

Conversion of synthesis gas to light olefins: impact of hydrogenation activity of methanol synthesis catalyst on the hybrid process selectivity over Cr-Zn and Cu-Zn with SAPO-34

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Highlights

- Syngas conversion to hydrocarbon/olefins over a hybrid catalyst
- Comparison of Cu-Zn vs. Cr-Zn catalyst in combination with SAPO-34
- Hydrogenation activity changes product composition and C₃/C₂ ratio
- Kinetic model proposed to describe the selectivity patterns

1. Introduction

Light olefins (C₂-C₃) are industrially vital feedstocks for production of plastics, functional materials, and as platform chemicals for production of other derivatives. The use of alternative feedstocks decreases oil dependence and facilitates new technologies for production of olefins. Short chain hydrocarbons can be produced from synthesis gas by using a hybrid catalyst combining Cu-based methanol synthesis and SAPO-34 [1]. Recently it was shown that direct conversion of synthesis gas to light olefin is also possible by combining Zn-Cr based catalyst and SAPO-34 [2].

In the present study, we aim to compare two bifunctional catalytic mixtures containing a Cu-Zn (here and after the catalyst is referred as “Cu-Zn”) catalyst designed for low temperature methanol synthesis [3] or a Cr-Zn catalyst designed for high temperature methanol synthesis [3] in combination with a zeolite component SAPO-34 for the direct conversion of synthesis gas to olefins. The focus of this study is the distribution of products and kinetics of product formation [4].

2. Methods

Cu-based methanol catalyst “HiFuel R120” (Johnson Matthey, sold by Alfa Aesar) and Cr-Zn catalyst (prepared by co-precipitation [5]) were used. SAPO-34 was synthesized according to the literature procedures [6]. Materials were crushed and sieved to 60-80 mesh. Catalyst were characterized by N₂ physisorption, XRF, XRD, TPR and SEM techniques. Hybrid catalysts were prepared by mixing Cu-Zn or Cr-Zn with SAPO-34. Catalytic test were performed in a tubular stainless steel fixed-bed microreactor (i.d. 3 mm) at 370-410°C, 20 bar, GHSV = 1200 h⁻¹ and different H₂/CO ratio. Online GC analysis of components (N₂, H₂, He, CO, CO₂, C₁-C₅ alkanes and olefins) was performed periodically. Mass balance in all experiments was 95-105% based on carbon.

3. Results and discussion

For Cu-Zn/SAPO-34 only saturated hydrocarbons (C₁-C₅) and carbon dioxide (water-gas-shift) were observed while for Cr-Zn/SAPO-34 system olefins were also present among reaction products (Figure 1). We observed, that the C₃/C₂ ratio is consistently higher for Cr-Zn/SAPO-34 systems compared to Cu-Zn/SAPO-34 systems at the same conversion level for all measured conditions (Figure 1). The difference in C₃/C₂ ratios between the Cr-Zn/SAPO-34 and Cu-Zn/SAPO-34 catalyst systems demonstrates the role of the relative hydrogenation behavior in affecting SAPO-34 product distributions. We propose that C₃/C₂ ratio is predominantly controlled by the relative rates of olefin cycle propagation and the rate of cycle termination by the formation of paraffins on the Cr-Zn catalyst – loading additional SAPO-34 at low conversions increases the relative contribution of olefin cycle propagation on the reactor effluent [4].

To better understand and describe the observed patterns in product distribution a kinetic model was built Cr-Zn/SAPO-34 system [4]. To simplify the reaction network, a variety of assumptions were made. Model parameter fits were performed using standard Bayesian techniques employing the Athena Visual Studio software package (M. Caracotsios and W.E Stewart, v14.2).

The parity plots for conversion, combined paraffin carbon yield, and combined olefin carbon yield show considerable scatter around perfect model prediction. Considering these kinetic model shortcomings, improving the quantitative description of this reaction network, potentially necessitating SAPO-34 transport restriction analysis, will be a useful avenue of future investigation to predict C₃/C₂ product distributions as a function of process conditions.

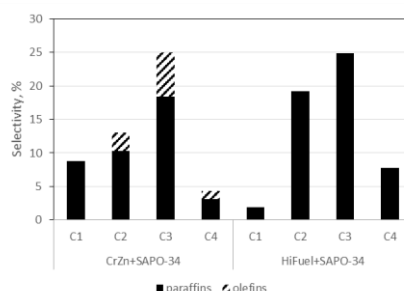


Figure 1. Product composition (C mol%) in conversion of synthesis gas over bifunctional catalysts (left: Cr-Zn/SAPO-34, right: Cu-Zn/SAPO-34). Full bar: paraffins, upward diagonal texture: olefins. Conversion of syngas 40-50%. CO₂ selectivity was 45-50%.

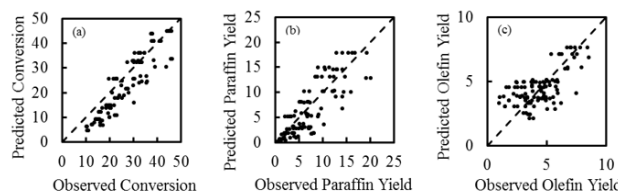


Figure 2. Parity plots for (a) conversion (%), (b) combined paraffin (ethane, propane, and butane) carbon yield (%), and (c) combined olefin (ethylene, propylene, and butene) carbon yield (%) for the kinetic model for Cr-Zn/SAPO-34 system data. The dashed lines represent perfect model prediction.

4. Conclusions

The choice of methanol synthesis catalyst alters product selectivity and distribution (the C₃/C₂ yield ratios). The relative rates of propagation of olefin methylation and cracking (olefin cycle) in SAPO-34 and olefin hydrogenation on the methanol synthesis catalyst dictates the observed C₃/C₂ ratio. A simplified kinetic model for the hybrid system is proposed to describe the observed selectivity patterns. We identify the balance of methanol synthesis rates compared to those of olefin hydrogenation on the mixed-metal-oxide catalysts as a potentially strong factor to control the product distribution in synthesis gas-to-olefin/paraffins technologies.

References

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Keywords

Olefins, syngas, mechanism, kinetic model