**BIMETALLIC Ru:NI/MCM-48 CATALYSTS FOR THE EFFECTIVE HYDROGENATION OF D-GLUCOSE INTO SORBITOL**

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ALBERTO ROMERO CAMACHO

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1. INTRODUCTION

2. OBJECTIVES

3. MATERIALS AND METHODS

4. RESULTS AND DISCUSSION

5. CONCLUSIONS

**BIMETALLIC Ru:NI/MCM-48 CATALYSTS FOR THE EFFECTIVE HYDROGENATION OF D-GLUCOSE INTO SORBITOL**

**CELLULOSE**

- Depletion of fossil fuels
- Global warming

**Biomass**

- Energy fuels
- Chemicals

**Hexitols** (Sorbitol and Mannitol)

- Toothpaste
- L-Ascorbic Acid
- Lower polyols

- Food industry
- Drugs
- Cosmetics

**Most abundant resource of biomass**

- Attractive reaction routes
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BIMETALLIC Ru:Ni/MCM-48 CATALYSTS FOR THE EFFECTIVE HYDROGENATION OF D-GLUCOSE INTO SORBITOL
Design of bimetallic Ru:Ni/MCM-48 catalysts as alternative to monometallic Ni/MCM-48 for the catalytic hydrogenation of D-Glucose into sorbitol

Synthesis and characterization of the catalysts

Study the influence of different amounts of Ru over Ni/MCM-48 in order to improved the catalytic behavior of the monometallic catalyst in D-Glucose hydrogenation

Recycling of Ru:Ni/MCM-48
**MCM-48 Preparation**

- Hydrolysis
- Condensation
- Calcination

**Ni/MCM-48 and Ru: Ni/MCM-48 Preparation (Wet impregnation)**

- Suspension MCM48
- Ultrasound for 10 min
- Solution Metal precursors
- Drying at 105 °C
- Milling
- Reduction (TPR)

**Bimetallic Ru: Ni/MCM-48 Catalysts for the Effective Hydrogenation of D-Glucose into Sorbitol**
HYDROGENATION TESTS

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**HYDROGENATION TESTS**

**Reactor BR-25**

- Stainless steel
- $V = 25 \text{ mL}$
- $P_{\text{max}} = 20 \text{ MPa}$
- $T_{\text{max}} = 300 \degree \text{C}$

**Experimental conditions**

- $T = 120–140 \degree \text{C}$
- $P = 2.5 \text{ MPa}$
- $[C/Ru] = 142 \text{ (mol·mol}^{-1})$
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ANALYSIS AND CHARACTERIZATION TECHNIQUES

- Composition
  - AA

- Morphology
  - TEM – MAPPING

- Textural properties
  - \( A_{\text{BET}} \) and \( V_p \)
  - XRD and SAXS

- Composition
  - AA

- Surface acidity
  - TPD-NH\(_3\)

- Species identification
  - TPR-H\(_2\)

- Analysis of reaction products
  - HPLC
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<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ru (%)</th>
<th>Ni (%)</th>
<th>Ru:Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/MCM-48</td>
<td>-</td>
<td>2.95</td>
<td>-</td>
</tr>
<tr>
<td>Ru:Ni/MCM-48 (0.15)</td>
<td>0.38</td>
<td>2.48</td>
<td>0.15</td>
</tr>
<tr>
<td>Ru:Ni/MCM-48 (0.45)</td>
<td>0.76</td>
<td>1.67</td>
<td>0.45</td>
</tr>
<tr>
<td>Ru:Ni/MCM-48 (1.39)</td>
<td>1.63</td>
<td>1.17</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Ni/MCM-48
- 255 ºC - Reduction of (Ni(NO₃)₂·4H₂O·2(SiOH)

Ru:Ni/MCM-48
- 100 ºC – Reduction of RuCl₃
- 175 ºC – Reduction of Ru/Ni alloys
- 255 ºC – Reduction of (Ni(NO₃)₂·4H₂O·2(SiOH)

TPR-H₂

Temperature (ºC)
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XRD

Main peaks of Ni⁰ and Ru⁰ overlapped

Ni⁰ (FCC) \(2\theta = 44.5^\circ, 51.7^\circ\) and \(76.1^\circ\) (JCPDS card No. 4-850)
Ru⁰ (HCP) \(2\theta = 38.8^\circ, 42.2^\circ, 43.8^\circ, 58.2^\circ, 69.6^\circ\) and \(78.4^\circ\) (JCPDS card No. 06–0663)
TEM Ni/MCM-48

Catalyst | Ni (%) | $S_{\text{BET}}$ (m$^2$·g$^{-1}$) | $V_{\text{pore}}$ (cm$^3$·g$^{-1}$) | $\phi$ pore (nm)
---|---|---|---|---
MCM-48 | - | 1289 | 0.87 | 2.2
Ni/MCM-48 | 2.95 | 572 | 0.44 | 4.4

$\bar{d}_p^{Ni} = 2.4$ nm (2.7 nm XRD-Scherrer)
TEM Ru: Ni/MCM-48 (0.15)

\[ \bar{d}_p_{Ni} = 20.6 \text{ nm} \]

