



# **The Use of Iron Ore as a Catalyst in Fischer–Tropsch Synthesis—A Review**

Chike George Okoye-Chine <sup>1,\*</sup> and Samuel Mubenesha <sup>2</sup>

- <sup>1</sup> Department of Chemical and Life Science Engineering, Virginia Commonwealth University (VCU), 737 North 5th Street, Richmond, VA 23219, USA
- <sup>2</sup> Institute for the Development of Energy for African Sustainability (IDEAS), University of South Africa (UNISA), Florida 1710, South Africa
- \* Correspondence: okoyechinec@vcu.edu

Abstract: The use of iron ore as an alternative to conventional Fischer–Tropsch synthesis (FTS) iron catalyst has been identified as a way to achieve a cost-effective catalyst. In recent times, considerable progress has been made to build a strong case for iron ore as a viable alternative to traditional iron catalysts. Nevertheless, there are still opportunities to enhance the current iron ore low-temperature Fischer–Tropsch (LTFT) catalysts and pave the way for optimal performing catalysts. In this study, we thoroughly examined the various publications on iron ore catalysts used for FTS and highlighted the research gaps in the studies. The study identified the progress made so far, opportunities, and challenges regarding the use of iron ore as a catalyst in FTS. One of the critical areas that needs to be addressed from the review is establishing the deactivation pathways of these catalyst systems. The application of advanced spectroscopic and computational methods is also suggested to elucidate the relationship between the synthesis conditions, active catalytic sites, reaction intermediates, and catalytic performance to fabricate optimized iron ore LTFT catalysts.

Keywords: activity; Fischer-Tropsch synthesis; iron ore; product selectivity; stability



Citation: Okoye-Chine, C.G.; Mubenesha, S. The Use of Iron Ore as a Catalyst in Fischer–Tropsch Synthesis—A Review. *Crystals* **2022**, *12*, 1349. https://doi.org/10.3390/ cryst12101349

Academic Editor: Bo Chen

Received: 26 August 2022 Accepted: 20 September 2022 Published: 24 September 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).

## 1. Introduction

Fischer–Tropsch synthesis (FTS) is an established technology that has been around for almost 100 years and is commercially spearheaded by renowned companies such as Sasol, Shell, and Synfuels China. The process involves the catalytic conversion of syngas (i.e., a mixture of CO and H<sub>2</sub>) derived from natural gas, coal, and biomass into valuable hydrocarbon products such as gasoline, diesel, lubricants, and chemicals [1–7]. FTS relies on iron and cobalt as the catalysts to convert syngas into a myriad of hydrocarbons due to their economic competitiveness over other transition metals such as ruthenium, nickel, etc. [4,6]. Among cobalt and iron, the latter is favored for FTS due to its cost, availability, and compatibility with hydrogen deficient feedstocks such as coal and biomass [1,2,8,9]. Moreover, its compatibility with biomass is attractive because it provides the opportunity to produce cleaner fuels with no sulfur, nitrogen, or aromatics as pollutants [2,9–12].

Nevertheless, biomass-to-liquid Fischer–Tropsch (BTL-FT) technology is still relatively more expensive to implement on a large scale compared to coal-to-liquid Fischer–Tropsch (CTL-FT) and gas-to-liquid Fischer–Tropsch (GTL-FT) technologies [9,13–16]. One of the ways to address this issue is to substitute conventional iron catalysts with cheaper iron ore [1-3,6,7,17]. Precipitated iron catalyst is one of the conventional iron-based catalysts used in FTS [4], and it requires the use of various chemicals for its preparation, which increases its cost [1–6]. On the other hand, iron ore is a source of iron, and the use of iron ore as a catalyst for FTS is fast gaining the attention of researchers due to its natural abundance and low price [1-3,6,7,17].

The FT catalytic performance of any catalytic material is directly linked to its properties, which rely on the catalyst synthesis method and precursor chosen from the beginning [3,9,10,18–20]. Thus, an optimized catalyst design and development process must be in place to achieve an excellent performing catalyst [1,3,16,19–25]. It is imperative to have an optimized catalyst to make the overall FT application economical for the practitioner by ensuring high production of the desired hydrocarbons [3,10,16,20,25]. Catalytic performance is defined as a function of its activity, selectivity, and stability [9,16,19,20,26–31]. These principles are also applicable to iron ore catalysts used in FT, which will be scrutinized to improve the current research on this type of iron catalyst.

It is observed that most of the research work carried out on the use of iron ore as a catalyst in FTS did not give significant attention to its stability. Apart from looking at the activity and selectivity of the iron ore as a catalyst in FTS, its stability is a very crucial aspect for the development of a practical reaction system [1,3,19,24,25,27,30,32,33]. A catalyst's stability can be defined as a function of the chemical and physical aspects [18,24,27,29,34]. The chemical element focuses on its durability during reactions before it starts losing its functionality, while the latter emphasizes maintaining its physical structure throughout the reactions [11,24,30,35]. The deactivation of catalysts is dependent on these two aspects. Therefore, studies that examine the iron ore catalyst's deactivation pathways during FTS would provide useful information for the FT community [19,24,30,35–37] to improve existing iron ore FT research. This review paper identifies the progress made so far, opportunities, and challenges regarding the use of iron ore as a catalyst in FTS.

#### 2. Raw Iron Ore Catalysts Application in Low-Temperature FTS

Iron-based FT catalysts are usually not regenerated due to their rapid rate of deactivation, which makes it difficult and expensive to reverse their deactivation mechanisms [5,17,25], and, thus, most of the time they are discarded instead [5]. Some of their deactivation mechanisms are due to the oxidation of the active phase, sintering, carbon deposition, and fouling by pollutants such as sulfur and nitrogen [4,19,24,25,27,30]. Consequently, it is important to find viable alternatives to a conventional iron-based catalysts that are cheaper and easily disposable, such as raw iron ore [1-3,5,6,17]. The use of iron ore in FTS has been widely used in high-temperature scenarios to target olefins, but in recent times, there have been a few studies that have looked at its application in the lowtemperature range [1,2,5,6,17]. Temperature ranges for FTS vary from author to author but fall within a similar range. Some authors state that the low-temperature mode is generally between 220 and 270 °C, the medium temperature between 270 and 295 °C, and the high temperature between 300 and 340 °C [33,38–41]. However, some other FT practitioners have defined the low-temperature mode as the low temperature being between 200 and 280 °C [4,42] and cite that the application of iron ore in FT is attractive to practitioners because, when optimized, it can yield  $C_{5+}$  hydrocarbons in a cheaper and much more environmentally friendly way [6,7]. These C<sub>5+</sub> hydrocarbons can further be processed downstream into in-demand high-value middle distillates such as diesel and jet fuels [20]. Low-temperature Fischer–Tropsch (LTFT) practitioners mainly use fixed-bed reactors to perform their studies due to their economic attractiveness in terms of operation and ease in scalability [3,18,22,25,35,43,44]. As a result, all LTFT iron ore investigations reported in the scientific literature so far have only used fixed-bed reactors [1,2,5–7,17].

#### 2.1. Characterization, Activity, and Stability of Raw Iron Ore

Before we look at the catalyst's FT activity, the textural and physicochemical properties were assessed to link it to its catalytic performance. The pore characterization of raw iron ore FTS catalysts as reported by some authors is shown in Table 1.

Table 1 shows that the natural ore catalysts used for FTS had low surface areas and pore volumes. In a bid to improve the surface area and pore volume of the natural iron ore, Hong et al. [5] carried out milling and promoted the iron ore with copper and potassium in order to obtain a similar texture and catalytic performance to that of the conventional precipitated iron catalysts. The deficient properties of natural iron ore signify that it must be modified to attain a comparable performance with precipitated iron catalysts. On the

other hand, Ramutsindela et al. [2,7] reported on natural iron ores with promising chemical properties that favored their catalytic performance. Ramutsindela et al. [2] observed that the presence of magnesium as an impurity in iron ore enhanced its overall performance compared to that reported by Hong et al. [5] and Bae et al. [6], which was confirmed by Yang et al. [31], reporting that an appropriate amount of magnesium can enhance the activity and stability of iron-based catalysts. Meanwhile, the textural properties of the iron ore were not reported by Kulikova et al. [7], but it is believed that the promoting effect of magnesium was responsible for increasing the surface area and improving carburization [2,31,45–47]. Table 2 summarizes the influence of alkaline earth metals in iron ore and conventional Fe catalysts on their properties and overall catalytic performance.

