂ hydrogenation rate was much lower than that observed for CO hydrogenation. ¹³CO₂ tracer experiments indicated that CO₂ is hydrogenated to hydrocarbons via the reverse water-gas shift even when present in small concentration (1.8 vol%). ¹³C enrichment was observed in both CO and C₁-C₄ hydrocarbons.

1. Introduction

Fischer-Tropsch Synthesis (FTS) converts synthesis gas (CO and H₂) from various carbon-containing feedstocks (i.e., natural gas, coal, and biomass) to hydrocarbons. However, CO₂, CH₄, light hydrocarbons, tar, and other minor contaminants (e.g., NH₃, NO_x, HCN, H₂S, COS, HCl, NaCl, KCl) can also be present in the raw synthesis gas [1]. The amount of CO₂ in the raw synthesis gas varies from 1.7 to 46 vol%, depending on the carbon source [1–4], and is usually removed by a physical solvent absorption process (AGR – acid gas removal). Therefore, if the purification step for CO₂ removal could be avoided, without affecting the FTS activity, a possible economic benefit could be reached. Furthermore, the utilization of CO₂-rich syngas or CO₂ feedstock would contribute to mitigating greenhouse gas emissions [5].

Iron-based catalysts are reported to be more effective than cobalt for converting CO₂ and CO/CO₂ gas mixtures to long-chain hydrocarbons [6–13]. This is mostly attributed to their intrinsic activity for the reverse water-gas shift (RWGS) reaction [6,9,10]. Lower conversion rates and lighter saturated hydrocarbons are formed during CO₂ hydrogenation compared to CO on unpromoted bulk iron [13–16] and promoted iron with a low K/Fe ratio (<0.1 mol/mol) [10]. In contrast, high potassium loading (>0.5 mol/mol) improves the CO₂ conversion, suppresses CH₄ selectivity, while increases olefin/paraffin ratio and long-chain hydrocarbons [6,17,18]. Very few studies appeared in the literature

investigating the reactivity of CO₂-rich syngas on Fe-based catalyst to the best of our knowledge. A general agreement is that CO₂ can only be hydrogenated at low CO partial pressures, while different results are reported about the effect on the CO conversion rate and product distribution when CO₂ is cofed [6,7,10,15,19,20].

The mechanism of CO₂ hydrogenation to hydrocarbons is still debated because of the complex nature of reactions involving a large number of adsorbed species. CO₂ hydrogenation to hydrocarbons could proceed via direct or indirect pathways. In the direct pathway, CO₂ is directly converted to hydrocarbons (Eq. (1)), while in the indirect route, CO₂ is first converted to CO through RWGS (Eq. (2)) followed by FTS (Eq. (3)). Since the direct conversion of CO₂ to hydrocarbons is kinetically more complicated, the RWGS followed by FTS seems a more plausible pathway [21].



The isotope tracer technique can provide some vital information on the mechanism of a heterogeneous catalytic reaction. Isotopic tracer experiments (e.g., ¹⁴C or ¹³C labelled molecules and deuterium) [22] and the Steady-State Isotopic Transient Kinetic Analysis (SSITKA)

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technique [23–25] were carried out to investigate mechanistic issues of the Fischer-Tropsch synthesis. ^{14}C -labelled CO_2 was cofed during FTS on Fe catalyst by Xu et al. [26], and the authors concluded that $^{14}\text{CO}_2$ acted as an initiator in the chain growth, but it was not involved in the chain propagation. Later, Krishnamoorthy et al. [27] found no significant isotopic enrichment in the hydrocarbon products suggesting no competitive reactions of CO_2 when $\text{H}_2/\text{CO}_2/\text{CO}$ gas mixtures were tested. Thus, additional isotopic experiments are needed to understand the mechanism better when CO_2 is present in the feedstock. In this work, a state-of-the-art iron-based catalyst was tested at representative FTS process conditions for the hydrogenation of CO/CO_2 gas mixtures. ^{13}C -labelled CO_2 was cofed during CO hydrogenation in order to have further insights on the mechanism at hand.

