



Application of Machine Learning in Analysis of the Effects of Co/SiO₂ Catalyst Surface Area on CO Conversion during Fischer Tropsch Synthesis

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Abstract. Cobalt is one of the most common catalysts used in the Fischer-Tropsch (FT) process and the primary catalyst investigated in this study. Machine learning (ML) was used to analyze the variables that affect the FT process. This study investigates how surface area impacts CO adsorption and hydrocarbon product diffusion under dynamic reaction conditions such as temperature or pressure. 410 data points were collected from publications involving Co catalysts where 36 key input parameters related to the feed gas, catalyst properties, pretreatment, and reaction conditions were investigated to predict the CO conversion during the FT process. Random Forest algorithm was used for both feature importance analysis and regression tasks. An optimum surface area in the range of 430 - 450m²/g resulted in the highest CO conversion. The observed trends and prediction models can help design more selective catalysts for CO conversion via FT process and provide a guide in identifying the key descriptors in the Co catalyst design and operating conditions to enhance the CO conversion.

Keywords: Surface area, Catalyst, Machine learning

1 Introduction

The Fischer-Tropsch synthesis (FTS) process has long been a cornerstone of industrial chemistry for converting synthesis gas (CO and H₂) into hydrocarbons, making it crucial for producing synthetic fuels and chemicals from biomass, coal, and natural gas [1]. Cobalt-based catalysts supported on silica (Co/SiO₂) are among the most widely used and effective catalysts in FTS, due to their high activity, selectivity for long-chain hydrocarbons, and resistance to deactivation under FTS operating conditions [2].

The performance of cobalt-supported catalysts in FTS is strongly influenced by the surface area of the catalyst, which directly correlates with the number of active sites available for CO adsorption and subsequent hydrogenation [3]. However, catalyst

surface area is not the only factor that affects CO conversion; the performance of Co/SiO₂ catalysts is also influenced by a multitude of other parameters, such as catalyst particle size, cobalt dispersion, metal loading, pore size, the reducibility of cobalt oxides, and various reaction conditions including temperature, pressure, and the H₂/CO ratio [4]. The complex, nonlinear interactions between these variables make it challenging to predict catalytic performance and optimize catalyst formulations using traditional methods, which typically involve trial-and-error experimental procedures.

ML has emerged as a powerful tool for predicting catalyst performance by leveraging large datasets to uncover hidden relationships between input parameters and reaction outcomes [5]. ML approaches offer significant advantages over traditional modeling techniques, as they can process large amounts of data, account for nonlinear interactions, and provide accurate predictions based on a compilation of experimental results [6]. In this study, machine learning was employed to predict CO conversion and other performance metrics as a function of catalyst properties and reaction conditions, mainly focusing on the effects of the surface area of the SiO₂ support, offering a more systematic and data-driven approach to catalyst optimization.

The findings highlight the potential of ML as a tool for accelerating the development of highly efficient cobalt-based catalysts for FTS, improving both the process economics and the environmental sustainability of synthetic fuel production.

2 Methodology

In order to determine what range of silica surface area values during FT synthesis and composition of the catalyst will be optimal for the maximum CO conversion in this work, experimental results based on work done on cobalt catalyst supported on silica for the past ten years were compiled, 36 parameters were used. Their relative contribution towards CO conversion was investigated. The benefit of using silica as the study's basis is that it can be synthesized using various techniques (such as hydrothermal and sol-gel), which allows researchers to systematically examine how surface area affects catalytic activity and hydrocarbon selectivity [7].

Moreover, silica has a well-known and straightforward surface chemistry that is mostly made up of siloxane bridges (Si–O–Si) and silanol groups (Si–OH), this makes it easier to functionalize or modify the surface to investigate the role of surface area and surface chemistry in CO adsorption and catalytic activity [8]. ML was applied to a dataset comprising 410 data points and 36 input parameters collected from various Co/SiO₂ publications to predict the effects of catalyst surface area and other variables on CO conversion during the FTS process. The 36 input parameters included a broad range of catalyst characteristics (such as cobalt particle size, surface area, pore size, and metal loading) as well as reaction conditions (including temperature, pressure, gas flow rates, and the H₂/CO ratio), making this dataset a comprehensive representation of the factors that influence FTS performance. A random forest machine learning algorithm was employed to develop predictive models based on the various input parameters that affect CO conversion. Cross-validation was carried out with $cv = 5$ to prevent overfitting and ensure the robustness of the model's predictions. A two-way partial dependence

analysis using `sklearn.inspection`, integrated with the Random Forest model, was used to estimate the model's predictions by averaging over the distribution of all other features while varying the selected features of interest.