Table 1. Pore characterization of raw iron ore FTS catalysts <sup>*a*</sup>.

Reference	BET Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Average Pore Size (nm)	
Ramutsindela et al. (2022) [2]	59.0	0.0882	9.15	
Bae et al. (2019) [6]	47.6	0.0961	8.08	
Hong et al. (2016) [5]	25.3	0.0701	11.1	

Note: <sup>*a*</sup> Analyzed by N<sub>2</sub> Physisorption.

**Table 2.** The effect of alkaline earth metals on the properties of iron ore and conventional Fe-FT catalysts and their overall performance.

			Proper				
Type of Catalyst	Promoter(s)	BET Surface Area (m²/g)	Mossbauer Spectroscopy (Phases)	Carburization	Mean Catalytic Performance (CO Conversion%)	Overall Effect	Reference
Iron ore-CAT 1	Ca and Mg	59.0	N/A	Improved carburization was confirmed by TEM	76.4	Improved	Ramutsindela et al. (2022) [2]
Iron ore-CAT 2	Ca and Mg	N/A	N/A	N/A	60	Improved	Kulikova et al. (2021) [7]
Conventional FT Fe-CAT 1	Mg, Ca, Sr, and Ba	55.5	${ m Fe}^{2+}$ , ${ m Fe}^{3+}$ and $\chi-{ m Fe}_5{ m C}_2$ Species identified	Improved with increasing atomic number of Alkali	24.2	Improved	J. Li et al. (2013) [46]
Conventional FT Fe-CAT 2	Mg	N/A	Fe <sup>2+</sup> and Fe <sup>3+</sup> Species identified	Improved carburization was confirmed by chemisorption	N/A (Reported as TOF)	Improved	Gallegos et al. (1996) [47]

The reducibility of any Fe-FT catalyst is influenced by the activation conditions, the catalyst synthesis, and the catalyst precursor used, ultimately determining its catalytic performance [2,48,49]. This section focuses on how activation conditions such as reductants and catalyst precursors affect the overall reducibility of the catalysts. One of the most common methods to measure the reducibility of catalysts is the use of temperature-programmed reduction (TPR) characterization studies [2]. Hong et al. [5] activated their catalysts with CO and reported no TPR results for fresh iron ore. However, its reducibility is expected to be more difficult than copper-doped iron ore, as evidenced by poor CO conversion and  $C_{5+}$  selectivities of 36.4% and 27%, respectively. This assertion was confirmed by Bae et al. [6], and it is shown in Figure 1.

Generally, the hematite reduction process follows a three-step mechanism:  $3Fe_2O_3 \rightarrow 2Fe_3O_4 \rightarrow 6FeO \rightarrow 6Fe$ . With the H<sub>2</sub>-TPR profile, the reducibility of the raw iron ore, promoted iron ore, and precipitated iron catalysts were estimated by the temperatures of the H<sub>2</sub> consumption peaks. The lower temperature is an indication of the higher reducibility of the catalyst. The TPR profile shown in Figure 1 delineates that raw iron ore is much more difficult to reduce than both the promoted iron ore and precipitated iron. The higher reduction temperature denotes that attainment of the active phase will be much more difficult and result in a meager overall catalytic performance as shown in Figure 2 and Table 3. The CO conversion of both raw iron ore catalysts (i.e., ROI-3 and ROI-1 in

Table 3) reported by Hong et al. [5] and Bae et al. [6] was reported to be 36.4% and 27.1%, respectively, which improved significantly to 89.9% (IO-CAT 4) and 75.4% (IO-CAT 1) after copper promotion. Both authors used CO as the reductant and did not investigate other reducing agents such as hydrogen and syngas, nor the link to their catalytic performance.



**Figure 1.** H<sub>2</sub>-TPR Comparison: (a) raw iron ore, (b) promoted iron ore, (c) precipitated iron catalyst [6]. Reproduced with permission from Elsevier.



**Figure 2.** Comparison of CO conversation versus Time [6]. IO-U, IO-CAT, and PFe-CAT represented promoted iron ore after milling prior to calcination, promoted iron ore after calcination, and precipitated iron catalyst, respectively. Reproduced with permission from Elsevier.

		Reaction Conditions			60	Selectivity (%)				
Catalysts	Т (°С)	GHSV (NL/g <sub>cat</sub> .h)	P (Bar)	H <sub>2</sub> /CO	CO Conversion (%)	CO <sub>2</sub>	CH <sub>4</sub>	C2-C4	C <sub>5+</sub>	Reference
RIO-1	275	2.8	15	1.0	27.1	28.9	20.8	41.9	21.2	Bae et al. (2019) [6]
RIO-2	260	N/A	30	1.0	60	N/A	7	13.1	80	Kulikova et al. (2021) [7]
RIO-3	275	2.8	15	1.0	36.4	32.2	35.9	36.5	27.6	Hong et al. (2016) [5]
RIO-4	270	2.5	20	2.0	94.2	32.4	13.7	33.3	53.0	Ramutsindela et al. (2022) [2]
PFe-CAT 1	275	2.8	15	1.0	85.0	44.2	9.25	20.0	68	Bae et al. (2019) [6]
PFe-CAT 2	270	2.8	13	0.7	78.7	47.5	36.0	N/A	64	Luo et al. (2009) [50]
PFe-CAT 3	270	2.0	13	0.7	74.7	47.7	5.8	N/A	72	Ma et al. (2018) [51]
PFe-CAT 4	275	2.8	15	1.0	85.0	44.2	9.25	N/A	68	Bae et al. (2019) [6]
PFe-CAT 5	280	12	20	1.0	68.8	36.7	11.8	26.5	61.7	Perez et al. (2019) [17]
IO-CAT 1	275	2.8	15	1.0	75.4	42.6	9.05	N/A	71	Bae et al. (2019) [6]
IO-CAT 2	270	3.6	20	2.0	72.1	48.6	5.0	N/A	83.2	Mubenesha et al. (2021) [1]
IO-CAT 3	280	12	20	1.0	46.5	30	11.7	25.9	62.4	Perez et al. (2019) [17]
IO-CAT 4	275	2.8	15	1.0	89.9	42.1	15.1	28.2	56.7	Hong et al. (2016) [5]

**Table 3.** FT catalytic performance of raw iron ore during LTFT conditions versus conventional iron catalysts.

RIO denotes raw iron ore, IO-CAT signifies promoted iron ore after calcination, and PFe denotes conventional low-temperature Fischer–Tropsch catalysts prepared by precipitation.

Moreover, it is postulated that the promoting effect of magnesium in the work conducted by Kulikova et al. [7] was responsible for the superior FT performance compared to other iron ore studies reported by previous authors. The average CO conversions reported by Hong et al. [5] and Bae [6] were 36.4% and 27.1%, respectively, which are lower than the average CO conversion of 79.3% for precipitated catalysts [6]. These lower CO conversions are strongly linked to raw iron ore's inferior properties and validate the need for them to be tuned like their counterparts to favor better overall FT performance.

Conversely, Kulikova et al. [7] reported a CO conversion of approximately 60% at their optimized operating conditions, mainly credited to its naturally occurring promoters such as magnesium [2,31]. It is believed that magnesium improved the surface area and carburization of this catalyst [2,31,52]. Therefore, it had a significantly better catalytic performance than the other iron ores cited in this work. Additionally, these findings highlight the fact that the origin of raw iron influences its catalyst performance. Despite this promising result, the effect of the activation condition on overall catalytic activity was not reported, and only hydrogen was used as a reducing agent. It is worth mentioning that the chemical stability of the iron ore catalyst was not reported by Kulikova et al. [7] under their optimized FT operating conditions. The times on streams for most of the studies reporting on raw iron ore were too short to deduce the stability of these catalyst systems and thus deemed inappropriate to compute deactivation mechanisms from them. The omission of stability studies of iron ore as an FT catalyst confirms a gap in the literature that has to be addressed urgently.

