



Towards Sustainable Fuels from Fischer-Tropsch Synthesis

Zahra Teimouri*

Department of Chemical Engineering, McMaster University, Canada

Abstract

Fischer-Tropsch Synthesis (FTS) is a non-crude oil-based technique for conversion of syngas to a wide range of hydrocarbons including light olefins, and liquid transportation fuels. Syngas, which is a combination of H₂ and CO gases can be produced through natural gas reforming, biomass or coal gasification processes. FTS is a catalytic polymerization reaction, therefore rational design of the catalyst including active sites, support and promoters plays a significant role in improving the selectivity of the process to desired range of products. This mini review presents a summary of the different catalyst designs in FTS to synthesize light olefins or heavier hydrocarbons. Iron and cobalt are the industrially used active metals for FTS, due to the lower price and higher hydrogenation activity, respectively. Supports are a key factor in designing efficient FTS catalysts, which provide mechanical, thermal strength for the active sites and a high surface area for dispersion of the active metal particles. Herein we discuss two categories of the widely used support material for FTS: metal oxide supports and carbon materials. Another significant element in formulating a high-performance catalyst for FTS process is the promoters, which can be divided into electronical and structural promoters. This work highlights the roles of active metal, support and promoters in understanding the structure-activity correlations to design high-performance FTS catalysts for production clean and sustainable fuels.

Keywords: Fischer-Tropsch synthesis; Light olefins; Liquid fuels; Catalyst design; Active metal; Support materials; Promoter; Sustainable fuels

Introduction

Increase in the world's population and global warming have motivated scientists and industries to seek for renewable and sustainable energy resources instead of fossil fuels. Fischer-Tropsch Synthesis (FTS) is one of the non-crude oil-based technologies, which converts syngas to a wide range of hydrocarbons with almost zero amounts sulfur and aromatics [1]. During last decades, FTS has drawn much attention because of: higher operational costs of the crude-oil-based technologies for fuel production, increased number of the discovered natural gas fields around the world, fluctuations in the price of the crudeoil and environmental obligations for CO_2 -neutral fuels production [2,3]. Syngas is produced through natural gas reforming, biomass or coal gasification followed by purification step before entering to FTS reaction [4,5]. FTS is a catalytic polymerization reaction, which syngas molecules are converted to monomers and initiators on the surface of the catalyst, the monomers then polymerize to produce a variety of hydrocarbons such as paraffins, olefins, wax and oxygenates. The reaction that are involved in this process are summarized in Table 1. Catalyst design is one of the fundamental steps in FTS to improve the selectivity of the desired products, which will be discussed in the following parts.

Table 1: Involved reactions in Fi	scher-Tropsch Synthesis (F	FTS).
-----------------------------------	----------------------------	-------

Reaction	Equation
Paraffins	$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$
Olefins	$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$
Water gas-shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$
Oxygenates	$nCO + 2nH_2 \rightarrow H(CH_2)_nOH + (n-1)H_2O$
Boudouard	$2CO \leftrightarrow CO_2 + C$

ISSN: 2637-8035



*Corresponding author: Zahra Teimouri, Department of Chemical Engineering, McMaster University, Canada

Submission: H March 11, 2024 Published: H March 22, 2024

Volume 6 - Issue 2

How to cite this article: Zahra Teimouri*. Towards Sustainable Fuels from Fischer-Tropsch Synthesis. Progress Petrochem Sci. 6(2). PPS. 000632. 2024. DOI: 10.31031/PPS.2024.06.000632

Copyright@ Zahra Teimouri, This article is distributed under the terms of the Creative Commons Attribution 4.0 International License, which permits unrestricted use and redistribution provided that the original author and source are credited.

Active Metals

Among transition metals, only Fe, Co, Ni and Ru have capability of CO hydrogenation. Ru as one of the active metals for FTS, can produce long chain hydrocarbons at lower operation temperatures. But higher price of this metal along with its limited sources has prevented the industrial application Ru in FTS. Ni is another candidate for CO hydrogenation reaction, which leads to high selectivity to methane instead of more economically feasible products such as light olefins and liquid hydrocarbons [6]. Therefore, Co and Fe are the only suitable candidates for industrial application in FTS process. Fe has a relatively lower price, Water Gas-Shift (WGS) activity, abundant availability, and capable of being operated at different temperatures and pressures for synthesis of lighter olefins and oxygenates. On the other hand, Co has higher price compared to Fe and CO hydrogenation capability, but it can only be employed at lower operating temperatures (230-250 °C) for production of mainly linear paraffins [7].

