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Debunking the impact of crystallite/particle size in cobalt-based Fischer-Tropsch synthesis

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ABSTRACT

This review examines the relationship between the crystallite size of cobalt and the distribution of products produced by Fischer-Tropsch synthesis (FTS). The ideal range for the average cobalt crystallite diameter is between 6 and 8 nm. Deviating from this range, whether by increasing or decreasing the crystallite size, influences the carbon monoxide (CO) turnover frequency and the selectivity of CH₄, C₂-C₄, and C₅₊. To ensure the development of a consistent catalyst, careful monitoring and adjustment of the morphology, particle size, and metal loading on the support particles are essential. For experimental repeatability during FTS applications, it would be ideal if catalyst particles had crystallites of a uniform size. Methods for crystallite characterization and catalyst synthesis were also addressed in detail. The diameter of the cobalt crystallite appears to be a crucial parameter that influences cobalt oxidation, the thermodynamics of cobalt reduction and oxidation are reported. Conducting a Design of Experiment (DOE) with Design Experts on available literature led to determining optimal conditions for enhancing the primary target product of FTS—C₅₊ selectivity.

KEYWORDS

C₅₊ selectivity; cobalt oxidation; cobalt reduction; crystallite size Fischer-Tropsch synthesis (FTS); design of experiments

Introduction

Fischer-Tropsch Synthesis (FTS) is a catalytic process transforming syngas (carbon monoxide and hydrogen) into valuable hydrocarbons (Deugd et al. 2001). Transition metals like cobalt, iron, or ruthenium serve as catalysts in this reaction. With a growing emphasis on sustainable energy solutions globally, FTS plays a significant role in generating clean and renewable hydrocarbons, helping reduce reliance on conventional fossil fuels and addressing environmental concerns (Hu et al. 2012). The Fischer-Tropsch reaction scheme involves a series of reaction steps where syngas react over a suitable catalyst to yield hydrocarbons. The generalized reaction can be represented as shown in Equation (1). There has been a proliferation of studies on the effect of the size of cobalt crystallite in FTS catalytic systems when tailoring

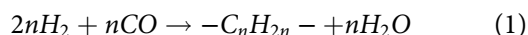
product distribution by controlling both particle and crystallite size (Bezemer et al. 2006; Herranz et al. 2009; Rane et al. 2012; Fischer et al. 2014; Fu et al. 2014; Yang et al. 2016; Fang et al. 2020). Different synthesis methods have been employed to yield the required cobalt crystallite size or a specific cobalt diameter on the surface of different supports. For instance, various 10%Co/ITQ-2 zeolites model catalysts were synthesized by combining reverse micellar and surface-silylated ITQ-2 delaminated zeolite to yield a Co⁰ crystallite size distribution in the 5–11 nm range (Prieto et al. 2009). In another study, cobalt crystallite ranging from 2.6 to 16 nm was prepared, using incipient wetness impregnation, by controlling the cobalt loading from 1 to 22 wt% and varying the cobalt precursor used (Co(NO₃)₂·xH₂O or Co(CH₃CO₂)₂·4H₂O) or the solvent used (H₂O or EtOH)

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(J. Den Breejen et al. 2009). Borg et al. (2008) prepared cobalt catalysts with crystallite sizes of 3 to 18 nm using one-step incipient wetness impregnation of alumina supports (γ and α -Al₂O₃), with a variety of cobalt nitrate solutions-such as water, ethylene glycol, diethylene glycol, or their combinations. The general observation in all these experiments is the intricacies of preparing a catalyst with crystallites of a certain size.



where n represents the number of carbon atoms in the hydrocarbon product.

The literature shows that different crystallite sizes of the supported cobalt catalyst behave differently during reduction and the Fischer-Tropsch (FT) reaction. Smaller cobalt crystallites (less than 6 nm) are more difficult to reduce than larger crystallites (20–70 nm) (Jacobs et al. 2007a). During the FT reaction, cobalt crystallites with a spherical shape and diameter less than 4.4 nm oxidize easily when $P_{H_2O}/P_{H_2} < 1.5$, according to van Steen et al. (2005). This suggests that controlling the size of the crystallite is important. The pore size of the support governs the diameter of the Co₃O₄ cobalt crystallite, with small crystallites forming in narrow support pores and large crystallites forming in wide pores (Borg et al. 2007).

The effect of support particle size is equally essential in FTS, as it affects reactant conversion selectivity. The smaller the support particle size, the larger the specific surface area of the support. Soykal et al. (2012) conducted experiments to evaluate the effect of the support particle sizes of Co/CeO₂ catalysts in ethanol steam reforming. When comparing two support particles of different sizes (μ m range and nm range), they observed that particles in the nm range show better ethanol reforming activity and deliver a higher ethylene yield. The benefit of being highly resistant to coking was observed with catalysts supported on particles in the nm range, whereas larger ceria particles in the μ m range were prone to coke formation.

Researchers use a wide range of support particle sizes in FTS systems. For instance, in a study by Tsubaki et al. (2001), they employed silica gel particles ranging from 74 to $\pm 590 \mu$ m, with support particles smaller than 149 μ m. Den Breejen et al. (2009) utilized carbon nanofibers with a

fraction size of 90–150 μ m. Fu et al. (2014) opted for carbon nanotubes (CNT) with a particle size of 180–425 μ m. Saib et al. (2002) used silica with a particle size ranging from 212 to 250 μ m. Rane et al. (2012) used utilized alumina with a size range of 53–90 μ m mixed with silicon carbide particles sized 75–150 μ m. Because of these variations in particle size, further studies are needed to determine the statistical significance of such wide variations in support size. This analysis will face the challenge of metal-support interaction with different supports, each support having distinct surface properties, acidity levels, and metal-support interactions. Moreover, we also recognize the multifaceted interplay between cobalt particle size and support size. The correlation between these two parameters adds another layer of complexity to the analysis. Table 1 gives examples that demonstrate the effect of cobalt crystallite size on FTS reaction.

The choice of support size in FTS systems at industrial scale is a crucial aspect that is also dependent on the type of reaction system employed, whether it's a fixed-bed, Continuous Stirred-Tank Reactor (CSTR), or microchannel system, plays a pivotal role in determining the optimal support particle size. In fixed-bed systems, larger support particles might be preferred to minimize pressure drop but these large pellet diameters lead to greater diffusion limitations. Brunner et al. (2015b) also showed that the catalyst shape affected the amount of catalyst required to achieve a specified conversion. The typical pellet size range is 1 to 4 mm (Pratt 2012; Brunner et al. 2015b; Stamenić et al. 2018). On the other hand, in CSTRs or microchannel systems, where heat and mass transfer limitations can be more pronounced, using smaller support particles can be advantageous. The smaller particles facilitate improved heat and mass transfer, ensuring efficient contact between the reactants and the catalyst surface (Ratchananusorn 2007).

The particle size of catalysts remains a crucial factor in catalysis, even when these particles are aggregated into pellets. Various effects arise from the particle sizes that make up the pellets in catalysis, influencing key aspects of catalyst performance. The surface area of catalysts is significantly impacted by particle size, with smaller

Table 1. Effect of cobalt crystallite size on different supports in FTS.

Support type	Reaction conditions, pressure, temperature, SV	Cobalt (Co) crystallite size	Characterisation method used to measure crystallite size	Effects in FTS	References
Silica	239.83 °C, H ₂ /CO = 2), 1 bar	1.4–10.5 nm	TEM	The water vapour easily oxidises smaller Co particles (1.4–2.5 nm) during FTS. A 1.4–2.5 nm particle size results in lower TOF and higher selectivity to CH ₄ . Larger Co particles in the 3.5–10.5 nm range show no oxidation during FTS. A 3.5–10.5 particle size does not affect TOF and CH ₄ selectivity. The maximum activity displayed for Co particles of 10–11 nm in size. CO ₂ hydrogenation increases with an increase in Co crystallite size from 3 to 11 nm. C ₅ + maximum extent at 11 nm. When Co particle size increases, C ₅ + selectivity is maximised at a crystallite size of 8–9 nm. With larger particles, selectivity to C ₅ + decreases before approaching a constant value.	(Z. J. Wang et al. 2012)
Silica	250 °C, H ₂ /CO = 2:1) 5 bar	3–11 nm	TEM	The selectivity of CH ₄ varies inversely with a decrease in crystallite size and C ₅ + selectivity. 7–8 nm Co particles yielded maximum C ₅ + selectivity. C ₅ + selectivity is constant for a crystallite size larger than 9–10 nm. The activation energies Co ₃ O ₄ reduction to CoO and Co crystallite size dependent, for particles ranging from 5.6 to 141 nm. FTS is not influenced by Co crystallite size >6 nm at 1 bar and >8 nm at 35 bar. Both TOF and C ₅ + selectivity decreased when the crystallite size was decreased from 16 to 2.6 nm. Co particles <6 nm result in decreased TOF and increased CH ₄ selectivity.	(Melaet et al. 2014)
Alumina	210 °C, H ₂ /CO = 2:1 20 bar PS = 53–90 µm	2–14 nm	XRD, H ₂ -chemisorption	CO ₂ hydrogenation increases with an increase in Co crystallite size from 3 to 11 nm. C ₅ + maximum extent at 11 nm. When Co particle size increases, C ₅ + selectivity is maximised at a crystallite size of 8–9 nm. With larger particles, selectivity to C ₅ + decreases before approaching a constant value.	(Rane et al. 2012b)
Alumina	190 °C, H ₂ /CO = 2, 9.9 bar PS = 150–200 µm	2.3–11.7 nm	XRD, TEM	The selectivity of CH ₄ varies inversely with a decrease in crystallite size and C ₅ + selectivity.	(Fischer et al. 2013)
Alumina	210 °C, 20 bar, and H ₂ /CO = 2.1 PS = 53 and 90 µm	3 to 18 nm	XRD, TEM, XPS	7–8 nm Co particles yielded maximum C ₅ + selectivity. C ₅ + selectivity is constant for a crystallite size larger than 9–10 nm.	(Borg et al. 2008b)
Silica delaminated ITQ-2 zeolite.	220 °C, H ₂ /CO = 2 20 bar PS = 0.25–0.42 mm	5.6–141 nm	XRD, H ₂ -chemisorption and (HR)TEM	The activation energies Co ₃ O ₄ reduction to CoO and Co crystallite size dependent, for particles ranging from 5.6 to 141 nm.	(Prieto et al. 2009c)
Carbon nanofibers	210, 220 and 250 °C, H ₂ /CO = 2), 1 and 35 bar PS = 0.5–1.0 mm	2.6–27 nm	(TEM), EXAFS, XPS and H ₂ chemisorption	FTS is not influenced by Co crystallite size >6 nm at 1 bar and >8 nm at 35 bar. Both TOF and C ₅ + selectivity decreased when the crystallite size was decreased from 16 to 2.6 nm. Co particles <6 nm result in decreased TOF and increased CH ₄ selectivity.	(G. Leendert Bezemer et al. 2006)
Carbon nanofiber	220 °C, H ₂ /CO = 2), 1 and 35 bar PS = 90–150 µm	2.6–16 nm	TEM, H ₂ -chemisorption	Co crystallite up to 7 nm displayed higher TOF and C ₅ + selectivity. No effect was observed for a Co crystallite size greater than 7 nm on TOF and C ₅ + selectivity.	(J. P. Den Breejen et al. 2009)
Activated carbon and on CNTs	230 °C, H ₂ /CO = 2, 20 bar PS = 180–425 µm	2.5 – 20.3	XRD, TEM	Co crystallite up to 7 nm displayed higher TOF and C ₅ + selectivity. No effect was observed for a Co crystallite size greater than 7 nm on TOF and C ₅ + selectivity.	(Fu et al. 2014b)