Similarly, Ramutsindela et al. [2] reported good catalytic performance of raw iron ore, which was mainly credited to the presence of natural impurities such as magnesium and calcium with a mean CO conversion of 76.1%. These alkaline earth metals are believed to have increased their catalyst's basicity, thereby improving its carburizing effect [2,7,31,45,53]. Moreover, as previously mentioned earlier, the magnesium was responsible for improving the surface area of their catalyst by creating extra pores resulting from the effective diffusion of Fe species [2,11,52,54,55]. The combination of these two factors yielded a good-performing catalyst. Moreover, the main crux of the investigation was to explore the effect that various reducing agents have on the iron ore catalyst to establish a correlation between temperature-programmed reduction studies and the overall catalytic performance of iron catalysts [2]. Therefore, the study reported on syngas-TPR, CO-TPR, and H<sub>2</sub>-TPR to establic.

lish the relationship between the catalytic performance and their reducibility under these reducing environments.

Figure 3 shows that the TPR spectra reveal that the syngas-reduced iron ore was the most difficult to reduce, followed by the hydrogen-reduced catalyst, and then the CO-reduced one. The findings suggest a direct proportionality between CO conversion and its reducibility, which is expected. Furthermore, Figure 4 bolsters these findings and shows that CO-reduced iron ore with a CO conversion of 94.2% was the best performing catalyst, followed by the H<sub>2</sub>-reduced catalyst with a CO conversion of 80.1%, while the syngas-reduced catalyst exhibited the lowest CO conversion at 54.8% [2]. The authors did a good job demonstrating the significance of detailed TPR studies, which correlate the FT catalytic performance of iron ore catalysts and their reducibility. Our research group also attempts to explain the interplay between the various iron phases during the different reducing conditions to explain their findings. However, the study would have been more fascinating if the phase changes were monitored in situ. Additionally, the comparative study that our research group carried out shows that the FT reactions were not performed at much longer times on streams than all the other predecessors. Thus, this necessitates the need to address it in future studies. Gorimbo et al. [49] recommend a time stream of 12,400 h for reliable stability studies for iron FT catalysts. So, a similar approach should be applied for fresh iron ores that show promising catalytic performance to ascertain their stability/deactivation behavior during FTS and help model better-performing catalysts.



Figure 3. TPR profiles under varying reducing agents [2]. Reproduced with permission from Elsevier.

The overall suboptimal catalytic performance of raw iron ore compared to the conventional precipitated LTFT catalysts was attributed to the precursor's deficient physicochemical properties (raw iron ore). The promotion of iron catalysts, in general, should improve the properties of the ores and, in turn, improve their overall catalytic performance [4,9,11,12,18,19,24,30,55–58]. There was an exception with the fresh iron ore studied by Ramutsindela et al. [2] and Kulikova et al. [7] due to impurities such as magnesium, which other natural iron ore reported by previous authors did not have. A comparative analysis of the activation conditions versus catalytic performance and hydrocarbon selectivities for all LTFT raw iron ores reported in the literature could not be determined due to differences in the precursors, reducing agents, and non-iso conversion reaction studies. However, based on Ramutsindela et al. [2], CO is the most favorable reducing agent due to the higher carburization effect, so a better FT catalytic performance was observed.



**Figure 4.** CO conversions of raw iron ore under varying reducing agents [2]. Reproduced with permission from Elsevier.

## 2.2. Product Selectivity of Raw Iron Ore

The product selectivity of raw iron ore toward CH<sub>4</sub>, CO<sub>2</sub>, and C<sub>5+</sub> hydrocarbons is analyzed and compared to precipitated iron ore catalysts to assess its applicability as an LTFT catalyst. An excellent performing catalyst will exhibit high selectivity toward C<sub>5+</sub> hydrocarbons and lower selectivity toward CH<sub>4</sub> and CO<sub>2</sub>. Table 3 summarizes the FT performance of raw and modified iron ore reported in the literature so far.

The conventional iron catalysts' mean that CH<sub>4</sub> and CH<sub>5+</sub> selectivities outperformed the natural iron ore, as shown in Table 3. The difference in these selectivities is expected because of the superior textural properties of the precipitated iron catalyst over fresh iron ores. The selectivity mismatch between the conventional iron catalysts and the natural ores has been attributed to K and Cu additions in the traditional catalysts that were absent in their competitors [4,9,59]. It is believed that K increases the basicity of the catalyst surface, which promotes CO adsorption and eventually the formation of iron carbides, which are responsible for increased FT activity [9,56,59,60]. On the other hand, Cu is believed to improve the reducibility of iron catalysts through the spillover effect of Fe species on the surface [9,56,59,61]. Some reports suggest that the CuO conversion to metallic copper during the reduction of the Cu-promoted iron catalyst increases dissociation sites for  $H_2$  into its atoms and, in turn, enhances the reduction of  $Fe_2O_3$  on its surface [56,59,61]. Thus, the presence of these two promoters in the conventional catalyst improved their reducibility, carburization ability, and overall selectivity for desirable products [4,9,12,17,19,24,40,42,51,61–66] compared to the natural ores. The outlier was the natural iron ore reported by Ramutsindela et al. [2] and Kulikova et al. [7], which had a significantly better overall hydrocarbon selectivity than its counterparts due to its superior physio-chemical properties. Contrarily, a different trend is observed for  $CO_2$  selectivity, in which the raw iron ore exhibited  $CO_2$  selectivity of 30.6%, and the precipitated ones reported a higher CO<sub>2</sub> selectivity of 46.5%. This pattern is consistent with other promoted iron catalysts reported by other researchers [4,9,10], and this is ascribed to the increased activity of the water–gas shift reaction. Compared to their counterparts, the lower  $CO_2$ formation due to the reduced water-gas shift activity in raw ores reported in Table 3 could be attributed to the absence of K as a promoter, which is believed to increase both the FT

and water-gas shift activity in iron catalysts [56,60,64,67,68]. Many FT practitioners have reported that potassium suppresses hydrogen adsorption on the catalyst surface but favors CO adsorption on its surface This, in turn, enhances the formation of Fe carbides and Fe<sub>3</sub>O<sub>4</sub> on the surface, which are thought to be active for FT and WGS reactions [40,60,67]. The average  $C_2$ – $C_4$  selectivities of fresh iron ore reported by Hong et al. [5] and Bae et al. [6] were 38.9% compared to the 24.1% of the conventional precipitated iron catalysts discussed by the same authors. These studies aimed to validate the application of iron ore as an alternative catalyst in LTFT, which targets its yield towards  $C_{5+}$  hydrocarbons. Therefore, it signifies that a lower selectivity towards  $C_2$ - $C_4$  hydrocarbons will favor the long-chain hydrocarbons ( $C_{5+}$  hydrocarbons), which is desirable. These findings justified the need to promote their respective iron ores to match the selectivities of the precipitated iron catalyst. Conversely, Kulikov et al. [7] reported  $CH_4$  and  $C_{5+}$  selectivities for fresh iron ore of 6–7% and 80%, respectively, which is relatively reasonable and comparable to other precipitated iron catalysts in the literature. Moreover, its  $C_2$ – $C_4$  selectivity was about 13%, which was expected considering the high  $C_{5+}$  selectivity. Thus, as mentioned earlier, the inherent properties of this fresh ore favored its catalytic performance compared to previous authors.

Most of the comparisons performed by authors regarding the product selectivities of the raw iron, doped iron ore, and precipitated iron catalysts were not carried out as isoconversions. To better compare the hydrocarbon selectivities of the various iron ore catalysts discussed in this section, they have to be performed at iso-conversions levels to expose the active sites to similar partial pressures of the reactants and products [54,55]. Likewise, a similar approach should compare the natural iron ores' hydrocarbon selectivities versus the precipitated iron catalysts.

