New Mechanism Insight for the Hydrogenation of CO/CO\textsubscript{2} Gas Mixtures to Hydrocarbons over Iron-Based Catalyst

Sandeep Badoga  
*University of Kentucky*

Michela Martinelli  
*University of Kentucky*, michela.martinelli@uky.edu

Muthu Kumaran Gnanamani  
*University of Kentucky*, muthu.gnanamani@uky.edu

Young Koh  
*Asbury University*

Wilson D. Shafer  
*Asbury University*

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Short communication

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

Sandeep Badoga a, Michela Martinelli a, *, Muthu Kumaran Gnanamani a, Young Koh b, Wilson D. Shafer b

a University of Kentucky Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511, United States of America
b Science and Health Department, Asbury University, One Maclenn Drive, Wilmore, KY 40390, United States of America

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A B S T R A C T

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°C, P = 175 psi and SV = 3 NL/h/gcat). 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 C₇-C₉ 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, NOₓ, 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 utilisation 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].

\[
\begin{align*}
nCO₂ + 3nH₂ & \rightarrow CₙH₂ₙ + 2nH₂O \quad (1) \\
CO₂ + H₂ & \rightarrow CO + H₂O \quad (2) \\
nCO + 2nH₂ & \rightarrow CₙH₂ₙ + nH₂O \quad (3)
\end{align*}
\]

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)
technique [23–25] were carried out to investigate mechanistic issues of the Fischer-Tropsch synthesis. $^{13}$C-labelled CO$_2$ was cofed during FTS on Fe catalyst by Xu et al. [26], and the authors concluded that $^{13}$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 H$_2$/CO$_2$/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 100Fe:4.4Si:1.2K catalyst (SSA = 117 m$^2$/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 NL/h/gcat) at 270 °C and 175 psi for 24 h. After this pretreatment, the feed was switched to a H$_2$/CO/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$_2$ hydrogenation was investigated with the following gas mixtures, whose compositions are reported in Table 1: H$_2$/CO$_2$, H$_2$/CO/N$_2$, H$_2$/CO/$^{13}$CO$_2$/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 abundance of $^{13}$C in the gas was estimated by GC-MSD equipped with GS-GASpro (60 m × 0.32 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. 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 $^{13}$C was quantified by a 3000A micro-GC-TCD (Agilent). The abundance of $^{13}$C to $^{12}$C was calculated using a relative abundance for the presence of $^{13}$C.

3. Results and discussion

3.1. CO and CO$_2$ hydrogenation

CO$_4$ 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 H$_2$/CO/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 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 conversion/selectivity, (b) hydrocarbon selectivity, and (c) olefin/paraffin ratio evolution with TOS during the hydrogenation of CO$_2$ gas mixtures; process conditions: T = 270 °C, P = 175 psi, SV = 3 NL/h/gcat.

![Fig. 1.](image-url)

Table 1

| Mixture  | H$_2$ | CO | N$_2$ | CO$_2$ | $^{13}$CO$_2$ |
|----------|-------|----|-------|-------|--------------|
| Mix 1    | 25    | 25 | 50    | –     | –            |
| Mix 2    | 75    | –  | –     | 25    | –            |
| Mix 3    | 50    | 25 | 25    | –     | –            |
| Mix 4    | 50    | 25 | 23.2  | –     | 1.8          |

After the CO conversion reached a pseudo-steady state, the feed gas mixture was switched from H$_2$/CO/N$_2$ (Mix 1, Table 1) to H$_2$/CO$_2$ (Mix...
Under this condition, CO$_2$ conversion had an initial value of 17%, which progressively decreased to 13% in 100 h (Fig. 1a). The CO$_2$ conversion was found lower than CO, indicating that CO$_2$ 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 CO$_2$ 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. CH$_4$ was the main product among hydrocarbons as its selectivity reached ~62%, moreover, C$_2$–C$_4$ selectivity increased to 37% after switching from Mix 1 to Mix 2.

Light saturated hydrocarbons (C$_1$–C$_4$) were the main products during CO$_2$ 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/H$_2$ to CO$_2$/H$_2$ 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 CO$_2$ hydrogenation on Fe-based catalyst can be correlated to the adsorption strength of CO$_2$ and CO on the catalyst surface. It is well-known that CO adsorbs strongly than CO$_2$, 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 C$_5$+ selectivity.

3.2. CO/CO$_2$ gas mixture hydrogenation

The effect of co-feeding $^{13}$CO$_2$ during FTS was investigated by comparing the performance of H$_2$/CO/N$_2$ (Mix 3, Table 1) with H$_2$/CO/CO$_2$/N$_2$ (Mix 4, Table 1). The presence of CO$_2$ 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 CO$_2$ reacted in the presence of CO. However, the addition of CO$_2$ in the feed decreased CO$_2$ selectivity from 42 to 34% (Fig. 1a), improving the atom efficiency of CO converted to hydrocarbons [6,27]. Furthermore, the presence of CO$_2$ had a negligible effect on the olefin/paraffin ratio.

