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Direct conversion of syngas to lower olefins precursors of jet fuel and chemicals

September 2023

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Abstract

This study investigates the direct conversion of syngas to olefins as a pathway to produce sustainable aviation fuels. This approach combines methanol/ dimethyl ether synthesis with methanol-to-olefins into one unit operation to avoid the equilibrium limitation of methanol synthesis and the Anderson–Schulz–Flory distribution limitations from the Fischer Tropsch process. The ability to combine reactor functionalities into a single step are also projected to significantly lower capital costs over current synthesis approaches for the syngas to olefins process.

Summary

We developed multifunctional catalyst systems using metal oxide catalysts mixed in with zeolite based catalyst support material and tested the catalytic performance for the direct conversion of syngas to olefins. Different metal oxide ratios for the metal oxide catalyst and silica-alumina ratios for the zeolite support of the I3T catalyst were investigated with no improvement on reducing hydrogenation activity. A different zeolite was then investigated and exhibited reduced hydrogenation activity compared to the I3T baseline catalyst. Overall, this study demonstrates a new catalyst system that further suppresses hydrogenation of C=C bonds in the olefins produced compared to the baseline catalyst and improves the CO₂ free olefins selectivity. However, this catalytic system also displays increased water gas shift activity and improvements are still needed to reduce undesired high CO₂ selectivity to improve overall olefins selectivity.

Acknowledgments

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1.0 Introduction

Conventionally, olefins as jet fuel precursors are produced from syngas through the Fischer-Tropsch synthesis (FTS) process, which is limited to a selectivity of 58% for light (C_2 to C_4) olefins due to the Anderson–Schulz–Flory (ASF) distribution from polymerization. Other methods of syngas conversion to olefins include Alcohol to Jet (ATJ) and Methanol to Olefins (MTO) followed by Olefins to Gasoline /Distillate (MOGD). [1] These are not limited to the same limitations as FTS but do have higher capital and operation costs due to having multiple unit operations such as first producing methanol from syngas in a preceding unit operation. Instead, we explore the direct conversion of syngas of olefins combining MTO with methanol synthesis into one unit operation, combining both reaction into one step is projected to reduce capital costs on olefin production.

In prior work, PNNL has explored the direct conversion of syngas to light olefins through the MTO process, using a composite Pd-ZnO/ Al_2O_3 –HZSM-5 catalytic system.[2] This system provides catalytic active sites for a direct conversion to gas range hydrocarbons from syngas: methanol synthesis from Pd-Zn, methanol dehydration from Al_2O_3 , and Dimethyl Ether to gasoline from HZSM-5. This catalytic system resulted in high CO conversion, excellent stability over 100 hours on stream, and a C_2 - C_4 hydrocarbon selectivity of 80%. That said, while this selectivity does surpass the ASF limitation of 58% selectivity, much of the olefins undergoes saturation to alkanes which can limit subsequent steps of oligomerization that leads to products such as sustainable aviation fuels.

Recently, Bao et. al demonstrated direct olefin production from syngas using a metal oxide/zeolite catalyst system.[3] However, a high olefin selectivity was obtained only at a low conversion and a high selectivity of CO_2 is also reported. With recent I3T funding, we demonstrated that a reasonable conversion of 30% can be achieved while maintaining an olefin/paraffin ratio of 1.37. The presence of paraffins is caused by the hydrogenation of olefins to alkanes and thus the purpose of this work is to improve upon this investigated catalyst, which will be referred here as the I3T baseline catalyst, by reducing hydrogenation of olefins and thereby improving olefin selectivity. The first action to explore is to tune the metal oxide catalyst and the SiO_2/Al_2O_3 (Si/Al) ratio from the baseline. Controlling these variables to alter catalyst acidity and observe any improvements in CO conversion and product selectivity.

2.0 Experimental

Catalysts are tested on their performance on syngas conversion to olefins in a fixed bed reactor. The catalytic bed consists of 0.3 grams of the metal oxide catalyst and 0.15 grams of the zeolite support which are mixed well before being added as a catalytic bed inside a Swagelok cylindrical 3/8-inch stainless steel tube. The reactor is pretreated under nitrogen at 450 °C for 8 hours and lowered to 410 °C thereafter. It is then reduced under 10% H₂ in N₂ for 1 hour. After reduction, the flow was switched to syngas and flushed for 10 minutes to remove hydrogen and nitrogen in the system and the system was then brought to the desired reaction temperature and pressure. Pressurization of the reactor is done at the same rate as the reaction flowrate and official Time on Stream (TOS) begins once the reaction pressure is reached. Reaction total TOS has a lower bound of 72 hours and an upper bound to the point when the ratio of olefins and paraffins being produced stops increasing.

