Fischer-Tropsch synthesis: foregoing calcination and utilizing reduction promoters leads to improved conversion and selectivity with Co/silica

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Introduction

SYNGAS: CO and H₂

Steam Reforming / Partial Oxidation
- CH₄ + H₂O → CO + 3H₂
- CH₄ + 1/2O₂ → CO + 2H₂

Hydrogen
- Water-gas Shift / Preferential Oxidation
  - CO + H₂O → H₂ + CO₂
  - CO + 1/2O₂ → CO₂

FT Catalyst

Methanol, Ethanol
- Oxygenate Synthesis
  - CO + 2H₂ → CH₃OH

Diesel, Jet Fuel
- PEM Fuel Cells/SOFC
- Portable Power

Waxes, Lubricants
- Fischer-Tropsch Synthesis
  - CO + 2H₂ → [CH₂]ₙ + H₂O

Natural Gas

Coal

Biomass

Co, Ru, Fe
Introduction

Catalyst support and promoter:
- Cobalt often supported on metal oxide carriers like \textit{alumina} or \textit{titania}.

\begin{itemize}
  \item \textbf{Co/Al}_2\textbf{O}_3
  \item \textbf{Co/TiO}_2
  \item \textbf{Co/SiO}_2
\end{itemize}

Problem: The weak interaction between SiO\textsubscript{2} and cobalt oxides on calcined catalysts leads to agglomerated Co\textsuperscript{0} after activation. Productivity is lower.

We consider 3 aspect:
\begin{itemize}
  \item Activity (CO conversion per gram of cat.)
  \item Product Selectivity
  \item Stability
\end{itemize}

Promoter:
- Ru
- Re
- Ag
- Pt

Past efforts\textsuperscript{1,2} showed that direct reduction of cobalt nitrate led to small, difficult-to-reduce Co species.

We revisit the possibility of direct cobalt nitrate reduction, but utilize promoters to facilitate activation of the difficult-to-reduce Co species.

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Experimental

Catalyst preparation

To prepare 0.5 wt.% (calcined basis) Pt promoted catalysts, tetraamineplatinum (II) nitrate was added by IWI to the dried Co(NO$_3$)$_2$/silica parent batch, and the material was dried again in the rotary evaporator.

<table>
<thead>
<tr>
<th></th>
<th>Calcined</th>
<th>12%Co/SiO$_2$</th>
<th>0.5%Pt-12%Co/SiO$_2$</th>
<th>0.276%Ag-12%Co/SiO$_2$</th>
<th>0.477%Re-12%Co/SiO$_2$</th>
<th>0.259%Ru-12%Co/SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncalcined</td>
<td>12%Co/SiO$_2$</td>
<td>0.5%Pt-12%Co/SiO$_2$</td>
<td>0.276%Ag-12%Co/SiO$_2$</td>
<td>0.477%Re-12%Co/SiO$_2$</td>
<td>0.259%Ru-12%Co/SiO$_2$</td>
<td></td>
</tr>
</tbody>
</table>
**Experimental**

- **BET surface area and porosity measurements**
  BET surface area and porosity characteristics were measured using a Micromeritics 3-Flex system.

- **Temperature programmed reduction**
  TPR profiles of calcined catalysts were recorded using a Zeton-Altamira AMI-200 unit equipped with a thermal conductivity detector (TCD).

- **Hydrogen chemisorption and percentage reduction by pulse reoxidation**
  Hydrogen chemisorption was conducted by using temperature programmed desorption (TPD), also measured with the Zeton-Altamira AMI-200 instrument.

- **TPR-EXAFS/ TPR-XANES spectroscopies**
  In-situ H2-TPR XAFS studies were performed at the Materials Research Collaborative Access Team (MR-CAT) beamline at the Advanced Photon Source, Argonne National Laboratory.

- **Catalytic activity**
  FTS reaction tests were conducted using a 1 L CSTR equipped with a magnetically driven stirrer with turbine impeller.
**Results**

**BET surface area and porosity measurements**

If the support is the main contributor to the area, then after adding 12.3 wt. % Co and assuming no pore blocking, the specific surface area should decrease to 291 m$^2$/g for the air calcined Co catalyst and 225 m$^2$/g for the uncalcined catalyst.

XRD analysis of the catalysts.