Information not given. PS = particle size.

particles generally providing a larger surface area per unit mass. This heightened surface area enhances catalytic activity by exposing more active sites for reactions to occur (García-Sánchez and Baldovino-Medrano, 2023). Even when assembled into pellets, the overall surface area is influenced by the arrangement and packing of particles within the pellet.

Particle size also affects diffusion rates within the catalyst pellet. Smaller particles may mitigate diffusion limitations, facilitating easier access of reactants to active sites. However, the packing arrangement in the pellet can alter diffusion pathways, influencing overall diffusion rates (Thiele, 1939; Mitchell et al. 2013). The catalytic activity is closely linked to the size of active sites on the catalyst surface. Smaller particles may expose a higher proportion of active sites, potentially leading to increased catalytic activity (Zhou et al. 2010; García-Sánchez and Baldovino-Medrano, 2023). The arrangement of particles within the pellet, however, can impact the accessibility of these active sites to reactants. In some instances, smaller particles may result in higher mass transfer limitations due to increased fluid flow resistance. The assembly of these particles into pellets affects the porosity and permeability of the catalyst bed, influencing mass transfer limitations (Satterfield et al. 1969; Yang et al. 2010). The size of catalyst particles can influence the selectivity of catalytic reactions. Different particle sizes expose varying crystal facets or surface structures, impacting the selectivity for specific reaction pathways (Wang and Lu 2020).

The particle sizes constituting catalyst pellets in catalysis have multifaceted effects on overall catalyst performance. Achieving the desired catalytic performance involves a delicate balance between maximizing active surface area, ensuring efficient mass transfer, and maintaining stability within the catalyst bed. The design and optimization of catalysts take into account these factors to meet specific catalytic requirements.

The morphology and metal loading on support particles are other critical parameters for designing and developing catalysts for the FTS. The FTS process converts synthesis gas into liquid fuels and chemicals. These parameters play a crucial role in determining the activity, selectivity,

stability, and lifetime of the catalysts. They also significantly impact the product distribution and quality of the FTS outcomes. Therefore, the optimization of these parameters is essential for the successful implementation of the FTS process (Parker et al. 2019).

The morphology of the catalyst refers to the shape and structure of the metal particles and the support. The morphology can influence the surface area, the dispersion, the coordination number, the electronic structure, and the exposure of different facets of the metal particles, which in turn affect the adsorption, activation, and dissociation of the reactants, the chain growth and termination of the products, and the rate and extent of the secondary reactions, such as cracking, isomerization, hydrogenation, and water-gas shift (Modekwe et al. 2021). The metal loading on the support refers to the amount or the weight percentage of the metal on the support. The metal loading can influence the dispersion, the reducibility, the stability, and the lifetime of the catalyst. Generally, higher metal loading leads to higher dispersion and reducibility, but lower stability and lifetime. Lower metal loading leads to lower dispersion and reducibility, but higher stability and lifetime. Therefore, carefully monitoring and adjusting the morphology, particle size, and metal loading on support particles for consistent catalyst development is crucial for achieving the desired FTS outcomes, such as high yield and quality of liquid fuels, low yield of methane and carbon dioxide, and optimal catalyst performance and durability.

Finally, the thermodynamics of cobalt catalyst reduction in FTS holds significant importance for several reasons. Firstly, the reduction process is a crucial step in activating the cobalt catalyst, transforming it from oxidized states to metallic cobalt. This activated state is what is active in FTS. The specific thermodynamic conditions during reduction, including temperature and pressure, impact the efficiency of the catalyst activation. Understanding and optimizing these conditions are vital for achieving the desired catalytic activity which then directs a certain product selectivity and stability of the cobalt catalyst. Therefore, a detailed understanding of the thermodynamics of cobalt catalyst reduction is

instrumental in designing and improving catalytic systems for efficient and economically viable Fischer-Tropsch processes.

In summary, understanding the impact of morphology, catalyst loading, crystallite and particle size in cobalt-based Fischer-Tropsch synthesis is crucial for optimizing catalytic performance. It allows for the tailoring of catalysts to enhance specific reaction pathways, ultimately improving product selectivity. By investigating size-dependent phenomena, researchers can gain insight into the intricate interplay between surface area, active sites, and catalytic activity, paving the way for more efficient and sustainable processes. Ma and Dalai (2021) recently reported a review on the effect of structure and particle size with an emphasis on TOF for Co, Fe and Ru. The current work reviewed the effect of crystallite size on carbon monoxide (CO) turnover frequency and selectivity of CH₄, C₂-C₄ and C₅+

This research aims to understand the effect of cobalt crystallite size on performance and selectivity in the FTS process, which converts synthesis gas (CO and H₂) into liquid fuels and chemicals. The size of the cobalt crystallites is a significant factor affecting the catalyst's activity, stability, and selectivity, along with the rate and extent of secondary reactions such as cracking, isomerization, hydrogenation, and water-gas shift. By comprehending how the size of cobalt crystallites influences product distribution, the study offers insights for future catalyst design and the development of more efficient and selective catalysts for FTS. This, in turn, can improve the economic and environmental viability of the process. The work further looked at the thermodynamics of cobalt catalyst reduction and characterization techniques for determining crystallite size. Understanding the thermodynamics of cobalt catalyst reduction is crucial for optimizing catalyst activation, improving energy efficiency in FTS and contributing to the fundamental understanding of the process.

Influence of cobalt particle size in FTS

Several catalyst preparation methods are used for FTS reactions. The different catalysts are made up of active components (usually transition metals), which are deposited on inert supports, such

as titania, silica, alumina, and carbon. These supports improve certain properties, such as the stability of the active component and its dispersion. Precipitation and deposition impregnation are the main methods used to prepare the catalyst (Bianchi et al. 2001), though other methods exist, specifically for the FTS reaction (Bianchi et al. 2001; Tsubaki et al. 2001; Brunner et al. 2015a; Deraz 2018). The chosen synthesis method and cobalt loading affects catalyst morphology, i.e., crystallite size, pore size distribution, pore volume, surface area and promoter distribution (Deraz 2018), which eventually affects product distribution (Zhai et al. 2013; Ghogia et al. 2021). A review done by Deraz (2018) on the comparative jurisprudence of catalyst preparation methods focused on impregnation and precipitation methods and clarified the advantages and disadvantages of each technique. The goals of a study should define the selection of the catalyst preparation method. The impregnation method is often chosen because of its simplicity: the procedure is quicker and cheaper than some other methods and the catalyst properties and configuration can be tailored.

Figure 1 presents the effect of cobalt crystallite size on methane selectivity. The figure suggests that CH₄ selectivity is favorable for a cobalt crystallite size less than 6 nm and there is a negligible effect on larger crystallite sizes. The methane selectivity shown in Figure 1 differs in magnitude, but more importantly, the significant aspect is the pattern displayed and the flattening of the curve after approximately 8 nm. The tabulated literature results (Table 1) show that crystallite size affects catalyst activity and product selectivity. Larger cobalt particles (>7 nm) favor higher TOF and C₅+ selectivity. For cobalt crystallites ≥7 nm, CH₄ selectivity is suppressed (Fu et al. 2014). In a study carried out by Wang et al. (2012) using steady-state isotopic transient kinetic measurements, it was reported that reduced TOF for Co crystallite <6 nm is attributable to lower intrinsic activity at the small terraces and to the blocking of edge/corner sites (to a significant extent). The proclivity of small Co crystallite (<6 nm) to favor high production of CH₄ under FTS conditions is mainly due to higher coverage of the surface by hydrogen (Den Breejen et al. 2009). It should be

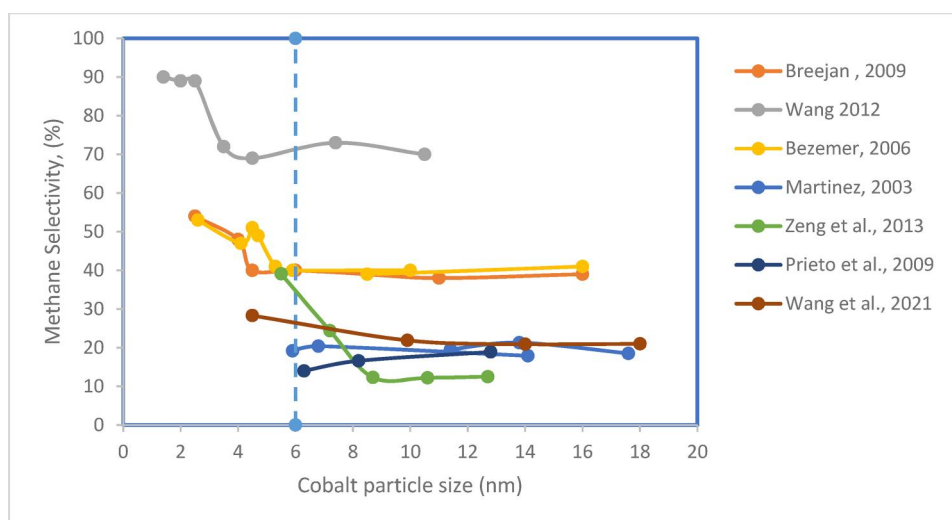


Figure 1. The increase in cobalt crystallite size on CH_4 selectivity: 220 °C, $\text{H}_2/\text{CO} = 2$, 1 bar (Bezemer et al. 2006); 210 °C, $\text{H}_2/\text{CO} = 2$, 1 bar (Den Breejen et al. 2009); 220 °C, $\text{H}_2/\text{CO} = 2$, 1 bar (Martínez et al. 2003); 239 °C, $\text{H}_2/\text{CO} = 2$, 1 bar $\text{H}_2/\text{CO} = 2$, $P = 20$ bar, 210 °C (Zeng et al. 2013); 220 °C, $\text{H}_2/\text{CO} = 2$, 20 bars (Prieto et al. 2009); 240 °C, $\text{H}_2/\text{CO} = 2$, $P = 20$ bar (Wang et al. 2021) [data used to generate this graph was obtained from the references given].

noted that turnover rates in FTS are not affected by Co crystallite dispersion and the type of support used over the accessible dispersion range under typical FTS conditions (Iglesia 1997a).