Very few studies investigated different CO$_2$/CO (CO$_2$/CO$_2$) gas ratio on an iron-based catalyst, and it was concluded that CO$_2$ can be reactive only at low CO partial pressures [10,15]. For instance, Yao et al. [15] found that CO$_2$ behaved as an inert for CO$_2$/CO (CO$_2$) 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 CO$_2$ production (lower CO$_2$ selectivity) for Mix 4. Indeed, the total net production of CO$_2$ obtained by the WGS reaction, could be higher than the total net consumption of CO$_2$.

To understand the role of added CO$_2$ during CO hydrogenation, the $^{13}$C abundance in the hydrocarbon products was estimated by GC/MS analysis for both Mix 3 and Mix 4. The natural abundance of $^{13}$C isotope is 1.1% for each carbon atom. The amount of $^{13}$C 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 C$_1$–C$_4$ hydrocarbons of Mix 4 (Fig. 2). This trend suggests that CO$_2$ was hydrogenated even if a low CO$_2$/CO (CO$_2$) gas ratio was used. Xu et al. [26] observed a linear increase in the radioactivity/mol for C$_1$–C$_4$ during an isotopic experiment with $^{13}$CO$_2$. However, in their operating conditions, WGS was very close to equilibrium, and consequently, $^{13}$C in CO$_2$ and CO was at equilibrium as well. Under such reaction conditions, it is difficult to conclude the role of $^{13}$CO$_2$ in chain initiation and chain growth. In our work, WGS was far from equilibrium; thus, the $^{13}$C distribution in the hydrocarbons suggested that CO$_2$ is involved in the chain initiation. Furthermore, the presence of $^{13}$C in CO suggested that this species could be the intermediate for hydrocarbon formation from CO$_2$ on an iron catalyst.

The adsorbed CO is subsequently hydrogenated to hydrocarbons following the pathway known for FTS. The situation is totally different for Co-FTS. Chakrabarti et al. [31] did not observe any $^{14}$C in CO when similar isotopic tracer experiments were carried out on 0.5%Pt-25%Co/$\gamma$-Al$_2$O$_3$ catalyst. The $^{13}$C abundance in the products at different TOS is shown in Fig. 3. The $^{13}$C abundance slightly increased in the first 2.5 h, and then it reached a steady-state value for all the hydrocarbons. Finally, $^{13}$CO$_2$ co-feeding did not deactivate the catalyst since both CO conversion and product selectivity remained stable with TOS. Moreover, a similar catalytic performance was observed when $^{13}$CO$_2$ was excluded from the reaction feed gas mixture (i.e., H$_2$/CO/N$_2$ (Mix 3, Table 1)). This behavior seems to suggest that $^{13}$CO$_2$ 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 CO$_2$ could be activated on Fe$_3$O$_4$ phase, which usually is associated with WGS/RWGS activity [34].

The effect of co-feeding $^{13}$CO$_2$ was also investigated during CO$_2$ hydrogenation (data not shown), where $^{13}$C was detected in both CO and C$_1$–C$_4$ hydrocarbons confirming that CO$_2$ 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 H$_2$/CO and H$_2$/CO/CO$_2$/N$_2$ was compared at the same process conditions (T = 270°C, P = 175 psi, SV = 3 NL/h/gcat). CO$_2$ can be hydrogenated but with much
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 C<sub>5</sub> selectivity close to 75%. On the contrary, methane and light-saturated chain hydrocarbons were obtained in the presence of CO with C<sub>5</sub> composition significantly influenced the product selectivity. The long-chain hydrocarbons were the main products for the CO<sub>2</sub>/H<sub>2</sub> gas mixture. Isotopic enrichment was reversible in terms of catalytic performance. When CO<sub>2</sub>-C 12-co-feeding was analyzed for CO conversion, product distribution and deactivation. Both CO conversion and chain growth probability were not affected by CO<sub>2</sub> addition, while the decrease of the net CO<sub>2</sub> production suggested an improved atom efficiency of CO converted to hydrocarbons. Isotopic enrichment was observed for CO and C<sub>5</sub>-C<sub>4</sub> hydrocarbons suggesting that <sup>13</sup>CO<sub>2</sub> was converted to hydrocarbons via the RWGS even if present in small concentration (1.8 vol%). However, the effect of adding <sup>13</sup>CO<sub>2</sub> was reversible in terms of catalytic performance. When <sup>13</sup>CO<sub>2</sub> was removed from the feed gas stream, the previous performance of <sup>13</sup>CO 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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