Support Materials

Support materials in heterogeneous catalysis are employed to provide a high surface area for dispersion of active sites, stabilizing active phase under harsh reaction conditions and improving mechanical and thermal strength for the active sites, which also facilitate mass and heat transfer during reaction. Therefore, catalyst support can play a key role in the activity and selectivity of the FTS. Two classes of the widely used supports for FTS process are refractory metal oxides and carbon materials. Metal oxides such as Al₂O₃, SiO₂, TiO₂, ZrO₂, etc. with high thermal strength and acidic surface properties can lead to the high metal-support interactions, decreasing the agglomeration possibility of the active sites during reaction, hampering deactivation of the catalyst [8]. On the other hand, high metal-support interactions result in the difficult reduction of the active sites, which can negatively affect the selectivity of the process. Another class of the common support materials for FTS catalysts is carbonaceous materials, which due to the higher surface areas, suitable porous structure, versatile surface chemistry and stability at high-temperature reaction conditions have drawn interest in FTS. Unlike metal oxide supports, carbon materials lead to the weaker metal-support interactions, which can facilitate the reduction of the active sites [9]. Various types of carbon materials consist of graphite, carbon black, Activated Carbon (AC), Carbon Nanotube (CNT), carbon fibers, Ordered Mesoporous Carbon (OMC) and Carbon Encapsulated Metal Nanoparticles (CEMNPs) that have been employed as support of Fe- and Co-based FTS catalysts. Physicochemical properties of the catalyst support play a significant role in improving performance of FTS, which can be achieved by tailoring the textural characteristics and surface chemistry of the catalyst support.

Promoters

Promoters are added to the formulation of FTS catalysts in small loadings to improve the structural and chemical properties of the active sites. While structural promoters decrease the agglomeration of the active sites by improving their dispersion, electronical promoters impact the intrinsic activity of the active sites, altering 631

Alayat A et al. [10] concluded that the that promotion of Fe catalyst with Cu, Mo, Co and Ru shifted the selectivity of the process to olefins and paraffins instead of the aromatics. Promoting Fe catalyst with K is reported to strengthen the Fe-C bond, while weakening the Fe-H and C-O bond by increasing the electron density on Fe sites. K also has a positive effect on surface basicity of the FTS active sites shifting selectivity of the process to heavier hydrocarbons [11].

Conclusion

Fischer-Tropsch synthesis provides a sustainable route for converting carbon-rich feedstocks to liquid fuels and light olefins with almost zero amounts of sulfur, nitrogen and aromatics, considered as clean fuels. In this process, a wide range of hydrocarbons from methane to heavier waxes are produced simultaneously through a catalytic polymerization reaction. Three key elements in designing an efficient catalyst for FTS are active metal, support and promoters. Fe and Co are the only economically feasible active sites for FTS with high selectivity to light olefins, and longer chain paraffins, respectively. Support material on the other hand can provide a high surface area for dispersion of the active sites, improving their thermal and mechanical strength during FTS. Promoters also are added in small amounts to the catalyst formulation to improve the structural characteristics and intrinsic activity of the active sites. By modifying the physicochemical properties of catalysts, including engineering active sites, catalyst support and promoters; high-quality sustainable liquid fuels and light olefins can be achieved from FTS process.

References

- Teimouri Z, Abatzoglou N, Dalai AK (2023) Green synthesis of Cu-Mo promoted Fe catalyst for production of the gaseous and liquid fuels through fischer-tropsch synthesis. Energy Convers Manag 286: 117079.
- Vosloo AC (2001) Fischer-tropsch: A futuristic view. Fuel Process Technol 71(1-3): 149-155.
- Teimouri Z, Abatzoglou N, Dalai AK (2023) Computational fluid dynamics simulation of fischer-tropsch synthesis coupled with a novel reaction kinetics using trimetallic catalyst over a biomass-based support. Energy Convers Manag 296: 117659.
- Nitsche KR, Hofbauer H, Rauch R, Goritschnig M, Koch R, et al. (2007) BTL-biomass to liquid (fischer tropsch process at the biomass gasifier in güssing. Proceedings of the 15th European Biomass Conference & Exhibition, Berlin, Germany.
- Teimouri Z, Abatzoglou N, Dalai AK (2024) Insights to the reaction kinetics of fischer-tropsch synthesis using an integral system over Cu-Mo promoted Fe catalyst. Fuel 360: 130512.
- Shafer WD, Gnanamani MK, Graham UM, Yang J, Masuku CM, et al. (2019) Fischer-tropsch: Product selectivity-the fingerprint of synthetic fuels. Catalysts 9(3): 259.
- Laan GP, Beenackers AA (1999) Kinetics and selectivity of the fischertropsch synthesis: A literature review. Catal Rev 41(3-4): 255-318.
- Soled SL, Iglesia E, Fiato RA, Baumgartner JE, Vroman H, et al. (2003) Control of metal dispersion and structure by changes in the solid-state chemistry of supported cobalt fischer-tropsch catalysts. Top Catal 26: 101-109.
- Bezemer GL, Bitter JH, Kuipers HP, Oosterbeek H, Holewijn JE, et al. (2006) Cobalt particle size effects in the fischer-tropsch reaction studied with carbon nanofiber supported catalysts. J Am Chem Soc 128(12): 3956-3964.

- 10. Alayat A, Echeverria E, Mcllroy DN, McDonald AG (2018) Enhancement of the catalytic performance of silica nanosprings (NS)-supported iron catalyst with copper, molybdenum, cobalt and ruthenium promoters for fischer-tropsch synthesis. Fuel Process Technol 177: 89-100.
- 11. Gong W, Ye RP, Ding J, Wang T, Shi X, et al. (2020) Effect of copper on highly effective Fe-Mn based catalysts during production of light olefins via fischer-tropsch process with low $\rm CO_2$ emission. Appl Catal B Environ 278: 119302.