Carbon Nanotubes Activation and its Influence on the Catalytic Performances of Pt/CNT Catalysts for Selective Hydrogenation

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Why CNT in catalysis?

Inverse structure of a traditional catalyst support

Conventional support

No mass transfer limitation
No pore blocking

Structurally dynamic support

- Mechanical properties
- Electronic properties
- Thermal conductivity

Resistant (attrition)
Conductive support (e⁻ transfer)
Exothermicity of chemical reactions

MSI
Specific reactivity?
Pt/CNT catalysts for selective hydrogenation

As grown CNT purification Pure CNT Support

1

Nitric acid treatment Air oxidation Ball-milling

CNT activation

Impact on...
• Specific surface area
• Length/Opening
• Surface chemistry

2

Activated Support new properties

3

Selective Hydrogenation

4

Grafting procedure
• Surface Organometallic Chemistry

Pt/CNT

Activated catalyst

Supported catalyst

CATALYSIS

Supported catalyst
Purified CNT powder

Purity: 95% (5% metal catalyst)

Pore volume: 0.8 cm³/g
Pore diameter: 6-20 nm

TPD: few oxygenated surface groups

S_{BET}: 180 m².g⁻¹
Length: tenth of µm

8 nm < Ø_{ext} < 21 nm
4 nm < Ø_{int} < 12 nm

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CNT activation (I) – HNO₃ treatment

HNO₃, 65%, 1g C/50 mL
0 to 8h, 140°C

XPS Chemical titration

2 kinetic regimes
- fast oxidation
- slow oxidation

• XPS
• TEM
• TGA
• XRD
• IR, Raman
CNT activation (I) – HNO$_3$ treatment

Raman

$\frac{I_D}{I_G}$ provides information on the disorder in CNTs

Decrease of $\frac{I_D}{I_G}$ (zone A) due to the oxidation of amorphous carbon
CNT activation (I) – HNO$_3$ treatment

significant CO$_2$ evolution during the first minutes of the reaction

Native carbon removal

C + “O$_2$” → CO$_2$
**CNT activation (I) – HNO₃ treatment**

- Slightly oxidized MWCNTs after 30 min treatment.
- Functionalization of carbon at MWCNTs defects, -CHₙ groups.

**Zone A**

Functionalization of carbon at MWCNTs defects, -CHₙ groups
**CNT activation (I) – HNO$_3$ treatment**

- Damaged tips of MWCNTs
- CNT opening
- Functionalization at reactive sites such as pentagons
- Some iron dissolution
- Moderately oxidized MWCNTs – 1 h
- Zone A/B

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CNT activation (I) – HNO₃ treatment

Zone B

highly oxidized MWCNTs

CNT walls damaged Burn-off
CNT activation (I) – HNO$_3$ treatment

<table>
<thead>
<tr>
<th>Support</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>CO (µmol g$^{-1}$)</th>
<th>CO$_2$ (µmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT</td>
<td>179</td>
<td>211</td>
<td>62</td>
</tr>
<tr>
<td>MWCNT-HNO$_3$</td>
<td>220</td>
<td>2132</td>
<td>1296</td>
</tr>
<tr>
<td>I.&amp;II. Carboxylic strong acidic, 560-700K</td>
<td></td>
<td>120</td>
<td>1017</td>
</tr>
<tr>
<td>IV. Lactones, 935K</td>
<td></td>
<td>-</td>
<td>108</td>
</tr>
<tr>
<td>III. Anhydrides, 790K</td>
<td></td>
<td>163</td>
<td>163</td>
</tr>
<tr>
<td>V. Phenols, 885K</td>
<td></td>
<td>917</td>
<td>-</td>
</tr>
<tr>
<td>VI. Carbonyl/Quinones, 1050K</td>
<td></td>
<td>920</td>
<td>-</td>
</tr>
</tbody>
</table>

TPD

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CNT activation (II) – ball-milling

1. CNT shortening

2. CNT opening
   ~ 20%

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### CNT activation (II) – ball-milling

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>0</th>
<th>12</th>
<th>24</th>
<th>60</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNTs aggregates mean diameter (µm)</td>
<td>37</td>
<td>15</td>
<td>10</td>
<td>4.7</td>
<td>4.5</td>
</tr>
<tr>
<td>MWCNTs length (µm)</td>
<td>~ 50</td>
<td>-</td>
<td>-</td>
<td>0.1-1</td>
<td>-</td>
</tr>
<tr>
<td>MWCNTs S\textsubscript{BET} (m\textsuperscript{2}/g)</td>
<td>177</td>
<td>180</td>
<td>201</td>
<td>260</td>
<td>240</td>
</tr>
<tr>
<td>I\textsubscript{D}/I\textsubscript{G} (Raman)</td>
<td>1.64</td>
<td>-</td>
<td>1.84</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>at. O % (XPS)</td>
<td>1.1</td>
<td>-</td>
<td>1.35</td>
<td>2.1</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Low amount of oxygenated groups
CNT activation (III) – air oxidation