3 Results and discussion

The distribution of the catalyst pore size and pore volume as the surface area increases were analyzed, as shown in Fig. 1, indicating that there is an inverse relationship between the surface area and the catalyst pore size and a direct relationship between the catalyst surface area and the silica pore volume. In Fig 1a, the dominant pore size is below 15 nm, as indicated by the dark-colored dots, whereas Fig 1b shows a range of 0.6 to around 1.3 cm^3/g as the predominantly used pore volume. The inverse relationship between pore volume and surface area holds because a larger surface area often corresponds to a greater number of silica pores or a more extended internal surface structure, increasing the total pore volume [10]. Higher CO conversions were mostly observed at around $300 \text{ m}^2/\text{g}$ – $450 \text{ m}^2/\text{g}$ and a pore volume of around 10 nm, however, due to the complexity of the FT process, the dependence on one or two variables could not explicitly show the impact on the CO conversion.

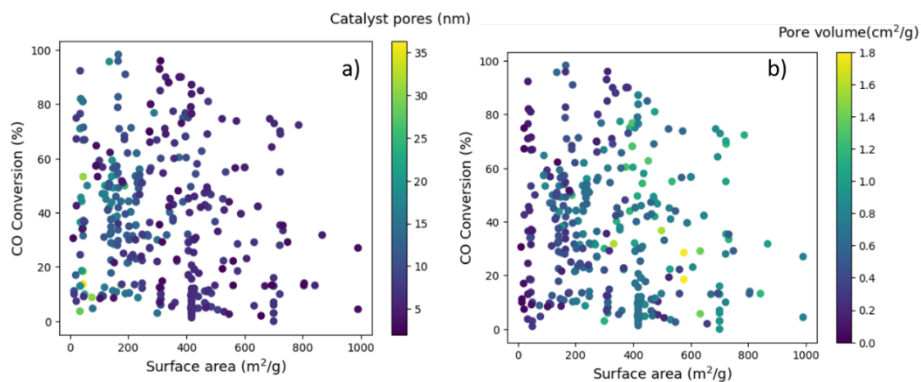


Fig. 1. a) Partial dependence of CO conversion on surface area and catalyst pore width, b) Partial dependence of CO conversion on surface area and catalyst pore volume

3.1 Data analysis and evaluation of parameters

It was imperative to identify the significant parameters influencing the CO conversion and assess the ability of Random Forest to predict the trends from the input variables. There was a fair positive correlation with an R^2 value of 0.67 between the predicted CO conversion and actual experimental values, see Fig 2. This low R^2 value shows that the RF model is not capturing all of the patterns; this could be caused by the complexity of the FT process and the limitation in the input variables used for this study. However, expanding the input variables to include the atomic and electro properties of metals and promoters would be expected to improve the correlation.

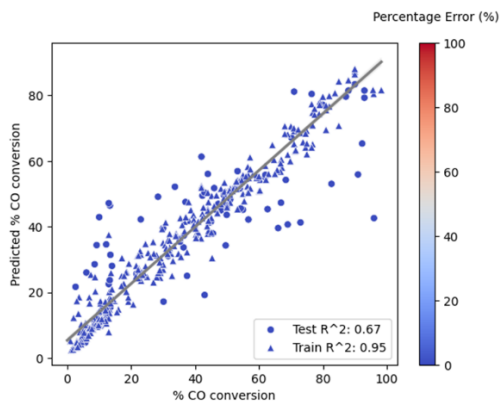


Fig. 2. Random forest regression prediction values of CO conversion

The RF model was used to carry out a feature importance analysis of the dependent variables used in the study. Fig 3 shows all the input parameters used against the respective relative feature importance. There is such a big distinction in the influence of the components, with the top 15 components having a contribution of almost 80% of the variance and the remaining 20%, which mainly consists of the catalyst promoters. The analysis showed that catalyst loading percentage, crystallite size, reaction temperature, surface area, and pore size were the top five parameters influencing CO conversion during Co/SiO₂-catalyzed FT reactions.