2. Experimental

The catalytic experiments were carried out in a lab-scale 1 L continuously stirred tank reactor (CSTR). Additional details about the lab-scale set-up are reported elsewhere [10]. Briefly, 8 g of calcined $100\text{Fe}:4.4\text{Si}:1.2\text{K}$ catalyst ($\text{SSA} = 117 \text{ m}^2/\text{g}$) was loaded into the 1 L CSTR and mixed with 310 g of melted Polywax 3000. The catalyst was activated by flowing CO ($3 \text{ NL}/\text{h}/\text{g}_{\text{cat}}$) at 270°C and 175 psi for 24 h. After this pretreatment, the feed was switched to a $\text{H}_2/\text{CO}/\text{N}_2$ gas mixture (Mix 1, Table 1). This condition was maintained until a pseudo-steady-state CO conversion was reached. Then, the catalytic performance during CO_x hydrogenation was investigated with the following gas mixtures, whose compositions are reported in Table 1: H_2/CO_2 , $\text{H}_2/\text{CO}/\text{N}_2$, $\text{H}_2/\text{CO}/^{13}\text{CO}_2/\text{N}_2$.

The flowrates of the incondensable products and the unconverted reactants were measured by a dry-test meter, while the gas composition was quantified by a 3000A micro-GC-TCD (Agilent). The oil and the water fraction were analyzed by 7890 GC-FID (Agilent) and SRI 8610 GC-TCD, respectively. The abundance of ^{13}C in the gas was estimated by GC-MSD equipped with GS-GASPro ($60 \text{ m} \times 0.32 \text{ mm}$, Agilent) column. The samples were collected in an inert foil gas sampling bag specific for hydrogen, and then injected into a GC-MSD using an electron impact as the ionization source set at 70 eV. The mass was tuned before each run to ensure the mass was corrected down to 0.7AMU. Theoretically, given the natural abundance of ^{13}C , the M+1 should display a 1.1% abundance when directly compared to the parent ion, "M". Yet, this is not always the case, so to dispel any anomalies in the MS, a comparison was made between the labelled iron, and a nonlabelled run. The comparison for each sample was completed by the spectral intensity of the M+1 ion to the parent (M), for both the labelled and unlabeled runs. The comparison of the intensity of the M to the M+1 provides a good relative abundance for the presence of ^{13}C .

3. Results and discussion

3.1. CO and CO_2 hydrogenation

CO_x conversion versus time-on-stream (TOS) for the different CO_x -containing gas mixtures is shown in Fig. 1(a). After CO activation, the feed was switched to $\text{H}_2/\text{CO}/\text{N}_2$ (Mix 1, Table 1). This condition was maintained for at least 200 h. The conversion of CO progressively increased from 42.5% to a pseudo-steady-state value of 62.8%. This trend suggests that iron carbides, the active phase, were still forming

Table 1
Composition (vol%) of the different mixtures tested for CO_x hydrogenation.

Mixture	H_2	CO	N_2	CO_2	$^{13}\text{CO}_2$
Mix 1	25	25	50	–	–
Mix 2	75	–	–	25	–
Mix 3	50	25	25	–	–
Mix 4	50	25	23.2	–	1.8

