Oxidation of organic compounds in a microstructured catalytic reactor
Goals of this work

- Development of microstructured catalytic reactor (MCR) with Cu-Cr oxide catalyst for oxidation of organic compounds (potential applications – heat generation, fuel processing, etc.)
- Kinetic studies of oxidation of organic compounds of different classes: n-butane, ethanol, i-propanol, 1,1-dimethylhydrazine (unsymmetrical dimethylhydrazine – UDMH)

Concept scheme of integrated microprocessor for UDMH oxidation
Introduction
• MCR design
• preparation of catalyst coatings on microstructured plates
• screening of coatings in n-butane oxidation

Results
• assembling of MCR with optimal catalyst
• kinetic study of n-butane oxidation
• ethanol oxidation
• i-propanol oxidation
• 1,1-dimethylhydrazine oxidation

Conclusions

Acknowledgements
Introduction: MCR design

Microstructured Al51st alloy plates as main components of MCR

1. Formation of microchannels by electro discharge machining (EDM)
2. Anodic oxidation
3. Catalyst deposition
4. Polishing
5. Assembly by stacking in MCR housing and diffusion bonding

Semi-circle shaped
Circle shaped

- Optimization of number and length of microchannels by gas phase plug flow reactor model in MathCad® 12
- Optimization of inlet flow diffuser configuration by Navier-Stokes model in FLUENT® 6.1

Porous alumina layer was produced by anodic oxidation of microstructured Al51st alloy plates in 3.5 wt.% oxalic acid solution at 1.0 ± 0.1°C for 23 hrs under current control conditions. This layer has uniform thickness of 29 ± 1 µm. Its texture is represented by hexagonal cylindrical pores with average diameter of ca. 40 ± 5 nm, $S_{\text{BET}} = 95 \text{ m}^2/\text{cm}^3$ (30 m$^2$/g), pore volume ~ 14 % of layer.
Introduction: **CuCr$_2$O$_4$** catalyst deposition on anodized Al$_2$O$_3$ plates

Catalysts were prepared by impregnation of anodized plates by aqueous solution of copper dichromate. Excess solution was wiped off, followed by drying under IR lamp for 1 h and calcination at 450°C for 4 h.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Level of implementation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C of impregnation solution, g/l</td>
<td>Low (No*)</td>
</tr>
<tr>
<td></td>
<td>High (Yes*)</td>
</tr>
<tr>
<td>Impregnation time, h</td>
<td>T (0.25)</td>
</tr>
<tr>
<td></td>
<td>T (1.0)</td>
</tr>
<tr>
<td>Number of impregnations (1 or 2)</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>M</td>
</tr>
<tr>
<td>Washing off excess solution *</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>W</td>
</tr>
</tbody>
</table>

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

- Washing removes most of active component (a.c.)
- Concentrated solution – excess a.c. on surface (confirmed by XPS, UV-Vis, XRD)
- Low concentrations deposit a.c. mostly in pores of Al$_2$O$_3$
Optimal wt.% of CuCr₂O₄ has to be found in order to provide highest activity without decreasing catalyst dispersion and blocking pores of alumina. Characterization of these coatings by activity tests, XPS, UV-Vis and X-ray microprobe analysis showed that optimum catalyst contains uniformly distributed a.c. at total content of ca. 5 wt.% with respect to alumina layer.
Results: **MCR assembling**

MCR housing made of same Al51st alloy as plates, for thermal expansion uniformity

Flow diffuser with vertical and horizontal slits matching reaction channel positions

Quench section thermally insulated from outlet of plates, to decrease secondary reactions
Results: n-butane oxidation in air, reaction products

\[
\text{C}_4\text{H}_{10} + 6.5 \text{ O}_2 \rightarrow 4 \text{ CO}_2 + 5 \text{ H}_2\text{O}
\]

Only products of deep oxidation were detected at MCR outlet. Presence of inlet flow diffuser improves n-butane conversion by several % in whole studied temperature range.

\[\text{C}_{0,\text{C}_4\text{H}_{10}} = 0.2 \text{ mmol/l, GHSV} = 5360 \text{ h}^{-1}\]
Results: n-butane oxidation, Arrhenius plots

Reaction rate equation (no radial ΔT, ΔC): \( W = k \cdot C_{\text{C}_4\text{H}_{10}} \), which gives \( E = 71–84 \, \text{kJ/mol}, \ k_0 = 3.4 \cdot 10^7–6.6 \cdot 10^9 \, \text{s}^{-1} \).

