Optimization of anodic oxidation and Cu-Cr oxide catalyst preparation on structured aluminum plates processed by electro discharge machining

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Introduction

Microreactors: tools for both basic research and safe process development, opportunity to safely study the kinetics of catalytic total oxidation:

- small unit size
- channel diameter < 500 μm (large surface-to-volume ratio) => gas-phase reactions, including explosive ones, can be avoided
- highly exothermic reaction => efficient heat removal

- Spinel catalyst
  CuCr$_2$O$_4$/γ-Al$_2$O$_3$
  high oxidation activity

(E.V. Rebrov et al., Catal. Today 69 (2001) 183)
Outline

- Fabrication and characterization of microstructured plates

- Anodic oxidation of metal plates
  - Oxidation of flat aluminum plates
  - Adaptation of oxidation procedure with the AlMgSi1 alloy

- Development of preparation methods of catalytic coatings
  - Preparation of Cu-Cr oxide catalytic coatings on flat aluminum plates
  - Adaptation of catalysts synthesis procedure for microstructured plate
Microreactor fabrication

1. Channel formation by spark erosion

2. Anodic oxidation

3. Catalyst deposition

4. Polishing

5. Diffusion bonding

6. Assembly

Microreactor geometry based on plug-flow model:
channel internal diameter 400 µm,
catalyst/support layer thickness 25 µm,
76 half-plates (400 µm thick)/2 =
38 full-plates (800 µm thick),
45 channels per plate =>
assembled 26.6 mm wide, 40 mm long,
30.4 mm high, 1710 channels
Fabrication of microstructured plates

**Al microreactor material:**
- high heat conductivity (230 W/m·K)
- can be used up to 450 °C (m.p. 660 °C)
- microchannels easily made (e.g., by spark erosion)
- anodic oxidation allows formation of external porous $\gamma$-$\text{Al}_2\text{O}_3$ layer for catalyst active component deposition

- Material
  - Al 99.5
  - AlMgSi1 alloy (Al51 st)

- EDM procedure
  - 1 incision
  - 2 incisions
  - 3 incisions
Single sided plates $h = 0.42$
Fabrication of microstructured plates

- 1st series: 21+63 microstructured plates (1 incision)

Dimensions: 45 channels with R=208 micron, L = 40 mm

Ra >3
Plate weight after EDM

![Bar graph showing the weight of 25 plates after EDM.]
2\textsuperscript{nd} series

2 incisions

Ra = 2.0

2 incisions + micro-powder jet treatment

Ra = 2.0
Summary

- Fabrication of long (40 mm) microchannels in Al 99.5 (code: 1050A) is not possible.
- Method “1 incision” gives surface roughness $Ra > 3.2$ with the Al51st alloy.
- It is possible to reach $Ra = 2.0$ with fabrication method “2 incisions” in Al51st.
Anodic oxidation

**Anode:** Al flat (or microstructured) plate

Pt cathode

3.5 wt.% oxalic acid ($H_2C_2O_4$) solution

Pt cathode

10 cm 10 cm

**Anode:**

\[ 2 \text{Al} + 3 \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6 \text{H}^+ + 6\text{e} \]

\[ \text{C}_2\text{O}_4^{2-} \rightarrow 2 \text{CO}_2 + 2\text{e} \]

**Cathode:**

\[ 2 \text{H}^+ + 2\text{e} \rightarrow \text{H}_2 \]

\[ 2 \text{Al} + 3 \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3 \text{H}_2 \]
Temperature vs. time

Temperature, °C vs. Time, min

-2 -1 0 1 2 3 4 5

p 5, 6
p 7, 8
p 9, 10
p 11, 12
p 13, 14
p 15, 16
p 17, 18
p 19, 20
p 21, 22
p 23, 25
Voltage vs. time

Current density: 4.2 mA/cm$^2$ (one side protected)
$T = 0.5 \, ^\circ C$

Electrolyte: 3.5 wt.% oxalic acid

- 444 hrs #17,18
- 306 hrs #11,12
- 168 hrs #5,6
- 92 hrs #24,25
- 46 hrs #21,22
- Fresh #19,20
Oxidation time 29 hrs