The activity of the FTS catalyst and its selectivity to desirable C_{5+} hydrocarbons are important production design criteria to consider. Figure 2 shows the relationship between cobalt crystallite size and C_{5+} selectivity. Borg et al. (2008) conducted a series of studies on Co supported on $\gamma\text{-Al}_2\text{O}_3$ and observed that C_{5+} selectivity increases sharply with an increase in crystallite size up to about 7 nm (Figure 2), with the optimum crystallite size being about 8 nm. The figure also shows a negligible increase in selectivity for crystallites larger than 9–10 nm (Borg et al. 2008).

A correlation between CH_4 and C_{5+} selectivity can be deduced from the available literature. Thus, a minimum CH_4 selectivity and maximum C_{5+} selectivity are recorded with larger cobalt crystallites, while the opposite is true for smaller sizes. A similar pattern is observed during FTS in a packed bed: when indigenous water accumulates, C_{5+} selectivity increases, whereas CH_4 selectivity decreases (Iglesia 1997a). A study done by Bezemer et al. (2006) supports the view that turnover frequency (TOF) and CH_4 selectivity remain unchanged for catalysts with a cobalt crystallite size greater than 6.0 nm, while a crystallite size of less than 6 nm results in variations in both

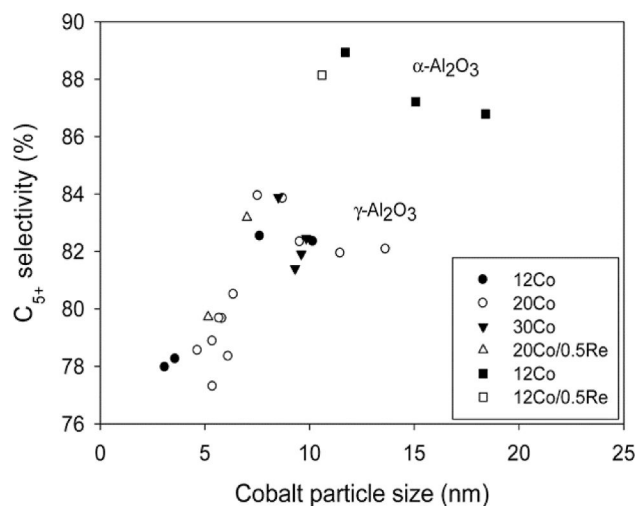


Figure 2. Depiction of the relationship between C_{5+} selectivity and cobalt crystallite size. Source: Reproduced from (Borg et al. 2008) with permission from [Elsevier]. Copyright [2008].

selectivity and activity. It can, therefore be concluded that the ideal cobalt crystallite size should be greater than 6 nm. A study done by Bezemer et al. (2006) revealed that the TOF for hydrogenation of CO was not affected by a cobalt crystallite size greater than 6 nm at 1 bar and greater than 8 nm at 35 bar. Several researchers agree that TOF, a surface-specific activity, decreases with a decrease in cobalt crystallite size from about 1 to 7 nm (Den Breejen et al. 2009; Fu et al. 2014). Factors like the type of support used and metal dispersion have been reported to not have an effect on the turnover rate; hence, the activity of

the catalyst ought to be proportionate to the number of active sites (Martínez et al. 2003).

Co_3O_4 crystallite size is influenced significantly by the pore size of the support. A larger pore favors the formation of larger Co_3O_4 crystallites. A study by Song and Li (2006) indicated that catalysts with a 6–10 nm pore size produce a moderate Co_3O_4 crystallite diameter, consequently yielding the required selectivity. In a study done by Liu et al. (2007), increasing the pore size of the FTS catalyst from 2.9 to 12.6 nm had a positive impact: catalytic activity, C_{5+} , $\text{C}_{12}\text{--C}_{18}$, and C_{18+} selectivity increased, and an antagonistic effect on CH_4 selectivity was observed. The higher α values obtained in a study by Rytter et al. (2018) were attributed to larger pore size and larger cobalt crystallites, which positively affect CO activation. Therefore, pore size is generally a selectivity director. The pore size of the support may control the size of the Co_3O_4 cobalt crystallite, as smaller crystallites form in narrow pores, whereas larger crystallites form in larger pores (Borg et al. 2007).

The data used to construct Figures 3 to 5 were extracted from various literature sources (Saib et al. 2002; Martínez et al. 2003; Song and Li 2006; Lira et al. 2008; Witton et al. 2011). These sources provided the experimental conditions, catalyst type, catalyst analysis results and product distribution in terms of C_1 , $\text{C}_2\text{--C}_4$, and C_5 selectivity. FT data for DOE was based on prior research on cobalt-impregnated silica support structures done by a group of academics, as reported in the available literature. Using the response surface approach, the effects of numerous independent and dependent variables were investigated. Design-Expert 13 was used to generate the 3-D plots. In terms of the data given, smaller cobalt crystallites of less than 12 nm proved to be more selective to methane. Increasing the crystallite size resulted in a decrease in methane selectivity. This observation concurs with the details provided in Table 1. Increasing pressure has a negligible effect on the conditions given.

$\text{C}_2\text{--C}_4$ selectivity decreases as crystallite size increases from 3 nm to about 15.8 nm, then gradually increases until it reaches 26 nm, see Figure 4. Smaller crystallites of 3 to 7.6 and larger

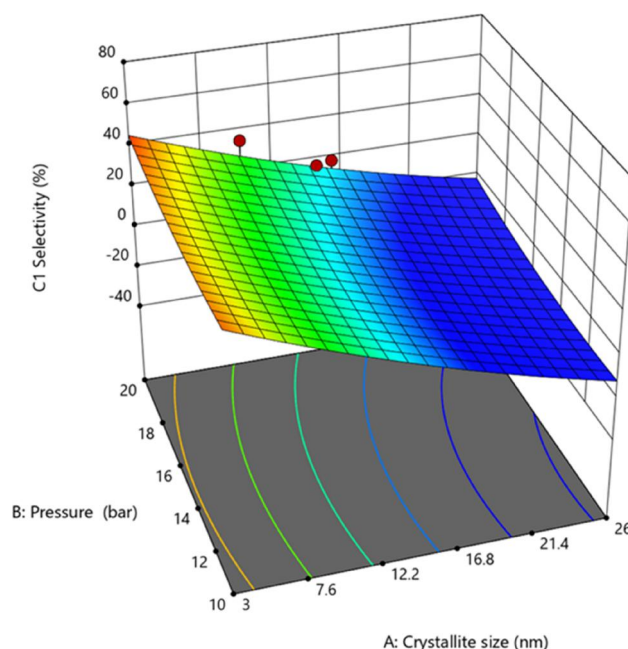


Figure 3. Three-dimensional (3-D) plot showing the effect of crystallite size and pressure on C1 selectivity (%). The 3-D plot was generated using design-expert 13. The red circles are data points above the predicted values, respectively.

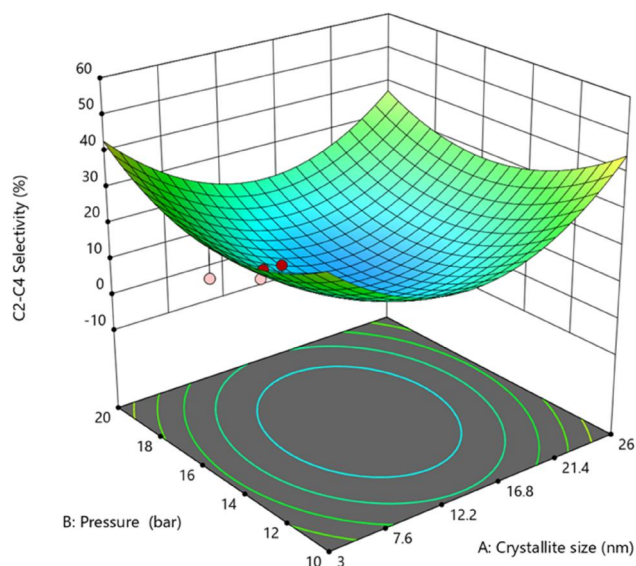


Figure 4. 3-D plot showing the effect of crystallite size and pressure on $\text{C}_2\text{--C}_4$ selectivity (%). The 3-D plot was generated using Design-Expert 13. The red and pink circles are data points above and below the predicted values, respectively.

crystallites of 21.4 to 26 are more selective to $\text{C}_2\text{--C}_4$ hydrocarbons. The data for this plot was extracted from various sources (Saib et al. 2002; Martínez et al. 2003; Song and Li 2006; Lira et al. 2008; Witton et al. 2011).

