Fischer-Tropsch Synthesis: Is a Single Site Responsible for FTS and WGS on Iron Catalysts?

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Introduction

The iron catalyst under steady-state working conditions contains Fe_3O_4 and iron carbides. Since Fe_3O_4 is, at high temperatures, a catalyst for the WGS reaction, many have the view that FTS and WGS occur on different catalytic sites. Thus, Fe_3O_4 provides the catalytic sites for WGS and the iron carbides provide sites for FTS. From a catalyst design point of view, it is desirable that the two reactions occur on different sets of catalytic sites since that should allow catalyst preparation and activation conditions to control the extent of the two reactions, and therefore the selectivity of the FTS reaction with iron catalysts.

In order to study this issue, the conversion of syngas with both low and high alpha iron catalysts was conducted. In order to keep the reaction conditions essentially the same during the study, an inert gas was included in the feed gas stream. Thus, the water pressure could be varied by the addition of some amount of water together with the reduction of the flow of inert gas by the same molar amount. Under these experimental conditions, if the reactions occur on different sites, the increase in the partial pressure of water should increase the rate of the WGS reaction but the FTS rate should not change. On the other hand, if a common site is responsible for both reactions the addition of water should increase the WGS rate and decrease the FTS rate.

Materials and Methods

The precipitation method for the preparation of the iron catalyst, its activation using CO, and the reactor system have been described previously [1]. In the present study two catalysts were utilized: one with low alkali content (K/Fe =1.0) and high alkali content (K/Fe = 5). The reaction was conducted in a CSTR at 270^oC, $H_2/CO = 0.7$, 1.3 MPa and 5.05 L/h/g-iron. Conversion was determined using gc analysis. The WGS rate was defined by the production of CO_2 and the FTS rate as $CO_{in} – CO_{2out} – CO_{out}$.

Results and Discussion

The FTS reaction was conducted for at least a week until the iron catalyst attained essentially steady-state activity. Then increasing amounts of water was added to the feed stream and the flow of the inert gas was decreased by a corresponding amount. Using this procedure, the conversion could be effected with increasing amounts of water pressure while keeping the concentrations of the reactants nearly constant. Since the additional water increased the WGS conversion, the conversion of CO was not completely the same as more water was added to the feed gas. The results for typical runs are shown in Figure 1. As can be seen, for both catalysts the FTS conversion decreases while the WGS conversion increases. This leads one to the tentative conclusion that the FTS and WGS reactions occur on the same site. This conclusion is supported by the results of additional CSTR runs with other iron catalysts.

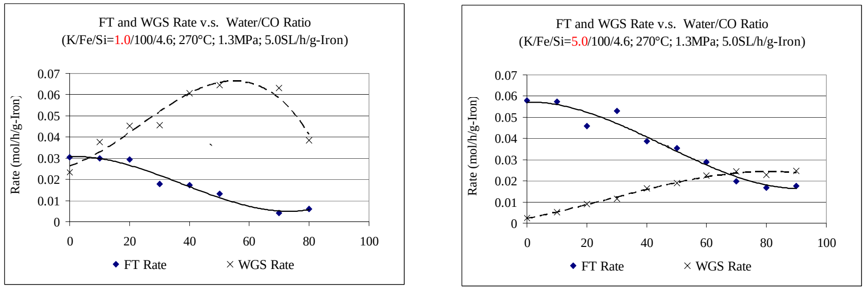

Figure 1. FTS and WGS rate for a low alpha (left) and high alpha (right) iron catalyst with increasing water partial pressure.

References

1. Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts, Final Report, 2002, DE-FC26-40308.