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Conversion of Syngas and CO₂ to Light Olefins using Multi-Functional Catalysts

September 2023

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Abstract

This report describes our effort in developing a novel catalyst for the conversion of syngas to light olefins. We have adopted a ligand assisted synthesis protocol in which first metal-amine was prepared using metal salts and suitable amine ligands. The stable metal-amine complex thus prepared was then used as the seed for the growth of zeolite in alkaline solution. We have optimized the synthesis condition as well as different amine ligand to identify the condition to obtain stable metal-amine complex. Catalytic activity of these catalysts was evaluated for syngas conversion reaction and compared with a baseline catalyst. The activity of the novel catalyst shows very different activity trend compared to the baseline catalyst. While a distribution of products with different carbon number was obtained with baseline catalyst, the novel catalyst shows ethylene as the major product. While ~73% selectivity to C₂-C₆ products were obtained with the novel catalyst, only 53% selectivity was obtained for the corresponding products with the baseline silica-alumina supported Fe catalyst. Not only higher carbon selectivity, but the novel catalyst was also selective towards C₂ products (ethylene/ethane) among light olefins.

Summary

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Acknowledgments

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Acronyms and Abbreviations

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1.0 Introduction

Light olefins—generally referring to ethylene, propylene and butylene—are not only basic building blocks for chemical industry, but also precursors for production of sustainable aviation fuel (SAF). With the depleting of fossil fuels, the direct synthesis of light olefins from syngas (a mixture of H_2 and CO) has wide attentions, because syngas can be obtained from multiple sources including coal, natural gas and sustainable biomass. Fischer-Tropsch process (FTP) is a classic process for the syngas-to-hydrocarbon transformation since 1925.^[1-6] However, the “Fischer-Tropsch to olefins” (FTO) technology is still challenged by the product selectivity to light olefins, because the hydrocarbon products typically follow the so-called Anderson-Schulz-Flory (ASF) distribution, which is basically a statistic distribution of the polymerization of CH_x ($x = 1, 2, \text{ or } 3$) monomers on an unconfined catalyst surface, with a maximum C_2 – C_4 hydrocarbon fraction of about ~58%.^[1, 4, 5] Therefore, development of catalyst that allows to break the ASF distribution is critical to improve the selectivity of light olefins. Researchers have put many efforts and made some progress in modifying the conventional Co- and Fe- FTP catalysts to increase the light olefin selectivity, but still suffers from generation of undesired products, mainly due to the trade-off between the over-hydrogenation (forming CH_4) and overgrowth of carbon chain (forming C_{5+} hydrocarbons). For instance, Zhong et al.^[7] synthesized a cobalt carbide nanoprism catalyst for FTO and achieved an improved C_2 – C_4 olefin selectivity of 60.8% and a low CH_4 selectivity of 5%, but the selectivity to C_{5+} hydrocarbon was as high as 31.4%. In contrast, Galvis et al.^[8] reported a carbon nanofiber (CNF)-supported Fe nanoparticle catalyst which showed a C_2 – C_4 olefin selectivity of 61% but meanwhile a CH_4 selectivity of 22%. Despite research activities, it is critical to develop a catalyst system that produces light olefins with higher selectivity.

Research design and Methodology

The two tasks for this project were following.

- (1) Synthesis and characterization of novel catalysts
- (2) Evaluate the performance of these novel catalysts for syngas conversion.

Catalyst Characterization

The composition of the catalyst was analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES) on a Perkin Elmer Optima 7300DV instrument. Before ICP measurements, the bimetallic catalysts were digested in concentrated nitric acid in a sealed vessel using CEM MARS 6 microwave digestion unit. The crystal structure of the catalysts was studied using a benchtop Rigaku MiniFlex 600 X-ray diffractometer equipped with a $Cu K_\alpha$ X-ray source (wavelength of 1.54 Å). To obtain X-ray diffraction (XRD) patterns, the was placed on a glass sample holder and diffraction patterns were collected over the scattering angle range of 5° to 80° , with a scan rate of $0.1^\circ \text{ min}^{-1}$ and a step size of 0.01° . Microscopic characterization of the catalysts were performed using JEOL TEM instrument.

Catalytic activity test

All the catalytic experiments were performed using a flow reactor. Experiments were performed using syngas as the feedstocks where $CO:H_2$ ratio was maintained as 2:1. The experiments were carried out at different temperature ranging from 100-400 °C and at different pressure such as 7-20 bar. Prior to the reaction the catalyst was pelletized and sieved. The catalysts were loaded in

the reactor and reduced under H₂ to obtain the metallic phase. The products were analyzed by micro-GC, GC-FID and GC-MS.