![XRD analysis of catalysts](image)
**Cobalt Reducibility:**

Figure reveals that the air calcined catalyst reduced at a relatively low temperature.

\[
\text{Co}_3\text{O}_4 + \text{H}_2 = 3\text{CoO} + \text{H}_2\text{O} \\
3\text{CoO} + 3\text{H}_2 = 3\text{Co}^0 + 3\text{H}_2\text{O}
\]

For uncalcined, promoter addition did not shift the peak for nitrate decomposition (black) but did shift the peaks for reduction of cobalt oxides (red) derived from nitrate decomposition.
Cobalt Reducibility:
H$_2$-TPR Mass Spectrometry

- The hydrogen has two consumption peaks, associated with H$_2$O production for the calcined sample.
- These peaks are due to the two reduction steps from Co$_3$O$_4$ to Co involving CoO as an intermediate, as previously discussed.
- There is a small peak on H$_2$O profile at temperatures lower than 100°C. This is probably due to some adsorbed water on the catalyst.
Cobalt Reducibility:

TPR Mass Spectrometry

At temperatures lower than 180 °C, there are at least six major events, whereby:

6- Between 300 °C and 750 °C, there is a series of hydrogen uptakes with corresponding evolution of H₂O peaks, these are assigned to reduction of CoO species
The ranking of promoter effectiveness for CoO reduction from TPR-MS is: Pt > Re > Ru > Ag > unpromoted
TPR XANES

This calcined catalyst starts with a line shape resembling the cobalt oxide spinel structure of $\text{Co}_3\text{O}_4$, with conversion to CoO being achieved below $250\, ^\circ\text{C}$. Next, because of the larger weakly interacting Co clusters, Co$^0$ metal is rapidly formed by $\sim 300\, ^\circ\text{C}$ (final dark blue spectrum to first green spectrum for CoO to Co$^0$).
TPR XANES

With the uncalcined catalysts, \( \text{Co(NO}_3\text{)}_2 \) slowly converts to \( \text{CoO}_x \) decomposition products that are oxidized to a spinel (e.g., \( \text{Co}_3\text{O}_4 \)) – final light blue spectrum. Afterwards, a typical two step reduction of \( \text{Co}_3\text{O}_4 \) was observed, with \( \text{CoO} \) as the intermediate (final dark blue spectrum).

Relative to the calcined catalyst, reduction of cobalt oxides occurs over a wider range, indicating smaller, interacting \( \text{Co} \) oxide species.
Results

TPR XANES

CoO converted to Co$^0$ (final dark blue spectrum to green spectra) with vastly different final extents of reduction by 500 °C depending on the presence or absence of promoter, as well as the promoter identity.

Pt > Re, Ru > Ag
**Results**

**TPR XANES**

(1) uncalcined unpromoted catalyst, and uncalcined catalysts promoted with (2) Pt, (3) Ag, (4) Re, and (5) Ru

The point of maximum CoO following cobalt nitrate decomposition

Co(NO$_3$)$_3$*nH$_2$O in the initial spectra of uncalcined catalysts

The point of maximum spinel (e.g., Co$_3$O$_4$) following reduction of the spinel

Reference spectra Calcined 12%Co/SiO$_2$
Results

Temp. vs Composition

(a) 0.5%Pt-12%Co/SiO\textsubscript{2} calcined
(b) 12%Co/SiO\textsubscript{2} uncalcined
(c) 0.5%Pt-12%Co/SiO\textsubscript{2} uncalcined
(d) 0.276%Ag-12%Co/SiO\textsubscript{2} uncalcined
(e) 0.477%Re-12%Co/SiO\textsubscript{2} uncalcined
(f) 0.259%Ru-12%Co/SiO\textsubscript{2} uncalcined

- 268°C
- 297°C
- 453°C
- 520°C
- 520°C
- 370°C
TPR EXAFS

With the calcined catalyst, Co$_3$O$_4$ is converted to CoO (final dark blue spectrum), with resulting slight shifts in the distances of Co-O and Co-Co coordination.

CoO is a short-lived intermediate, and with a slight increase in temperature, a large peak for Co-Co metal coordination is formed (Green).
TPR EXAFS

With the uncalcined unpromoted catalyst, cobalt nitrate slowly converts to \( \text{CoO}_x \) that oxidizes to a spinel (e.g., \( \text{Co}_3\text{O}_4 \)) (first dark blue spectrum). The spinel converts to CoO (final dark blue spectrum).

Once formed, CoO converts very slowly to the metal (green spectra). Even at 500°C, Co-O coordination is still observed.
TPR EXAFS
By adding the promoter, the major difference is that significant Co-Co metal coordination peaks begin to form at lower temperature as expected from the TPR and TPR-XANES results, including Pt-promoted 300°C, Re-promoted ~400°C, Ru-promoted ~370°C.
TPR EXAFS

(1) uncalcined unpromoted catalyst, and uncalcined catalysts promoted with (2) Pt, (3) Ag, (4) Re, and (5) Ru

(a) Co(NO$_3$)$_n$H$_2$O in the initial spectra (b) the point of maximum spinel following cobalt nitrate decomposition, (c) the point of maximum CoO and (d) the point of maximum Co$^0$ content.
# Results