The effect of pressure and crystallite size produced a dome-shaped distribution, contrary to

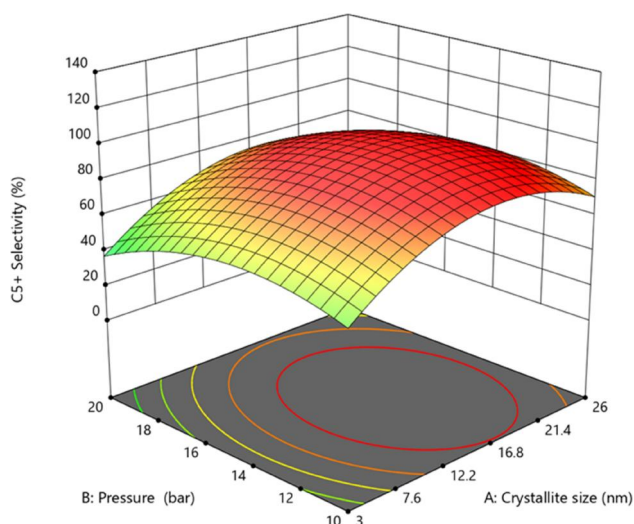


Figure 5. 3-D plot showing the effect of crystallite size and pressure on C_{5+} selectivity (%). The 3-D plot was generated using Design-Expert 13.

the pattern observed for C_2 - C_4 selectivity (on a carbon basis). Increasing pressure increased C_{5+} to about 16 bar, then gradually decreasing until it reached 20 bar. C_{5+} selectivity increased with an increase in crystallite size until 15.2 nm; it then decreased until it reached 26 nm. Analysis of the literature yielded Figures 3 to 5 (Saib et al. 2002; Martínez et al. 2003; Song and Li 2006; Lira et al. 2008; Witoon et al. 2011). Cobalt crystallite size appears to be an important factor that influences product distribution. This novel approach provides insight into selectivity being dependent on pressure and crystallite size in cobalt-catalyzed FTS.

In summary, maintaining the cobalt crystallite diameter within the specified range is crucial for optimizing FTS outcomes. This range ensures an optimal balance between catalytic activity, selectivity toward desired hydrocarbons, and resistance to deactivation mechanisms (to be discussed in the following section). Deviations from this range may lead to undesirable changes in CO turnover frequency and hydrocarbon selectivity, affecting the overall efficiency and performance of the Fischer-Tropsch synthesis process. Moreover, using unnecessarily large particle sizes also has these disadvantages (1) reduced active surface area since active sites for catalytic reactions are typically located on the surface of the catalyst; (2) diffusion limitations since large particles may

tend to block the pores of the support material, and (3) large particles have a cost implication.

Proneness of cobalt catalyst to oxidation

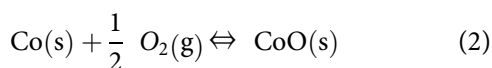
Cobalt catalyst oxidation has been studied extensively as a deactivation mode in FTS (Van Berge et al. 2000; Lira et al. 2008; Rytter and Holmen 2015; C. Kliever et al. 2019; Choudhury et al. 2020; Okoye-Chine et al. 2023). The literature analysis suggests that, in general, the catalytic properties of small cobalt crystallite differ from that of larger ones in terms of activity, selectivity and deactivation. Table 1 shows that smaller Co particles are easily oxidized by the indigenous water vapor during FTS. A study done by Wang et al. (2012) concluded that with smaller Co crystallite (1.4–2.5 nm), the cobalt metal was easily oxidized by the indigenous water vapor, which led to reduced TOF and increased CH_4 selectivity. Wang et al. (2012) also observed that larger Co crystallites of 3.5–10.5 nm are immune to oxidation during FTS and do not affect TOF and CH_4 selectivity.

Thermodynamic analysis done by van Steen et al. (2005) showed that cobalt crystallites with a spherical shape and measuring < 4.4 nm in diameter are prone to oxidation during FTS ($P_{H_2O}/P_{H_2} < 1.5$, $T = 493$ K). The same qualitative observation was recorded by Iglesia (1997a), who reported rapid deactivation by oxidation during FTS of cobalt metal crystallite with a diameter of less than 5–6 nm. A high P_{H_2O}/P_{H_2} ratio is needed to re-oxidize bulk cobalt metal, but these ratios are not encountered under normal FTS conditions (Iglesia 1997b; Hilmen et al. 1999; van Steen et al. 2005). High P_{H_2O}/P_{H_2} ratios are possible at high per-pass conversions but the ranges of P_{H_2O}/P_{H_2} ratios that may cause oxidation are not experienced in normal FT. The ratios of P_{H_2O}/P_{H_2} experienced in normal FTS and P_{H_2O}/P_{H_2} ratios required for oxidation are 3 and 123, respectively (van Steen et al. 2005). The thermodynamic feasibility of oxidizing small cobalt crystallites or forming an oxide shell may occur under conditions where the oxidation of bulk metallic cobalt is not feasible. This phenomenon is associated with the influence of surface energy on the overall process, which is lower for bulk

metal oxides compared to their corresponding bulk metals. Consequently, it is anticipated that nanosized crystals exhibit lower oxidation resistance compared to bulk crystalline materials.

Cobalt crystallite size significantly affects activation energy in stepwise reduction: $\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}^0$ [8] (Prieto et al. 2009). Thermodynamically, the oxidation of CoO by water during FTS is not favored as evidenced by a positive change in free energy (ΔG), indicating a non-spontaneous reaction, this is due to the weak reduction ability of Co^0 and the relatively feeble oxidizing potential of water. However, observations indicate that under a very low $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ ratio, where the partial pressure of hydrogen (P_{H_2}) is much lower than the partial pressure of water vapor ($P_{\text{H}_2\text{O}}$) in the gas phase, oxidation occurs (Van Berge et al. 2000). These conditions create circumstances in which the chemical potential of hydrogen is low, and the chemical potential of water is high. As a result, the oxidation of CoO by water moves toward equilibrium, despite being thermodynamically unfavorable.

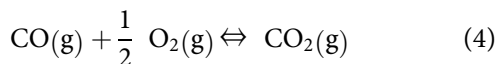
Cobalt oxidation by H_2O and CO_2 is governed by the $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ and $P_{\text{CO}}/P_{\text{CO}_2}$ ratios in the reactor. Cobalt oxidation follows Equation (2) below.



From Equation (2), the minimum oxygen partial pressure required to effect oxidation can be given by Equation (3):

$$\text{Log } P_{\text{O}_2} - \text{log } K(T) \quad (3)$$

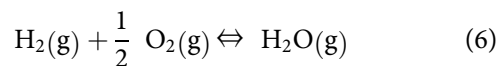
For the oxidation of carbon monoxide (CO), it would be (Equation (4)):



The O_2 partial pressure can be given by Equation (5):

$$\text{Log } P_{\text{O}_2} = 2\text{log } (P_{\text{CO}_2}/P_{\text{CO}}) - \text{log } K_{\text{CO}} \quad (5)$$

Equation (6) can be used for the oxidation of hydrogen:



The oxygen partial pressure can be given by Equation (7):

$$\text{Log } P_{\text{O}_2} = 2\text{log } (P_{\text{H}_2}/P_{\text{H}_2\text{O}}) + \text{log } K_{\text{H}_2} \quad (7)$$

The oxygen partial pressure corresponds to $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ and $P_{\text{CO}_2}/P_{\text{CO}}$ ratios under certain conditions. The plot of O_2 partial pressure versus temperature with different partial pressures of H_2 , H_2O , CO and CO_2 can be used to predict the stability of varying cobalt phases.

The parameters in Table 2 indicate that all the given reactions are thermodynamically feasible in the temperature ranges given. According to the three equations, the oxygen partial pressure can be related to $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ and $P_{\text{CO}_2}/P_{\text{CO}}$ in the reactor at any point during the reaction. From the theoretical calculations of the thermodynamic properties, the oxidation of cobalt catalysts at different $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ and $P_{\text{CO}_2}/P_{\text{CO}}$ ratios were plotted—see Figure 6 (The $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$, $P_{\text{CO}_2}/P_{\text{CO}}$ ratios correspond to a particular partial pressure of O_2). The thermodynamic calculations for CoO oxidation to Co_3O_4 are not presented, as they are approximately four orders of magnitude higher than for Co^0 to CoO.

The theoretical calculations show that it is impossible to oxidize a Co-based catalyst under normal FT conditions, as the $\text{H}_2\text{O}/\text{H}_2$ ratios are usually less than 10. This concurs with van Steen et al. (2005) calculations. This observation does not agree with many FT practitioners, who recorded catalyst oxidation after characterizing the spent catalyst. For our theoretical calculations to agree with the experimental data, the effects of crystallite size (that changes the surface energy of particles) on thermodynamic properties must be considered. (Here, crystallite size refers to the size of the cobalt metal clusters on the support surface.)

Table 2. Variation of thermodynamic parameters from 100 to 400 °C.

Equation	Thermodynamic parameters (range 100–400°C)		
	Log (K _{eq})	ΔH (kJ)	ΔG (kJ)
$\text{Co(s)} + \frac{1}{2} \text{O}_2(\text{g}) = \text{CoO(s)}$	58.34 to 28.94	−473.83 to −468.00	−416.70 to −372.85
$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{H}_2\text{O(g)}$	63.04 to 32.64	−485.13 to −490.55	−450.33 to −420.54
$\text{CO(g)} + \frac{1}{2} \text{O}_2(\text{g}) = \text{CO}_2(\text{g})$	70.18 to 34.80	−566.70 to −567.05	−501.30 to −448.40

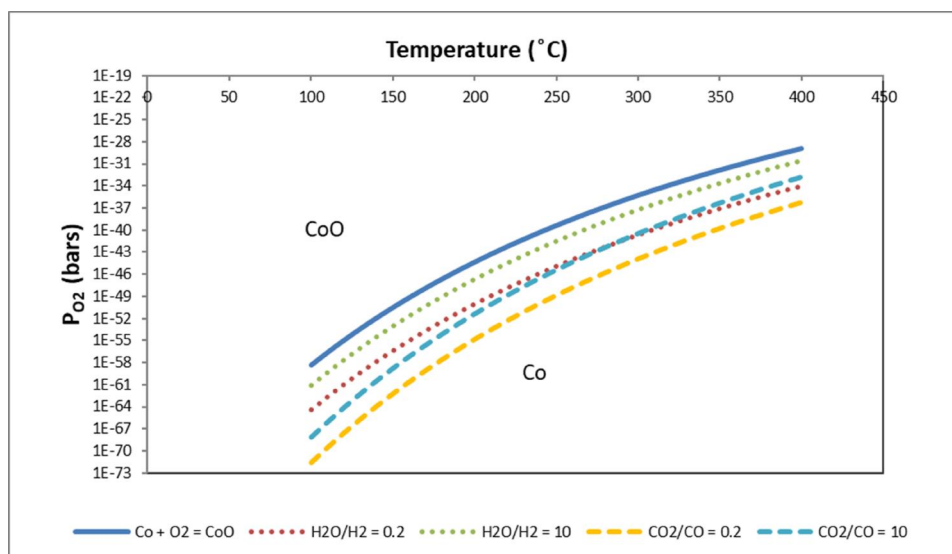


Figure 6. Theoretical study of the effect of $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ and $P_{\text{CO}_2}/P_{\text{CO}}$ on cobalt catalyst oxidation.