In high temperature region, activity of microstructured catalyst is higher than that of pelleted catalyst due to low diffusion limitations in former one.
Results: ethanol oxidation, kinetic scheme, model parameters

Models using modified method of "quickest descent"

<table>
<thead>
<tr>
<th>Model</th>
<th>$k_{0,1}$, s$^{-1}$</th>
<th>$k_{0,2}$, s$^{-1}$</th>
<th>$E_1$, kJ/mol</th>
<th>$E_2$, kJ/mol</th>
<th>$N_{O2}$</th>
<th>$M_{O2}$</th>
<th>Mean absolute deviation of concentrations, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.7·$10^9$</td>
<td>2.14·$10^1$</td>
<td>92.1</td>
<td>143.6</td>
<td>1</td>
<td>1</td>
<td>5.5</td>
</tr>
<tr>
<td>2</td>
<td>6.6·$10^7$</td>
<td>8·$10^{13}$</td>
<td>75.4</td>
<td>142.4</td>
<td>0.4</td>
<td>0.8</td>
<td>3.5</td>
</tr>
<tr>
<td>3</td>
<td>1.8·$10^8$</td>
<td>1.6·$10^{15}$</td>
<td>79.5</td>
<td>153.7</td>
<td>0.5</td>
<td>1</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Deep oxidation: $C_2H_5OH + 3 O_2 \rightarrow 2 CO_2 + 3 H_2O$

Overall mechanism: $C_2H_5OH + 1/2 O_2 \rightarrow CH_3CHO + H_2O$ (1) (CH$_3$CHO – acetaldehyde)

$CH_3CHO + 5/2 O_2 \rightarrow 2 CO_2 + 2 H_2O$ (2)

$W_1 = k_1 \cdot C_{C2H5OH} \cdot C_{O2}^N$ $W_2 = k_2 \cdot C_{CH3CHO} \cdot C_{O2}^M$

$W_i (i = 1,2)$ are reaction rates, $k_i$ are rate constants, $k_i = k_0 \cdot \exp(-E_i/RT)$

$C_j$ are concentrations in gas phase, $M$ and $N$ are rate orders
Results: ethanol oxidation, composition of products, experiment vs. model

Model 3:

\[ W_1 = k_1 \cdot C_{\text{C}_2\text{H}_5\text{OH}} \cdot C_{\text{O}_2}^{0.5} \]

\( k_{0,1} \sim 1.8 \cdot 10^8 \text{ s}^{-1}, \quad E_1 \sim 79.5 \text{ kJ/mol} \)

\[ W_2 = k_2 \cdot C_{\text{CH}_3\text{CHO}} \cdot C_{\text{O}_2} \]

\( k_{0,2} \sim 1.6 \cdot 10^{15} \text{ s}^{-1}, \quad E_2 \sim 153.7 \text{ kJ/mol} \)
Results: i-propanol oxidation, kinetic scheme

Deep oxidation:

\[ C_3H_7OH + 9/2 \, O_2 \rightarrow 3 \, CO_2 + 4 \, H_2O \]

Overall mechanism:

\[
\begin{align*}
C_3H_7OH & \xrightarrow{k_1} C_3H_6 + H_2O \quad (C_3H_8 \text{ – propane}) \\
C_3H_7OH + 1/2 \, O_2 & \xrightarrow{k_2} C_3H_6O + H_2O \quad (C_3H_6O \text{ – acetone}) \\
C_3H_6 + 9/2 \, O_2 & \xrightarrow{k_3} 3 \, CO_2 + 3 \, H_2O \\
C_3H_6O + 4 \, O_2 & \xrightarrow{k_4} 3 \, CO_2 + 3 \, H_2O
\end{align*}
\]