Layer thickness: 41±1 µm
R = 408 µm
Oxidation time 23 hrs

Layer thickness: 29±1 μm, R = 415 μm
Coating thickness vs. oxidation time

Flat plates

Microstructured plates
Weight gain after routine oxidation

![Bar graph showing weight gain over different plate numbers with fresh electrolite indicated. The x-axis represents plate numbers from 6 to 24, and the y-axis represents weight gain in mg. The graph includes a note for 'n/d' for plate number 6.](image)
SEM: anodic oxidation of microstructured Al plates

15 μm of γ-Al₂O₃ have been formed (low thickness due to the other, non-porous Al₂O₃ produced by spark erosion procedure) => anodic oxidation conditions are being optimized to form required 25 μm of γ-Al₂O₃
Anodized flat aluminum plates: $S_{sp}$, porosity, SEM

$S_{sp}$ ($\gamma$-Al$_2$O$_3$/Al plate) = 95 m$^2$/cm$^3$ (30 m$^2$/g), pore volume ~ 14 %, pore (cylindrical shape) distribution maxima at 15 nm and 46 nm.

Result: Close to expected from literature, input data for catalyst active component deposition.
Summary

- Low current density (I= 4 mA/cm²) is required for anodic oxidation of Al51 st
- Low temperature (close to the melting point of the electrolyte) is required to decrease the rate of undesirable reaction with oxalic acid
- Temperature control within ±0.5 K is crucial during oxidation to get reproducible results
- Higher voltage is required in subsequent runs due to copper deposition on the cathodes and copper dissolution in the electrolyte.
Development of spinel catalyst synthesis method using $\text{Al}_2\text{O}_3/$Al plates

1. Finding initial synthesis conditions by testing different methodologies of catalyst active component deposition using conventional pelleted $\gamma$-$\text{Al}_2\text{O}_3$ supports

2. Synthesis using the flat plates, catalysts characterization (physical methods, catalytic activity), optimization of synthesis conditions

3. Synthesis using the microstructured plates
Catalyst active component deposition on pelleted $\gamma$-Al$_2$O$_3$ supports

- Limiting condition: on $\gamma$-Al$_2$O$_3$/Al plates, catalyst calcination T not to exceed 500 °C, because m.p. of Al is ~ 600 °C (especially for microstructured Al plates)

- Method tested on pelleted (1.0-1.6 mm) $\gamma$-Al$_2$O$_3$: low-T formation of CuCr$_2$O$_4$ spinel (impregnation with solution of copper dichromate, drying and calcination at T = 450°C for 4 h)

- XRD, BET results: at T = 450°C dominate low-T solid solutions based on spinel structure $(\text{Cu,Cr,Al})[\text{Cr,Al}]_2\text{O}_4$ with lattice parameter $a = 7.905$-$7.960$ Å, particle size $D < 50$ Å and $S_{sp} \sim 130$ m$^2$/g

- Reference catalyst composition 26%CuCr$_2$O$_4$/$\gamma$-Al$_2$O$_3$
Catalyst active component deposition on $\gamma$-Al$_2$O$_3$/Al supports

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Level of implementation</th>
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<tbody>
<tr>
<td></td>
<td>Low (No*)</td>
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<tr>
<td>C of impregnation solution, g/l</td>
<td>C (250)</td>
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<tr>
<td>Time of impregnation, h</td>
<td>T (0.25)</td>
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<tr>
<td>Multiplicity of impregnation *</td>
<td>M</td>
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<tr>
<td>Washing off excess solution *</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>High (Yes*)</td>
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<tr>
<td>C of impregnation solution, g/l</td>
<td>C (500)</td>
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<tr>
<td>Time of impregnation, h</td>
<td>T (1.0)</td>
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<tr>
<td>Multiplicity of impregnations *</td>
<td>M</td>
</tr>
<tr>
<td>Washing off excess solution *</td>
<td>W</td>
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</tbody>
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Examples (with resulting wt.% of a.c.):
- C T M W: 0.4
- C T M W: 2.5
- C T M W: 5.3

Results:
- Washing removes most of active component (a.c.)
- Concentrated solution – excess a.c. on surface (confirmed by XRD)
- Low concentrations deposit a.c. mostly in pores of $\gamma$-Al$_2$O$_3$
XPS and UV-Vis: Cr cations