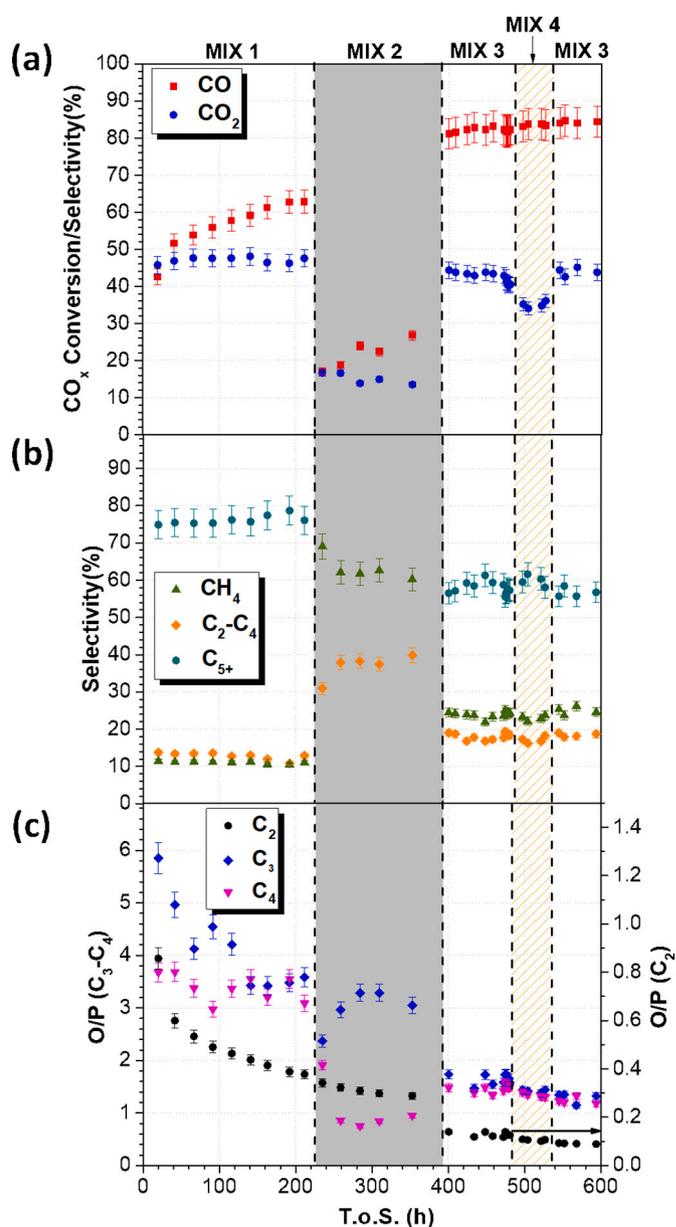


Fig. 1. (a) CO_x conversion/selectivity, (b) hydrocarbon selectivity, and (c) olefin/paraffin ratio evolution with TOS during the hydrogenation of CO_x gas mixtures; process conditions: $T = 270^\circ\text{C}$, $P = 175 \text{ psi}$, $\text{SV} = 3 \text{ NL}/\text{h}/\text{g}_{\text{cat}}$.

even after the switch from CO to the syngas mixture [28]. The initial induction period is a typical phenomenon occurring in the first few days of FT activity for an iron-based catalyst [29,30]. Indeed, the activation has a crucial role in obtaining a moderate reduction/carburization of the catalyst. Insufficient carburization would lead to long induction time, whereas excess carburization would result in rapid catalyst deactivation. The product selectivities were quite stable with TOS, CO_2 selectivity slightly increased from 45.7 to 47.5% (Fig. 1a), CH_4 and $\text{C}_2\text{-C}_4$ selectivities were close to 10%, while the C_{5+} selectivity was 75% (Fig. 1b). Moreover, the olefin/paraffin ratio for $\text{C}_2\text{-C}_4$ species (Fig. 1c) progressively decreased as the CO conversion was increasing. As expected, the low potassium-containing Fe catalyst in this study yielded a low methane selectivity. The potassium is a well-known promoter used to suppress secondary hydrogenation reaction by favoring the formation of long-chain hydrocarbons [6–8,29].

After the CO conversion reached a pseudo-steady state, the feed gas mixture was switched from $\text{H}_2/\text{CO}/\text{N}_2$ (Mix 1, Table 1) to H_2/CO_2 (Mix

2, Table 1). Under this condition, CO₂ conversion had an initial value of 17%, which progressively decreased to 13% in 100 h (Fig. 1a). The CO₂ conversion was found lower than CO, indicating that CO₂ was more difficult to be hydrogenated as the reaction rate is usually about two times slower for both unpromoted and promoted iron-based catalysts [8,10,13–15]. The product distributions during CO₂ and CO hydrogenation were also very different (Fig. 1b). CO was detected in the product pool, whose selectivity reached up to 26%, because of the RWGS activity. CH₄ was the main product among hydrocarbons as its selectivity reached ~62%, moreover, C₂-C₄ selectivity increased to 37% after switching from Mix 1 to Mix 2.

