Effect of catalytic site position of carbon nanotubes supported cobalt catalysts in Fischer-Tropsch synthesis

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Worldwide decrease in oil reserves and high demand of clean energy reinforce the interest of Fischer-Tropsch (FT) synthesis to produce viable and clean-energy.

**Importance of FTS:**

- Syngas produced from non-petroleum sources
- Sulfur- and nitrogen-free high quality fuels (diesel and gasoline)
- Petrochemicals (olefins)

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Fischer-Tropsch is a heterogeneous catalytic process for the transformation of synthesis gas (H₂+CO with different ratio)

Reactions involved in Fischer-Tropsch Synthesis (FTS)

- **Paraffins formation:** \((2n + 1)\text{H}_2 + n\text{CO} \rightarrow C_n\text{H}_{2n+2} + n\text{H}_2\text{O}\)
- **Olefins formation:** \(2n\text{H}_2 + n\text{CO} \rightarrow C_n\text{H}_{2n} + n\text{H}_2\text{O}\)
- **Alcohols formation:** \(2n\text{H}_2 + n\text{CO} \rightarrow C_n\text{H}_{2n+2}\text{O} + (n - 1)\text{H}_2\text{O}\)
- **WGS reaction:** \(\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\)
- **Methanation:** \(\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}\)

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Catalysts for FTS: active phase

Group VIII metals (Co, Ru and Fe)

Cobalt

- High activity and selectivity to linear hydrocarbons
- Low activity for WGS reaction
- More stable toward deactivation by water
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Catalysts for FTS: supports

- Carbon nanotubes
  - SWNT (bundle)
  - MWNT

Most commonly used supports:
- SiO$_2$
- Al$_2$O$_3$
- TiO$_2$

Properties:
- High purity
- High mechanical strength
- Good electrical conductivity
- High thermal stability
- High surface area

AIM OF THIS WORK: Study the effect of the deposition of cobalt catalytic sites (on the inner and outer surface of the CNTs) for Fischer-Tropsch synthesis

KNOWLEDGE GAP

✓ Deviation of the graphene layers from planarity causes π electron density to shift from the concave inner surface to the convex outer surface

✓ Confinement could increase the density of reactants, which favor syngas conversion

✓ Deposition of catalytic sites inside the narrow channels could result in higher mass transfer restriction

Electron-deficient in-surface electron-enriched out-surface

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**Catalyst preparation**

**Support pre-treatment**
- Close cap CNTs
- $\text{HNO}_3$ 30 wt%, 100 °C, 16 h
- Open cap CNTs

**RESULTS**

**out-10Co/CNT**
- Co particles outside the pores
- Open cap CNTs
- Water addition
- Co salt solution
- Drying, calcination

**in-10Co/CNT**
- Co particles inside the pores
- Co salt solution
- Drying, calcination

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FTS study

Fixed bed reactor (450 mm L, 22-mm i.d.)

- Mass flow controllers
- Pressure Gauges
- BP Valve
- Fixed bed reactor (450 mm L, 22-mm i.d.)

EXPERIMENTAL

- T = 210-240 ºC
- Feed: H\textsubscript{2}/CO ratio: 2 (30%CO, 60%H\textsubscript{2}, 10%Ar) 30 ml/min
- P = 2 MPa
- TOS = 48 h

- Reduction: 30 ml/min H\textsubscript{2}, 380 ºC, 1 ºC/min
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Evaluation criteria used for catalytic performance

- **CO conversion:** \[ \% \text{CO} = \frac{\text{CO}_{\text{in}} - \text{CO}_{\text{out}}}{\text{CO}_{\text{in}}} \]

- **Product selectivity:** \[ S(C_i) = \frac{\text{mass of component } C_i}{\sum C_i} \]

- **FTS rate:** \[ \text{FTS rate} = \frac{\text{g of HC produced}}{\text{g of catalyst min}} \]

- **WGS rate:** \[ \text{WGS rate} = \frac{\text{g CO}_2 \text{ produced}}{\text{g of catalyst min}} \]
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Catalyst characterization

