

Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts

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Burtron H. Davis

Enrique Iglesia (UC/B Subcontract)

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University of Kentucky Research Foundation

201 Kinkead Hall

Lexington, KY 40506

University of California-Berkeley (Subcontract)

Laboratory for the Science and Application of Catalysis

Department of Chemical Engineering

University of California at Berkeley

Berkeley, CA 94720

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Abstract

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Iron Fischer-Tropsch synthesis (FTS) catalysts with different potassium loadings showed different induction periods during which the conversion increased from a low initial level to a peak value before declining to attain a lower activity that was stable at the reaction conditions. A lower K loading produced a higher peak conversion and a shorter induction period. Although the induction period and the peak conversion were slightly dependent on the K loading for the iron catalyst, the stabilized conversions and the stabilization periods were independent of potassium content. The C₂-C₄ olefin to paraffin ratio of the gaseous products and the CO₂ selectivity did not change significantly as the potassium content increased from 5 to 10%. An increase in reaction temperature produced a new induction period and a higher conversion than that before the reaction temperature was increased. The H₂:CO ratio also had an important influence on FTS conversions. Increasing the H₂:CO ratio in the feed gas lowered the H₂ utilization. A higher H₂:CO ratio feedstock gas produced lower FTS catalyst activity compared to a low H₂:CO ratio gas.

The effects of group II alkali metals (barium, beryllium, calcium and magnesium) and potassium promoted iron catalysts on Fischer-Tropsch Synthesis (FTS) product selectivity, reaction conversions and productivity was investigated. Iron FTS catalysts promoted with group II alkali metals produced lower CO conversions, less diesel and heavier fraction products than potassium promoted catalysts. Slightly higher alpha value was observed for potassium promoted catalysts than group II alkalis promoted catalysts. Beryllium and barium promoted iron catalysts, however, showed the best stability among all alkali metal promoted catalysts based on the results of over 500 hours of FTS.

It is also found that a potassium promoted iron catalyst produced higher water gas shift and FTS activities than group II alkali promoted catalysts. Among the group II alkalis, barium showed

the highest water gas shift activity. All group II alkalis generated similar hydrocarbon, CO₂ and methane rates. It was also shown that group II alkali promoted catalysts produced similar oxygenates, except that Ba yielded more ethanol and Mg and more normal propanol than other group II alkali metal promoters. The olefin ratio, however, did not reveal any difference among group II alkalis and potassium. Higher WGS activity for potassium promoted catalysts may cause a lower carbon utilization rate than group II alkalis because a significant amount of CO was consumed in the water gas shift reaction. A slightly higher alpha value was obtained from potassium promoted catalysts than that from group II alkalis.

TPR and H₂ chemisorption with pulse reoxidation were used to study the reducibility of cobalt Fischer Tropsch catalysts. Different supports (e.g., Al₂O₃, TiO₂, SiO₂, and ZrO₂ modified SiO₂) and a variety of promoters, including noble metals and metal cations, were screened. Addition of Ru and Pt exhibited a similar catalytic effect on decreasing the reduction temperature of Co₃O₄ and for CoO species where a significant CoO-support interaction was present, while Re mainly catalyzed the reduction of CoO. A slight decrease in cluster size was evidenced in H₂ chemisorption/pulse reoxidation with noble metal promotion for catalysts reduced at the same temperature, indicating that smaller Co oxide species that interact with the support were reduced with the aid of the promoter. Increasing the cobalt loading, and therefore the average Co cluster size, was found to exhibit improved reducibility, by decreasing interactions with the supports. Addition of metal oxides such as B, La, K, and Zr were found to decrease the cobalt cluster size, and caused reduction to shift to higher temperatures.

During this reporting period, the SBCR modifications detailed in the previous quarterly report, were completed. In this report we describe results and operating experiences for a 404-hour SBCR shakedown run that was completed in December. Special emphasis was placed on maintaining a constant catalyst inventory within the reactor vessel while reducing slurry holdup

within the wax separation system. A new system for measuring the SBCR slurry level using a differential pressure transducer was implemented and thoroughly tested. The differential pressure signal was also found to give important information regarding the liquid recirculation rate and gas holdup within the reactor system.