Kinetic parameters:

\[
\begin{align*}
W_1 &= k_1 \cdot C_{C3H7OH} \\
&(k_{0.1} \sim 8.3 \cdot 10^7 \, s^{-1}, \quad E_1 \sim 81.2 \, kJ/mol) \\
W_2 &= k_2 \cdot C_{C3H7OH} \cdot C^{0.5}_{O2} \\
&(k_{0.2} \sim 4.4 \cdot 10^7 \, s^{-1}, \quad E_2 \sim 71.2 \, kJ/mol) \\
W_3 &= k_3 \cdot C_{C3H6} \cdot C_{O2} \\
&(k_{0.3} \sim 6.7 \cdot 10^9 \, s^{-1}, \quad E_3 \sim 95.5 \, kJ/mol) \\
W_4 &= k_4 \cdot C_{C3H6O} \cdot C_{O2} \\
&(k_{0.4} \sim 9.5 \cdot 10^{19} \, s^{-1}, \quad E_4 \sim 209.3 \, kJ/mol)
\end{align*}
\]
Results: i-propanol oxidation, composition of products, experiment vs. model

Concentration, mole fraction vs. Temperature, °C

Experiment vs. model:
- i-C₃H₇OH
- CO₂
- C₃H₆O
- C₃H₆

Temperature, °C

0.000
0.005
0.010
0.015
0.020
0.025
0.0275

Temperature, °C

100
150
200
250
300
350
400
Results: 1,1-dimethylhydrazine oxidation, background

- 1,1-dimethylhydrazine \((\text{CH}_3)_2\text{N–NH}_2\) (unsymmetrical dimethylhydrazine, UDMH) - principal component of liquid rocket fuels in Russia, USA and PR China

- Large amounts of UDMH, extremely toxic (MPC 0.1 ppm in air, 0.01 mg/l in water), explosive and flammable. Need for utilization: one of the best options – catalytic oxidation by air (Z.R. Ismagilov et al., Catal. Today 75 (2002) 277)

- Main catalytic reaction: \((\Delta H = -1799 \text{ kJ/mol})\)
  \[(\text{CH}_3)_2\text{N–NH}_2 + 4\text{O}_2 = \text{N}_2 + 2\text{CO}_2 + 4\text{H}_2\text{O}\]
  \(X \sim 100 \%\) achieved only at \(T = 300-400 \, ^\circ\text{C}\),
  \(T \sim 200 \, ^\circ\text{C}\) – up to 14 intermediate products

RSM-50 (SS-N-18 "Stingray“ (State Rocket Center “Makeyev Design Bureau”, Miass, Russia)
Results: 1,1-dimethylhydrazine oxidation, composition of products at high $C_{0,\text{UDMH}}$

Concentrations of products of UDMH oxidation (mmol/l) at different temperatures, $C_{0,\text{UDMH}} = 0.4$ mmol/l, $C_{0,\text{O}_2} = 8.9$ mmol/l (20 vol.%), balance – He, GHSV = 5360 h$^{-1}$

<table>
<thead>
<tr>
<th>T, °C</th>
<th>CH$_4$</th>
<th>DMA</th>
<th>DDA</th>
<th>MDMH</th>
<th>CO$_2$</th>
<th>N$_2$</th>
<th>$C_{\Sigma C}$</th>
<th>$C_{\Sigma N}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.0039</td>
<td>0.12</td>
<td>0.03</td>
<td>0.16</td>
<td>0.028</td>
<td>0.11</td>
<td>0.652</td>
<td>0.720</td>
</tr>
<tr>
<td>240</td>
<td>0.002</td>
<td>0.156</td>
<td>0.03</td>
<td>0.09</td>
<td>0.045</td>
<td>0.12</td>
<td>0.599</td>
<td>0.636</td>
</tr>
<tr>
<td>260</td>
<td>0.002</td>
<td>0.014</td>
<td>0.12</td>
<td>0.10</td>
<td>0.063</td>
<td>0.14</td>
<td>0.533</td>
<td>0.734</td>
</tr>
<tr>
<td>300</td>
<td>0.0005</td>
<td>0.0007</td>
<td>0.16</td>
<td>0.02</td>
<td>0.18</td>
<td>0.17</td>
<td>0.541</td>
<td>0.701</td>
</tr>
</tbody>
</table>

$$(\text{CH}_3)_2\text{N–NH}_2 + 4\text{O}_2 = \text{N}_2 + 2\text{CO}_2 + 4\text{H}_2\text{O}, \quad \Delta H = -1799.15 \text{ kJ/mol}$$