Light saturated hydrocarbons (C₁-C₄) were the main products during CO₂ hydrogenation in agreement with previous studies [6,7,10,13–16]. However, the difference in product distribution could be more pronounced based on the catalyst formulation. For instance, Herranz et al. [16] found that the chain growth probability decreased from 0.62 to 0.29 by switching from CO/H₂ to CO₂/H₂ on an unpromoted iron catalyst, whereas it decreased only from 0.62 to 0.56 for a Fe-Mn-1.3K catalyst. Visconti et al. [6] proposed that the difference in the product distribution between CO and CO₂ hydrogenation on Fe-based catalyst can be correlated to the adsorption strength of CO₂ and CO on the catalyst surface. It is well-known that CO adsorbs strongly than CO₂, thus resulting in a lower local H/C ratio on the catalyst surface during CO hydrogenation [6], which favors the chain growth probability, and thus high C₅₊ selectivity.

3.2. CO/¹³CO₂ gas mixture hydrogenation

The effect of co-feeding ¹³CO₂ during FTS was investigated by comparing the performance of H₂/CO/N₂ (Mix 3, Table 1) with H₂/CO/¹³CO₂/N₂ (Mix 4, Table 1). The presence of CO₂ in the feed gas mixture did not affect the CO conversion, which is 83% for both systems (Fig. 1a). There was no evidence from GC analysis that CO₂ reacted in the presence of CO. However, the addition of CO₂ in the feed decreased CO₂ selectivity from 42 to 34% (Fig. 1a), improving the atom efficiency of CO converted to hydrocarbons [6,27]. Furthermore, the presence of CO₂ had a negligible effect on the olefin/paraffin ratio.

Very few studies investigated different CO₂/(CO+CO₂) gas ratio on an iron-based catalyst, and it was concluded that CO₂ can be reactive only at low CO partial pressures [10,15]. For instance, Yao et al. [15] found that CO₂ behaved as an inert for CO₂/(CO+CO₂) gas ratio lower than 0.5–0.7. In this work, the investigated ratio was 0.07, and on-line GC analysis showed a decrease of net CO₂ production (lower CO₂ selectivity) for Mix 4. Indeed, the total net production of CO₂, obtained by the WGS reaction, could be higher than the total net consumption of CO₂.

To understand the role of added CO₂ during CO hydrogenation, the ¹³C abundance in the hydrocarbon products was estimated by GC/MS analysis for both Mix 3 and Mix 4. The natural abundance of ¹³C isotope is 1.1% for each carbon atom. The amount of ¹³C in the products of Mix 3 was almost proportional to the number of carbon atoms in each hydrocarbon. On the contrary, an isotopic enrichment was detected for C₁-C₄ hydrocarbons of Mix 4 (Fig. 2). This trend suggests that CO₂ was hydrogenated even if a low CO₂/(CO+CO₂) gas ratio was used. Xu et al. [26] observed a linear increase in the radioactivity/mol for C₁-C₄ during an isotopic experiment with ¹⁴CO₂. However, in their operating conditions, WGS was very close to equilibrium, and consequently, ¹⁴C in CO₂ and CO was at equilibrium as well. Under such reaction conditions, it is difficult to conclude the role of ¹⁴CO₂ in chain initiation and chain growth. In our work, WGS was far from equilibrium; thus, the ¹³C distribution in the hydrocarbons suggested that CO₂ is involved in the chain initiation. Furthermore, the presence of ¹³C in CO suggested that this species could be the intermediate for hydrocarbon formation from CO₂ on an iron catalyst.

The adsorbed CO is subsequently hydrogenated to hydrocarbons following the pathway known for FTS. The situation is totally different

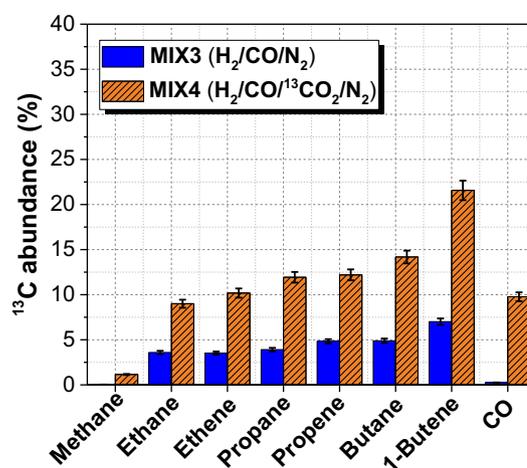


Fig. 2. ¹³C abundance in the gas products for H₂/CO/N₂ (Mix 3) and H₂/CO/¹³CO₂/N₂ (Mix 4).