Irregular geometry of ruthenium areas
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BIMETALLIC Ru:Ni/MCM-48 CATALYSTS FOR THE EFFECTIVE HYDROGENATION OF D-GLUCOSE INTO SORBITOL
### Textural properties bimetallic catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ru (%)</th>
<th>Ni (%)</th>
<th>Ru:Ni</th>
<th>( S_{\text{BET}} ) (m²·g⁻¹)</th>
<th>( V_{\text{pore}} ) (cm³·g⁻¹)</th>
<th>( \phi_{\text{pore}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-48</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1289</td>
<td>0.87</td>
<td>2.2</td>
</tr>
<tr>
<td>Ru:Ni/MCM-48 (0.15)</td>
<td>0.38</td>
<td>2.48</td>
<td>0.15</td>
<td>931</td>
<td>0.59</td>
<td>2.2</td>
</tr>
<tr>
<td>Ru:Ni/MCM-48 (0.45)</td>
<td>0.76</td>
<td>1.67</td>
<td>0.45</td>
<td>1112</td>
<td>0.69</td>
<td>2.2</td>
</tr>
<tr>
<td>Ru:Ni/MCM-48 (1.39)</td>
<td>1.63</td>
<td>1.17</td>
<td>1.39</td>
<td>1184</td>
<td>0.74</td>
<td>2.2</td>
</tr>
</tbody>
</table>

### Acidity features

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Acidity (mmol·g⁻¹)</th>
<th>TCD (a.u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (170 -250 ºC)</td>
<td>II (520-590 ºC)</td>
<td>Total</td>
</tr>
<tr>
<td>MCM-48</td>
<td>0.157</td>
<td>0.343</td>
</tr>
<tr>
<td>Ni/MCM-48</td>
<td>0.546</td>
<td>0.462</td>
</tr>
<tr>
<td>Ru:Ni/MCM-48 (0.15)</td>
<td>0.396</td>
<td>0.756</td>
</tr>
<tr>
<td>Ru:Ni/MCM-48 (0.45)</td>
<td>0.320</td>
<td>0.882</td>
</tr>
<tr>
<td>Ru:Ni/MCM-48 (1.39)</td>
<td>0.334</td>
<td>0.918</td>
</tr>
</tbody>
</table>
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**Evolution of the conversion of D-Glucose**

**Pseudo-first order fitting**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Specific reaction rate $\cdot 10^{13}$ (mol$_{sorbitol}$·cm$^{-2}$·Ni$^{-1}$·s$^{-1}$)</th>
<th>$k\cdot 10^3$ (dm$^3$·g$^{-1}$·min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/MCM-48</td>
<td>2.24</td>
<td>9.7</td>
<td>0.998</td>
</tr>
<tr>
<td>Ru:Ni/MCM-48 (0.15)</td>
<td>3.35</td>
<td>2.3</td>
<td>0.976</td>
</tr>
<tr>
<td>Ru:Ni/MCM-48 (0.45)</td>
<td>19.8</td>
<td>18.3</td>
<td>0.996</td>
</tr>
<tr>
<td>Ru:Ni/MCM-48 (1.39)</td>
<td>24.9</td>
<td>66.3</td>
<td>0.985</td>
</tr>
</tbody>
</table>

C:Ru = 142, 120 °C, 2.5 MPa H$_2$ and 1400 rpm

- ● Ni/MCM-48,
- ■ Ru:Ni/MCM-48 (0.15),
- ▲ Ru:Ni/MCM-48 (0.45) and
- ▼ Ru:Ni/MCM-48 (1.39).

Pseudo-first order fitting
**Effect of reaction temperature**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Glucose Conversion (X%)</th>
<th>Sorbitol Selectivity (S%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>60%</td>
<td>100%</td>
</tr>
<tr>
<td>130</td>
<td>70%</td>
<td>100%</td>
</tr>
<tr>
<td>140</td>
<td>80%</td>
<td>100%</td>
</tr>
</tbody>
</table>

**Arrhenius plot D-Glucose hydrogenation**

\[ k_{\text{Ru:Ni/MCM-48 (0.45)}} = 36689457 \cdot e^{-70/RT} \]

\[ k_{\text{Ni/MCM-48}} = 592 \cdot e^{-36/RT} \]

**C:Ru = 142, 2.5 MPa H\(_2\), 90 min and 1400 rpm**

**Ni/MCM-48**
- Clear decrease of selectivity to sorbitol (95 – 86 %)

**Ru:Ni/MCM-48 (0.45)**
- Conversion of D-Glucose increased from 31 % to 59 % between 120 and 140 ºC
- Selectivity to sorbitol remained constant (100 %)

**E\(_a\) >> 12 -21 KJ/mol**

Reaction was controlled by the kinetics on the metal surface
Recycling of Ru:Ni/MCM-48 (0.45)

Sligth decrease of yield to sorbitol from 31 to 29 % after three reaction cycles

Selectivity to sorbitol remained constant (100 %)

C:Ru = 142, 120 °C, 2.5 MPa H₂ and 1400 rpm
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Improvement of reducibility of Ni and Ru

Ru:Ni/MCM-48 stands as a good material for the hydrogenation of carbohydrate sugars into sugar alcohols

Good stability of the bimetallic catalyst

$\text{SORBITOL} (S = 86\%)$
$\text{MANNITOL} (S = 14\%)$

$\text{SORBITOL} (S = 100\%)$

$\text{D-GLUCOSE} + H_2$

$T = 140 \degree C$, $P = 2.5 \text{ MPa}$ $H_2$ and $t = 90 \text{ min}$

Ru:Ni/MCM-48 (0.45) improved reaction rate remaining the selectivity constant from 120 to 140 $\degree C$

$\uparrow$ Ru:Ni than 0.45 improved catalytic behaviour of the Ni/MCM-48 (reaction rate and selectivity)
Thank you for your attention
Bimetallic Ru: Ni/MCM-48 catalysts for the effective hydrogenation of D-glucose into sorbitol

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