2.0 Results and Discussion

All the novel catalysts were synthesized and characterized in detail using microscopy and spectroscopy techniques prior to their testing. Baseline catalysts i.e., Fe supported on Silica-Alumina (Fe-SiAl) was synthesized via wet impregnation technique.

Both the novel catalysts and Fe-SiAl catalyst was then tested for syngas conversion reaction. Figure 3 shows activity comparison of these two catalysts when the reaction was carried out at 14 bar and at 150 °C. As shown in Figure 3 rate of CO conversion is nearly same in both the catalyst. Although both the catalysts activity is similar their difference is significant on product selectivity. While Fe-SiAl catalysts demonstrates distribution of product, novel catalysts produced ethylene as the major product. Another notable feature of the novel catalysts is the absence of methane formation which could be considered as the loss of carbon. Both these catalysts also formed CO₂ as one of the products which could be resulted due to Boudart reaction in which first dissociative chemisorption of CO on the metal surface generates C* and O*. C* further reacts with another CO to generate CO₂. Currently, our analysis accurately determines C₂-C₆ products, and we attributed the remaining amount as the missing products of which we require more detailed analysis. These products could be larger products >C₆ or coke species. Further detailed analysis is required to identify the exact nature of the compounds. However, from Figure 4 it is apparent that, selectivity to these products is higher in case of Fe-SiAl compared to the novel catalysts. Thus, we concluded that the novel catalyst is more efficient in the formation of light olefins. We next consider C₂-C₆ products as the light olefins which shows nearly 70% of these products are in these range in case of the novel catalyst. This is nearly 1.3 times higher compared to Fe-SiAl. It is also interesting to note that among C₂-C₆ products, the novel catalysts only produce C₂ products whereas Fe-SiAl produces distribution of products with C₂ being the major one. It is also apparent that olefin produces herein also undergoes further hydrogenation to produces alkanes. This is consistent with previous literature where both olefin and alkane were obtained during syngas conversion.

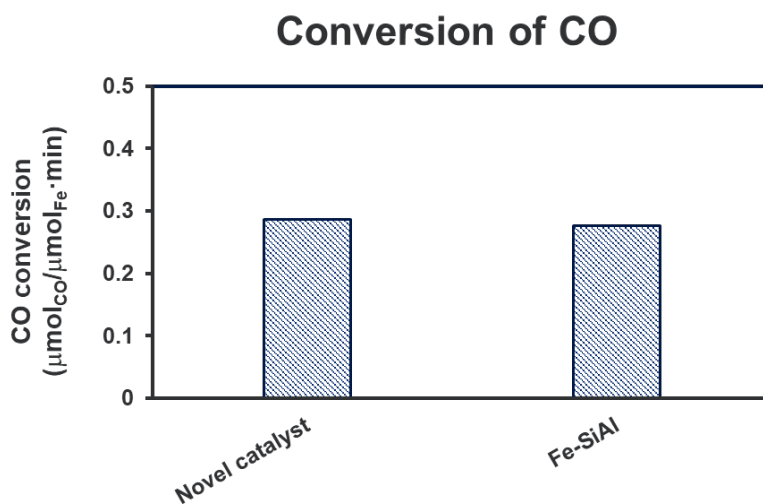


Figure 3. Activity comparison of the novel catalyst and Fe-SiAl catalyst towards syngas conversion reaction. Reaction condition: 14 bar, 150 °C, CO:H₂ = 2

