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Higher alcohols synthesis from syngas over carbon-nanotube supported Iron-Chromium catalysts

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Introduction
Higher alcohols synthesis (HAS) from syngas has recently drawn considerable attention for its application in the field of biofuel and bioadditive production [1-3]. Higher alcohols may be produced directly from syngas, which may be obtained by gasification of renewable sources such as biomass and waste. In the 1980s van der Riet et al. [4] studied the HAS with a K/Fe/Cr2O3 catalyst and achieved a high total selectivity to C2+ oxygenates of 83.4 wt% at 5 mol% CO conversion, but after these very promising, initial results there have been no subsequent reports on HAS with the K-Fe-Cr system. Recently, carbon-nanotubes (CNTs) have been reported as a novel interesting carrier for catalysts due to the unique chemical and physical properties of the nanotubes [5]. Here, CNT-supported K-Fe-Cr catalysts have been investigated. The investigations include high pressure (100 bar) activity evaluations, BET surface area measurements, X-ray diffraction (XRD) studies, and transmission electron microscopy (TEM) evaluations.

Experimental
Fe-Cr supported on CNTs or silica were prepared by co impregnating the supports with a precursor solution containing the metal salts. Additionally, CNTs were purified by refluxing CNTs in 37 wt% nitric acid at 110 °C for 5 h, followed by filtering, washing and drying. Performance of catalysts for HAS from syngas has been evaluated in a fixed-bed continuous-flow reactor with a GC-FID/TCD detection system [6]. Prior to the reaction the catalysts precursor were in-situ subjected to a reducing treatment in a flow of 20% H2 in N2 for 12-14 h at 400 °C. Typical operating conditions are: P = 100 bar; T = 250-400 °C; GHSV = 5000 h⁻¹; Feed: H2/CO=1 (v/v).

Results and Discussion
Table 1 shows the catalytic properties of K2CO3/Fe3Cr2/CNTs catalyst in CO hydrogenation at steady state. From 300 °C to 400 °C the selectivity to alcohols decreased from 83.7 % to 68.9 %, while the hydrocarbon (HC) selectivity increased from 13.4 % to 30.3 %. The selectivity to C2+-oxygenates reached 42.8 mol% at 300 °C. The alcohol space time yield reached 87 g·kgcath⁻¹·h⁻¹. The production of alcohols or hydrocarbons followed Anderson-Schulz-Flory (ASF) distributions. The chain growth probabilities for both alcohols and hydrocarbons are different, which may indicate that the intermediates for the alcohols and hydrocarbons are different. Figure 1 shows that the catalytic particles mainly are spread inside the CNTs. In the calcined catalyst, Fe3O4 particles were identified by XRD. No chromium-related reflections were observed in the XRD patterns indicating that Cr compounds in the catalyst were amorphous or finely dispersed. The particle sizes are in the range of 3-10 nm.
Additionally, the opened/impregnated CNTs did not seem to have agglomerated compared to the raw CNTs.

Table 1. Behavior of K$_2$CO$_3$/Fe$_1$Cr$_2$/CNTs catalyst in CO hydrogenation at steady state at $P = 100$ bar, $H_2/CO = 1.0$ vol/vol, and GHSV = 5000 h$^{-1}$.

<table>
<thead>
<tr>
<th>T [$^\circ$C]</th>
<th>CO conv. [mol%]</th>
<th>Space time yield [g/kg$_{cat}$ h$^{-1}$]</th>
<th>Carbon based, CO$_2$-free selectivity [mol%]</th>
<th>Chain growth probability ($\alpha$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Overall alcohols</td>
<td>Hydro-carbons</td>
<td>C$_2$+-oxygenates</td>
</tr>
<tr>
<td>300</td>
<td>3.6</td>
<td>11</td>
<td>83.7</td>
<td>13.4</td>
</tr>
<tr>
<td>325</td>
<td>4.4</td>
<td>26</td>
<td>85.0</td>
<td>13.2</td>
</tr>
<tr>
<td>350</td>
<td>4.7</td>
<td>32</td>
<td>81.9</td>
<td>17.7</td>
</tr>
<tr>
<td>400</td>
<td>8.2</td>
<td>87</td>
<td>68.9</td>
<td>30.3</td>
</tr>
</tbody>
</table>

Figure 1. TEM images of the raw CNTs (left) and the fresh K$_2$CO$_3$/Fe$_1$Cr$_2$/CNTs (right, the individual catalytic particles highlighted with black arrows).

Conclusions

A carbon-nanotube supported iron-chromium alcohol synthesis catalyst was synthesized, tested and characterized. At 300 °C it showed up to 43.8 mol% and 39.9 mol% selectivity to methanol and higher alcohols, respectively (3.6 mol% CO conversion). The production of alcohols or hydrocarbons followed ASF distributions. Chromium compounds in the catalyst were in the form of either amorphous or finely dispersed particles. Fe$_3$O$_4$ particles are mainly spread inside of the CNTs.

References