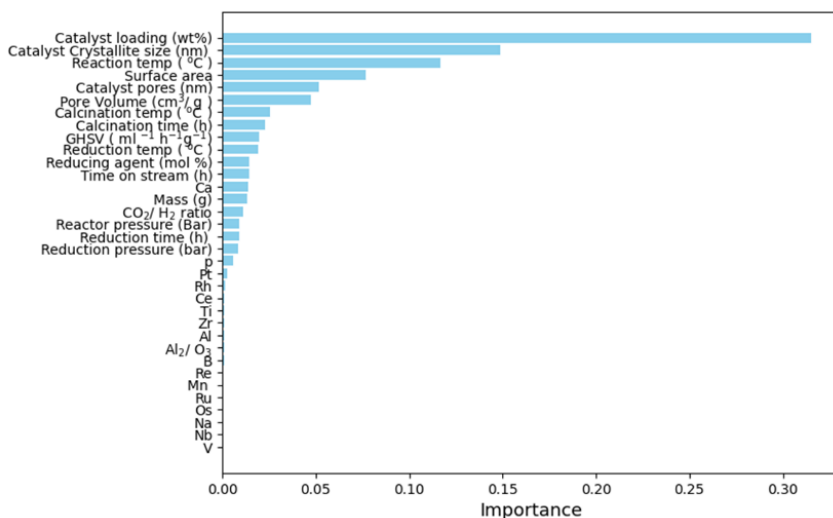


Fig. 3. Feature importance of the input parameters

3.2 Two-way partial dependence of the CO conversion on top 5 most influential parameters

The Partial Dependence Plot in machine learning is a graphical illustration that shows the effects caused by one or two input features on the predicted outcome, showing whether the relationship between the target features will be linear, monotonic, or complex. [10]. In Fig 4a, there is generally a higher dependence of CO conversion on surface area in the range 100 – 450 m²/g within a temperature range of 175 °C to 225 °C after which an even further increase in the dependence is observed on temperatures higher than 225 °C. After 450 m²/g, a drop in activity was observed, suggesting surface area becomes independent of temperature. The greatest values of CO conversion on surface area and reaction temperatures were observed at a surface area of around 450 m²/g and a temperature of 230 °C at which a peak is observed, and it decreases to a steady value thereafter. Lower temperatures have a lesser dependence on the surface area towards CO conversion. However, increasing the temperature above 230°C would also cause a drop on influencing the CO conversion. Dry suggested that in FTS, optimal CO conversion typically occurs in the temperature range of 200 – 250 °C for Co-based catalysts; below this range, the reaction slows considerably due to insufficient activation energy [1]. On the other hand, although high temperatures increase reaction rates, when it becomes too high, the sintering of cobalt particles is promoted, reducing surface area, increasing methane production (via methanation), and accelerating carbon deposition, leading to catalyst deactivation and lower CO conversion. It was also observed that very high surface areas above 450 m²/g have a generally low dependence on reaction temperature towards the CO conversion and that there is a gradual decrease in the dependence as the surface area further decreases below the value of 450 m²/g. This observation is attributed to the decline in the number of available active sites, because catalysts with lower surface areas are less prone to sintering at high temperatures, as they typically contain larger cobalt particles that are more thermally stable hence, the overall number of active sites is lower, limiting CO conversion regardless of the reaction temperature [11].