1. CNT opening ~ 40%

2. CNT shortening
**CNT activation (III) – air oxidation**

**TGA - Raman**

- Important burn-off ($T_{ox} = 500^\circ C$)
- CNT surface damaged
**CNT activation – Surface chemistry**

Type and concentration of groups are different (TPD)

- CO
  - \( \text{HNO}_3 \) (-COOH) > air (-CO) >> ball-milling
CNT activation - Comparison

- HNO$_3$
  - Oxygenated groups
  - Non destructive

- Ball-milling
  - Length

- Air oxidation
  - Opening
  - Destructive

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CNT activation – CNT dispersibility (EtOH)

24h

Functionalized (-COOH) CNT

Short CNT
# Pt/CNT catalysts

**Diagram:**

- **COOH**
- **[PtII\(\text{Me}_2\)(COD)]**
- **N\(_2\) - 400°C**
- **H\(_2\) - 350°C**

**Table:**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(S_{\text{BET}}) (m(^2) g(^{-1}))</th>
<th>Pt load (wt. %)</th>
<th>TPD (µmol g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO</td>
</tr>
<tr>
<td>MWCNT-COOH</td>
<td>241 (225)</td>
<td>-</td>
<td>1960</td>
</tr>
<tr>
<td>Pt/MWCNT-COOH</td>
<td>241</td>
<td>4.8±0.1</td>
<td>1448</td>
</tr>
<tr>
<td>MWCNT-air</td>
<td>311 (225)</td>
<td>-</td>
<td>1584</td>
</tr>
<tr>
<td>Pt/MWCNT-air</td>
<td>297</td>
<td>2.1±0.1</td>
<td>1144</td>
</tr>
<tr>
<td>MWCNT-bm</td>
<td>201 (177)</td>
<td>-</td>
<td>792</td>
</tr>
<tr>
<td>Pt/MWCNT-bm</td>
<td>226</td>
<td>2.7±0.1</td>
<td>788</td>
</tr>
</tbody>
</table>

**Notes:**

- No pore blocking, except CNT-air (open)
- Oxygenated groups decreases upon Pt grafting
Pt/CNT catalysts

Influence of the concentration of oxygenated groups on Pt dispersion
Selective hydrogenation of cinnamaldehyde

Difficult since reaction kinetics and thermodynamics both favor hydrogenation of the C=C double bond.

Building block in organic synthesis (perfumery, pharmaceuticals)
Selective hydrogenation of cinnamaldehyde

**Catalysts activation** (thermal treatment – 700°C N₂)

- Elimination of surface groups (adsorption)
- Mean NP size (selectivity)

**TPD**

- CO₂ (µmol.g⁻¹.s⁻¹)
- CO (µmol.g⁻¹.s⁻¹)
## Selective hydrogenation of cinnamaldehyde

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NP diam (nm)</th>
<th>CO+CO₂ (µmol/g)</th>
<th>TOF (s⁻¹)</th>
<th>Selectivity (%), X_{CAL} = 50%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>COL</td>
</tr>
<tr>
<td>4.8%Pt/MWCNT-COOH</td>
<td>5.2</td>
<td>1916</td>
<td>3.6</td>
<td>15</td>
</tr>
<tr>
<td>Pt/MWCNT-COOH700</td>
<td>8.5</td>
<td>513</td>
<td>21.2</td>
<td>43</td>
</tr>
<tr>
<td>2.1%Pt/MWCNT-air</td>
<td>9.7</td>
<td>1388</td>
<td>12.1</td>
<td>4</td>
</tr>
<tr>
<td>Pt/MWCNT-air700</td>
<td>17.2</td>
<td>645</td>
<td>7.2</td>
<td>69</td>
</tr>
<tr>
<td>2.7%Pt/MWCNT-bm</td>
<td>13.5</td>
<td>1048</td>
<td>13.9</td>
<td>19</td>
</tr>
<tr>
<td>Pt/MWCNT-bm700</td>
<td>18.5</td>
<td>453</td>
<td>10.4</td>
<td>65</td>
</tr>
</tbody>
</table>

### Rate
Linear increase of catalyst activity when the amount of oxygenated groups on the support surface decreases (Pt: 5-13 nm)

### Selectivity/Rate
Balance between: the concentration of oxygenated groups, the mean particle size and CNT morphology
Conclusions

CNT activation affects CNT characteristics such as $S_{\text{BET}}$, length, C/O ratio...

Impact on characteristics of catalyst

- Metal dispersion
- Adsorption
- Dispersibility

Impact on catalyst properties

- Activity & Selectivity
- Activity & Selectivity
- Activity
THANK YOU FOR YOUR KIND ATTENTION