Novel Application of Bio-char as a Catalyst in the Low Temperature SRC-deNO$_x$ Process

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• SCR unit located up stream of air pre-heaters, FGD and particulate control devices to meet temperature requirements (300 – 400 °C).

• SCR unit aids in the conversion of SO$_2$ to SO$_3$ and the production of ammonia salts (\((\text{NH}_4)\text{SO}_4 / (\text{NH}_4)\text{HSO}_4\)) known for their respective corrosive and fouling nature.

• SCR unit replacement costly and performed during an outage.
• Low temperature SCR (100 – 200 °C) down stream of air pre-heaters, FGD and particulate control devices.

• Low temperature SCR avoids conversion of SO₂ to SO₃ and the production of ammonia salts.

• Novel use of a waste derived SCR catalyst represents a way of combining waste disposal, energy recovery and pollution control (NO) in one process.

• Oxides of Manganese (Mn) and Ceruim (Ce) demonstrate excellent performance at low temperatures due to unique redox and acid-base properties.
Chemical Activation and Co-activation Processes
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Structure of talk

Chemical Activation and Co-activation Processes

Phosphoric Acid (0.75, 1.5 and 3.0 wt%) + Cotton Stalk

Precursor Cotton Stalk Material

Chemical Activation (5°C/min to 800°C, N₂ 200 cm³/min)

CACS-Carbon Support

Phosphoric Acid (0.75, 1.5 and 3.0 wt%) + Cotton Stalk

Precursor Cotton Stalk Material

Chemical Activation (5°C/min to 800°C, Steam/N₂ 200 cm³/min)

Washed in NaOH (0.1 M)
Oven Dried 105°C, 24 hrs

CO-ACS-Carbon Support

Metal (Mn/Ce) 4 wt% Dissolved in Deionised H₂O + CACS-Carbon Support

Semi-solid Precursor Mixture Continuously Stirred

Oven Dried, Air, 105°C, 12 hrs

Solid Precursor Mixture (Mn/Ce-CACS)

Precursor Mixture (Mn/Ce-CACS) Calcined (Nb, 500°C, 5 hrs)

Biorenewable SCR Catalyst (CACS-Mn/Ce)

Metal (Mn/Ce) 4 wt% Dissolved in Deionised H₂O + COACS-Carbon Support

Semi-solid Precursor Mixture Continuously Stirred

Oven Dried, Air, 105°C, 12 hrs

Solid Precursor Mixture (Mn/Ce-CO-ACS)

Precursor Mixture (Mn/Ce-CO-ACS) Calcined (Nb, 500°C, 5 hrs)

Biorenewable SCR Catalyst (CO-ACS-Mn/Ce)
Modified Fixed Bed Reactor Co-activation
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Fixed Bed SCR Reactor

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### Chemical Activation

<table>
<thead>
<tr>
<th>SCR-deNO(_x) Catalyst</th>
<th>Ce/Mn (Molar Ratio)</th>
<th>Temperature (°C)</th>
<th>H(_3)PO(_4) (wt% Ratio)</th>
<th>Hold Time (Hrs)</th>
<th>Atmosphere</th>
<th>BET Surface Area (m(^2) g(^{-1}))</th>
<th>Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CACS(_{0.75})-Mn/Ce</td>
<td>1:2</td>
<td>800</td>
<td>0.75:1</td>
<td>2</td>
<td>N(_2)</td>
<td>826.95</td>
<td>2.74</td>
</tr>
<tr>
<td>CACS(_{1.5})-Mn/Ce</td>
<td>1:2</td>
<td>800</td>
<td>1.5:1</td>
<td>2</td>
<td>N(_2)</td>
<td>1100.63</td>
<td>3.79</td>
</tr>
<tr>
<td>CACS(_{3.0})-Mn/Ce</td>
<td>1:2</td>
<td>800</td>
<td>3.0:1</td>
<td>2</td>
<td>N(_2)</td>
<td>1184.83</td>
<td>5.26</td>
</tr>
</tbody>
</table>

### Co-Activation

| CO-ACS\(_{0.75}\)-Mn/Ce | 1:2                | 800              | 0.75:1                      | 2               | N\(_2\)/Steam | 1293.90                              | 2.46              |
| CO-ACS\(_{1.5}\)-Mn/Ce  | 1:2                | 800              | 1.5:1                       | 2               | N\(_2\)/Steam | 1613.63                              | 3.45              |
| CO-ACS\(_{1.5}\)-Mn/Ce  | 1:2                | 800              | 3.0:1                       | 2               | N\(_2\)/Steam | 1541.00                              | 4.61              |

