Kinetics of Main Reaction and Deactivation by Carbon of Cobalt Fischer-Tropsch Catalyst

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Introduction
One of the foremost technical challenges to the successful, economical practice of Fischer-Tropsch Synthesis (FTS), as with most catalytic processes, is catalyst life and activity. Understanding the chemistry of activation/deactivation pathways and modeling catalyst activation/deactivation rates are imperatives to the design of more stable catalysts and the development of robust, realistic reactor models which facilitate FT reactor/process design and optimization. Carbon deposition on FT catalysts is not sufficiently understood well enough to enable its quantification. There are only a few studies which have investigated the kinetics of Co deactivation [1, 2]. Our goal is to develop a rate model for the main reaction and for the deactivation which predicts the deactivation of Co FT catalysts by carbon deposition as a function of reactant partial pressures and temperature.

Materials and Methods
Reaction kinetic experiments were carried out in a fixed-bed reactor (X_Co < 24%) for 25 wt% Co/0.25 wt% Pt/Al_2O_3 (63-90 μm) using a fractional factorial design with four levels of temperature (210, 220, 230, 240°C) and three levels of P_H_2 (6, 8, 12 bar) and P_CO (2.7, 4, 6 bar). To determine deactivation rates, eight samples of the cobalt catalyst were tested over a period of 800-900 h, each at a different set of CO and H_2 partial pressures and temperature (in the range of 220-250°C) while the space velocity was held constant.

The FTS reaction kinetics and deactivation kinetics can be linked by the activity of the catalyst. Activity (a) is a function of time, temperature, and concentrations and is defined as the CO depletion rate normalized by the initial rate. The rate of the main reaction (r_m) and deactivation rate (r_d) are defined as follows:

\[ -r_m = k(T)f(T, C) a \]
\[ -r_d = -\frac{da}{dt} = k_d f_d(T, C) (a - a_\infty) \]

where the constant \( a_\infty \) represents the asymptotic or steady state catalyst activity as time approaches infinity.

Results and Discussion
Activity of the catalyst increases with increasing P_H_2 and the H_2 order becomes more positive as temperature increases (Figure 1); H_2 order (proportional to the slope of rate vs P_H_2) ranges from 0.56 to 0.77. At low temperatures (210-220°C) the CO consumption rate increases with increasing CO partial pressure (positive CO order), while the rate decreases with increasing P_CO (negative CO order) at high temperatures (230-240°C). In fact, CO order changes from a positive value of 0.31 at 210°C to a negative value of -0.64 at 240°C.

Since the CO order becomes more negative as the temperature increases, in a Langmuir-Hinshelwood framework, this suggests a denominator term including the partial pressure of CO with a rate constant coefficient (rather than adsorption coefficient). On the other hand, the reaction order for H_2 increases at higher temperatures suggesting an adsorption coefficient (heat of adsorption temperature dependence) for H_2 in the denominator, which will become less important at higher temperatures and result in a more positive overall H_2 order.

A realistic sequence of elementary steps which includes hydrogen-assisted dissociation of adsorbed CO and a parallel step which leads to carbon on the surface was used to derive the following three-parameter kinetic model. It includes a P_CO term with rate constant \( k' \) and adsorption coefficient \( K'' \) for P_H_2. It was used to fit all 24 data points over the entire temperature range and the fit was excellent with a correlation coefficient (r^2 value) of 0.996.

\[ -r_{CO} = \frac{k_{PO} P_CO^{0.5}}{(1 + k' P_CO + K'' \frac{P_H_2^{0.5}}{2})} \]

Significance
H_2 partial pressure dependence increases and CO pressure dependence decreases as temperature increases, and these observations are consistent with the proposed model. At 230°C, deactivation rate increases with either increasing P_CO or increasing P_H_2.

References