As per Table 1, activity and selectivity can change with changes in crystallite size. Oxidation of cobalt only happens with substantial $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratios, and these ratios are not encountered under normal FTS conditions as stated earlier. The literature analysis done by Van de Loosdrecht et al. [39] revealed that, with FTS, P_{H_2} ranges from 6.5 to 9.2 bar, and a $P_{\text{H}_2\text{O}}$ between 4.6 and 7.6 bar, which corresponds to a $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio between 0.5 and 1.2. Cobalt particles of less than 4–5 nm are oxidized if the $\text{H}_2\text{O}/\text{H}_2$ ratio is 1–1.5 (van Steen et al. 2005). Schanke et al. (1995) observed no oxidation on 15 and 25 nm particles at a $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ of 0.33. Hilmen et al. (1999) experimented with 10 and 16 nm particles using a $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio of 10 and observed no Co oxidation. Bian et al. (2003) studied larger Co-crystallites (10 and 29 nm) using a high $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ of 6.11 and observed no oxidation. A cobalt particle smaller than 4 nm oxidized at a $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio of 0.74 (Iglesia 1997a). A study done by Jacobs et al. (2003) on a 6 nm Co particle showed that a $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio of 0.56 resulted in no oxidation, whereas a $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ of 0.60 resulted in oxidation. Therefore, cobalt oxidation of crystallites less than 6 nm can be avoided by ensuring the correct combination of reactor partial pressures of $P_{\text{H}_2\text{O}}$ and P_{H_2} .

A study done by Lu (2011) on FT product distribution (using 10%Co/TiO₂) resulted in different $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratios when using a continuously stirred tank reactor (CSTR) and tubular fixed-bed

reactor (TFBR) at $\text{H}_2/\text{CO} = 2$ and 20 bar and different pressure levels. In the same study, it was shown that the $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio increases with temperature. With a TFBR, the ratios are significantly higher than with a CSTR. When using a CSTR, the proportions are comparatively lower and tend to approach an asymptote as the temperature increases toward 240 °C. The distribution of FT products is influenced by several parameters, including the type of reactor employed thus affecting the $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio. The impact of temperature on the FT product distribution may vary between the Fixed Bed Reactor (FBR) and the Continuous Stirred Tank Reactor (CSTR) due to the inherent characteristics of these reactors. The Anderson-Schulz-Flory (ASF) model suggests that the distribution of FT products conforms to a geometric distribution, with a chain growth probability factor (α) that declines with an increase in temperature. As a result, higher temperatures tend to promote the formation of lighter hydrocarbons, such as methane and ethane, while lower temperatures favor the production of heavier hydrocarbons, such as waxes and diesel. The model for the ASF synthesis serves as an elementary representation of the FT synthesis. It omits the secondary reactions that occur within the reactor, such as cracking, isomerization, hydrogenation, and water-gas shift. These reactions can significantly impact the FT product distribution, causing it to differ from the ideal ASF distribution. For instance, the process

of cracking can break down long-chain hydrocarbons into shorter ones, isomerization can alter the structure of the hydrocarbons from linear to branched, hydrogenation can decrease the olefin content, and water-gas shift can consume CO and H₂O while producing CO₂ and H₂.

The extent of secondary reactions in chemical reactors is influenced by the reactor type and operating conditions. FBRs experience temperature variations influenced by factors such as heat transfer, reaction kinetics, and reactant concentration. This enhances the rate of secondary reactions, such as cracking and isomerization, leading to a more diverse and complex distribution of products. Conversely, in CSTRs, catalyst particles are well-mixed, resulting in a more uniform temperature. As a result, secondary reactions occur at a lower rate, yielding a more predictable and consistent product distribution. The CSTR exhibits little variation in pH₂O/PH₂ with an increase in reaction temperature, and this could be attributed to the fact that the CSTR has a lower rate of secondary reactions than the FBR, making it less sensitive to temperature changes.

The effect of cobalt-support interaction

In studying the effect of cobalt crystallite, Bezemer et al. (2006) opined that these types of experiments are better carried out using inert materials such as graphitic or carbon-based supports. Oxidic supports, silica and alumina tend to form mixed oxides that are not reducible - such as cobalt aluminate or cobalt silicate - which may affect the observations (Van Berge et al. 2000; Li et al. 2002; Wolf et al. 2021). The strength of cobalt-support interaction has been found to increase in the order SiO₂ < Al₂O₃ < TiO₂ (Jacobs et al. 2007; James and Maity 2016; Kliever et al. 2019; Petersen et al. 2019; Yan et al. 2021). Deductions from the literature indicate that strong Co-support interaction of Al₂O₃, and particularly TiO₂, results in increased dispersion and there is a tendency to form cobalt aluminates and titanates, respectively. This affects the density of the Co⁰ surface sites. Comparatively speaking, the interaction of cobalt on silica support is weaker, which is ideal for complete cobalt oxide reducibility. However,

there is a problem with the agglomeration of cobalt crystallites during catalyst preparation, which also happens at high temperatures during calcination (Martínez et al. 2003). This sintering leads to low Co crystallite dispersion.

Crystallite size measurement techniques

The characterization of crystallites involves a range of techniques for determining their size, morphology, and structure. Among the most commonly used methods, X-ray diffraction (XRD) allows for the analysis of crystal structure and the determination of lattice parameters, as well as peak broadening, which can provide indications of crystallite size. Transmission electron microscopy (TEM), on the other hand, provides high-resolution imaging of individual crystallites, revealing information about their shape, size, and defects. Scanning electron microscopy (SEM) is a useful method for obtaining surface morphological information. In addition, techniques such as atomic force microscopy (AFM) and dynamic light scattering (DLS) can be employed to study the size and shape of crystallites.

Transmission electron microscopy (TEM), X-ray diffraction (XRD) and H₂-chemisorption are often employed to measure crystallite size before running FTS. These analytical techniques often show consistency with crystallite sizes (Miller et al. 1993; Schanke et al. 1995; Jacobs et al. 2003; Bezemer et al. 2006; Den Breejen et al. 2009; Saib et al. 2010) with X-ray absorption studies giving results that are within the experimental error. Powder XRD has been reported to measure millions of crystals and provide the precise size distribution of nanomaterials (Chauhan and Chauhan 2014). The terms particle size and crystallite size are often used interchangeably to mean the same thing, but these refer to two distinct properties of a material. Particles comprise of several small crystallites, and nanomaterial properties depend and comprise several small crystallites, and nanomaterial properties depend on crystallite size, not particle size (Chauhan and Chauhan 2014).

Due to the principle of measurement, crystallite size calculated with XRD is always smaller than when using the chemisorption method. This

is expected because the XRD measurements also record dislocations in the crystal structure that are not registered by chemisorption (Geyer et al. 2012). The crystallite size given by TEM analysis agrees with the size derived from XRD (Rozita et al. 2010). Usually, in a minimal particle size regime (nanometer scale), there is close agreement between the TEM and XRD measurements. However, for larger particle size regimes, TEM tends to provide a comparatively larger average particle size than XRD. The discrepancy is attributed to the size that is determined by XRD correlating with the average of the smallest undistorted regions in the material. In contrast, TEM measurements relate to scanned areas separated by more-or-less sharp contours in the micrograph (Rozita et al. 2010).

Characterization of cobalt crystallite size

In FTS, precision catalyst development with defined crystallite size is an area of interest that researchers continue to look at. From the previous sections, it is clear that knowledge of the crystallite size distribution is crucial for interpreting the experimental results of FTS. Various synthetic pathways have been adopted for the preparation of catalysts with good uniform dispersion and controlled crystallite size. Examples include incipient wetness impregnation (Xiong et al. 2005; Song and Li 2006; Lira et al. 2008; Fu et al. 2014; Gavrilović et al. 2018; Rytter et al. 2018); the sol-gel technique (Okabe et al. 2004; Liu et al. 2010; Bykova et al. 2012; Sukkathanyawat et al. 2015); the chemical deposition method (Kazemnejad et al. 2019); the precipitation method (Li et al. 2017); and the impregnation method (Bian et al. 2003). A review by Ghogia et al. (2021) provides an overview of these methods along with a detailed description of each. Different characterization techniques are used to measure crystallite size accurately. The techniques include TEM, XRD and H_2 -chemisorption as stated earlier. Each technique has certain advantages and disadvantages, as there are limitations, given that they are prone to operational and other fundamental uncertainties. So, it is recommended that more than one technique is used to verify the agreement of the data.

Agreement of the data, which is determined using various methods, proves the absence of significant errors in the methods used for each supported metal catalyst. After analyzing various experiments conducted to determine crystallite sizes using the XRD Scherrer formula and TEM, it was concluded that both methods yield similar crystallite size values, especially for sizes smaller than 60 nm (Vorokh 2018). Thus, a combination of at least two methods is needed to determine catalyst crystallite size accurately.

TEM application in determining crystallite size

TEM has been applied to image crystallite size directly on the supported catalyst. However, for accuracy and reproducibility, there is a need for accurate crystallite size distribution analysis. TEM has the advantage of the real-space visualization of nanoparticles. Nevertheless, to ensure accurate results, the operator must still select the correct magnification and have reasonable choices regarding the type of imaging (bright vs dark field), method of analysis, and a manual or automated method (Pyrz and Buttrey 2008). These choices have an impact on resolution, the contrast between the background and the particles, the particle population in each image, the efficiency of the analysis and proper background-particle boundary determination (Pyrz and Buttrey 2008). It is important to note that images visualized at coarse magnifications clearly show all the particles in that given area, but the reliability of the quantification was severely limited, as high magnification imaging results in sampling fewer particles. This limitation contributes to errors or bias in determining the crystallite size of a given sample. Therefore, the statistical significance of the crystallite size determination will be compromised if the particle population is not captured and it is not representative of the particle population. Therefore, all variables should be considered, in order to measure particle size distribution with statistical significance and accuracy.