Main products: CO$_2$, H$_2$O, N$_2$
Intermediate products: methane, dimethylamine (DMA), methylenedimethylhydrazine $(\text{CH}_3)_2\text{N–N=CH}_2$ (MDMH), 1,2-dimethylidiazene $\text{CH}_3\text{–N=N–CH}_3$ (DDA)
Results: 1,1-dimethylhydrazine oxidation, composition of products at low $C_{0,UDMH}$

$C_{0,UDMH} = 0.16 \text{ mmol/l}$, $C_{O_2} = 9.7 \text{ mmol/l}$, balance – He, GHSV = 11570 h$^{-1}$
Results: \(1,1\text{-dimethylhydrazine oxidation, tentative kinetic scheme}\)

\[
\text{(CH}_3\text{)}_2\text{N–NH}_2 + [ ] \rightarrow [(\text{CH}_3\text{)}_2\text{N–NH}_2]_{\text{ads}}
\]

\[
[(\text{CH}_3\text{)}_2\text{N–NH}_2]_{\text{ads}} + [\text{O}]_{\text{ads}} \rightarrow [(\text{CH}_3\text{)}_2\text{N=N}]_{\text{ads}} + [\text{H}_2\text{O}]_{\text{ads}}
\]

\[
[(\text{CH}_3\text{)}_2\text{N=N}]_{\text{ads}} + [(\text{CH}_3\text{)}_2\text{N=N}]_{\text{ads}} \rightarrow [(\text{CH}_3\text{)}_2\text{N–N=CH}_2]_{\text{ads}} + [\text{CH}_3\text{N=NH}]_{\text{ads}}
\]

\[
[(\text{CH}_3\text{)}_2\text{N=N}]_{\text{ads}} \rightarrow \text{CH}_3–\text{N=N–CH}_3 + [ ]
\]

\[
[(\text{CH}_3\text{)}_2\text{N–N=CH}_2]_{\text{ads}} \rightarrow (\text{CH}_3\text{)}_2\text{N–N=CH}_2 + [ ]
\]

\[
[(\text{CH}_3\text{)}_2\text{N–N=CH}_2] + [\text{O}]_{\text{ads}} \rightarrow (\text{CH}_3\text{)}_2\text{NH} + \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2 + \text{NO}_x
\]

\[
[\text{CH}_3\text{N=NH}]_{\text{ads}} \rightarrow \text{CH}_4 + \text{N}_2
\]

\[
[\text{CH}_3\text{N=NH}]_{\text{ads}} + [\text{O}]_{\text{ads}} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2 + \text{NO}_x
\]

where [ ] denotes active site of catalyst
Conclusions

1. Kinetics of deep oxidation of organics n-butane, ethanol, and i-propanol was studied in MCR with Cu-Cr oxide catalyst. Intermediate reaction products in reactions of alcohols oxidation were identified and reaction schemes were proposed.

2. Kinetic parameters of reactions were estimated using kinetic modeling based on modified method of "quickest descent".

3. Kinetic studies of oxidation of 1,1-dimethylhydrazine (UDMH) were performed. Intermediate reaction products were identified: methane, dimethylamine, formaldehyde, methylenedimethyhydrazine, 1,2-dimethylidiazene. Tentative reaction scheme was proposed.

4. UDMH was shown to convert mainly to N-containing organic compounds at temperatures below 300°C, but mainly to CO₂, H₂O and N₂ at higher temperatures of 350-375°C.

In summary, this work provides one of illustrative examples how MCRs can be successfully used for catalytic combustion of organic compounds, which can be applied for energy production, safe and efficient abatement of hazardous VOCs, as well as for kinetic studies.