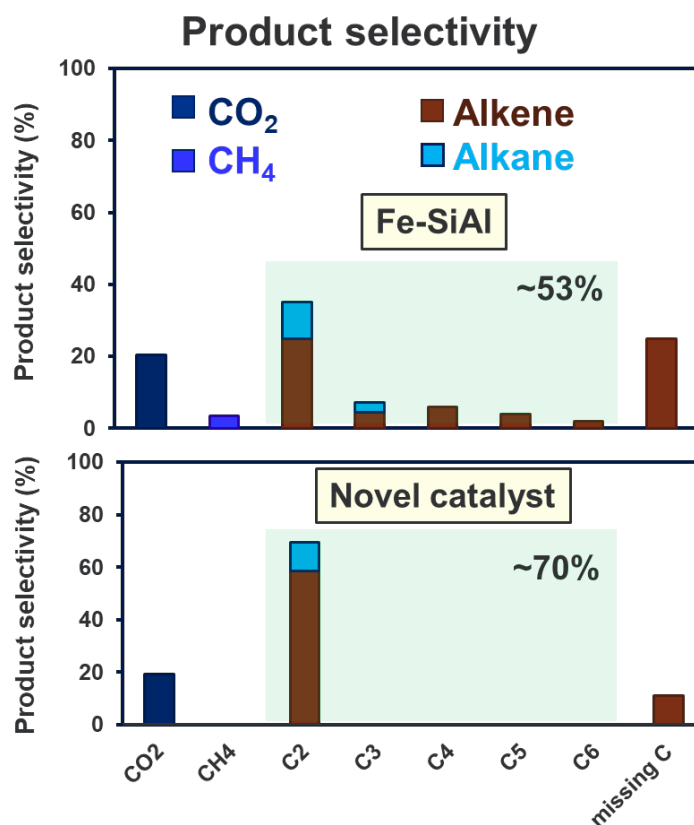


Figure 4. Product selectivity obtained during syngas conversion reaction for both Fe-SiAl and the novel catalyst. Reaction condition: 200 psig, 150 °C, CO:H₂ = 2

We next evaluated the effect of reaction parameter on the product selectivity obtained during the reaction with the novel catalyst. Figure 5 shows the effect both temperature and pressure on the performance of the novel catalysts specifically on the product selectivity. The reaction was carried out at 14 bar at different temperature ranging from 100-350 °C.

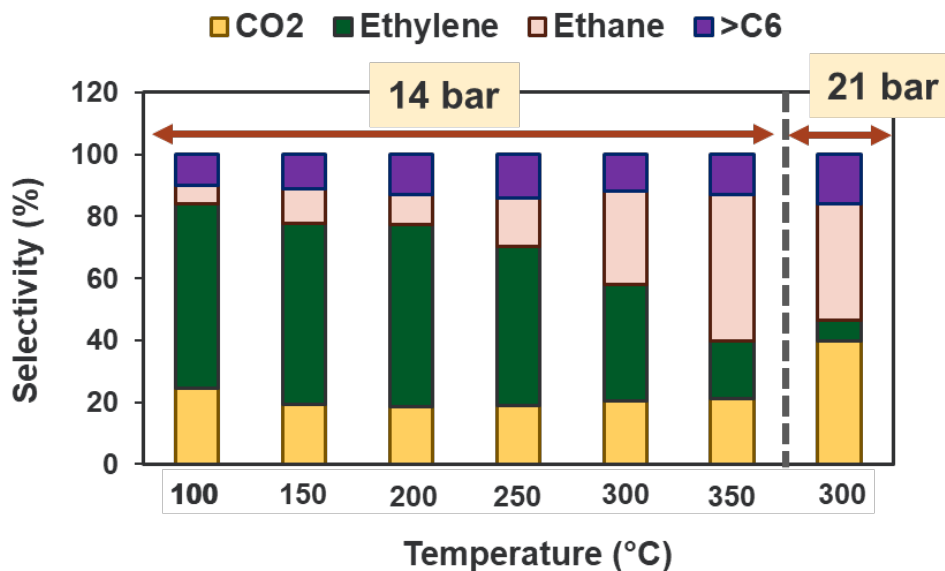


Figure 5. Effect of temperature and pressure on the product selectivity obtained during syngas conversion with the novel catalyst.

When reaction temperature was increased from 100 °C to 350 °C, selectivity to alkane was increased continuously as evidenced by the decrease in ethylene/ethane ratio. Alkane formation was also facilitated by increasing the reaction pressure from 14 to 21 bar. Thus, both reaction temperature and pressure have significant effect on hydrogenation reaction and increasing in either temperature or pressure facilitates the alkane formation. On the other hand, it is apparent that reaction temperature does not have significant impact on the CO₂ production as it remained insensitive (~20% selectivity) when the reaction temperature was increased from 100 °C to 350 °C. However, increase in reaction pressure from 14 bar to 21 bar, resulted in ~2x increase in CO₂ selectivity. Although the results show here is interesting more detailed catalytic experiments are required to understand the catalytic performance of this catalyst

3.0 Conclusion

In conclusion, we have prepared a novel catalyst and compare their activity with Fe-SiAl as a baseline catalyst. Performance evaluation of these catalysts towards syngas conversion demonstrated a unique reactivity with novel catalysts which shows the formation C_2 only products among light olefins (C_2 - C_6). While the baseline Fe-SiAl catalyst resulted only ~53% of the product among C_2 - C_6 , ~73% selectivity was obtained with the novel catalyst further demonstrated its effectiveness towards the formation of light olefins. Reaction temperature and pressure also shows significant effect on product selectivity obtained with the novel catalyst. Increase in either pressure and temperature facilitate hydrogenation reaction and favored the alkane formation, thus, decreases olefin/alkane ration. On the other hand, reaction pressure has strong effect on CO_2 formation as increase in selectivity to CO_2 formation was noted with increase in reaction pressure.

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Appendix A – Title

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