Greener Detergents – Gold-based Catalysts for the Production of Ether Carboxylic Acids

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- Non-ionic surfactants such as fatty-alcohol ethoxylates constitute the second largest class of detergents. They can be oxidized to ether carboxylic acids which belong to the group of anionic surfactants.
- Current production process: Williamson’s ether synthesis with ecologically questionable chlorinated substrates, excess use of chloroacetic acid, incomplete conversion and by-products and corrosion through NaCl formation.
- Pt- & Pd-based catalysts show only moderate selectivity, low activity and insufficient stability due to over-oxidation and leaching.
- Here we show a new environmentally sound fundamental technology for the oxidation of fatty-alcohol ethoxylates to ether carboxylic acids via active, selective and stable ceria-supported gold-platinum catalysts.

Catalyst optimisation

Variation of preparation conditions
- supports (Al2O3, TiO2, AC, CeO2, BaSO4, Y2O3, etc.)
- preparation methods (IW, DP Urea/NaOH, wet imp.)
- metal loadings (0.05 – 2 wt-%)
- Au:Pt ratios (100:0 – 1:100)

Optimised catalyst
- wet impregnation method
- CeO2 as support
- 0.1% AuPt(90:10) metal loading

Reaction scheme

Oxidation of primary alcohol function of polyethylene-glycols (PEGs), alkyl-PEGs or fatty alcohol ethoxylates to corresponding ether carboxylic acids

\[
\text{R-OCH}_2\text{CH}_2\text{OH} \text{ cat/O} \rightarrow \text{R-OCH}_2\text{CH}_2\text{OH} = \text{COOH}
\]

AuPt/CeO2 for oxidation of various substrates

<table>
<thead>
<tr>
<th>name</th>
<th>R</th>
<th>n</th>
<th>Activity(^a)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG M 350</td>
<td>methyl-</td>
<td>~7</td>
<td>495</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>PEG M 500</td>
<td>methyl-</td>
<td>~11</td>
<td>495</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>PEG M 1000</td>
<td>methyl-</td>
<td>~22</td>
<td>145</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>PEG S 2000</td>
<td>-OH</td>
<td>~45</td>
<td>210</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>Butyldiglycol</td>
<td>butyl-</td>
<td>2</td>
<td>220</td>
<td>&gt; 99 %</td>
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<tr>
<td>Hexanol + 7 EO</td>
<td>hexyl-</td>
<td>7</td>
<td>375</td>
<td>&gt; 99 %</td>
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<tr>
<td>Octanol + 7 EO</td>
<td>octyl-</td>
<td>7</td>
<td>145</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>Genapol LA 030</td>
<td>lauryl-</td>
<td>~3</td>
<td>12</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>Genapol LA 070</td>
<td>lauryl-</td>
<td>~7</td>
<td>260</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>Sapogenat T 080</td>
<td>tributylphenyl-</td>
<td>~6</td>
<td>2</td>
<td>&gt; 99 %</td>
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</table>

- Varying activity but always excellent selectivity for a broad variety of substrates.

Reactors and reaction conditions

Batch (slurry STR)
- 1000 g charge size
- 5 – 20 % substrate
- 25 g catalyst
- pH 11 (titration)
- 80 °C
- p(O2): 8 bar
- 1000 rpm

Continuous-flow trickle-bed
- Oxidation of PEG M 1000 @ c0 = 5 wt%, T = 100 °C, p = 18 bar, residence time = 18 min, pH = 13, variations see diagram

- Good long-term stability @ varying conditions for 57 days
- Selectivity for PEG M 1000 oxidation > 99 %
- TEM analysis → no sintering of metal particles
- ICP-OES analysis → no significant metal leaching detected

Summary

- Optimized catalyst AuPt/CeO2 opt. 130x as active as a Pt-catalyst from patent literature
- Excellent selectivity (> 99 %) of all gold-based catalysts
- Satisfactory long-term stability under continuous-flow conditions, no metal leaching if ceria is used as support
- Broad range of ether carboxylic acids accessible by this route

Catalyst comparison

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<tr>
<td>Selectivity</td>
<td>85 – 95 %</td>
<td>&gt; 99 %</td>
<td>&gt; 99 %</td>
<td>&gt; 99 %</td>
<td>&gt; 99 %</td>
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<tr>
<td>Activity(^b)</td>
<td>&lt; 2</td>
<td>10(^c)</td>
<td>40(^d)</td>
<td>60(^e)</td>
<td>260(^f)</td>
</tr>
<tr>
<td>Me-leaching</td>
<td>significant small reduced no no</td>
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<td></td>
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</table>

\(^a\) from patent literature for comparable fatty-alcohol ethoxylates and reaction conditions
\(^b\) in mmol min\(^{-1}\) gcat\(^{-1}\)
\(^c\) under optimized reaction conditions for Genapol LA070

Introduction

- Analytical methods
- Reactor systems

Experimental

Results

Conclusion

- Parameter:
- Production
- Greener
- * corr.
- Experimental
- Results
- Conclusion

Prüße1*, Pt- & Pd-based catalysts show only moderate selectivity, low activity and insufficient stability due to over-oxidation and leaching.

Au:Pt ratios

Reaction scheme

Optimised catalyst

wet impregnation method

CeO2 as support

0.1% AuPt(90:10) metal loading

Varying activity but always excellent selectivity for a broad variety of substrates.

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<th>Parameter</th>
<th>Pt- &amp; Pd-based cats</th>
<th>Au/TiO2</th>
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<th>AuPt/CeO2</th>
<th>AuPt/CeO2 opt</th>
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