TEM limitations

Generally, measuring the crystallite diameter on the supported catalyst and understanding the

distribution using TEM can be a challenging exercise. To obtain statistically meaningful data from TEM, many points should be analyzed, many particles should be analyzed and many crystallites should be measured. Other challenges with TEM image analysis are the presence of crystallites as clusters at different heights; crystallites that are sometimes embedded in support material; crystallites that overlap; and an uneven background. In order to address these issues, Gontard et al. (2011) invented an image-processing algorithm to assist in measuring crystallite size and their distribution using TEM images. The algorithm reportedly allows crystallites to be detected and characterized with greater accuracy than when using other conventional methods. In another study, Fisker et al. (2000) developed an automated image analysis technique built on a deformable ellipse model to accurately and robustly estimate crystallite size distribution from thousands of crystallites. This method has also proved to be very useful.

Figure 7 shows synthesized uniform-sized cobalt crystallites on mesoporous SiO_2 supports. The number of crystallites varies per given area at the same magnification. There is a correlation between

crystallite size and selectivity, so the ability to tune the crystallite size controls the selectivity of the products. However, a correlation between shape and product selectivity is not mentioned in the available literature. Another, disadvantage of TEM is sometimes a lack of contrast between crystallites and the support, and it is difficult to see tiny particles of 0.5 nm (Mustard and Bartholomew 1981). In principle, TEM can measure the size of a discrete particle, which can be used to determine the average particle size. However, different points or locations need to be imaged to avoid bias and the pictures studied should be representative of the whole sample.

X-ray diffraction (XRD)

XRD is another technique that is often used to measure the mean size of crystallites by applying the Scherrer equation to XRD data. The history of applying the Scherrer equation in determining crystallite size is documented in articles written by Alexander and Klug (1950), and Langford and Wilson (1978). The Scherrer equation is the most commonly used modulus operandi in FT reported in the literature for extracting crystallite size

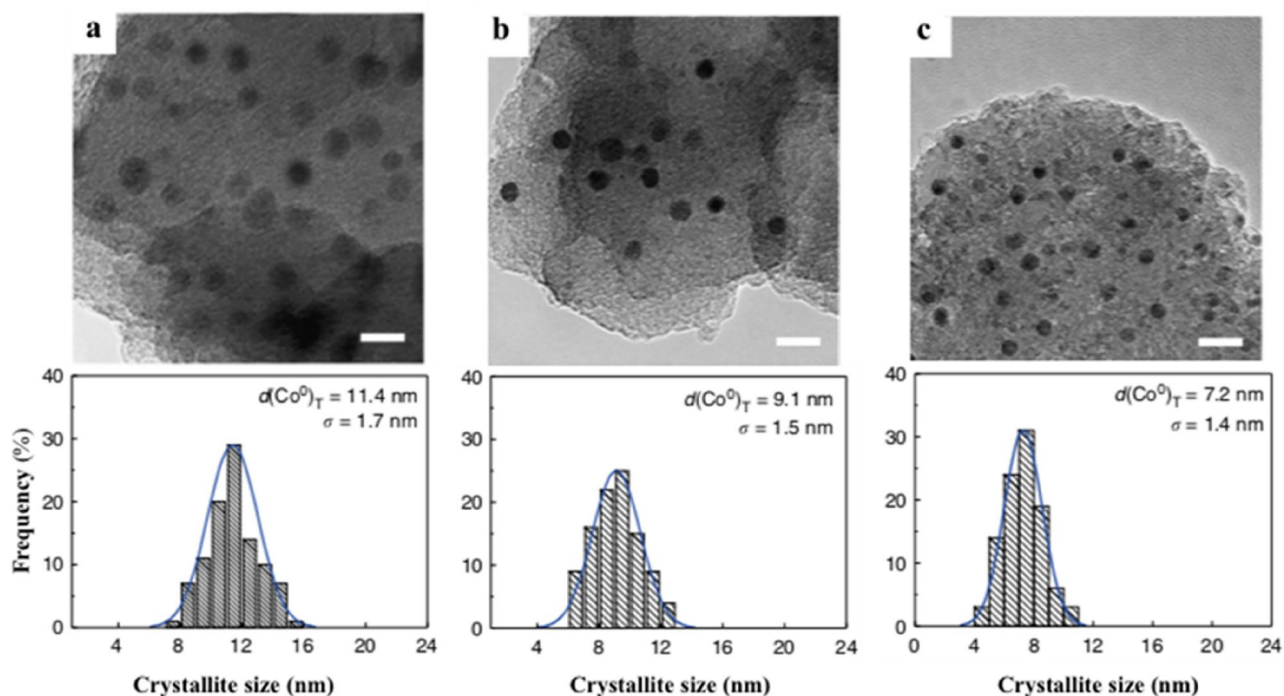


Figure 7. Images obtained from TEM and a reduced catalyst's corresponding cobalt crystallite size distribution. Crystallite size decreases from a > b > c, and metallic cobalt crystallites are dispersed almost homogeneously with a narrow size distribution. The figure was modified with permission from (Cheng et al. 2018).

information from XRD data. The Scherrer Equation was formulated in 1918 to compute the diameter of crystallite. It is given in Equation (8).

$$L = \frac{K\lambda}{\beta \cdot \cos\theta} \quad (8)$$

Where L is the average crystallite size (crystallite diameter in nanometer (nm)); K is the crystallite shape-related constant, normally taken as 0.9 (depending on the shape of the crystallite); λ is the wavelength of the X-ray, usually in nm; β is the Full Width at Half Maximum (FWHM) at 2θ in radians (β = value of FWHM $\times \pi/180$), and β varies inversely with crystallite diameter (L); θ is the Bragg angle for the peak at 2θ (in degrees); θ = ($2\theta/2$) FWHM, and θ can be expressed in radians or degrees, since the value of $\cos\theta$ corresponds to the same value (Monshi et al. 2012).

Uncertainties in calculating crystallite size

The accuracy of the familiar Scherrer Equation is limited by the uncertainties in K (the crystallite shape factor) and β (the pure diffraction broadening) (Alexander and Klug 1950). In reality, crystallites are not usually uniformly perfect but have irregular shapes. However, the Scherrer Equation assumes a regular shape for all samples. Although crystallite shape is usually irregular, shapes are often approximated as spheres, triangular prism, cubes, tetrahedrons and octahedrons, and in some cases include shapes that do not have cubic symmetry (Lele and Anantharaman 1962; Wilson 1969; Louër et al. 1972). Special cases of non-cubic symmetry crystallite shapes that have been considered are parallelepipeds such as needles and plates (Langford and Wilson 1978).

The K value depends on the determined width, crystallite shape and distribution of the size. The values often used for K (the shape factor) are 0.94 for crystallites that are spherical and 0.89 for other shapes. These values can be approximated to be 1 after rounding off. K varies from 0.62 to 2.08. A detailed discussion of K is given by Langford and Wilson (1978). The literature survey shows that, when using the Scherrer Equation, the estimates are usually that crystallites are spherical; however, prior analysis using other methods (TEM, SEM, and AFM) to determine the average crystallite shape can assist in determining the most accurate value of K .

The accuracy of Equation (8) (the Scherrer crystallite size equation) is restricted partly by the uncertainty regarding the β value, which varies inversely with crystallite size (Alexander and Klug 1950). FWHM is defined as the diffraction peak width, in radians, at a height halfway between the base and the maxima of the peak (Muniz et al. 2016). FWHM of the broadened line has been criticized for giving unreliable crystallite size values. Therefore, it was proposed that the integral breadth be used together with the Scherrer equation to reduce errors in determining crystallite size (Bushroa et al. 2012). Moreover, the line shape of an XRD pattern is affected by the uneven distribution of crystallite and the wide distribution of size (Bushroa et al. 2012). The Scherrer formula has a lower limit of applicability, which has been established. It has been shown that the error when using the Scherrer formula non-linearly increases with a crystallite size of less than 4 nm (Vorokh 2018). In another study, XRD was reported to be insensitive to low metal loading and small particles (<3 nm) (Mustard and Bartholomew 1981).

Crystallite definition

Here, the phrases crystallite size and particle size, and the word size are synonymous with the diameter of the crystallite, with the diameter being defined as the length of a straight line traversing through the middle of the mass of the crystallite and ending at the crystallite boundary (Green 1927; Heywood 2010). For non-uniform crystallite that cannot be completely defined by a single mean value, a mathematical shape factor for defining the geometric shape can be applied if accuracy is important (Hatch 1933). Several definitions of particle size exist in the literature, but the most appropriate is governed by the system being examined and the analysis technique employed (Matyi et al. 1987). For instance, XRD is sensitive to the crystallite size on the surface or inside any given particle. However, the phrase crystallite size seems more accurate, since individual particles can be made up of many crystallites or domains with a non-identical orientation. This distinction is significant if the diameter measured from diffraction broadening is juxtaposed with that obtained using other methods.

Figure 8 shows that an increase in the size of particles tends to result in the narrowing of the peaks to resemble a coarse crystalline material. Smaller particles less than 1.5 nm tend to produce broad peaks synonymous with amorphous substances (Vorokh 2018). This phenomenon is observed even if the particles or crystallites are not the same shape and size. The peak width varies with particle or crystallite size, and a narrow peak corresponds with a bigger crystallite diameter. When the peaks are broader, there is a limit to the smallest nanoparticles that can be measured by XRD, (<3 nm) (Mustard and Bartholomew 1981).

H₂ chemisorption

Many catalyst characterization studies have used H₂ chemisorption as a crystallite size measuring technique (Bezemer et al. 2006; Den Breejen et al. 2009; Prieto et al. 2009; Rane et al. 2012). H₂ chemisorption measurements relate the consumption of H₂ gas molecules to the available surface area of the supported metal crystallites. The relationship that exists between H₂ consumption and the exposed surface area is governed by the chemisorption stoichiometry of the hydrogen-to-metal atom. This technique is useful for small particles when the size is difficult to estimate through electron microscopy or XRD (Almuthn and Hibbitts 2018). The approximation of active crystallite size calculation is a geometrical assumption that is based on the shape of the crystallite having a regular geometry, with the ideal geometry being a sphere (Webb 2003).

