Biomass-derived Porous Carbonaceous Materials: Synthesis and Catalytic Applications

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COST Action FP1306 «LIGNOVAL»

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ORGANISATION
COST Action FP1306

WG1
Pre-treatment/fractionation

WG2
Hemicellulose valorisation

WG3
Lignin valorisation

WG4
LCA & Techno-economic analysis
Furfural production

- Chemistry and mechanisms of formation and destruction
- Novel process concepts including downstream processes
- **Novel solid acid catalysts** with high hydrothermal stability!!!
Today’s industrial chemical products are largely based on oil & gas

- Background: biomass derived porous materials
- Starbons: new functional mesoporous carbons
- MAGBON: synthesis and applications
- Conclusions
BACKGROUND

THE INITIAL CONCEPT

Biomass Derived Polysaccharides

Novel Nano Porous Materials

Graphite-like materials
Microporous carbons
Mesoporous carbons

Temperatures of preparation

Carbonaceous materials
Charcoals

Mesoporosity $V_{\text{meso}}/V_{\text{total}}$

Starbons

ChemSocRev 2009, 38, 3401
ChemCatChem 2015, in press

TAKEN TO THE DESIGN OF ADVANCED FUNCTIONAL MATERIALS

ChemCatChem 2014;
ChemComm. 2015,
Mesoporous carbons from biomass: Starbons®

Hydrophobicity of starbons functional groups

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°C</td>
<td>Stable in aprotic solvents, alcohols, acetone.</td>
</tr>
<tr>
<td>150°C</td>
<td>Stable in boiling toluene.</td>
</tr>
<tr>
<td>170°C</td>
<td>Stable in boiling water.</td>
</tr>
<tr>
<td>220°C</td>
<td>Stable to acid and base solutions</td>
</tr>
<tr>
<td>300°C</td>
<td></td>
</tr>
<tr>
<td>450°C</td>
<td></td>
</tr>
<tr>
<td>600°C</td>
<td></td>
</tr>
<tr>
<td>700°C</td>
<td></td>
</tr>
</tbody>
</table>


My name is BON, MAGBON

Synthesis of catalysts

**Carbonaceous Materials**

- **Steps**
  - Gelatinization in water of starch and cooling 5°C
    - (140°C, 2 hours)
    - (overnight)

- **Solvent-exchange steps**

  - STARCH
  - Fe₃O₄-STARCH

**Mesoporous carbons from biomass: Magbons®**

*ChemCatChem 2014*
FORMATION OF A POROUS MAGNETIC GEL

1. Starch/H₂O; 140°C, 2 h

2. Cooling down; 5°C, 24 h

3. Addition of Fe₃O₄

PREPARATION OF THE MESOPOROUS MAGNETIC HYBRID

MAGSTAR
CONTROLLED CARBONISATION OF MAGSTAR AT 450°C

N₂ FLOW; 450°C, 2 h

MAGBON450

FUNCTIONALIZATION OF MAGBON450

H₂SO₄; 80°C, 4 h

MAGBON450-S
Synthesis of catalysts

Carbonization
(200-450°C, under N₂ flow)

MAGBON-200
MAGBON-450
## Materials characterization

### TEXTURAL PROPERTIES

<table>
<thead>
<tr>
<th>Materials</th>
<th>$S_{BET}$ (m²/g)</th>
<th>Pore diameter (nm)</th>
<th>Pore Volume (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous STARCH</td>
<td>120</td>
<td>9.1</td>
<td>0.38</td>
</tr>
<tr>
<td>STARBON450</td>
<td>568</td>
<td>4.5</td>
<td>0.35</td>
</tr>
<tr>
<td><strong>STARBON450-S</strong></td>
<td><strong>309</strong></td>
<td><strong>4.9</strong></td>
<td><strong>0.21</strong></td>
</tr>
<tr>
<td>MAGSTAR</td>
<td>114</td>
<td>10.9</td>
<td>0.46</td>
</tr>
<tr>
<td>MAGBON450</td>
<td>248</td>
<td>5.0</td>
<td>0.32</td>
</tr>
<tr>
<td><strong>MAGBON450-S</strong></td>
<td><strong>115</strong></td>
<td><strong>4.5</strong></td>
<td><strong>0.25</strong></td>
</tr>
</tbody>
</table>
Table 2. XPS analysis of the novel materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Atomic concentrations (%)</th>
<th>C1s HiRes components (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O 1s</td>
<td>C 1s</td>
</tr>
<tr>
<td>MAGBON450</td>
<td>21.5</td>
<td>66.8</td>
</tr>
<tr>
<td>MAGBON450-S</td>
<td>20.0</td>
<td>76.8</td>
</tr>
</tbody>
</table>

Correlation graph: C-C vs. O/C
(A-C) MAGBON450-S  (D) STARBON450
## Selective oxidation of benzyl alcohol

![Chemical reaction diagram](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (min)</th>
<th>Conversion (mol%)</th>
<th>Sel. Benzaldehyde (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Blank (no catalyst)</td>
<td>60</td>
<td>&lt;10</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>STARBON450</td>
<td>5</td>
<td>&lt;10</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>STARBON450S</td>
<td>5</td>
<td>&lt;15</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4</td>
<td>MAGBON450</td>
<td>5</td>
<td>28</td>
<td>93</td>
</tr>
<tr>
<td>5</td>
<td>MAGBON450S</td>
<td>5</td>
<td>74</td>
<td>66</td>
</tr>
<tr>
<td>6</td>
<td>MAGBON450S</td>
<td>5</td>
<td>45&lt;sup&gt;a&lt;/sup&gt;</td>
<td>86</td>
</tr>
<tr>
<td>7</td>
<td>MAGBON450S</td>
<td>5</td>
<td>50&lt;sup&gt;b&lt;/sup&gt;</td>
<td>79</td>
</tr>
<tr>
<td>8</td>
<td>Fe/MCM-41&lt;sup&gt;[12]&lt;/sup&gt;</td>
<td>60</td>
<td>25</td>
<td>98</td>
</tr>
<tr>
<td>9</td>
<td>MW-Fe/Al-SBA-15&lt;sup&gt;[13]&lt;/sup&gt;</td>
<td>3</td>
<td>51</td>
<td>89</td>
</tr>
<tr>
<td>10</td>
<td>IMP-Fe/Al-SBA-15&lt;sup&gt;[13]&lt;/sup&gt;</td>
<td>5</td>
<td>42</td>
<td>95</td>
</tr>
</tbody>
</table>

**Reaction conditions:** 2 mmol benzyl alcohol, 0.3 mL H<sub>2</sub>O<sub>2</sub> 50%, 0.05 g catalyst, 2 mL acetonitrile, 130 °C; <sup>a</sup>: H<sub>2</sub>O<sub>2</sub> 33%; <sup>b</sup>100 °C, reaction temperature.

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**Balu et al. ChemCatChem 2014, accepted**
**Xylose (X) conversion to Furfural (F)**

**Reaction conditions:**
23mg X, 3mL water, 23mg Catalyst, temperature monitored by FO

**MAGBON-SO$_3$H**

**Microwave irradiation Monowave 300**

**Goal of this research:**
Kinetic study of Xylose conversion to Furfural

**F YIELD:** 20-50%

Diagram showing the conversion of Xylose (X) to Furfural (F) using MAGBON-SO$_3$H under microwave irradiation. The yield of Furfural is indicated as 20-50%. The reaction conditions include 23mg of Xylose, 3mL of water, 23mg of Catalyst, and temperature monitored by FO.
Acknowledgments

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THANK YOU FOR YOUR ATTENTION!