In Fig 4b, there is a general increase in the dependence of CO conversion on the surface area from 20 – 450 m²/g after which there is a steep drop to a generally constant value. There is also a general increase in the dependence on crystallite size as the size increases to 7.5 nm after which it becomes constant; the maximum CO conversion on the surface area and crystallite sizes is observed at a surface area of around 450 m²/g against a crystallite size in the range of 10 to 17.5 nm. Very small crystallite sizes do not have a significant dependence on the surface area towards CO conversion since they exhibit weaker interaction with the silica support, leading to metal size reduction and migration. This effect is exacerbated in high-surface-area supports, where small particles are prone to sintering or agglomeration at high temperatures during FTS, reducing the number of active sites and lowering CO conversion [12]. The smaller the crystallite, the higher its likelihood of oxidation, thus reducing the catalyst's ability to convert CO [13]. The optimum surface area that can yield a high dependence of CO

conversion on the crystallite size is between 350 and 450 m^2/g . In Fig 4c generally, there is a relatively high dependence observed on catalyst loading, it can also be noted that a similar trend is observed on the surface area as to what is observed in Fig 4a and b that at 450 m^2/g there is a sharp decrease in the dependence on the catalyst loading with the maximum occurring at 430 – 450 m^2/g , then, there is a general increase in the dependence as the catalyst loading increases from 2 percent to 10%. The reason for the low dependence of CO conversion on low metal loadings, even with large surface areas, is that there is insufficient active metal available to achieve high CO conversion, even if the dispersion is good. Furthermore, for most of the research, which was conducted with a metal loading of 10 - 20% catalyst loading, we can observe that there is a higher dependence on the surface area due to an increase in the number of active sites available. In Fig 4d, from the dependence of the surface area and catalyst pore size we can observe almost the same general trend on the surface area axis as that observed with the crystallite sizes partial dependence graph. There is also a low dependence of CO conversion on very small pore sizes. Generally, too small pores lead to poor diffusion of reactants and products, resulting in reduced CO conversion due to mass transfer limitations, poor cobalt dispersion, and pore blockage by long-chain hydrocarbons [14] On the other hand, while they alleviate diffusion limitations, too large pores do lead to poor cobalt dispersion and lower surface area, ultimately decreasing the number of active catalytic sites and reducing CO conversion.

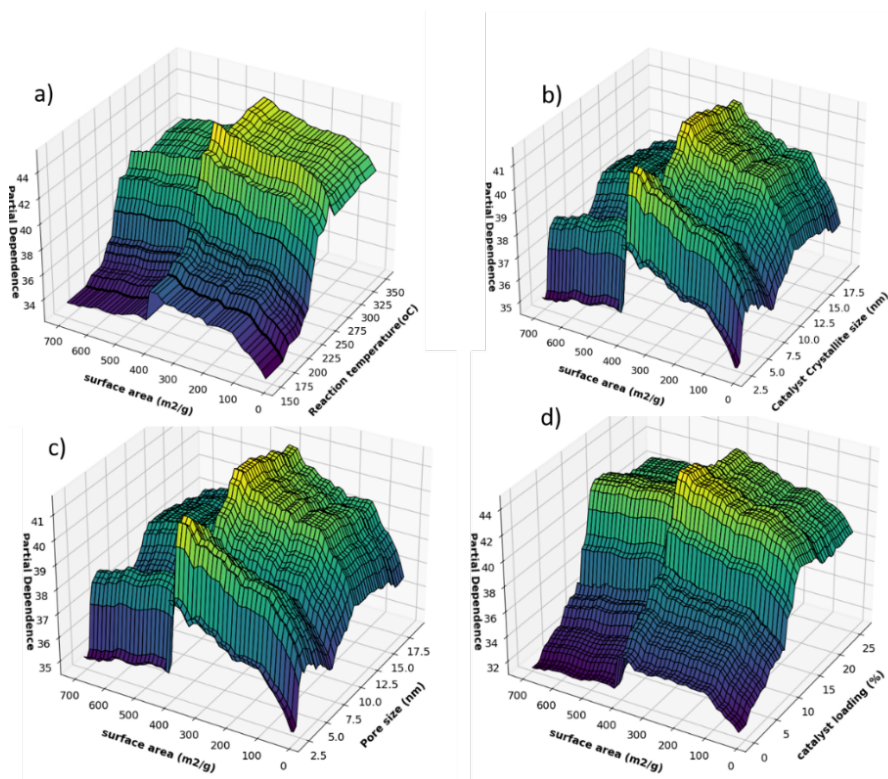


Fig. 4. Three-way Partial dependence plots of CO conversion on surface area and the other top four most important parameters