Experimental conditions employed to chemically activate (CACS) and co-activate (CO-ACS) cotton stalk impregnated with Ce/Mn.
NO conversion (%) of chemically activated (CACS$_x$-Mn/Ce) and co-activated (CO-ACS$_x$-Mn/Ce) cotton stalk derived SCR-deNO$_x$ catalysts impregnated with Mn/Ce. A = CACS$_x$-Mn/Ce, B= CO-ACS$_x$-Mn/Ce.
X-ray diffraction patterns of chemically activated (CACS$_x$-Mn/Ce) and co-activated (CO-ACS$_x$-Mn/Ce) cotton stalk derived SCR-deNO$_x$ catalysts impregnated with Mn/Ce. A = CACS$_{1.5}$-Mn/Ce, B = CO-ACS$_{1.5}$-Mn/Ce.
• NO conversion efficiencies were seen to range from ~48% to 68% for both CACS$_x$-Mn/Ce and CO-ACS$_x$-Mn/Ce.

• The catalysts ability to oxidize NO to NO$_2$ is crucial for the overall conversion of NO to N$_2$:

\[
\text{NH}_3(\text{aq}) + \text{O} (\text{aq}) \rightarrow \text{NH}_2 (\text{aq}) + \text{OH} (\text{aq}) \quad \text{RQ-1}
\]

\[
2\text{NO} (\text{g}) + 2\text{O}_2 (\text{g}) \rightarrow 2\text{NO}_2 (\text{aq}) \quad \text{RQ-2}
\]

\[
\text{NH}_2 (\text{aq}) + \text{NO} (\text{g}) \rightarrow \text{NH}_2\text{NO} (\text{aq}) \rightarrow \text{N}_2 (\text{g}) + \text{H}_2\text{O} (\text{g}) \quad \text{RQ-3}
\]

\[
\text{OH} (\text{aq}) + \text{NO}_2 (\text{aq}) \rightarrow \text{O} (\text{aq}) + \text{HNO}_2 (\text{aq}) \quad \text{RQ-4}
\]

\[
\text{NH}_3 (\text{aq}) + \text{HNO}_2 (\text{aq}) \rightarrow \text{NH}_4\text{NO}_2(\text{aq}) \rightarrow \text{NH}_2\text{NO} (\text{aq}) + \text{H}_2\text{O} (\text{g}) \rightarrow \text{N}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{g}) \quad \text{RQ-5}
\]

• The required excess of O$_2$ for reactions 1 and 2 to occur is significantly reduced impacting on reactions 3 to 5.
• The redox potential of the catalysts is dependent on the transition metals (valency) ability to maximize reaction rates between NO and NH$_3$ in the presence of O$_2$ on their respective active sites.

• Saturation of the active sites is suggested to occur rapidly allowing for an increased excess of NH$_3$ and NO to pass un-reacted over the catalyst.

• The low metal loading of 4 wt% is thought to be mainly responsible for the conservative NO reductions.

• Historical literature has demonstrated NO reductions >95% for metal loadings ranging from 10 - 30 wt% at temperatures between 150 and 230 °C.
• The raw cotton stalk and pyrolysed char have shown a potential for possible application in the low temperature SCR-deNO\textsubscript{x} process.

• NO reduction far more dependent on the wt% of the metal loading than the physical parameters such as the pore size, pore structure and surface area.

• The addition of phosphoric acid significantly increased the BET surface area (m\textsuperscript{2}g\textsuperscript{-1}) for CACS\textsubscript{x}-Mn/Ce and CO-ACS\textsubscript{x}-Mn/Ce catalysts.

• Higher NO reductions can be realised by an increase in the metal loadings of Mn/Ce.
• The influence of the activation methods in conjunction with H₃PO₄ on NO reduction are complex and require further investigation.

• Investigate the highest NO reductions associated with metal loading (4 wt% - 30 wt%).

• SCR experiments using a variety of other waste materials as a catalytic support (MSW, waste plastics and waste tyres).

• SCR experiments to be conducted in a synthesised flue gas containing both particulates, SO₂ and H₂O as well as Hg.

• Investigate application of low temperature catalyst in NO emission control from heavy duty vehicle engines.
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