#### 3. Modified Iron Ore Catalysts in FTS

In this section, the effect of promoting iron ores with chemical and structural dopants was studied to highlight their influence on the iron ore catalyst's overall activity. After that, they are compared to the traditional precipitated catalysts. Traditional precipitated catalysts are also promoted and modified to be functional [39,65,66]. Various copper-free precipitated catalysts reported by many FT practitioners have shown that they are not rapidly reduced due to a prolonged induction of the reaction, and result in below-average catalytic performance [63,69,70]. Very low olefin rates were also reported for catalysts free of potassium, resulting in higher methane production instead of desirable C5+ hydrocarbons [4,63]. Copper usually enhances the hydrogenation of iron catalysts and facilitates the reduction of the hematite phase by creating additional surface vacancies via the spillover effect; on the other hand, potassium increases the basicity of the catalyst's surface and promotes CO adsorption, which eventually leads to carburization of the Fe species [4,63,71]. Therefore, both dopants must be in optimal ratios to ensure an excellent-performing precipitated iron FT catalyst [4]. In addition, precipitated catalysts are typically used in slurry beds and further treated by spray drying to ensure they are attrition resistant and function optimally. Therefore structural dopants such as silica and alumina are usually incorporated to ensure this [24,30,50,67]. Conversely, all the modified LTFT iron ore catalysts studied so far used oven drying after promotion. As discussed in the previous section, raw iron ore showed some promise as an LTFT catalyst. Still, to compete with precipitated iron catalysts, their properties must be modified to perform at par with their counterparts. One of the notable areas that needs attention is the iron ore catalyst systems' stability under LTFT reaction conditions directly linked to their physio-chemical properties determined at the catalyst preparation stage [22,24,30,34,42,44].

Another crucial aspect of stability for iron catalysts discussed in this work is the physical aspect of their stability, which also determines their longevity under process conditions [1,4,9,24,30,35]. During fixed-bed operation, especially in high-scale scenarios, solid catalysts must withstand the reaction conditions and maintain their structure to avoid mechanical failure. This is important to minimize downstream clogs that can cause downtime [1,2,9,18,22,35,43,72,73]. Additionally, fines of the catalyst pellets resulting from me-

chanical failure may also increase the overall pressure of reactants/products on the catalyst's surface and inside the fixed-bed reactor itself, which accelerates their deactivation [1,3,9,35]. Catalyst development and design are crucial in controlling the physio-chemical properties of iron FT catalysts to improve their longevity and yield the desired hydrocarbon selectivity [1,19,22,24,34,35,74,75]. For iron ore catalysts to be viable substitutes for traditional LTFT iron catalysts, they must be rigorously tested at all development stages of their synthesis, namely, the conceptual, laboratory, pilot, and commercial phases.

Most FT researchers have addressed this issue by incorporating structural and chemical promoters [4,6,11,24,26,44,54,57,76,77]. To date, the chemical promoters used for iron ore catalysts are copper and potassium, while the structural promoters are silica, alumina, and carbon [2,4,9,11,26,44,56,58]. There is still the chance of exploring more promoter additions for iron ore LTFT catalysts to provide more insights into their best catalyst configuration and optimal catalytic performance.

Copper promotion is used to facilitate the reduction of the precursor into the active phase, which, in turn, will also improve the overall catalytic performance [1,4,6,22,24,56,59]. On the other hand, potassium addition is believed to enhance the carburization of iron catalysts by increasing their basicity, which is also crucial for the catalyst's optimal catalytic performance [4,11,24,44,56,59,60,62]. The structural promoters effectively stabilize the active phase from sintering, and re-oxidation and spacing of the active sites of the catalysts [1,4,12,26,34,35,54,57,76,77]. They also provide mechanical stability to the catalysts throughout the reaction, which is important for upscaled fixed-bed LTFT applications [1,9,35,58].

## Activity and Stability of Modified Iron Ore

Most of the FT iron ore applications reported in the literature have been explored using iron ores with chemical and structural promoters [1,5,6]. The results of these reports are discussed in this section.

Hong et al. [5] modified natural iron ore by wet milling the precursor to open its pores and make it suitable for doping promoters. After that, copper and potassium were added to match the chemical composition of traditional precipitated iron catalysts. Natural iron ore naturally contains significant amounts of silica and alumina as impurities [1,2,5–7]. Consequently, structural promoters were not required, making them inexpensive. This promoted iron ore showed some improvements in the textural properties compared to its precursor [5]. The promoted iron's surface area and pore volumes increased to  $108 \text{ m}^2/\text{g}$ and 0.358 m<sup>3</sup>/g, respectively, which was significant from the 25.3 m<sup>2</sup>/g and 0.0701 m<sup>3</sup>/g of its precursor. High thermal stability of the crystallites before and after heat treatments was also observed and confirmed via  $N_2$  physisorption analyses [5]. There was a general improvement in the physio-chemical properties of the precursor in this case, which favored its overall FT catalytic performance, as shown in Table 3. It was shown in Table 3 that a notable increase in CO conversion from 36.4% to 89.9% was observed after milling and promoting the natural iron ore. The improvements were attributed to superior textural properties and the promotion of the precursor [6]. Despite this significant increment in CO conversion, the TOS was not enough to ascertain this catalyst's stability. Stability studies of this novel FT catalyst are crucial to validate it as a possible substitute for traditional iron catalysts. This highlights the lack of sufficient studies in the public domain that have investigated the chemical stability of iron ore under typical LTFT reaction conditions to delineate its deactivation pathway. Additionally, stability curves would make room for improvements in their catalyst design and overall life span [29,35]. Moreover, the CO conversion reported by Hong et al. [5] is not bolstered by temperature-programmed studies to evaluate this catalyst's reducibility throughout its synthesis. It would have been beneficial to track the reducibility just after milling and after promotion to see how these steps influence the iron ore's reducibility. Other in situ studies, such as X-ray absorption fine structure and wide-angle X-ray scattering, can bolster the TPR studies [4,30,34,40,52,60,78,79] and better understand the reducibility of this catalyst and how the various promoters influence it. These findings will help optimize the catalyst design to understand the synergistic effect of copper and potassium on the overall catalytic performance of this modified iron ore. A much more systematic approach is needed to validate this. Perhaps an in-depth study of how each step in the catalyst preparation affects the activity and stability will shed some light on this matter. After that, further analysis can be used to study how each chemical promoter affects the catalytic performance of this catalyst system, starting with doping iron ore with copper only, and evaluating its FT performance. In another experiment, iron ore doped only with potassium evaluated its FT performance to compare it with iron ore doped with copper. The final study would then combine the best optimized from each study to compare the synergistic effects of both promoters on their catalytic performance. As a result, an optimal amount of loading for copper and potassium will be achieved and contribute significantly to the current work conducted on iron ore as FT catalysts.

In general, the characterization studies reported by Hong et al. [5] were insufficient to support its FT catalytic performance. Thus, further investigation is needed to validate these findings. In addition, more in situ surface interaction studies need to be explored to elucidate the phase changes during the reactions to identify opportunities for improvements. One way of improving the stability research on this catalyst is via in situ XRD and other advanced temperature-programmed surface reaction studies [26,34,52,60,78]. This would reveal the phase changes on the catalyst's surface during the reaction to help model a much more stable catalyst and improve the current progress. Furthermore, extending the rate versus time during LTFT will also enlighten the stability of promoted iron ore and facilitate the comparison to conventional iron catalysts in the literature.

Bae et al. [6] adopted a similar catalyst preparation to Hong et al. [5] but improved the study by preparing a precipitated iron catalyst and comparing its catalytic performance. The comparative research with a commercial iron catalyst was a promising step toward justifying iron ore as a viable alternative for the FT community. This study obtained a similar CO conversion range of 75–90% to Hong et al. [5], and, unlike its predecessor, supported the FT activity with hydrogen temperature reduction characterization. As shown in Table 3, its hydrocarbon selectivities compared with conventional iron catalysts were promising. However, they were not performed at iso-conversions, thus rendering the findings incomparable with the product selectivities reported by other researchers who performed similar work. Moreover, just like its predecessor, the reaction time was not long enough to determine catalyst stability. To overcome these shortcomings, as mentioned earlier, extending the reaction time will solve this. Moreover, the deactivation behavior of this catalyst system will also be established and provide valuable data for the FT community [18,24,29,34,35,79,80]. Moreover, the comparison of catalytic performance undertaken by Bae et al. [6] versus the literature was not based on reaction rates as other studies have done [9,19,28,30,34,36,42,50,52,81]. So, future studies should investigate their reaction rates to obtain a more comprehensive catalytic performance versus traditional iron catalysts. In situ studies, such as XRD magnetization measurements, Mossbauer spectroscopy, XANES, and temperature-programmed surface reactions, would bolster the study [22,26,52,60,78,79,82]. Furthermore, the operando characterizations would also reveal the phase changes during reaction conditions and help link them to the catalyst properties [22,23,26,52,60,78,82-84].