4 Conclusion

It was observed that the CO conversion depends on several parameters, the most prominent being the metal loading, crystallite size, surface area, reaction temperature, and catalyst pore size. In Co/SiO₂-catalyzed FTS, very small surface areas lead to poor cobalt dispersion, diffusion restrictions, and larger particle sizes, all of which reduce CO conversion rates. Large surface areas, however, can potentially cause issues like excessive cobalt oxidation and difficulty in pore accessibility, even though they promote CO conversion and cobalt dispersion. Therefore, to maximize CO conversion and guarantee long-term catalyst performance in FTS, silica support surface area optimization is essential. From this study a normal range of the surface area that would give high CO conversion was found to be 430–450 m²/g. These findings can be useful in FT catalyst design during synthesis as well as predicting a certain catalyst surface area range for required CO conversions which can be used in process flowsheeting during industrial scale operations. The authors recommend further studies to be carried out using an extended dataset of maybe three or four times as many as these 410 data points used to increase the predictive accuracy of the model. Lastly, the findings should be validated experimentally.

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References

1. Dry, M. E. (2002). The Fischer-Tropsch process:1950-2000. *Catalysis Today*,71(3-4), 227-241.
2. Iglesia, E. (1997). Design, synthesis, and use of cobalt-based Fischer-Tropsch synthesis catalysts. *Applied Catalysis A: General*, 161(1-2), 59-78.
3. Bezemer, G. L., et al. (2006). Cobalt particle size effects on the activity of Co/SiO₂ .Catalysts in Fischer-Tropsch synthesis. *Journal of Catalysis*, 237(1), 152-161.
4. Prieto, G., et al. (2011). Cobalt particle size effects in Fischer-Tropsch synthesis: Structural and mechanistic aspects. *Journal of Catalysis*, 271(2), 191-198.
5. Jablonka, K. M., et al. (2020). Machine learning in catalyst discovery and design: From evolutionary to data-driven approaches. *ACS Central Science*, 6(8), 1317-1330.
6. Yang, K., et al. (2019). Predicting heterogeneous catalysis reaction outcomes using machine learning. *Nature Communications*, 10(1), 1-9.
7. Bezemer, G. L., et al. (2006). Cobalt particle size effects on the activity of Co/SiO₂ catalysts in Fischer-Tropsch synthesis. *Journal of Catalysis*, 237(1), 152-161
8. Christensen, C. H., Johannessen, T., Sørensen, R., & Schmidt, I. (2006). Fischer-Tropsch synthesis: a microemulsion-based preparation of H₂ reduction-promoted Co/SiO₂ catalysts with very small Co particles. *Catalysis Today*, 114(2-3), 141-144.

9. Zhao, D., et al. (1998). Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. *Science*, 279(5350), 548-552.
10. Friedman, J. H. (2001). Institute of Mathematical Statistics. *The Annals of Statistics*, 29(5), 1189–1232. <https://www.jstor.org/stable/2699986>
11. Davis, B. H. (2003). Fischer-Tropsch synthesis: comparison of performances of iron and cobalt catalysts. *Catalysis Today*, 84(1-2), 83-98.
12. Zhang, Y., et al. (2006). Influence of cobalt particle size on the catalytic performance of Co/SiO₂ for Fischer-Tropsch synthesis. *Journal of Catalysis*, 238(1), 60-70.
13. Schanke, D., et al. (1995). Fischer-Tropsch synthesis on cobalt catalysts: The influence of support, cobalt loading, and crystallite size. *Journal of Catalysis*, 156(1), 85-95.
14. Xu, L., et al. (2010). Effect of pore size on the catalytic properties of mesoporous silica supported cobalt catalysts for Fischer-Tropsch synthesis. *Applied Catalysis A: General*, 384(1-2), 131-139.

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