## Cobalt particle size differences

Results of hydrogen chemisorption and pulse re-oxidation.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\text{H}_2$ desorbed per $\text{g}\text{cat}$ [$\mu\text{mol}/\text{g}\text{cat}$]</th>
<th>Uncorr. Disp. [%]</th>
<th>Uncorr. Diam. [nm]</th>
<th>% Red. [%]</th>
<th>Corr. Disp. [%]</th>
<th>Corr. Diam. [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>12%Co/SiO$_2$ calcined</td>
<td>10.8</td>
<td>0.98</td>
<td>104.9</td>
<td>49.8</td>
<td>1.98</td>
<td>52.2</td>
</tr>
<tr>
<td>0.5%Pt-12%Co/SiO$_2$ calcined</td>
<td>19.3</td>
<td>1.91</td>
<td>54.0</td>
<td>51.4</td>
<td>4.29</td>
<td>24.0</td>
</tr>
<tr>
<td>0.5%Pt-12%Co/SiO$_2$ uncalcined</td>
<td>39.2</td>
<td>3.85</td>
<td>26.8</td>
<td>37.0</td>
<td>11.5</td>
<td>8.9</td>
</tr>
</tbody>
</table>

This table provides an estimate of the average Co metal particle size and extent of reduction obtained from hydrogen chemisorption with pulse reoxidation.
CO conversion and product selectivity for the tested catalysts (process conditions: T = 220°C, P= 300 psi, H₂/CO= 2 mol/mol, SV = 6 slph per g<sub>cat</sub>).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO Conv[%]</th>
<th>CH₄</th>
<th>C₂-C₄</th>
<th>C₅+</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>12%Co/SiO&lt;sub&gt;2&lt;/sub&gt; calcined</td>
<td>13.3</td>
<td>12.5</td>
<td>12.7</td>
<td>73.4</td>
<td>1.4</td>
</tr>
<tr>
<td>12%Co/SiO&lt;sub&gt;2&lt;/sub&gt; uncalcined</td>
<td>40.2</td>
<td>7.3</td>
<td>8.0</td>
<td>84.4</td>
<td>0.3</td>
</tr>
<tr>
<td>0.5%Pt-12%Co/SiO&lt;sub&gt;2&lt;/sub&gt; calcined</td>
<td>30.0</td>
<td>10.1</td>
<td>10.7</td>
<td>78.8</td>
<td>0.4</td>
</tr>
<tr>
<td>0.5%Pt-12%Co/SiO&lt;sub&gt;2&lt;/sub&gt; uncalcined</td>
<td>48.9</td>
<td>8.0</td>
<td>10.2</td>
<td>81.5</td>
<td>0.3</td>
</tr>
<tr>
<td>0.276%Ag-12%Co/SiO&lt;sub&gt;2&lt;/sub&gt; uncalcined</td>
<td>36.8</td>
<td>8.7</td>
<td>14.6</td>
<td>76.4</td>
<td>0.3</td>
</tr>
<tr>
<td>0.477%Re-12%Co/SiO&lt;sub&gt;2&lt;/sub&gt; uncalcined</td>
<td>51.3</td>
<td>6.8</td>
<td>11.7</td>
<td>81.2</td>
<td>0.3</td>
</tr>
<tr>
<td>0.259%Ru-12%Co/SiO&lt;sub&gt;2&lt;/sub&gt; uncalcined</td>
<td>36.8</td>
<td>9.3</td>
<td>9.1</td>
<td>81.2</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Results

Evolution with Time On Stream of carbon monoxide conversion for uncalcined and calcined samples

process conditions: $T = 220^\circ$C, $P = 300$ psi, $H_2/CO = 2$ mol/mol, $SV = 6$ slph per $g_{cat}$.

CO conversion of the unpromoted samples decreased with T.o.S., and the deactivation rate was 0.05%/h for the uncalcined catalyst relative to 0.025%/h for the calcined.
Foregoing calcination and utilizing direct reduction of cobalt nitrate led to the formation of smaller and more strongly interacting cobalt oxide nanoclusters in interaction with silica support as intermediates of the activation process to Co$^0$ nanoparticles; this was demonstrated by TPR, TPR-MS, TPR-XANES, and TPR-EXAFS experiments using hydrogen.

These intermediate cobalt oxides included a spinel (e.g., Co$_3$O$_4$) formed from oxidation of Co$^{2+}$ species by NO$_2$, which in turn converted to CoO prior to formation of the metal.

To improve the reducibility, metal promoters such as Pt, Re, Ru, and Ag were added.
The best catalysts were Re and Pt promoted 12%Co/SiO₂ catalysts utilizing direct reduction of the nitrate, where conversions in a CSTR were up to 3.8 times higher and 71% higher than unpromoted and Pt promoted air calcined catalysts, respectively.

At the same time, methane production was lower (6.8 and 8.0% for Re and Pt promoted catalysts by direct reduction versus 12.5 and 10.1% for unpromoted and Pt promoted air calcined catalysts) and C₅⁺ selectivity was higher (81.2 and 81.5% for Re and Pt promoted catalysts by direct reduction versus 73.4 and 78.8% for unpromoted and Pt promoted air calcined catalysts).
Thanks