Mubenesha et al. [1] expanded the work conducted by Bae et al. [6] by considering the mechanical strength of an iron ore catalyst during fixed-bed operations. A similar catalyst preparation method was used, but the natural iron ore emanated from the tailings of steelmakers based in South Africa. As a result, the physio-chemical properties of the iron ores used in this work differed significantly. The application of this catalyst system was optimized to be suited for pilot fixed-bed scenarios and was pelletized using a bentonite binder (silica-based inorganic binder). Despite having inferior physio-chemical properties to that of its predecessors, the overall catalytic performance of this catalyst was comparable to other iron ores reported by other researchers. The study presented an iron ore catalyst that evaluated its mechanical stability under LTFT fixed operations and compared it to a commercial catalyst to validate its suitability [1,9]. The solid iron ore catalyst was found to be at least three times stronger than the recommended mechanical strength [1]. This result was further quantified by an in-depth statistical analysis that bolstered the findings. An evaluation of the physical stability (mechanical strength) under process conditions is helpful for FT practitioners that need to upscale their laboratory catalyst formulations. Additionally, the physical stability profile of a new catalyst is essential to eliminate operation issues at both pilot and commercial implementation stages [1,9,35]. The work presented valuable data useful for iron ore FT applications to model their catalysts. Nevertheless, the reliable chemical stability of this catalyst system could not be established due to short reaction times, thus necessitating studies that can tackle this issue.

Mubenesha et al. [1] recorded a CO conversation of 72.1%, which was still in the same 70–85% range as other iron ore catalysts, as shown in Table 3. However, it is challenging to compare the catalytic performance reported by Mubenesha et al. [1] with their counterparts because the studies were not performed under similar operating conditions. The lack of reliable stability curves and comparative studies that can improve existing iron FT catalyst development and designs is highlighted and calls for efforts to address them to justify its application as a viable LTFT iron catalyst alternative.

Conversely, Mubenesha et al. [1] reported a mean CO reaction rate of  $5.68 \times 10^{-4}$  mol/min, unlike most of its predecessors. However, a definite comparison with others could not be established due to varying operating conditions. Keyvanloo et al. [34] compared the rates of various iron catalysts at similar operating conditions, conversions, and selectivities. So, a similar approach would improve the current research on iron ore FT catalysts.

The utilization of structural promoter iron catalysts among the FT community has been credited to improve overall catalytic performance [9,19,28,34,54,79,85]. Moreover, encapsulated catalysts that have the active metal surrounded by carbonaceous material are reported to chemically stabilize various active carbide phases formed during FT reaction and physically prevent their mechanical failures [11,12,18,57,79,86]. Iron catalysts encapsulated with carbon as a structural promoter also have an advantage over their counterparts by weakening metal–support interactions, which can improve the carburization of the iron oxide and lead to better catalytic performance [12,79,86].

To date, only one publication on encapsulated iron ore catalysts has been reported [17], emphasizing that their application as a viable iron-LTFT iron alternative is still in its infancy. The author studied an encapsulated iron ore catalyst with oxalic acid without the need for additional promoters such as copper or potassium to obtain a working FT catalyst. Moreover, the proposed catalyst synthesis provided a shorter route to attain the carbide phase using iron ore as a precursor with promising results [17]. Unlike previous authors [1,5,6], Perez et al. [17] provided a more detailed characterization study that correlates the catalytic performance to the catalyst properties. Another added advantage that this study has over its counterparts is that it did not need any activation before being catalyzed under LTFT reaction conditions. The temperature programmed reduction results reported were also much more insightful than their predecessors in that they provided CO-TPR instead of H<sub>2</sub>-TPR. The author also provided the thermal stability of their iron ore catalyst, which is vital for ensuring that it is resistant to sintering during reaction conditions [17,30,54]. In addition, Perez et al. [17] also provided a detailed characterization of the morphology changes of their catalyst to bolster their promising results. The overall characterization provided by Perez et al. is comprehensive and links the catalyst properties to the FT catalytic performance quite well [17]. Moreover, the reported average CO conversion of 66.8% by Perez et al. [17] is still comparable to other similar research (see Table 3). The study provided a characterization of the spent catalyst that revealed its stability after the reaction was over. These findings are crucial to ascertain the stability of the active phase [2,19,35,87]. Moreover, the  $CO_2$ ,  $CH_4$ , and  $CH_{5+}$  hydrocarbon selectivities reported by Perez et al. [17] were also comparable to the ones reported by similar research [1,5,6]. However, it is difficult to deduce conclusive comparisons because they were not performed at similar reaction conditions [2,54,55]. The reaction time of 100 h reported by Perez et al. [17] was also short to

ascertain their durability as with its predecessors. Lin et al. suggested that reporting the deactivation rate of the catalyst after at least 1000 h is sufficient to determine its chemical stability under realistic reaction conditions [30]. The overall catalytic performance of the iron ore reported by Perez et al. [17] is comparable to a precipitated iron catalyst, but a conclusive quantitative comparison could not be established due to variance in operating conditions. The current iron ore FT loopholes are apparent and need to be tackled to guide the rational design of optimized catalysts.

### 4. Outlook and Conclusions

Iron ore is a promising alternative to traditional precipitated iron FT catalysts. Due to the urgent need to reduce the catalyst synthesis cost associated with conventional iron catalysts, it has recently gained attention. The attempts to link its physicochemical properties and varying operating conditions to its catalytic performance in terms of activity and selectivity are also encouraging. A few researchers have reported raw iron as a viable option under typical LTFT reactions, and only a few so far have shown opportune results.

The current review has revealed that most iron ores need to be doped with promoters to match their catalytic performance with that of the precipitated iron catalysts and compensate for their deficient properties. These studies have incorporated chemical and structural promoters to fine-tune their electronic and geometric properties under various synthesis conditions to improve catalytic performance. However, there is still room to explore various other promoters under varying synthesis conditions to optimize their electronic and geometric properties and, in turn, their catalyst design. In addition, a few researchers have investigated catalytic performance in terms of the activity and selectivity of iron ore. However, this catalyst system's chemical stability is not well represented and needs to be addressed to provide a holistic rationale for designing better iron ore LTFT catalysts.

The stability studies of iron ore LTFT catalysts reported so far have been performed with reaction times of less than 1000 h. This 1000 h was suggested as the minimum reaction time to determine the durability of the iron catalyst under realistic industrial conditions. Thus, insufficient data are available to study the deactivation behavior of iron ore catalysts. Consequently, studies that provide a much more detailed understanding of structure interactions, diffusion, and stability will be beneficial in modeling much more efficient iron ore catalysts. The current characterization studies on these iron-based catalysts do not have the depth to reveal their structure–activity correlations. Therefore, coupling advanced spectroscopic and computational methods with extended reaction times of iron ore will help deepen the understanding of their surface chemistry.

Finally, most of the comparisons undertaken by authors with respect to the product selectivities of the raw iron ore, doped iron ore, and precipitated iron catalysts were not carried out at an iso-conversion level (i.e., same conversion level). Product selectivity is dependent on the conversion level. This means that for the comparison of the product selectivities of the catalysts to be valid, the product selectivities of the catalysts have to be compared at iso-conversion levels so that the active sites of the catalysts are exposed to similar partial pressures of the reactants and products.

Funding: This research received no external funding.

Data Availability Statement: The study did not report any data.

Acknowledgments: The authors would like to thank Virginia Commonwealth University (VCU) and the University of South Africa (UNISA) for their support.

Conflicts of Interest: The authors declare no conflict of interest.