This analysis makes use of an expression of grain geometry. Using the approximated regular geometry, the size (being the diameter) can then be computed in terms of volume and area (Webb 2003). The diameter computed is the average diameter of the active crystallite onto which hydrogen adsorption occurred. The significant economic advantages of using H₂ chemisorption in measuring particle size are that it is less expensive than TEM and XRD techniques, is fairly accurate, and measures particles of all sizes. However, it has disadvantages, as it is easily affected by contamination, there is metal support interaction and adsorption stoichiometry could vary with dispersion or metal loading (Mustard and Bartholomew 1981). The H₂ chemisorption method

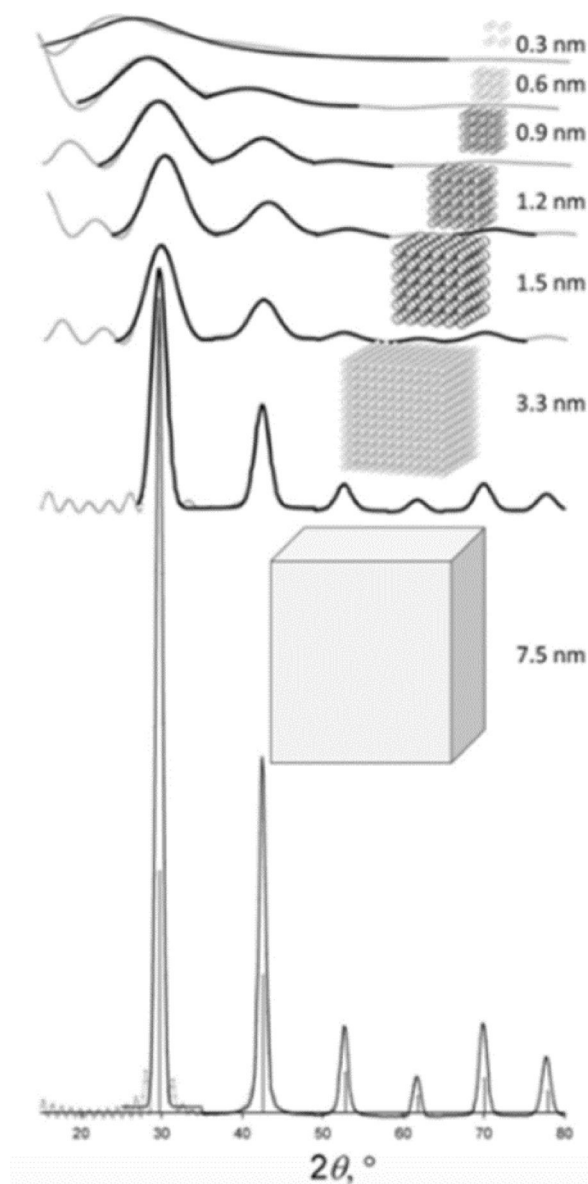


Figure 8. Diffraction curves of model particles with a cubic shape and a cubic unit cell structure. Particle size measurements are given in nm (Vorokh 2018).

also has other inherent difficulties that hinder its effective application, for example, in order for measurement by H₂ chemisorption to make sense, the probe gas should be adsorbed on the surface of the metal as a monolayer and gas desorption should be complete (Matyi et al. 1987).

Cobalt crystallite size determined by TEM, H₂ chemisorption and XRD

The crystallite sizes of cobalt-based catalysts are tabulated in Table 3. Various authors employed different preparation methods for the catalysts,

and distinct analytical techniques (TEM, H₂ chemisorption, and XRD) were utilized to determine the crystallite size. In comparing and computing differences obtained by using two or more methods for crystallite size determination, a statistical approach was employed to check for variations when specific techniques were applied. One-way ANOVA followed by post-hoc Bonferroni correction was used to analyze the results obtained from the literature.

Table 4 summarizes the one-way ANOVA results that compare different analysis methods used to determine crystallite size. A post-hoc Bonferroni correction test was performed to enable a comparison of the different techniques, and the results are tabulated. As shown in all the ANOVA tables, the P values are greater than 0.05 and F is less than F_{critical}, which provides strong evidence that the techniques yield almost similar measurements.

A one-way ANOVA, followed by a post-hoc Bonferroni correction test, indicated that any of the techniques (TEM, XRD and H₂ chemisorption) can be used to determine crystallite size with $P(T \leq t)$ two-tail values that are greater than an alpha value of 0.05, even after applying

the Bonferroni test (all are above 0.01666667). Any of the techniques discussed can be adopted to give measurements that are of statistical significance, as there are no differences within groups or any combination of techniques.

Cobalt catalyst reduction

Temperature-programmed reduction (TPR) is a technique applied in FT catalysis, with a catalyst precursor undergoing monitored reduction while the temperature is increased linearly with time. TPR studies of catalysts are a crucial step in FT technology as they produce the active catalyst. The method has been used extensively to study supported and unsupported catalysts, to extract qualitative information such as the oxidation state of the reducible species present (Jacobs et al. 2007; Jozwiak et al. 2007; Bao et al. 2009; Gorimbo 2018). The technique is highly sensitive to the presence of species in a reducible form and discussions on the sensitivity of the TPR profiles (peak shape, maximum temperature, resolution of reduction steps, etc.) have been published (Bosch et al. 1984; Malet and

Table 3. Cobalt crystallite size determined by TEM, H₂ chemisorption and XRD.

Co- based catalyst	Crystallite determination method (measurements in nm)			References
	TEM	H ₂ chemisorption	XRD	
Co/SiO ₂ -20	26	19.8	–	(A. M. Saib et al. 2002)
Co/SiO ₂ -40	3	5.9	–	
Co/SiO ₂ -60	6.7	6	–	
Co/SiO ₂ -100	6.9	7.3	–	
Co/SiO ₂ -150	8.3	10.6	–	
Co-silica ID	–	19.9	23.5	(Zhang et al. 2006)
Co-acetic acid	–	14.2	16.1	
Co-ethanol	–	19	22.3	
Co-1-propanol	–	15.6	18.2	
Co-1-butanol	–	14.9	16.5	
30% Co/SiO ₂	183	141	125	(Prieto et al. 2009c)
10% Co/ITQ(1)	12.8	10.4	12.5	
10% Co/ITQ(2)	8.2	8.9	9.9	
10% Co/ITQ(3)	–	7.3	9.1	
10% Co/ITQ(4)	6.3	5.6	6.8	
10% Co/ITQ(5)	–	–	5.9	(Cheng et al. 2018)
Cat-12 h	11.4	10.6	12.8	
Cat-8h	9.1	8.9	11	
Cat-4h	7.2	7.3	8.9	
Cat-1M	14.3	12.3	13.1	
HDP11	30	25	–	(G. Leendert Bezemer et al. 2006)
HDP9	14	12.5	–	
IWN13	7.5	8.5	–	
IEN4	3.6	4.4	–	
IWA1	3.7	6.1	–	
5Co/M	3	–	5	(Li et al. 2006)
10Co/M	4.5	–	11	
15Co/M	6.5	–	14	

Table 4. Analysis of variance (ANOVA): single factor.

Summary						
Groups	Count	Sum	Average	Variance		
TEM vs H ₂ Chemisorption	18	72.1	4.00555556	92.5923203		
TEM vs XRD	11	82.7	7.51818182	285.787636		
XRD vs H ₂ Chemisorption	14	41.8	2.98571429	14.6551648		
ANOVA						
Source of variation	SS	df	MS	F	P-value	F crit
Between groups	136.483561	2	68.2417803	0.59052311	0.55879474	3.23172699
Within groups	4622.46295	40	115.561574			
Total	4758.94651	42				
t-Test: Two-sample assuming equal variance						
	TEM vs H ₂ chemisorption		TEM vs XRD			
Mean	4.00555556		7.51818182			
Variance	92.5923203		285.787636			
Observations	18		11			
Pooled variance	164.146141					
Hypothesized mean Difference	0					
df	27					
t Stat	−0.7163911					
P(T<=t) one-tail	0.2399505					
t Critical one-tail	1.70328845					
P(T<=t) two-tail	0.47990099				0.01666667	FALSE
t Critical two-tail	2.05183052					
t-Test: Two-sample assuming equal variance						
	TEM vs H ₂ chemisorption		XRD vs H ₂ chemisorption			
Mean	4.00555556		2.98571429			
Variance	92.5923203		14.6551648			
Observations	18		14			
Pooled variance	58.8195529					
Hypothesized mean Difference	0					
df	30					
t Stat	0.37316165					
P(T<=t) one-tail	0.355826					
t Critical one-tail	1.69726089					
P(T<=t) two-tail	0.711652				0.01666667	FALSE
t Critical two-tail	2.04227246					
t-Test: two-sample assuming equal variance						
	TEM vs XRD		XRD vs H ₂ chemisorption			
Mean	7.51818182		2.98571429			
Variance	285.787636		14.6551648			
Observations	11		14			
Pooled variance	132.538848					
Hypothesized mean Difference	0					
df	23					
t Stat	0.97713251					
P(T<=t) one-tail	0.16933498					
t Critical one-tail	1.71387153					
P(T<=t) two-tail	0.33866996				0.01666667	FALSE
t Critical two-tail	2.06865761					

Bonferroni post hoc test.

Caballero 1988; Fierro et al. 1994; Christel et al. 1997; Giordano et al. 2000).

The TPR technique has been used as a successful fingerprint method for characterizing FT catalysts - mainly cobalt and iron. This section focuses on the cobalt-based catalyst in FTS only.

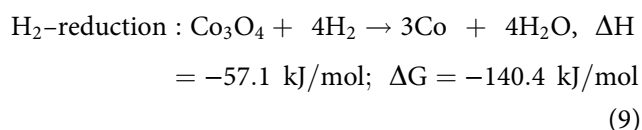
Several factors that influence the TPR profile have been studied, and sample weight, hydrogen concentration, carrier flow rate, total hydrogen consumption, and heating rate tend to have a greater degree of influence (Bosch et al. 1984). The conditions reported in the literature differ

widely; as a result, it is challenging to compare TPR profiles obtained by different researchers (Figure 9).

TPR with hydrogen is a commonly used technique for characterizing catalysts in FTS reactions. An in-depth understanding of the accurate reduction pathway of the FTS catalyst is an important piece of information. In the case of the cobalt-based catalyst, Co_3O_4 undergoes reduction to Co in two steps, with CoO being the intermediate species regardless of support type (SiO_2 , TiO_2 , and Al_2O_3) (Xiong et al. 2005; Jacobs et al. 2007; Kliewer et al. 2019). Using hydrogen (H_2) as the reduction gas yields two different reduction regions, as shown in Figure 9.