3.0 Results & Discussion

3.1 Metal Oxide Ratio Tuning

For the first part of the catalyst screening process 2 different ratios of our metal oxide were investigated, a ratio of R2 was compared to the I3T baseline catalyst ratio of R1. All other operating conditions remain the same as the I3T baseline catalyst in terms of space velocity, pressure, and temperature. Table 1 shows the conversion and selectivities to the primary products. As shown, R2 resulted in a much higher selectivity of paraffins giving an olefin to paraffin ratio of 0.58, contrasting with a ratio of R1 done in the same conditions and TOS which attained a ratio of 0.93. This ratio hence further enables hydrogenation of the olefins further into paraffins and is not desirable for olefin production. We chose to maintain the baseline ratio of R1 moving forward.

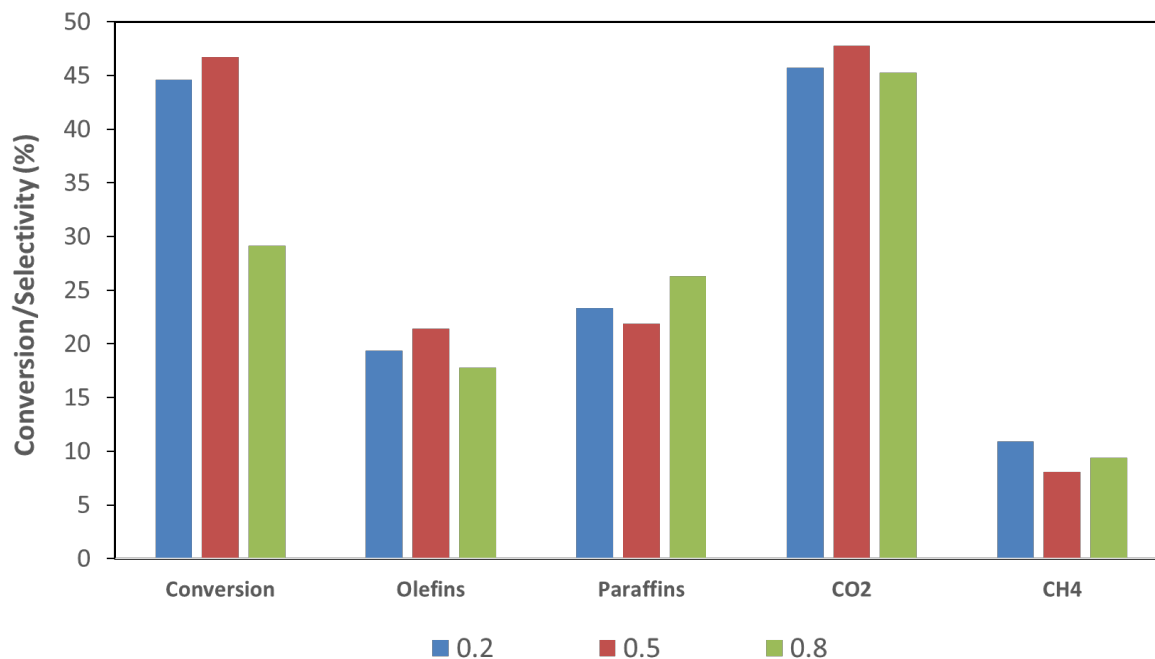
Table 1. Effect of Metal Oxide Ratios on the catalytic performance of syngas to olefins

Metal Oxide Ratio	Conversion	Selectivity	
		Olefins	Paraffins
R1	26.8	21.2	22.8
R2	30.2	17.9	31.0

Conditions: 430 psig, 410 °C, GHSV: 2427 L Lcat⁻¹ h⁻¹, syngas feed (64% H₂, 32% CO, 4% N₂), 48 h TOS

3.2 B1 Si/Al Ratio Tuning

For the next part of the screening process, the Si/Al ratio of the I3T baseline zeolite support (B1) is investigated on its impact on catalyst selectivity and hydrogenation activity. We will refer this catalyst as B1-X where X is the silica/alumina ratio of the catalyst where the I3T baseline catalyst is B1-0.5. B1-0.5 and ratios higher and lower than this value were studied. Figure 1 below presents the impact of catalysts with these ratios on catalytic performance for direct syngas conversion. Among the 3 catalysts, the conversion of a B1-0.5 is the highest at 47% while the conversion of B1-0.2 and B1-0.8 are 45% and 29% respectively. The olefins selectivity is highest and paraffins selectivity lowest for a ratio of 0.5 thus among the 3 ratios explored, B1-0.5 still possesses the lowest amount of hydrogenation activity. Overall, a lower Si/Al ratio provides slightly inferior catalytic performance compared to the baseline whereas a higher ratio performs much more poorly with a significant reduction in conversion while also having the highest amounts of hydrogenation.