## References

- 1. Mubenesha, S.; Okoye-Chine, C.G.; Ramutsindela, F.K.; Gorimbo, J.; Moyo, M.; Liu, X. The Potential Use of Raw Iron Ore in Fischer-Tropsch Synthesis. *Int. J. Pet. Technol.* **2021**, *8*, 99–115. [CrossRef]
- Ramutsindela, F.K.; Okoye-Chine, C.G.; Mbuya, C.O.L.; Mubenesha, S.; Gorimbo, J.; Okonye, L.U.; Liu, X.; Hildebrandt, D. The effect of reducing gases on raw iron ore catalyst for Fischer-Tropsch synthesis. J. Taiwan Inst. Chem. Eng. 2022, 131, 104163. [CrossRef]
- 3. Mubenesha, S. A Design and Development of Iron Ore Fischer Tropsch Catalyst. Master's Thesis, University of South Africa, Pretoria, South Africa, 2021.
- 4. Chun, D.H.; Rhim, G.B.; Youn, M.H.; Deviana, D.; Lee, J.E.; Park, J.C.; Jeong, H. Brief Review of Precipitated Iron-Based Catalysts for Low-Temperature Fischer–Tropsch Synthesis. *Top. Catal.* **2020**, *63*, 793–809. [CrossRef]
- Hong, S.Y.; Park, J.C.; Lee, H.T.; Yang, J., II.; Hong, S.J.; Jung, H.; Chun, D.H. Nanocrystalline Iron-Ore-Based Catalysts for Fischer-Tropsch Synthesis. J. Nanosci. Nanotechnol. 2016, 16, 2014–2018. [CrossRef] [PubMed]
- 6. Bae, J.S.; Hong, S.Y.; Park, J.C.; Rhim, G.B.; Youn, M.H.; Jeong, H.; Kang, S.W.; Yang, J., II.; Jung, H.; Chun, D.H. Eco-friendly prepared iron-ore-based catalysts for Fischer-Tropsch synthesis. *Appl. Catal. B Environ.* **2019**, 244, 576–582. [CrossRef]
- Kulikova, M.V.; Chudakova, M.V.; Kulikov, A.B.; Krylova, A.Y. Fischer–Tropsch Synthesis in the Presence of Catalysts Based on Unmodified Iron Ores. *Russ. J. Appl. Chem.* 2021, 94, 104–109. [CrossRef]
- 8. Gruber, H.; Groß, P.; Rauch, R.; Reichhold, A.; Zweiler, R.; Aichernig, C.; Müller, S.; Ataimisch, N.; Hofbauer, H. Fischer-Tropsch products from biomass-derived syngas and renewable hydrogen. *Biomass Convers. Biorefinery* **2021**, *11*, 2281–2292. [CrossRef]
- 9. Badoga, S.; Vosoughi, V.; Dalai, A.K. Performance of Promoted Iron/CNT Catalyst for Fischer-Tropsch Synthesis: Influence of Pellet Shapes and Binder Loading. *Energy Fuels* **2017**, *31*, 12633–12644. [CrossRef]
- 10. Mahmoudi, H.; Mahmoudi, M.; Doustdar, O.; Jahangiri, H.; Tsolakis, A.; Gu, S.; LechWyszynski, M. A review of Fischer Tropsch synthesis process, mechanism, surface chemistry and catalyst formulation. *Biofuels Eng.* **2017**, *2*, 11–31. [CrossRef]
- 11. Zhang, Q.; Deng, W.; Wang, Y. Recent advances in understanding the key catalyst factors for Fischer-Tropsch synthesis. *J. Energy Chem.* **2013**, *22*, 27–38. [CrossRef]
- 12. Chen, Y.; Wei, J.; Duyar, M.S.; Ordomsky, V.V.; Khodakov, A.Y.; Liu, J. Carbon-based catalysts for Fischer-Tropsch synthesis. *Chem. Soc. Rev.* 2021, *50*, 2337–2366. [CrossRef] [PubMed]
- 13. Okeke, I.J.; Mani, S. Techno-economic assessment of biogas to liquid fuels conversion technology via Fischer-Tropsch synthesis. *Biofuels Bioprod. Biorefining* **2017**, *11*, 472–487. [CrossRef]
- 14. Aliyu, A.K.; Modu, B.; Tan, C.W. A review of renewable energy development in Africa: A focus in South Africa, Egypt and Nigeria. *Renew. Sustain. Energy Rev.* 2018, *81*, 2502–2518. [CrossRef]
- Luque, R.; De La Osa, A.R.; Campelo, J.M.; Romero, A.A.; Valverde, J.L.; Sanchez, P. Design and development of catalysts for Biomass-To-Liquid-Fischer-Tropsch (BTL-FT) processes for biofuels production. *Energy Environ. Sci.* 2012, *5*, 5186–5202. [CrossRef]
- 16. Jahangiri, H.; Bennett, J.; Mahjoubi, P.; Wilson, K.; Gu, S. A review of advanced catalyst development for Fischer-Tropsch synthesis of hydrocarbons from biomass derived syn-gas. *Catal. Sci. Technol.* **2014**, *4*, 2210–2229. [CrossRef]
- Pérez, S.; Mondragón, F.; Moreno, A. Iron ore as precursor for preparation of highly active χ-Fe<sub>5</sub>C<sub>2</sub> core-shell catalyst for Fischer-Tropsch synthesis. *Appl. Catal. A Gen.* 2019, 587, 117264. [CrossRef]
- Yahyazadeh, A.; Dalai, A.K.; Ma, W.; Zhang, L. Fischer–Tropsch Synthesis for Light Olefins from Syngas: A Review of Catalyst Development. *Reactions* 2021, 2, 227–257. [CrossRef]
- 19. Teimouri, Z.; Abatzoglou, N.; Dalai, A.K. Kinetics and selectivity study of Fischer-Tropsch synthesis to C5+ hydrocarbons: A review. *Catalysts* **2021**, *11*, 330. [CrossRef]
- 20. De Klerk, A. Environmentally friendly refining: Fischer-Tropsch versus crude oil. Green Chem. 2007, 9, 560–565. [CrossRef]
- 21. Hensen, E.J.M.; Wang, P.; Xu, W. Research Trends in Fischer–Tropsch Catalysis for Coal to Liquids Technology. *Front. Eng. Manag.* **2016**, *3*, 321–330. [CrossRef]
- 22. Rytter, E.; Holmen, A. Deactivation and regeneration of commercial type fischer-tropsch co-catalysts—A mini-review. *Catalysts* **2015**, *5*, 478–499. [CrossRef]
- 23. Ojelade, O.A.; Zaman, S.F. A review on CO<sub>2</sub> hydrogenation to lower olefins: Understanding the structure-property relationships in heterogeneous catalytic systems. *J. CO<sub>2</sub> Util.* **2021**, *47*, 101506. [CrossRef]
- 24. Ferdous, D.; Dimirel, B. Deactivation of iron based Fischer-Tropsch catalyst: A critical problem. In Proceedings of the AIChE Spring Meeting and Global Congress on Process Safety, San Antonio, TX, USA, 25 March 2010.
- 25. Ghofran Pakdel, M.; Atashi, H.; Zohdi-Fasaei, H.; Mirzaei, A.A. Effect of temperature on deactivation models of alumina supported iron catalyst during Fischer-Tropsch synthesis. *Pet. Sci. Technol.* **2019**, *37*, 500–505. [CrossRef]
- Xu, K.; Sun, B.; Lin, J.; Wen, W.; Pei, Y.; Yan, S.; Qiao, M.; Zhang, X.; Zong, B. ε -Iron carbide as a low-temperature Fischer-Tropsch synthesis catalyst. *Nat. Commun.* 2014, 5, 5783. [CrossRef]
- 27. Dautzenberg, F.M. *Characterization and Catalyst Development*; ACS Symposium Series; American Chemical Society: Washington, DC, USA, 1989; Volume 411, pp. 99–119. [CrossRef]
- Javed, M.; Zhang, G.; Gao, W.; Cao, Y.; Dai, P.; Ji, X.; Lu, C.; Yang, R.; Xing, C.; Sun, J. From hydrophilic to hydrophobic: A promising approach to tackle high CO<sub>2</sub> selectivity of Fe-based Fischer-Tropsch microcapsule catalysts. *Catal. Today* 2019, 39–45. [CrossRef]