Various reducing agents have been used in FTS, including hydrogen, CO and syngas (Gorimbo 2016). In the case of hydrogen, the degree of reduction is determined by monitoring H_2 consumption while increasing the sample temperature at a constant rate. As a result, the reduction profiles are obtained at different temperatures. An elevated temperature is sometimes necessary for reduction, such as when strong metal-support interaction is experienced (Jacobs et al. 2007).

The stoichiometry of Equation (9) suggests that 1 mole of Co_3O_4 yields 4 moles of H_2O during reduction.



Co_3O_4 reduction to CoO consumes 1 mole of hydrogen and then reduces to metallic Co using

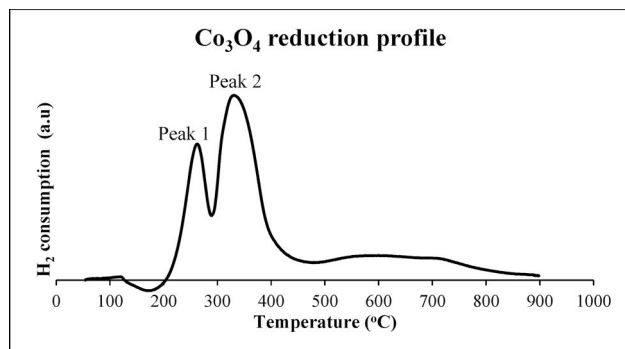
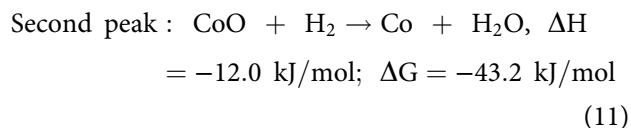
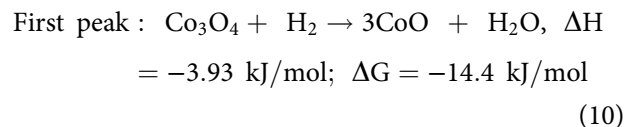


Figure 9. The pattern represents the TCD signal resulting from Co_3O_4 reduction in hydrogen for a cobalt-based catalyst (Gorimbo et al. 2020).

1 mole of H_2 - see Figure 10.



Thermodynamics of Co-based catalysts reduction

Gibbs free energy and enthalpy of the reaction system at specific temperature and pressure levels have been used to plot the mass balance-attainable region of the FT system (Gorimbo et al. 2020), while standard energies are provided in Equations 9–11. Gibbs free energy gives the work potential of the given scenario, while enthalpy presents the minimum reaction energy requirements of the system. So, $+\Delta H$ values indicate that work and energy should be supplied to the reaction system, whereas $-\Delta H$ values indicate that work and energy are released by the system. Pressure deviations are not considered significant in terms of enthalpy and Gibbs free energy at the temperature levels studied.

$$\Delta H^0 = \Delta H_0^0 + R \int_{T_0}^T \frac{\Delta C^0}{R} dT \quad (12)$$

Where ΔH^0 and ΔH_0^0 are heat of formation of the components at temperature T and reference temperature T_0 . The heat capacity term at temperature T is given by Equation (13).

$$\frac{\Delta C_p^0}{R} = A + BT + CT^2 + DT^{-2} \quad (13)$$

Where A, B, C, and D are heat transfer coefficients. Integrating Equations (11) and (12) to get ΔH^0 at temperature T gives Equation (13), where $T = \frac{T}{T_0}$

$$\begin{aligned} \Delta H^0 = \Delta H_0^0 + R \left[\Delta A * T_0 * (T-1) + \frac{\Delta B}{2} * T_0^2 * (T^2-1) \right. \\ \left. + \frac{\Delta C}{3} * T_0^3 * (T^3-1) + \frac{\Delta D}{T_0} * \left(\frac{T-1}{T} \right) \right] \end{aligned} \quad (14)$$

ΔG at various temperatures can be calculated using Equation (14). (15) (Smith et al. 2018).

Larger pores correspond to the formation of larger Co_3O_4 crystallite with decreased dispersion. Different pore sizes exhibited by supports result in varying CO adsorption properties. Supports with a pore size in the range of 6–10 nm have been shown to result in better FT activity and more selectivity to the desired C_{5+} . This observation is attributed to moderate crystallite size and CO adsorption on the catalyst (Song and Li 2006).

Effect of promoters on crystallite size

In FT, promoters are chemical additives that enhance the physical, chemical and catalytic properties of the catalyst. In a study done by Jacobs et al. (2002) reduction temperature was significantly reduced by incorporating small amounts of Ru and Pt during the synthesis of a cobalt-based catalyst. Adding Mn has been shown to enhance metal cluster dispersion, which results in a smaller average size of cobalt crystallite (Sukkathanyawat et al. 2015). Mn also influences FTS product distribution by promoting the formation of long-chain hydrocarbon on a cobalt-supported catalyst (Sukkathanyawat et al. 2015). Morales et al. (2007) reported that MnO species cause positive structural and electronic modification of the catalyst, resulting in improved FT catalytic performance. Morales et al. (2007) also observed that the water gas shift (WGS) reaction was catalyzed by MnO, which adjusts the H_2/CO ratio and alters overall FT catalytic performance. Alkali metals are also useful as FT catalyst chemical promoters, as they affect activity and selectivity. Performance evaluation of the $\text{Co}/\text{Al}_2\text{O}_3$ catalysts promoted Li, Na, K, Rb and Cs resulted in enhanced C_{5+} selectivity (Gholami et al. 2021). Generally, the literature provides definitive evidence that promoters facilitate Co reducibility at a lower reduction temperature than non-promoted catalysts. Several detailed reviews and work on the effect of promoters are available (Shimura et al. 2015; Yang et al. 2022).

Concluding remarks

The literature analysis indicates that the catalytic properties of small cobalt particles (<6nm) differ

from those of larger ones (>6nm) in FT synthesis. Oxidation of cobalt particles less than 6 nm in diameter can be minimized by correctly adjusting the hydrogen and water partial pressure in the FT reactor. The crystallite diameter of cobalt particle size appears to be a parameter of influence in controlling speciation by oxidation of the cobalt catalyst. From the literature surveyed, the general conclusion is that cobalt crystallite size significantly affects product selectivity. Cobalt crystallite with a size of <6–8 nm tends to favor the formation of methane and reduce C_{5+} selectivity. C_{5+} products are the most sought-after product nowadays; hence its increased selectivity is ideal.

H_2 adsorption is the most convenient, accurate and generally applicable technique for estimating the average crystallite size of several FT catalysts. However, TEM is a precise technique for measuring the average crystallite size and the distribution of the size of the metal catalysts in FT. XRD is widely used in FT to determine crystallite size, although it is generally insensitive to small metal particles that are <3 nm. It is apparent that no single method fully characterizes crystallite size and distribution in supported metal catalysts in the absence of inherent theoretical shortcomings, uncertainty in the experimental approach and ambiguity in the interpretation of results. Therefore, it is ideal to use multiple techniques whenever possible to validate the readings obtained.

There are still challenges in precisely controlling the crystallite size at the nanoscale this demands advanced synthesis methods to ensure easy synthesis, uniformity and reproducibility. Another challenge is attributing FT activity to initial crystallite size. Therefore there is a need to capture and comprehend dynamic changes in crystallite size during different stages of FT reaction, this requires sophisticated in-situ characterization techniques. The interaction between cobalt crystallites and catalyst supports adds complexity. Optimizing this interplay to enhance stability and catalytic activity is an ongoing challenge.

Demonstrating the impact of particle or crystallite size at the laboratory scale is just the beginning. The translation of these findings to industrial-scale reactors presents additional

challenges due to limitations in heat and mass transfer, reactor design considerations, and potential catalyst deactivation effects. Therefore, it is crucial to understand the scalability of particle size effects for practical implementation.

Perspectives:

1. Debunking the impact of particle and crystallite size in cobalt-based Fisher-Tropsch synthesis presents a crucial opportunity to deepen our fundamental understanding of the underlying mechanisms governing catalytic reactions. This understanding can greatly aid in designing more efficient and selective catalysts for industrial applications. By acquiring knowledge of the underlying processes that govern catalytic reactions, it becomes possible to optimize and improve the performance of catalysts for specific applications. Therefore, this study represents an important step toward the development of more effective and efficient catalytic processes, which can help to drive industrial innovation and progress.
2. The study of particle and crystallite size impact on catalyst optimization is crucial for identifying the optimal catalyst sizes that maximize desired product selectivity or improve activity. This knowledge is invaluable in the development of more efficient and cost-effective cobalt-based Fischer-Tropsch catalysts. By utilizing the insights gained from this study, it is possible to guide the development of optimized catalysts that will lead to higher product yields, lower costs, and increased sustainability.
3. Process intensification is a crucial aspect of chemical engineering, and understanding the role of particle/crystallite size can significantly aid in developing strategies for process intensification. By designing catalysts with tailored properties, it may be possible to achieve higher conversion and selectivity within smaller reactor volumes, especially if smaller particles exhibit higher activity. Therefore, particle/crystallite size should be a key consideration in the design of catalysts and reactors to achieve optimal process intensification.
4. The stability of a catalyst plays a crucial role in industrial and academic settings. The impact of particle/crystallite size on catalyst stability is a subject of significant research, as it provides valuable insights into potential deactivation mechanisms. Investigating this impact enables the identification of ways to enhance catalyst longevity by mitigating particle sintering, maintaining active site accessibility, or improving resistance to catalyst poisons. These insights can help design more robust catalysts and contribute to the development of efficient and sustainable chemical processes.
5. Catalyst design and engineering: Insights gained from studying particle/crystallite size effects can contribute to more rational catalyst design and engineering. Optimizing particle sizes, surface structures, and interactions can lead to enhanced catalytic performance and overall process efficiency.
6. Finally, the integration of cutting-edge techniques such as in-situ microscopy and spectroscopy offers a promising perspective for unraveling real-time changes in crystallite size during Fischer-Tropsch reactions.

The perspectives presented in this study highlight the potential for gaining fundamental knowledge, optimizing catalysts, improving process intensification, enhancing catalyst stability, and enabling rational catalyst design and engineering. Therefore, it is essential to consider these perspectives when exploring cobalt-based Fischer-Tropsch synthesis and its potential applications.

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Disclosure statement

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