Modulated Synthesis of Cr-MOF (MIL 101) for Hydrogen Storage Applications

Tshiamo Segakweng
Introduction

- Hydrogen South Africa (HySA)
  - DST
  - NWU / CSIR
  - UCT / Mintek
  - UWC

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- Council for Scientific and Industrial Research (CSIR)

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Objectives

• Prepare Cr-MOF with safe synthetic method
• Maximise the $\text{H}_2$ adsorption of the synthesised Cr-MOFs
• Maximise safety in the syntheses procedure to enable large scale production
Unique Facts about Cr-MOF

• Large pores that can be used for gas storage
• Open metal sites
• Relative large surface area
• Hydrogen storage potential
• H$_2$O as solvent
• Draw back is the use of HF as a modulator
Chromium-based MOF (MIL-101) (MIL= Matériaux de l’Institut Lavoisier)

Two types of mesoporous cages: 29Å and 34Å
MIL-101 Structure

- Hydrothermal synthesis in an autoclave
- Chromium salt (usually Cr(NO$_3$)$_3$·9H$_2$O), H$_2$BDC and H$_2$O
- 200–220 °C
- 8–20 h
- Formula: Cr$_3$F(H$_2$O)$_2$O[(O$_2$C)-C$_6$H$_4$-(CO$_2$)]$_3$.nH$_2$O (where n is ~25)
Hydro Fluoric acid

- HF acid is very reactive
- Special storage and apparatus
- Very toxic and harmful to the environment
- Safe use of HF in large scale results in more expenses and increased danger for all involved as well as the environment
# Fluorine Substitution

<table>
<thead>
<tr>
<th>Property</th>
<th>Fluorine</th>
<th>Sulphur</th>
<th>Chlorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic no.</td>
<td>9</td>
<td>16</td>
<td>17</td>
</tr>
<tr>
<td>Std. Atomic weight</td>
<td>18.99</td>
<td>32.06</td>
<td>35.45</td>
</tr>
<tr>
<td>Atom group</td>
<td>Halogen</td>
<td>Chalcogen</td>
<td>Halogen</td>
</tr>
<tr>
<td>Electron config.</td>
<td>[He] 2s2 2p5</td>
<td>[Ne] 3s2 3p</td>
<td>[Ne] 3s2 3p5</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>3.98</td>
<td>2.58</td>
<td>3.16</td>
</tr>
<tr>
<td>Oxidation state</td>
<td>-1 (Fluoride ion)</td>
<td>+6 (in H2SO4)</td>
<td>-1 (chloride ion)</td>
</tr>
<tr>
<td>Van de Waals Radii</td>
<td>135 pm</td>
<td>180pm</td>
<td>175 pm</td>
</tr>
</tbody>
</table>

- Chlorine is hence the best option
- Can be added via HCl or Salts ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$)
Initial experiments gave small sized crystals

To improve hydrogen storage, we had to obtain bigger sized crystals

An acid with a similar functional group to that of H₂BDC was needed to slow down the reaction to allow for bigger crystal growth
PXRD patterns of the obtained MIL-101

(a)

Intensity (a.u.)

2-Theta

100 eq
80 eq
50 eq
20 eq
10 eq
0 eq
Effect of different ratios of formic acid/CrCl$_3$
(a) $N_2$ and (b) $H_2$ sorption isotherms at 77 K and 1 bar
<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm³)</th>
<th>$S_{\text{BET}}$ (m²·g⁻¹)</th>
<th>Pore vol. (cm³·g⁻¹)</th>
<th>Micropore vol. (cm³·g⁻¹)</th>
<th>H₂ uptake (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-101 (0 eq)</td>
<td>1.55</td>
<td>1133.7</td>
<td>0.51</td>
<td>0.43</td>
<td>0.99</td>
</tr>
<tr>
<td>MIL-101 (50 eq)</td>
<td>1.58</td>
<td>1715.7</td>
<td>0.91</td>
<td>0.78</td>
<td>1.65</td>
</tr>
<tr>
<td>MIL-101 (100 eq)</td>
<td>1.60</td>
<td>2618.5</td>
<td>1.36</td>
<td>1.22</td>
<td>1.92</td>
</tr>
</tbody>
</table>

Thermo gravimetric analysis
CI-MIL-101 and F-MIL-101 FTIR
PXRD patterns of CrMOF samples obtained in 100 eq synthesis.
Time dependent reaction

Phase-transition from MIL-101 to MIL-53 observed at the longer synthesis time
Stability in H2O and DMF

(a) XRD patterns, and (b) N$_2$ adsorption isotherms of MIL-101 after exposure to 80 °C water and DMF for 5 days.
Confirmed synthesis

- Reagents: $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{H}_2\text{BDC}$, Formic Acid, $\text{H}_2\text{O}$
- Reaction time: 8hrs in high pressure autoclave
- Formic acid: $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ equivalents: 100eq
Conclusions

- Successful synthesis of Cr-MOF with no HF
- Water stability confirmed
- Economical and safe industrial production possible

GREEN INDUSTRIAL SYNTHESIS POSSIBLE
Acknowledgments

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HySA Infrastructure (CSIR, NWU, DST)

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