- 29. Gorimbo, J. Use of stability diagrams to predict catalyst speciation during Fischer Tropsch reduction stage: A mini-review. *Catal. Sci. Technol.* **2018**, *8*, 2022–2029. [CrossRef]
- Lin, Q.; Cheng, M.; Zhang, K.; Li, W.; Wu, P.; Chang, H.; Lv, Y.; Men, Z. Development of an iron-based Fischer–Tropsch catalyst with high attrition resistance and stability for industrial application. *Catalysts* 2021, 11, 908. [CrossRef]
- Yang, J.; Sun, Y.; Tang, Y.; Liu, Y.; Wang, H.; Tian, L.; Wang, H.; Zhang, Z.; Xiang, H.; Li, Y. Effect of magnesium promoter on iron-based catalyst for Fischer-Tropsch synthesis. J. Mol. Catal. A Chem. 2006, 245, 26–36. [CrossRef]
- 32. Gorimbo, J.; Lu, X.; Liu, X.; Yao, Y.; Hildebrandt, D.; Glasser, D. Low-Pressure Fischer-Tropsch Synthesis: In Situ Oxidative Regeneration of Iron Catalysts. *Ind. Eng. Chem. Res.* 2017, *56*, 4267–4274. [CrossRef]
- 33. Steynberg, A.; Dry, M. Fischer-Tropsch Technology; Elsevier: Amsterdam, The Netherlands, 2004.
- 34. Keyvanloo, K.; Hecker, W.C.; Woodfield, B.F.; Bartholomew, C.H. Highly active and stable supported iron Fischer-Tropsch catalysts: Effects of support properties and SiO<sub>2</sub> stabilizer on catalyst performance. *J. Catal.* **2014**, *319*, 220–231. [CrossRef]
- 35. Argyle, M.D.; Bartholomew, C.H. Heterogeneous catalyst deactivation and regeneration: A review. *Catalysts* **2015**, *5*, 145–269. [CrossRef]
- Storsæter, S.; Borg, Ø.; Blekkan, E.A.; Holmen, A. Study of the effect of water on Fischer-Tropsch synthesis over supported cobalt catalysts. J. Catal. 2005, 231, 405–419. [CrossRef]
- 37. Desai, M.B. Appendix 1 Equipment cost Estimates. Chem. Eng. 1981, 88, 65–70.
- Saeidi, S.; Nikoo, M.K.; Mirvakili, A.; Bahrani, S.; Saidina Amin, N.A.; Rahimpour, M.R. Recent advances in reactors for low-temperature Fischer-Tropsch synthesis: Process intensification perspective. *Rev. Chem. Eng.* 2015, 31, 209–238. [CrossRef]
- 39. Dry, M.E. The Fischer-Tropsch process: 1950–2000. Catal. Today 2002, 71, 227–241. [CrossRef]
- 40. Pendyala, V.R.R.; Jacobs, G.; Mohandas, J.C.; Luo, M.; Hamdeh, H.H.; Ji, Y.; Ribeiro, M.C.; Davis, B.H. Fischer-Tropsch synthesis: Effect of water over iron-based catalysts. *Catal. Lett.* **2010**, *140*, 98–105. [CrossRef]
- Pondini, M.; Ebert, M. Process Synthesis and Design of Low Temperature Fischer-Tropsch Crude Production from Biomass Derived Syngas. Master's Thesis, Chalmers University of Technology, Göteborg, Sweden, 2013.
- 42. Spadaro, L.; Arena, F.; Bonura, G.; Di Blasi, O.; Frusteri, F. Activity and stability of iron based catalysts in advanced fischer-tropsch technology via CO<sub>2</sub>-rich syngas conversion. *Stud. Surf. Sci. Catal.* **2007**, *167*, 49–54. [CrossRef]
- Zhang, Y.; Sirimanothan, N.; O'brien, R.J.; Hamdeh, H.H.; Davis, B.H. Study of Deactivation of Iron-Based Fischer-Tropsch Synthesis Catalysts. *Stud. Surf. Sci. Catal.* 2001, 139, 125–132. [CrossRef]
- 44. Méndez, C.I.; Ancheyta, J. Kinetic models for Fischer-Tropsch synthesis for the production of clean fuels. *Catal. Today* **2020**, *353*, 3–16. [CrossRef]
- 45. Tao, Z.; Yang, Y.; Zhang, C.; Li, T.; Wang, J.; Wan, H.; Xiang, H.; Li, Y. Effect of calcium promoter on a precipitated iron-manganese catalyst for Fischer-Tropsch synthesis. *Catal. Commun.* **2006**, *7*, 1061–1066. [CrossRef]
- Li, J.; Zhang, C.; Cheng, X.; Qing, M.; Xu, J.; Wu, B.; Yang, Y.; Li, Y. Effects of alkaline-earth metals on the structure, adsorption and catalytic behavior of iron-based Fischer-Tropsch synthesis catalysts. *Appl. Catal. A Gen.* 2013, 464–465, 10–19. [CrossRef]
- Gallegos, N.G.; Alvarez, A.M.; Cagnoli, M.V.; Bengoa, J.F.; Marchetti, S.G.; Mercader, R.C.; Yeramian, A.A. Selectivity to olefins of Fe/SiO<sub>2</sub>-MgO catalysts in the Fischer-Tropsch reaction. *J. Catal.* 1996, *161*, 132–142. [CrossRef]
- 48. O'Brien, R.J.; Xu, L.; Spicer, R.L.; Davis, B.H. Activation study of precipitated iron Fischer-Tropsch catalysts. *Energy Fuels* **1996**, *10*, 921–926. [CrossRef]
- 49. Gorimbo, J.; Lu, X.; Liu, X.; Hildebrandt, D.; Glasser, D. A long term study of the gas phase of low pressure Fischer-Tropsch products when reducing an iron catalyst with three different reducing gases. *Appl. Catal. A Gen.* **2017**, *534*, 1–11. [CrossRef]
- Luo, M.; Hamdeh, H.; Davis, B.H. Fischer-Tropsch Synthesis. Catalyst activation of low alpha iron catalyst. *Catal. Today* 2009, 140, 127–134. [CrossRef]
- 51. Ma, W.; Shafer, W.D.; Jacobs, G.; Yang, J.; Sparks, D.E.; Hamdeh, H.H.; Davis, B.H. Fischer-Tropsch synthesis: Effect of CO conversion on CH<sub>4</sub> and oxygenate selectivities over precipitated Fe-K catalysts. *Appl. Catal. A Gen.* **2018**, *560*, 144–152. [CrossRef]
- Al-Dossary, M.; Fierro, J.L.G.; Spivey, J.J. Cu-promoted Fe<sub>2</sub>O<sub>3</sub>/MgO-based Fischer-Tropsch catalysts of biomass-derived syngas. *Ind. Eng. Chem. Res.* 2015, 54, 911–921. [CrossRef]
- Zamani, Y.; Zamaniyan, A.; Bahadoran, F.; Shojaei, M. Effect of calcium promoters on nanostructured iron catalyst for Fischer-Tropsch synthesis. J. Petrol. Sci. Technol. 2015, 5, 21–27.
- Okoye-Chine, C.G.; Moyo, M.; Hildebrandt, D. Fischer–Tropsch synthesis: The effect of hydrophobicity on silica-supported iron catalysts. J. Ind. Eng. Chem. 2021, 97, 426–433. [CrossRef]
- Okoye-Chine, C.G.; Moyo, M.; Liu, X.; Hildebrandt, D. A critical review of the impact of water on cobalt-based catalysts in Fischer-Tropsch synthesis. *Fuel Process. Technol.* 2019, 192, 105–129. [CrossRef]
- Hole, N.A. Effects of Potassium and Copper Promoters on Iron Fischer-Tropsch Catalysts. Master's Thesis, NTNU: Norwegian University of Science and Technology, Trondheim, Norway, 2015.
- 57. Horáček, J. Fischer–Tropsch synthesis, the effect of promoters, catalyst support, and reaction conditions selection. *Mon. Chem.* **2020**, *151*, 649–675. [CrossRef]
- 58. Chun, D.H.; Park, J.C.; Hong, S.Y.; Lim, J.T.; Kim, C.S.; Lee, H.T.; Yang, J.I.; Hong, S.; Jung, H.J. Highly selective iron-based Fischer–Tropsch catalysts activated by CO<sub>2</sub>-containing syngas. *J. Catal.* **2014**, *317*, 135–143. [CrossRef]

