Effect of Potassium on Multicomponent Fe/C Catalysts for Hydrocarbons and Oxygenates from Fischer-Tropsch Synthesis

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Introduction

Most catalysts used for Fischer-Tropsch synthesis (FTS) give rise to hydrocarbons with a wide distribution of carbon numbers. Adjustment of the hydrocarbon chain length would result in gasoline- and diesel-range products being more selectively produced from syngas. The use of activated carbon (AC) as a support has been shown to result in such an effect [1]. Iron-based catalysts, with or without promoters, are one of the most widely used, primarily due to their lower cost. We have conducted a systematic study of the effects of components of the Fe-Cu-Mo-K/AC catalyst for FTS; see for example, Ref. [2] for the effect of Mo. The current work reports on the effect of K loading on catalyst performance. Specifically, activities for FTS and the water-gas shift reaction (WGS), stability, product distribution of hydrocarbons and product distribution of oxygenates have been considered.

Materials and Methods

The AC, peat-based and obtained from Sigma-Aldrich, was washed, calcined and sieved before use. AC-supported unpromoted and K-promoted iron catalysts were prepared by incipient wetness impregnation. In all cases, 15.7 wt% Fe was used. K loadings of 0 wt%, 0.9 wt%, and 2 wt% were used, termed 0K, 1K, and 2K catalysts, respectively. Reaction studies were carried out in a computer-controlled downflow fixed-bed reactor system. The catalyst was reduced *in-situ* by flowing H_2. Runs were carried out at 2 MPa, over the range 260-300°C, generally for 24h for each temperature. The exit stream passed through a product trap to condense liquids. These were analyzed every 24h. Inlet and outlet gases were analyzed every 2h. By the use of standards and by matching key components, vapor-phase hydrocarbons, liquid-phase hydrocarbons, and aqueous-phase oxygenates could be gathered together and selectivities obtained for the product stream as a whole.

Results and Discussion

The change of activity by K promotion depends greatly upon the K content. The best results were obtained for the 1K catalyst, see Figure 1. The ratio of WGS to FTS was also found to be greatest for the 1K catalyst. However, increasing K levels increases the deactivation rate, with the greatest drop in performance for the 2K catalyst. The kinetics of FTS were analyzed for all three catalysts using a simple first-order model, which has been shown to be valid for conversions of up to 80%. For the 1K catalyst, the decrease in activation energy (relative to 0K) increases the rate more than the decrease of the pre-exponential factor decreases the rate. For the 2K catalyst relative to the 1K catalyst, the opposite situation occurs.

The selectivity of liquid-phase hydrocarbons (C_{5+}) is greater for the 1K catalyst than for the 0K catalyst. This is important for fuel considerations. Only a slight improvement is noted in going

to the 2K catalyst. In all cases, the C_{5+} selectivity decreases with increase in temperature. At least for carbon numbers of 25 or less, increasing K increases the number of branched paraffins, with the greatest increase for the 1K catalyst. Olefin/paraffin ratios are greater for the 1K than for 0K catalyst; again, little improvement is observed in going to the 2K catalyst. Among the olefins, internal-olefins (*int*-olefins) are produced in larger amounts for the 0K catalyst, and the ratio *int*-olefins/1-olefins is least for the 2K catalyst. This indicates that the promoter is less active for secondary reactions. In all cases, total hydrocarbons obey Anderson-Schultz-Flory (ASF) distributions. The values of α for 1K and 2K catalysts are virtually the same, and higher than that for the 0K catalyst.
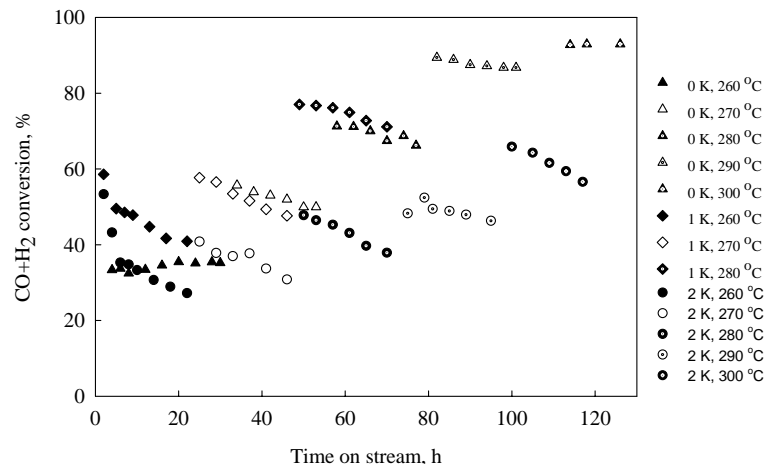

Figure 1. Syngas conversion with time on stream. 2 MPa, $3Nl.h^{-1}.gcal.^{-1}$

Alcohol products up to C_5 can be easily detected. Total alcohol yields and selectivities are higher at higher temperatures. In all cases, the C_2-alcohol predominates, followed by C_3, C_1, C_4 and C_5 in turn. As K increases, methanol is decreased and the higher alcohols are increased.

Significance

The effect of changing potassium levels in a multi-component iron-based, AC-supported catalyst has been quantified in long-term tests. An intermediate amount of K appears to work best, in terms of overall activity, liquid-phase selectivity, and ASF distributions. This can be related to the inter-relationship between activation energy and pre-exponential factor. The addition of K makes the catalyst less active for secondary reactions. For alcohols, addition of K increases the amounts of higher alcohols and decreases the amount of methanol formed.

References

1. Jung, H.J., Vannice, M.A., Mulay, L.N., Stanfield, R.M., Delgass, W.N. *J. Catal.* 76, 208 (1982).
2. Ma, W.P., Kugler, E.L., Wright, J., and Dadyburjor, D.B. *Energy Fuels* 20, 2299 (2006).