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

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Introduction

- 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
- Au/TiO_2 shows better activity, high selectivity but shows still metal leaching (Heidkamp et al. Eur. J. Lipid Sci. Technol. *112* 2010 51)
- 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

Experimental

Catalyst optimisation

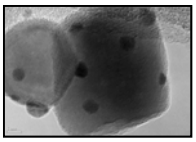
Variation of preparation conditions

- ➔ supports (Al_2O_3, TiO_2, AC, CeO_2, $BaSO_4$, Y_2O_3,…)
- ➔ preparation methods (IW, DP Urea/NaOH, wet imp.)
- ➔ metal loadings (0.05 – 2 wt.-%)
- ➔ Au:Pt ratios (100:0 - 0:100)

Optimised catalyst

- ➔ wet impregnation method
- ➔ CeO_2 as support
- ➔ 0.1% AuPt(90:10) metal loading

HR-TEM of the optimized catalyst AuPt/CeO_2 opt.



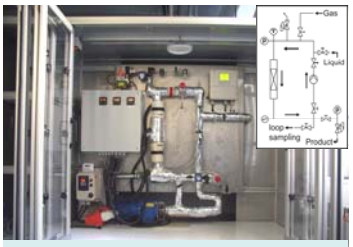
Reactors and reaction conditions

Batch (slurry STR)

Batch

- 1000 g charge size
- 5 – 20 % substrate
- 25 g catalyst
- pH 11 (titration)
- 80 °C
- p(O_2): 8 bar
- 1000 rpm

Continuous-flow trickle-bed



Parameter: T = 20–100 °C, p = 1–30 bar, V_{total} = 138 ml, V_{cat} = 16 ml, $flow_{gas}$ = 6–6000 ml, $flow_{liquid}$ = 0.06–600 ml

Results

Reaction scheme

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

$$\underset{\text{ethoxylate}}{R\text{-}(O\text{-}CH_2\text{-}CH_2)_n\text{-}OH} \xrightarrow{cat/O_2} \underset{\text{ether carboxylic acid}}{R\text{-}(O\text{-}CH_2\text{-}CH_2)_{n-1}\text{-}O\text{-}CH_2\text{-}COOH}$$

$AuPt/CeO_2$ for oxidation of various substrates

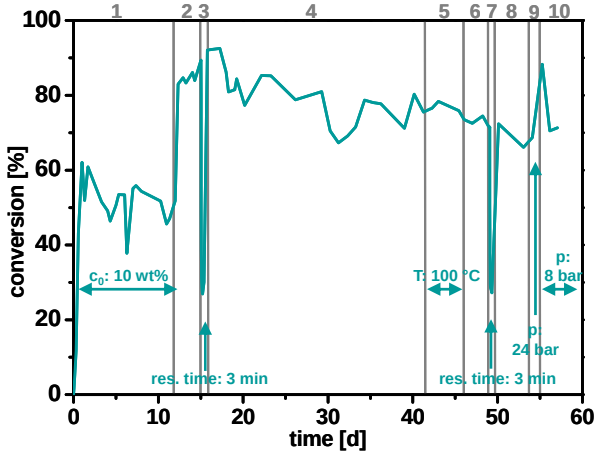
name	R	n	Activity[a]	Selectivity
PEG M 350	methyl-	~7	495	> 99 %
PEG M 500	methyl-	~11	495	> 99 %
PEG M 1000	methyl-	~22	145	> 99 %
PEG S 2000	-OH	~45	210	> 99 %
Butyldiglykol	butyl-	2	220	> 99 %
Hexanol + 7 EO	hexyl-	7	375	> 99 %
Octanol + 7 EO	octyl-	7	145	> 99 %
Genapol LA 030	lauryl-	~3	12	> 99 %
Genapol LA 070	lauryl-	~7	260	> 99 %
Sapogenat T 080	tributylphenyl-	~6	2	> 99 %

[a] in mmol min^{-1} g_{Me}^{-1}

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

Long-term stability studies (trickle-bed)

➔ Oxidation of PEG M 1000 @ c_0 = 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**

Conclusion

Summary

- Optimized catalyst $AuPt/CeO_2$ 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

Parameter	Pt- & Pd-based cats [a]	Au/TiO_2	$AuPt/TiO_2$	$AuPt/CeO_2$	$AuPt/CeO_2$ opt.
Selectivity	85 – 95 %	> 99 %	> 99 %	> 99 %	> 99 %
Activity[b]	< 2	10[c]	40[c]	60[c]	260[c]
Me-leaching	significant	small	reduced	no	no

[a] from patent literature for comparable fatty alcohol ethoxylates and reaction conditions
[b] in mmol min^{-1} g_{Me}^{-1}
[c] under optimized reaction conditions for Genapol LA070