- Chernavskii, P.A.; Kazak, V.O.; Pankina, G.V.; Perfiliev, Y.D.; Li, T.; Virginie, M.; Khodakov, A.Y. Influence of copper and potassium on the structure and carbidisation of supported iron catalysts for Fischer–Tropsch synthesis. *Catal. Sci. Technol.* 2017, 7, 2325–2334. [CrossRef]
- 60. Ribeiro, M.Z.L.L.; Souza, J.C.; Gnanamani, M.K.; Martinelli, M.; Upton, G.F.; Jacobs, G.; Ribeiro, M.C. Fischer–Tropsch Synthesis: Effect of the Promoter's Ionic Charge and Valence Level Energy on Activity. *Reactions* **2021**, *2*, 408–426. [CrossRef]
- Peña, D.; Jensen, L.; Cognigni, A.; Myrstad, R.; Neumayer, T.; van Beek, W.; Rønning, M. The Effect of Copper Loading on Iron Carbide Formation and Surface Species in Iron-Based Fischer–Tropsch Synthesis Catalysts. *ChemCatChem* 2018, 10, 1300–1312. [CrossRef]
- 62. Luo, M.; Davis, B.H. Fischer–Tropsch synthesis: Activation of low-alpha potassium promoted iron catalysts. *Fuel Process. Technol.* **2003**, *83*, 49–65. [CrossRef]
- 63. Bukur, D.B.; Mukesh, D.; Patel, S.A. Promoter effects on precipitated iron catalysts for Fischer-Tropsch synthesis. *Ind. Eng. Chem. Res.* **1990**, *29*, 194–204. [CrossRef]
- 64. Bukur, D.B.; Lang, X.; Mukesh, D.; Zimmerman, W.H.; Rosynek, M.P.; Lii, C. Binder/Support Effects on the Activity and Selectivity of Iron Catalysts in the Fischer-Tropsch Synthesis. *Ind. Eng. Chem. Res.* **1990**, *29*, 1588–1599. [CrossRef]
- 65. Hou, W.; Wu, B.; An, X.; Li, T.; Tao, Z.; Zheng, H.; Xiang, H.; Li, Y. Effect of the ratio of precipitated SiO<sub>2</sub> to binder SiO<sub>2</sub> on iron-based catalysts for fischer-tropsch synthesis. *Catal. Lett.* **2007**, *119*, 353–360. [CrossRef]
- Ma, W.; Kugler, E.L.; Dadyburjor, D.B. Promotional effect of copper on activity and selectivity to hydrocarbons and oxygenates for Fischer-Tropsch synthesis over potassium-promoted iron catalysts supported on activated carbon. *Energy Fuels* 2011, 25, 1931–1938. [CrossRef]
- 67. Bukur, D.B.; Todic, B.; Elbashir, N. Role of water-gas-shift reaction in Fischer–Tropsch synthesis on iron catalysts: A review. *Catal. Today* **2016**, *275*, 66–75. [CrossRef]
- Jacobs, G.; Pendyala, V.R.R.; Martinelli, M.; Shafer, W.D.; Gnanamani, M.K.; Khalid, S.; MacLennan, A.; Hu, Y.; Davis, B.H. Fischer–Tropsch Synthesis: XANES Spectra of Potassium in Promoted Precipitated Iron Catalysts as a Function of Time On-stream. *Catal. Lett.* 2017, 147, 1861–1870. [CrossRef]
- 69. Li, S.; Li, A.; Krishnamoorthy, S.; Iglesia, E. Effects of Zn, Cu, and K promoters on the structure and on the reduction, carburization, and catalytic behavior of iron-based Fischer-Tropsch synthesis catalysts. *Catal. Lett.* **2001**, 77, 197–205. [CrossRef]
- O'Brien, R.J.; Davis, B.H. Impact of copper on an alkali promoted iron Fischer-Tropsch catalyst. Catal. Lett. 2004, 94, 1–6. [CrossRef]
- Wan, H.; Wu, B.; Zhang, C.; Xiang, H.; Li, Y. Promotional effects of Cu and K on precipitated iron-based catalysts for Fischer-Tropsch synthesis. J. Mol. Catal. A Chem. 2008, 283, 33–42. [CrossRef]
- 72. Zakeri, M.; Samimi, A.; Shafiee Afarani, M.; Salehirad, A. Effects of porosity and pore size distribution on mechanical strength reliability of industrial-scale catalyst during preparation and catalytic test steps. *Part. Sci. Technol.* **2018**, *36*, 96–103. [CrossRef]
- 73. David, E. Mechanical strength and reliability of the porous materials used as adsorbents/catalysts and the new development trends. *Arch. Mater. Sci. Eng.* **2015**, *73*, 5–17.
- 74. De Klerk, A. Fischer Tropsch Refining; Wiley-VCH: Weinheim, Germany, 2011; ISBN 9783527307401.
- Schanke, D.; Hilmen, A.M.; Bergene, E.; Kinnari, K.; Rytter, E.; Ådnanes, E.; Holmen, A. Study of the deactivation mechanism of Al<sub>2</sub>O<sub>3</sub>-supported cobalt Fischer-Tropsch catalysts. *Catal. Lett.* 1995, 34, 269–284. [CrossRef]
- 76. Keyvanloo, K.; Huang, B.; Okeson, T.; Hamdeh, H.H.; Hecker, W.C. Effect of support pretreatment temperature on the performance of an iron Fischer-Tropsch catalyst supported on silica-stabilized alumina. *Catalysts* **2018**, *8*, 77. [CrossRef]
- 77. Gholami, Z.; Asmawati Mohd ZabiDi, N.; Gholami, F.; Ayodele, O.B.; Vakili, M. The influence of catalyst factors for sustainable production of hydrocarbons via Fischer-Tropsch synthesis. *Rev. Chem. Eng.* **2017**, *33*, 337–358. [CrossRef]
- Rochet, A.; Moizan, V.; Pichon, C.; Diehl, F.; Berliet, A.; Briois, V. In situ and operando structural characterisation of a Fischer-Tropsch supported cobalt catalyst. *Catal. Today* 2011, 171, 186–191. [CrossRef]
- 79. Yu, X.; Zhang, J.; Wang, X.; Ma, Q.; Gao, X.; Xia, H.; Lai, X.; Fan, S.; Zhao, T.S. Fischer-Tropsch synthesis over methyl modified Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> catalysts with low CO<sub>2</sub> selectivity. *Appl. Catal. B Environ.* **2018**, *232*, 420–428. [CrossRef]
- Pham, T.H.; Qi, Y.; Yang, J.; Duan, X.; Qian, G.; Zhou, X.; Chen, D.; Yuan, W. Insights into Hägg Iron-Carbide-Catalyzed Fischer-Tropsch Synthesis: Suppression of CH4 Formation and Enhancement of C-C Coupling on χ-Fe<sub>5</sub>C<sub>2</sub> (510). ACS Catal. 2015, 5, 2203–2208. [CrossRef]
- 81. Yan, B.; Ma, L.; Gao, X.; Zhang, J.; Ma, Q.; Zhao, T.S. Amphiphobic Surface Fabrication of Iron Catalyst and Effect on Product Distribution of Fischer–Tropsch Synthesis. *Appl. Catal. A Gen.* **2019**, *585*. [CrossRef]
- Lu, F.; Chen, X.; Lei, Z.; Wen, L.; Zhang, Y. Revealing the activity of different iron carbides for Fischer-Tropsch synthesis. *Appl. Catal. B Environ.* 2021, 281, 119521. [CrossRef]
- Cubeiro, M.L.; Goldwasser, M.R.; Zurita, M.J.P.; Franco, C.; González-Jiménez, F.; Jaimes, E. Mössbauer study of the evolution of a laterite iron mineral based catalyst: Effect of the activation treatment. *Hyperfine Interact.* 1994, 93, 1831–1835. [CrossRef]
- 84. Shroff, M.D.; Datye, A.K. The importance of passivation in the study of iron Fischer-Tropsch catalysts. *Catal. Lett.* **1996**, *37*, 101–106. [CrossRef]
- 85. Lyu, S.; Wang, L.; Li, Z.; Yin, S.; Chen, J.; Zhang, Y.; Li, J.; Wang, Y. Stabilization of ε-iron carbide as high-temperature catalyst under realistic Fischer–Tropsch synthesis conditions. *Nat. Commun.* **2020**, *11*, 1–8. [CrossRef]

- 86. Wang, Y.; Huang, S.; Teng, X.; Wang, H.; Wang, J.; Zhao, Q.; Wang, Y.; Ma, X. Controllable Fe/HCS catalysts in the Fischer-Tropsch synthesis: Effects of crystallization time. *Front. Chem. Sci. Eng.* **2020**, *14*, 802–812. [CrossRef]
- Cimenler, U.; Kuhn, J.N. Heterogeneous Catalysts Encapsulated in Inorganic Systems to Enhance Reaction Performances for XTL Processes. In *Encapsulated Catalysts*; Elsevier: Amsterdam, The Netherlands, 2017; pp. 505–524. ISBN 9780128039052.