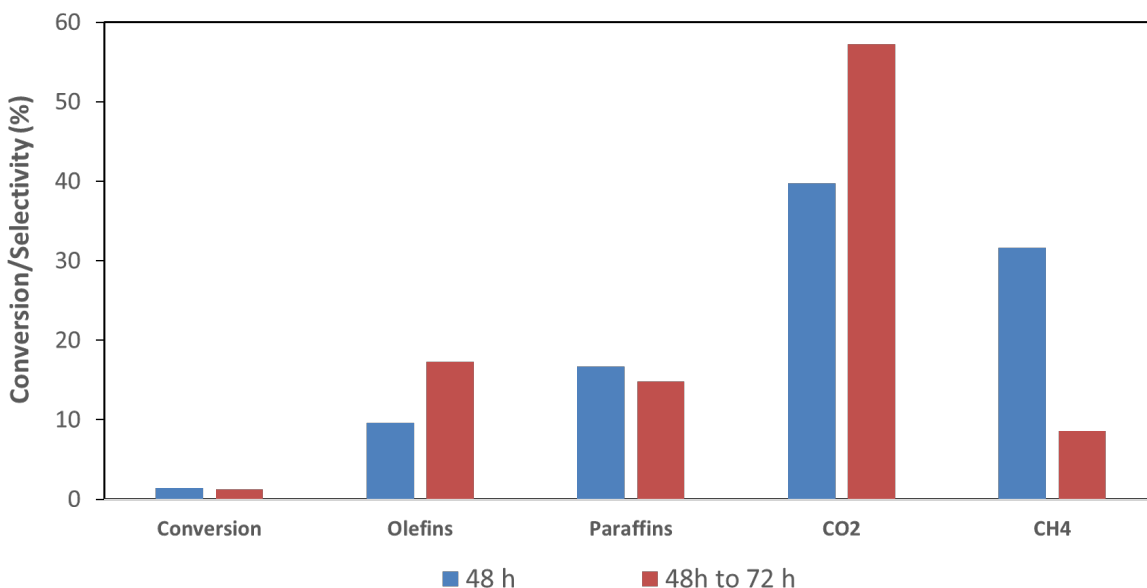


Conditions: 430 psig, 410 °C, GHSV: 2427 L Lcat⁻¹ h⁻¹, syngas feed (64% H₂, 32% CO, 4% N₂), 48h to 72h TOS

Figure 1. Effect of Silica-Alumina Ratios on the conversion of syngas and selectivities of major reaction products

3.3 Zeolite Support Catalyst M1

As the baseline B1-0.5 catalyst support held the best catalytic performance for syngas to olefins, similar zeolites that have shown promise in literature are investigated. M1 is one such catalyst support that was identified exhibiting high olefins to paraffins ratio on methanol conversion into olefins. M1 was tested on its catalytic performance at the same operating conditions as the I3T baseline runs (430 psig, 400 °C), the operating conditions were then changed for the next 24 hours on stream to that of the literature study (300 psig, 350 °C). Figure 2 highlights the differences between the catalytic performance under those 2 conditions. The whole run yielded a very low conversion of less than 5% but notably at the latter operating conditions olefins selectivity improves while paraffins selectivity falls, doubling the olefin to paraffin ratio from 0.58 to 1.17, demonstrating a large impact on the reduction of hydrogenation activity. Similarly, carbon dioxide selectivity rises while methane selectivity decreases, demonstrating an increase in water gas shift activity and decrease in methanation.



Conditions: GHSV: 2427 L Lcat⁻¹ h⁻¹, syngas feed (64% H₂, 32% CO, 4% N₂)

Figure 2. Catalytic Performance of catalyst support M1 under 430 psig and 400 °C (48h) and under 300 psig, 350 °C (48h to 72h)

A new run with a fresh batch of M1 was conducted at the literature conditions. Table 2 exhibits the catalytic performance of catalyst support M1 under these conditions and compared to that of the I3T baseline catalyst. Overall, zeolite illustrates increased conversion and olefins to paraffins ratio over the baseline, successfully demonstrating reduced hydrogenation activity with this new catalytic system with a ratio of 1.67 due to a reduction in the production of undesired alkanes. An increased CO₂ selectivity is also observed at over 50%, highlighting increased water gas shift activity.

Table 2. Comparison of Catalytic Performance between baseline catalyst supports B1 and M1.

Catalyst Support	Conversion	Selectivity				Olefins : Paraffins Ratio
		Olefins	Paraffins	CO ₂	CH ₄	
B1-0.5 ^a	29.9	32.4	23.7	41.8	0.2	1.37
M1 ^b	35.7	27.9	16.7	50.8	2.4	1.67

a: 430 psig, 425 °C, GHSV: 2427 L Lcat⁻¹ h⁻¹, syngas feed (64% H₂, 32% CO, 4% N₂)

b: 300 psig, 350 °C, GHSV: 2427 L Lcat⁻¹ h⁻¹, syngas feed (64% H₂, 32% CO, 4% N₂)

4.0 Conclusion & Future Work

This study demonstrated reduced undesirable hydrogenation activity over the I3T baseline catalyst on a direct syngas to olefins within one step through a novel catalytic system with zeolite support M1. Hydrogenation is limited further with an improved olefins to paraffins ratio of 1.67. Improved olefin selectivity is not observed due to increased water gas shift activity. Improvement is needed to reduce undesired water gas shift activity and reduce its predominance among the main products of direct syngas conversion. Planned future work to investigate promoters that inhibit water gas shift activity contributing to high CO₂ selectivity and improve olefin selectivity.

5.0 References

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