Synthesis of biofuels and fine chemicals over Supported Ionic Liquid Catalysts (SILCAs)

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IONIC LIQUIDS

- Ionic compounds
- Melting point below 100°C or room temperature
- Usually large organic cation and polyatomic inorganic or organic anion
- Negligible vapor pressure
- Wide liquidus range
- Unique solvation properties

Most commonly used cations

- 1-alkyl-3-methylimidazolium
- N-alkylpyridinium
- Tetraalkylammonium

Some commonly used anions

- $\text{CH}_3\text{CO}_2^-$
- $\text{CF}_3\text{CO}_2^-$
- $\text{Br}^-$, $\text{Cl}^-$, $\text{I}^-$
WHY IONIC LIQUIDS?

- More environmental benign processes
  - Less toxic and volatile solvents
- Reaction takes place at ionic atmosphere
  - Higher reaction rate
  - Better selectivity
- Different applications
  - Hydrogenation
  - Dehydration
  - Isomerisation
SUPPORTED IONIC LIQUID CATALYSTS

- A thin layer of ionic liquid immobilized on a solid support
- Metal compounds, metal nanoparticles or e.g. acid/alkaline modifiers residing in ionic liquid layer
BENEFITS OF SILCA

- Benefits of heterogeneous and homogeneous catalysis
- Easy separation of catalyst from the liquid phase
- Small amount of ionic liquid (IL) needed
- Two basic limitations
  - Decomposition temperature of the IL
  - IL should not be miscible with the reaction solvent
CATALYST PREPARATION

- Simple impregnation method is applied
- Ionic liquid and metal compound are dissolved into suitable solvent
- Solution is poured over support material (ACC or zeolite)
- Solvent evaporation
- Catalyst pretreatment/reduction if needed
CATALYST CHARACTERISATION (ACC)

- SILCA catalyst Pd in \([(C_3OH)Py][N(CF_3SO_2)_2]/KOH(1:4)\) on ACC in macro-, micro- and nanoscale
CATALYST CHARACTERISATION (ZEOLITES)

H-Beta-25 zeolite catalyst.

IL-H-Beta-25 zeolite catalyst.
SYNTHESIS OF BIOFUELS

HMF ETHERIFICATION TO t-BMF

HMF is a renewable building block for various (currently) petroleum derived chemicals.

**CATALYST ACTIVITY AND SELECTIVITY**

**Catalyst Conversion (%)**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Beta 25</td>
<td>36</td>
</tr>
<tr>
<td>H-Beta 150</td>
<td>30</td>
</tr>
<tr>
<td>H-Beta 300</td>
<td>25</td>
</tr>
<tr>
<td>IL-H-Beta 25</td>
<td>46</td>
</tr>
<tr>
<td>IL-H-Beta 150</td>
<td>35</td>
</tr>
<tr>
<td>IL-H-Beta 300</td>
<td>27</td>
</tr>
</tbody>
</table>

**Selectivity [tBMF] (%)**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>tBMF selectivity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL-H-Beta 25</td>
<td>83</td>
</tr>
<tr>
<td>IL-H-Beta 150</td>
<td>76</td>
</tr>
<tr>
<td>IL-H-Beta 300</td>
<td>72</td>
</tr>
</tbody>
</table>

Reaction time: 3h  
T = 120 °C, p(Ar) = 8 bar
CONCLUSIONS

- High selectivities of tBMF were obtained with zeolites modified with Lewis acidic ionic liquids.
- Formation of HMF ethers is associated with the presence of Lewis acid sites.
- Modification of zeolites with ionic liquid did not influence the morphology of the zeolites (XRD/SEM).
SYNTHESIS OF FINE CHEMICALS

CITRAL HYDROGENATION TO CITRONELLLAL

The reaction conditions were $T = 100 \, ^\circ C$, $p(H_2) = 10$ bar
The reaction conditions were

\[ T = 100 \, ^\circ\text{C}, \, p(H_2) = 5 \, \text{bar} \]
CONCLUSIONS

- Reaction rate can be influenced by different modifiers and also by different ionic liquids.
- Alkaline modifiers enhance the activity and increase the selectivity of citronellal.
- Highly selective reaction route was accomplished.
  - Only conjugated double bond is hydrogenated in the first phase.
SYNTHESIS OF FINE CHEMICALS

α-PINENE OXIDE ISOMERISATION TO CAMPHOLENIC ALDEHYDE

- Monoterpenes (e.g. α-pinene) are the major components of resin
- Epoxidation of monoterpenes to oxides (e.g. α-pinene oxide)
- Isomerization of terpene oxides to value-added compounds (e.g. campholenic aldehyde)

Activity and selectivity of the catalysts are dependent upon the nature of ionic liquid and Lewic acid modifier

Campholenic aldehyde molar yield ≈ 62 %
RESULTS

m(SnCl₂) = 68 mg
m(IL)= 150 mg

Reaction conditions were T=70 °C, p(Ar) = 5, C₀, α-Pinene =0.012 M and V_hexane = 250 ml.

Reaction time = 4 h
## RESULTS

Molar yields of products from α-pinene oxide isomerisation reactions (after 4 hours). n(IL):n(M_xCl_y) = 1:1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion [%]</th>
<th>Campholenic aldehyde yield [%]</th>
<th>Fencholenic aldehyde yield [%]</th>
<th>trans-Carveol yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FeCl_3/IL/ACC</td>
<td>81</td>
<td>44 (49)</td>
<td>7</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>CrCl_3/IL/ACC</td>
<td>83</td>
<td>40 (46)</td>
<td>8</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>SnCl_2/IL/ACC</td>
<td>100</td>
<td>51</td>
<td>12</td>
<td>19</td>
</tr>
<tr>
<td>4a</td>
<td>SnCl_2/IL/ACC</td>
<td>100</td>
<td>57</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td>5a,b</td>
<td>SnCl_y/IL/ACC</td>
<td>100</td>
<td>62</td>
<td>10</td>
<td>23</td>
</tr>
</tbody>
</table>

\[a\] m(SnCl_2)=135 mg. (n(IL):n(M_xCl_y)=1:2)

\[b\] Toluene as a solvent

IL= [N(3-OH-Pr)Py][NTf_2]
CONCLUSIONS

- Reusable catalysts with high selectivity towards campholenic aldehyde were accomplished
- The nature of the ionic liquid in SILCA influences the activity and selectivity of the catalyst
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