Deactivation Model for Co FT Catalysts
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Introduction
One of the foremost technical barriers to the successful, economical practice of Fischer-Tropsch Synthesis (FTS) is uncertainty regarding catalyst life. Understanding the chemistry of deactivation pathways and modeling catalyst 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, however, is not sufficiently quantitatively understood to effectively enable its management. The work of Saib et al. [1] identified three routes of deactivation; namely, (1) sintering of the Co active phase, (2) carbon deposition and (3) surface reconstruction.

Our goal is to develop a deactivation rate model which predicts the deactivation of Co FT catalysts by carbon deposition as a function of reactant partial pressures and temperature. To facilitate the accomplishment of this goal, four different cobalt catalysts will be prepared and tested, and one of them will be selected to obtain catalyst life data from which the model will be validated and rate constants obtained. The supported Co catalyst will be selected based on the best combination of activity, selectivity and stability.

Materials and Methods
To prepare the candidate catalysts, two kinds of alumina were used in this study (St. Gobein alumina stabilized with La (Al-StG) and a home-made alumina stabilized with silica (AlSi)). Each support was calcined at 700-1100 °C in air for 4 h prior to impregnation. The catalysts were prepared by slurry impregnation in a rotary evaporator in successive steps using an aqueous solution containing the appropriate amount of cobalt nitrate to get 25% Co. The sample was dried overnight in vacuum and calcined at 250 °C for about 16 h. The catalyst was also impregnated with Pt in the last impregnation step. The AlSi was also sometimes impregnated with Ca in which case it was designated as CaAlSi.

Activity studies were performed in a fixed-bed reactor. Reaction conditions were 180 to 220°C, 300 psig, H₂:CO=2.

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 rate normalized by the initial rate. The rate of the main reaction (r_{m}) and deactivation rate (r_{d}) are defined as follows:

\[-r_{m} = k(T)f_{a}(T,C)a\]
\[-r_{d} = -da/dt = k_{d}f_{d}(T,C)a^{d}\]

f_{a}(T,C) and f_{d}(T,C) are potentially functions of reactant and product concentrations and temperature which can lead to models with shifting reaction orders (e.g. Langmuir-Hinshelwood) which are more complex than models traditionally used such as power-law and generalized power-law models [2]. To verify and determine the constants for such a model, a wide range of rate data as a function of CO and H₂ partial pressures will be needed.

Results and Discussion
Table 1 shows the physical properties of the AlSi support and a 20% cobalt catalyst on that support after calcination. The alumina-silica support has high surface area and pore volume even though it was calcined at 1100 °C for 4 h, which makes it an excellent candidate for a highly loaded supported cobalt catalyst.

Table 1. Physical properties of the catalysts
<table>
<thead>
<tr>
<th>Sample</th>
<th>BET (m²/g)</th>
<th>V_p (cm³/g)</th>
<th>d_p (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlSi</td>
<td>167</td>
<td>0.61</td>
<td>17.4</td>
</tr>
<tr>
<td>20%Co/AlSi</td>
<td>102</td>
<td>0.41</td>
<td>18.2</td>
</tr>
</tbody>
</table>

The cobalt catalyst prepared on silica-alumina support has great stability; there is no significant activity change after 430 h (Table 2). To our surprise, the cobalt catalyst prepared on calcium pretreated silica-alumina support had very low activity (not shown here). Calcium was selected to lower the methane selectivity.

Table 2. Catalyst performance of AlSi25Co0.53Pt at 200 °C, 2.15 MPa, H₂/CO=2
<table>
<thead>
<tr>
<th>Property</th>
<th>Time on stream, h</th>
<th>Rate¹</th>
<th>H₂C. selectivity, mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>165</td>
<td>27</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>430</td>
<td>26</td>
<td>11</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.89</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>C₂⁺</td>
<td>85</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>Catalyst productivity</td>
<td>0.26</td>
<td>0.25</td>
<td></td>
</tr>
</tbody>
</table>

¹mmol (CO)/g cat/MPa/h
²gHC/ g cat/h

Significance
Due to the cost of both cobalt and noble metals, an extended catalyst life is required to make the FT process using cobalt catalysts more economically feasible. This highlights the importance of better understanding the deactivation pathways and accurately modeling the catalyst deactivation rates.

References