for Co-FTS. Chakrabarti et al. [31] did not observe any ¹⁴C in CO when similar isotopic tracer experiments were carried out on 0.5%Pt-25%Co/ γ -Al₂O₃ catalyst. The ¹³C abundance in the products at different TOS is shown in Fig. 3. The ¹³C abundance slightly increased in the first 2.5 h, and then it reached a steady-state value for all the hydrocarbons. Finally, ¹³CO₂ co-feeding did not deactivate the catalyst since both CO conversion and the product selectivity remained stable with TOS. Moreover, a similar catalytic performance was observed when ¹³CO₂ was excluded from the reaction feed gas mixture (i.e., H₂/CO/N₂ (Mix 3, Table 1)). This behavior seems to suggest that ¹³CO₂ hydrogenation does not exclude the active site for the CO hydrogenation. Under FTS conditions, a mixture of iron carbides and magnetite are reported [28,32,33]. CO activation occurs on iron carbide, while CO₂ could be activated on Fe₃O₄ phase, which usually is associated with WGS/RWGS activity [34].

The effect of co-feeding ¹³CO₂ was also investigated during CO₂ hydrogenation (data not shown), where ¹³C was detected in both CO and C₁-C₄ hydrocarbons confirming that CO₂ is hydrogenated to hydrocarbons via RWGS. However, additional investigation will be carried out in near future to have more consolidate results.

4. Conclusions

The catalytic performance of an iron-based catalyst for H₂/CO and H₂/CO₂ was compared at the same process conditions ($T = 270^\circ\text{C}$, $P = 175$ psi, $SV = 3$ NL/h/g_{cat}). CO₂ can be hydrogenated but with much

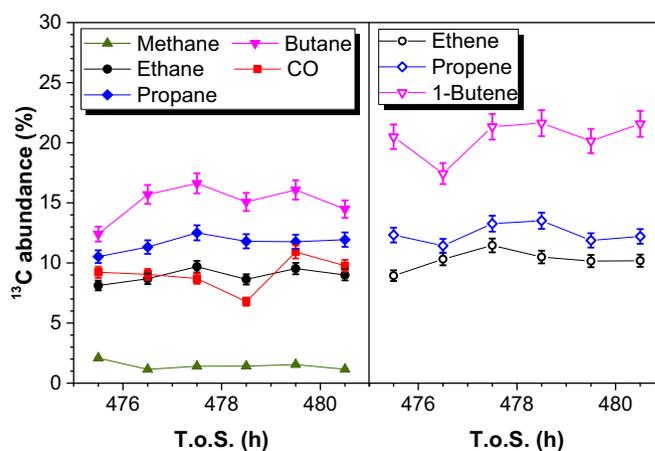


Fig. 3. ¹³C abundance with TOS in the gas products for H₂/CO/¹³CO₂/N₂ feed gas stream.

lower rates than those observed for the CO hydrogenation. The feed gas composition significantly influenced the product selectivity. The long-chain hydrocarbons were obtained in the presence of CO with C₅₊ selectivity close to 75%. On the contrary, methane and light-saturated hydrocarbons were the main products for the CO₂/H₂ gas mixture. The difference in selectivity can be ascribed to the change in the local H/C ratio on the catalyst surface.

The role of ¹³CO₂ co-feeding was analyzed for CO conversion, product distribution and deactivation. Both CO conversion and chain growth probability were not affected by CO₂ addition, while the decrease of the net CO₂ production suggested an improved atom efficiency of CO converted to hydrocarbons. Isotopic enrichment was observed for CO and C₁-C₄ hydrocarbons suggesting that ¹³CO₂ was converted to hydrocarbons via the RWGS even if present in small concentration (1.8 vol%). However, the effect of adding ¹³CO₂ was reversible in terms of catalytic performance. When ¹³CO₂ was removed from the feed gas stream, the previous performance of ¹²CO hydrogenation was restored.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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