Normal spinels: $XY_2O_4$
- $X(Cu^{2+}, T_d$ coordination),
- $Y(Cr^{3+}, O_h$ coordination),
- face-centered cubic unit cell
  (formed by close-packed $O^{2-}$)

Cr$_{2p_{3/2}}$ of $Cr^{3+}$: 576.5-577.5 eV (577.1 eV for $CuCr_2O_4$)
UV-Vis: $O_h$ $Cr^{3+}$ ~ 17000 cm$^{-1}$ and ~ 22000 cm$^{-1}$ (d-d transitions)

Cr$_{2p_{1/2}}$

Resulting wt.% of a.c.:
- C T M W: 5.3
- C T M W: 3.5
- C T M W: 0.4

Shift to lower BE with increase of active component (a.c.) loading
=> possibly, interaction with $\gamma$-$Al_2O_3$ support is stronger, than within a.c. particles themselves
Cu e\textsubscript{2p\textsubscript{3/2}} of Cu\textsuperscript{2+}: \sim 933 eV for CuCr\textsubscript{2}O\textsubscript{4}, \sim 935 eV for CuCO\textsubscript{3}

UV-Vis: T\textsubscript{d} Cu\textsuperscript{2+} \sim 13000 cm\textsuperscript{-1} (d-d transitions)

- For sample with low a.c. loading, the CuCO\textsubscript{3} signal overlaps with CuCr\textsubscript{2}O\textsubscript{4} signal, looking as 1 peak at 933.1 eV. With higher a.c. loadings, CuCO\textsubscript{3} signal becomes more pronounced.

- Maximum of Cu\textsuperscript{2+} content is observed for medium a.c. loading catalyst (XPS is surface-sensitive). Cu\textsuperscript{2+} is considered the most active part of spinel catalyst => probably, better a.c. dispersion and Cu\textsuperscript{2+} localization for this catalyst.

- Shift to higher BE with increase of a.c. loading – opposite to Cr\textsuperscript{3+}
XMA: Cu, Cr, Al distributions (sample C T M W: 3.5%CuCr$_2$O$_4$)

Across the plate:

Along the plate:
SEM: $\gamma$-Al$_2$O$_3$ surface before and after impregnation with CuCr$_2$O$_7$

Before: cylindrical pores are clearly visible

After (sample C T M W: 5.3%CuCr$_2$O$_4$): surface is covered with CuCr$_2$O$_7$
Catalytic activity: deep oxidation of \( \text{C}_4\text{H}_{10} \) on flat plate supported catalyst

Initial \( C(\text{C}_4\text{H}_{10}) = 2000 \text{ ppm in air, GHSV} = 120000 \text{ h}^{-1} \) with respect to volume of catalytic coating
Catalyst active component deposition on microstructured plates

anodized AlMgSiCu-alloy plate without catalytic coating

CTMW 3.7 wt. % CuCr$_2$O$_4$
Catalytic activity: deep oxidation of C₄H₁₀ on microstructured plate supported catalyst

\[ C(C₄H₁₀) = 2000 \text{ ppm in air, GHSV} = 120000 \text{ h}^{-1} \text{ with respect to volume of catalytic coating} \]
Catalytic activity: deep oxidation of $\text{C}_4\text{H}_{10}$ on microstructured plate supported catalyst

Initial $\text{C(C}_4\text{H}_{10}) = 2000$ ppm, GHSV = 120000 h$^{-1}$ vs. $\gamma$-$\text{Al}_2\text{O}_3$ with respect to volume of catalytic coating
Catalytic microreactor for total oxidation reactions
Conclusions

1. The alumina-supported Cu, Cr oxide catalysts for reactions of total oxidation in a microreactor were synthesized using flat and microstructured anodized Al plates and characterized.

2. The formation of CuCr$_2$O$_4$ active component on γ-Al$_2$O$_3$/Al plates produced by anodic oxidation was confirmed by XPS, UV-Vis, XRD, XMA and SEM.

3. The best catalyst synthesis method is via double impregnation for 15 min with a diluted aqueous solution of copper dichromate.

4. The C$_4$H$_{10}$ oxidation activities of coatings even at much less content of active component are superior to that of the reference pelleted catalyst.
Acknowledgements

Netherlands Organization for Scientific Research (NWO) and
Russian Foundation for Basic Research (RFBR)

for the financial support of this Project