PdZn/Mg(Al)(Pd)(Zn)O_x for ethanol conversion: reconstruction of the active phase upon a water containing feed

J. De Waele, V.V. Galvita, H. Poelman, J.W. Thybaut

Laboratory for Chemical Technology
Acetaldehyde as platform molecule
Acetaldehyde as platform molecule
Acetaldehyde as platform molecule
Acetaldehyde as platform molecule
Acetaldehyde as platform molecule
Acetaldehyde as platform molecule

... and many more

FOSSIL RESOURCES
Acetaldehyde as platform molecule

... and many more

BIO-BASED RESOURCES
Acetaldehyde as platform molecule

BIO-BASED RESOURCES: acetaldehyde

... and many more
Production from bio-ethanol

O₂

Metal oxide catalyst

H₂O

Ethanol

Acetaldehyde
Production from bio-ethanol

\[
\text{Ethanol} \xrightarrow{\text{Metal oxide catalyst}} \text{Acetaldehyde}
\]

\[
\text{O}_2 \quad \text{H}_2\text{O}
\]

\[
\text{Metal catalyst} \quad \text{H}_2
\]
Production from bio-ethanol

O₂ → Metal oxide catalyst → H₂O

Ethanol → Metal catalyst → Acetaldehyde

H₂
Overview

Catalyst selection
Overview

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Catalyst synthesis & activation

\[ \text{PdZnPdZnPdZnPdZnPdZnPdZn} \]
Overview

Catalyst selection

Catalyst synthesis & activation

Effect of water
Cu catalysts give high acetaldehyde selectivity…

Ethanol $\xrightarrow{\uparrow S_{Ac}}$ Acetaldehyde

$\text{H}_2$
Cu catalysts give high acetaldehyde selectivity...

Ethanol \[ \xrightarrow{\uparrow S_{\text{Ac}}} \] Acetaldehyde

... but sintering is a well-known problem.
PdZn has similar electronic properties as Cu

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... and Zn prevents the Pd-atoms from sintering.

PdZn/Mg(Al)(Pd)(Zn)O_x synthesis via co-precipitation
(1wt% Pd & 1.2wt% Zn, Pd/Zn=1/2 mol mol⁻¹)

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\[ \text{H}_2 \rightarrow \text{PdO} \rightarrow \text{ZnO} \]

\[ \text{H}_2 \rightarrow \text{Pd} \rightarrow \text{PdZn} \]

\[ \text{O}_2 \rightarrow \text{PdO} \rightarrow \text{PdZn} \]

Coking of unwanted Pd sites improves the selectivity

$T$: 533K, $P_{\text{tot}}$: 0.5MPa,
$W/F_{\text{EtOH}}$: 36 kg$_{\text{cat}}$ s mol$^{-1}$

I: freshly activated
II: after 1st regeneration
III: after 2nd regeneration

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Steady-state experiments on a high-throughput set-up

**Pretreatment @ 823K**

2x (30min $H_2$ – 15min $N_2$ – 30min $O_2$ – 15min $N_2$) – 30min $H_2$
Steady-state experiments on a high-throughput set-up

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**Conditions**
Temperature: 533K
Total pressure: 0.5 MPa
$N_2$ (or $N_2$+H$_2$O)/ethanol: 20
Space time: 36 kg$_{\text{cat}}$ s mol$^{-1}$
Steady-state experiments on a high-throughput set-up

**Pretreatment @ 823K**
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Temperature: 533K
Total pressure: 0.5 MPa
N\(_2\) (or N\(_2\)+H\(_2\)O)/ethanol: 20
Space time: 36 kg\(_{\text{cat}}\) s mol\(^{-1}\)

**Subsequent experiments**
Experiment 1: 100wt% ethanol
Experiment 2: 30wt%H\(_2\)O/ethanol
Experiment 3: 100wt% ethanol
Experiment 4: 100wt% ethanol after regeneration
100% ethanol gives a stable activity after 24h → catalyst structure is formed and stable.
Activity and selectivity changes

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With 30wt%H₂O/EtOH, the activity and acetaldehyde selectivity drops → catalyst changes or different reactions occurring?
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After regeneration, the activity and selectivity are as original, although the catalyst deactivates more rapidly. → catalyst fully restored?
PdZn alloy remains present in XRD, but less clear

- MgO
- γ-Al₂O₃
- PdZn

100wt% ethanol
30wt% H₂O/ethanol
100wt% ethanol regeneration-100wt% ethanol
## Surface area & particle size changes upon water feed

<table>
<thead>
<tr>
<th></th>
<th>BET surface area (m² g⁻¹)</th>
<th>Metal loading (%)</th>
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<tbody>
<tr>
<td></td>
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<td>Pd</td>
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<td>71.4 ± 1.66</td>
<td>1.25</td>
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<tr>
<td>30wt% H₂O/ethanol</td>
<td>45.9 ± 2.15</td>
<td>1.16</td>
</tr>
<tr>
<td>100wt% ethanol</td>
<td>44.9 ± 1.17</td>
<td>1.08</td>
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<tr>
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<td>5 ± 2</td>
<td></td>
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<tr>
<td>30wt% H₂O/ethanol</td>
<td>2 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100wt% ethanol</td>
<td>2.5 ± 1.2 &amp; 8 ± 3</td>
<td></td>
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<td>regeneration-100wt%</td>
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Hollow particles found for all samples

Kirkendall effect:
Due to the oxidizing & reducing environment hollow particles form via rapid diffusion of Pd compared to Zn
Zn clusters on particle upon water feed

Zinc seems to be partially removed from the particle and appears as a cluster on the surface.
Amount of cokes lower upon water feed

<table>
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The temperature at which the cokes is burned is the same
→ same interaction between cokes and Pd-sites for all catalysts.
What is now happening with the catalyst?

1. More methane formation
2. Less active
3. Smaller surface area
4. Smaller particle size
5. Zn-rich spots in border particles
6. Less cokes
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- Pd-rich alloy
- Zn-rich clusters
- Changes in support
- Desintegration of particles
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- Segregation of PdZn particles to Zn-rich clusters and an Pd-rich alloy on one particle
- Formation of smaller particles due to oxidizing and reducing environment in-situ
Conclusion

![Diagram showing conversion and acetaldehyde selectivity over time for different alloys.]

- **PdZn (1:1 alloy)**
- **PdZn (highly Pd-rich alloy)**
- **PdZn (Pd-rich alloy)**

The chart illustrates the conversion (%) and acetaldehyde selectivity (%) over time (h). The alloys are represented by different markers and colors, indicating their performance in the reaction process.
Acknowledgments

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Thank you for your attention!
Extra slide 1

Normalized Xµ(E)

Energy (eV)

Catalyst PdZn/Mg(Al)(Pd)(Zn)O_x
Reference Pd foil
Reference PdZn

Energy (eV)