TEM: Effect of acid treatment

- Open nanotubes caps and removes impurities from CNTs
- Introduces a large number of functional groups
- Decreases the hydrophobicity of the CNT, easier impregnation
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Catalyst characterization

TEM: Effect of catalytic site position

in-10Co/CNT

out-10Co/CNT
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**EXPERIMENTAL**

**RESULTS**

**CONCLUSIONS**

XRD results

- $\Delta \text{Co}_3\text{O}_4$
- $\square \text{CoO}$
- $\bigcirc \text{CNT}$

![XRD graph](attachment:image.png)

Intensity (arb. units)

2θ

0 10 20 30 40 50 60 70 80 90 100 110 120

out-10%Co/CNT
in-10%Co/CNT
Treated CNT
Fresh CNT
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**ICP, BET results**

<table>
<thead>
<tr>
<th>Supports/catalysts</th>
<th>Metal content (%)</th>
<th>BET (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh CNT</td>
<td>-</td>
<td>205</td>
<td>0.67</td>
<td>6.5</td>
</tr>
<tr>
<td>Treated CNT</td>
<td>-</td>
<td>264</td>
<td>0.73</td>
<td>5.5</td>
</tr>
<tr>
<td>in-10Co/CNT</td>
<td>9.5</td>
<td>218</td>
<td>0.56</td>
<td>5.1</td>
</tr>
<tr>
<td>out-10Co/CNT</td>
<td>8.5</td>
<td>197</td>
<td>0.56</td>
<td>5.7</td>
</tr>
</tbody>
</table>

\[ S_{BET} (\text{in}) > S_{BET} (\text{out}) \]
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TPR results

$T_{\text{reduction (in)}} < T_{\text{reduction (out)}}$

$Co_3O_4 + H_2 = 3CoO + H_2O$

$CoO + H_2 = Co + H_2O$

$1^{\text{st peak}}$

$2^{\text{nd peak}}$
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**FTS kinetic results**

**CO conversion & CH₄ selectivity**

![Graphs showing CO conversion and CH₄ selectivity for in 10Co/CNT and out 10Co/CNT as a function of temperature (T °C).](image)
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**Product selectivity**

<table>
<thead>
<tr>
<th>Product selectivity</th>
<th>210 °C</th>
<th>220 °C</th>
<th>230 °C</th>
<th>240 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in</td>
<td>out</td>
<td>in</td>
<td>out</td>
</tr>
<tr>
<td>CH₄</td>
<td>4.6</td>
<td>6.7</td>
<td>8.2</td>
<td>10.5</td>
</tr>
<tr>
<td>C₂-C₄</td>
<td>2.4</td>
<td>2.0</td>
<td>3.2</td>
<td>3.3</td>
</tr>
<tr>
<td>C₅⁺</td>
<td>89.9</td>
<td>86.6</td>
<td>83.6</td>
<td>79.6</td>
</tr>
<tr>
<td>CO₂</td>
<td>3.1</td>
<td>4.7</td>
<td>4.9</td>
<td>6.7</td>
</tr>
</tbody>
</table>

- **Increasing temperature**
  - CO conversion ↑
  - C₂-C₄, CO₂ and CH₄ ↑
  - C₅⁺ ↓

in-10Co/CNT more selective to C₅⁺ and less selective to CO₂ and CH₄
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**Experimental**

**Introduction**

**Results**

**Conclusions**

_in-10Co/CNT_ more selective to $C_{5+}$ (higher FTS rate) and less selective to CO2 (lower WGS rate)
The favourable behaviour of \textbf{in-10Co/CNT} are related to:

- \textit{Electron deficiency in the inner surface}
  improving the reduction behaviour of the CNT catalysts

- \textit{Confinement effects}
  increasing the contact time of the reactants with the active sites, resulting in production of heavier hydrocarbons

- \textit{No mass transfer limitations}
  due to high selectivity to \( \text{C}_{5+} \)
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