Activity decline of an iron-based FT catalyst during the shakedown run was documented and compared with that of previous CSTR and SBCR runs using the same catalyst and operating conditions. The activity decline measured in the revamped SBCR system was shown to be similar to that of the CSTR experiments.

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The reduction, carburization, and catalytic properties of Fischer-Tropsch synthesis (FTS) catalysts based on Fe-Cu were examined using kinetic and spectroscopic methods at reaction conditions. FTS reactions start to occur as Fe_3O_4 forms and then rapidly converts to FeC_x . The onset of FTS activity requires only the conversion of surface layers to an active structure, which consists of FeC_x with steady-state surface coverage of oxygen and carbon vacancies formed in CO dissociation and O-removal steps during FTS. The catalytic properties of these surface layers are largely independent of the presence of an oxide or carbide core.

The local structure and oxidation state of Fe_2O_3 precursors promoted by Cu and/or K was probed using *in situ* X-ray absorption spectroscopy during these processes. The initial rate of carburization, and the extent of carburization and the FTS rate at steady-state, were higher for Fe_2O_3 precursors containing either Cu or K. These effects were stronger when both promoters were present. K and Cu provide CO and H_2 activation sites, which lead to the nucleation of multiple carbide regions on Fe oxide surfaces. The larger number of nucleation sites leads to higher initial carburization rates and to smaller FeC_x crystallites. These smaller crystallites, in turn, provide higher active surface areas, shorter bulk diffusion distances, more complete carburization

of Fe_2O_3 precursors, and higher steady-state FTS rates. It appears that K and Cu act predominantly as structural promoters, which increase the surface area of the active FeC_x phase. Chemical promotion of catalytic rates by these additives is not required in order to account for the observed results. These structural promotion effects of Cu and K account for the apparent correlation between bulk FeC_x contents and FTS rates at steady-state.

The structure of unpromoted precipitated Fe catalysts was determined by Mössbauer emission and X-ray absorption spectroscopies after use in the Fischer-Tropsch synthesis (FTS) reaction for various periods of time in well-mixed autoclave reactors. The nearly complete formation of Fe carbides during initial activation in CO was followed by gradual re-oxidation to form Fe_3O_4 with increasing time on stream. It appears that the deactivation of Fe catalysts in FTS reactions parallels the conversion of Fe carbides to Fe_3O_4 ; the CO activation steps responsible for replenishing carbidic surface species and for removing chemisorbed oxygen are selectively inhibited by deactivation of surface sites, leading to the oxidation of Fe carbide even in the presence of a reducing reactant mixture.

Experiments conducted with Fe-Zn-Ru-K samples using different calcination temperatures showed no significant differences in FT rates and small differences in the product selectivities. The Fe-Zn-Ru-K is significantly more active than a Fe-Zn-Cu-K prepared using the same calcination temperature due to the achievement of a better Fe_xC crystallite dispersion on the Ru-based sample. A switch between synthesis gas and methane in an empty reactor conducted as a first step in our systematic switching experiments aimed at determining the effect of water on the reaction, showed a transient response that was identical to the step input. This suggested that no hydrodynamic corruptions interfere with our intended response measurements.

Table of Contents

	<u>Page</u>
Disclaimer	1
Abstract	2
Table of Contents	6
Executive Summary	7
Task 1. Iron Catalyst Preparation	13
Task 2. Catalyst Testing	13
A. High-Alpha Fischer-Tropsch Synthesis over Potassium Promoted Iron Catalysts	13
B. Group II Alkali Metal Promoted Iron Fischer-Tropsch Synthesis Catalysts ..	41
Task 3. Catalyst Characterization	70
A. TPR Study of Promoter and Support Effects on the Reducibility of Supported Cobalt Fischer-Tropsch Catalysts	70
Task 4. Wax/Catalyst Separation	91
A. Slurry Bubble column Reactor (SBCR) Activities	91
Task 5. Oxygenates	117
Task 6. Literature Review of Prior Fischer-Tropsch Synthesis with Co Catalysts	117
Task 7. Co Catalyst Preparation	117
Task 8. Co Catalyst Testing for Activity and Kinetic Rate Correlations	117
A. Co Kinetics	117
Task 9. Co Catalyst Life Testing	129
Task 10. Co Catalyst Mechanism Study	129
Task 11. University of California-Berkeley Subcontract	129
Task 12. Reporting and Management	188