

Enhanced Fischer-Tropsch Synthesis Using Transition Metal Modified Iron Catalysts

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Introduction

Gasification followed by Fischer-Tropsch synthesis (FTS) is the most promising route currently for converting natural gas, coal and biomass to liquid fuels and other chemical products [1]. Bulk Fe catalysts are the catalysts of choice for the conversion of low H₂/CO ratio syngas derived from coal or biomass due to their high water-gas shift (WGS) activity, high FTS activity and a relatively low cost of Fe-based catalysts comparing to Co catalysts [2].

Development of a bulk Fe FTS catalyst having high FT activity, low methane selectivity, and long-term stability is of importance. It appears that Fe carbides play a critical role in the activity of Fe-based catalyst for FTS [1]. Therefore, the ability of Fe catalyst to maintain the carburized surface may be key to the initial and long-term activity. In this study, we have focused on the effect of the addition of a transition metal (*Me*) which is known to form carbides and possibly Fe-*Me* mixed carbides. The catalysts studied had a formulation of 95Fe/5*Me*/5Cu/17Si compared to the benchmark catalyst, 100Fe/5Cu/17Si. The CO hydrogenation activity as well as the selectivity for hydrocarbon products of the Fe/*Me* catalysts were studied and compared to those of the standard unpromoted Fe catalyst.

Materials and Methods

Catalysts, 95Fe/5*Me*/5Cu/17Si, were prepared using the constant pH precipitation technique [2] where *Me* was Cr, Mo, Mn, Ta, V, W and Zr. A prepared catalyst was calcined under air 300°C for 5h and pretreated *in situ* under H₂ at 280°C for 12 h prior to the CO hydrogenation with a H₂:CO ratio of 2:1. A fresh calcined catalyst was sieved < 90 μm before testing. The reaction was carried out in a differential plug-flow reactor at 280°C and 1.8 atm.

Results and Discussion

The results showing the catalyst activities vs. TOS for the FTS and water-gas shift (WGS) reactions are given in Figs. 1 and 2, respectively. It can be clearly seen that adding the transition metal was able to improve the catalyst activity for both FTS (hydrocarbon formation) and the WGS reaction (CO₂ formation) in varying degrees, depending on the added metal, with the exception of W. This suggests that surface of the Fe/W catalyst was probably overcarburized leading to too much carbon deposition on the surface of catalyst. Adding metals also had a positive impact on α (chain growth probability). On the other hand, none of them affected significantly the BET surface area or the reducibility or the crystallinity of metal or the selectivity towards methane or the %C₂-C₄ olefins.

Zr, Cr and Mn offer the greatest improvement in FTS activity of the Fe catalyst. The catalyst activity was most enhanced by the addition of Zr. The Fe/Zr catalyst did not show any significant induction period behavior for the FTS activity while it was observed for all the rest. The existence of the induction period for a Fe catalyst with H₂ pretreatment was also reported

by Sudsakorn et al. [3]. This induction period was hypothesized to be due to the formation of active Fe carbides on the catalyst surface. It appears that a reduced surface of the Fe/Zr catalyst was able to carry out the FTS reaction as well. Catalyst characteristics and the impact of added metal on the Fe catalyst for FTS will be discussed in detail.

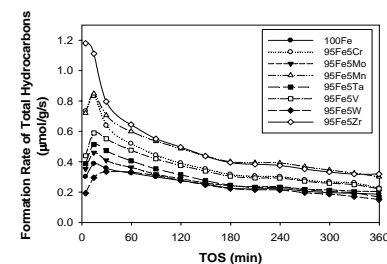


Figure 1. Formation rate of total hydrocarbon (C₁-C₈).

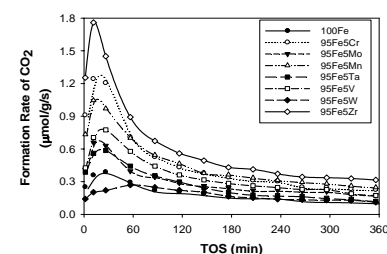


Figure 2. Formation rate of CO₂.

Significance

Catalyst formulation, 95Fe/5*Me*/5Cu/17Si, developed in this study should result in Fe FTS catalysts having potentially higher initial and steady-state activities with interesting product selectivities. Such catalysts should be able to operate at lower temperatures with better yield of desirable liquid fuels and minimize the production of light gaseous hydrocarbons, thereby resulting in lower cost for the production of liquid fuels derived from biomass or coal.

References

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- [2] Jothimurugesan, K., Goodwin, J.G. Jr., Gangwal, S.K., Spivey, J.J., *Catal. Today* 58, 335(2000).
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