Atomic Level Control of Catalyst Structure for Clean Fuel Production

Nuoya Yang
Bent research group, Department of Chemical Engineering
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Syngas conversion – convert carbon in waste to valuable chemical
Atomic Layer Deposition (ALD)--controllable modification of catalyst structure and composition

Data shown here are 5 cycles MnO
MnO improves activity and $C_{2+}$oxy selectivity
ALD-MnO support maintains Rh nanoparticle size

- MnO support didn’t change Rh size distribution
- co-IMP leads to smaller Rh size

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
<th>Count</th>
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<tbody>
<tr>
<td>Rh/SiO₂</td>
<td></td>
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<tr>
<td>Rh/MnO/SiO₂</td>
<td></td>
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<tr>
<td>Rh-Mn (co-IMP)/SiO₂</td>
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ALD-MnO overlayer — unstable upon CO adsorption

- XPS: MnO/Rh/SiO$_2$ before and after CO adsorption

![Graph showing Mn 3d and Rh 3d peaks before and after CO adsorption]

- Mn/Rh atomic ratio:
  - 1.95 before CO
  - 1.15 after CO

- MnO not stable upon CO adsorption
Infrared spectra -- CO adsorption on Rh surface

- Rh-MnO interface sites weaken CO bond, increase activity.
- Some stepped/defect sites on Rh nanoparticles may be blocked by MnO during impregnation.
- Blocking stepped sites could decrease methane selectivity.
DFT – MnO stabilizes key transition state

Rh-MnO interface:
• MnO stabilizes the transition state for $C_{2+}$oxy synthesis, improves selectivity.

Transition state

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\text{CH}_2$-$\text{H}^*$ (CH$_4$ selectivity)</th>
<th>$\text{H-CH}<em>2$CO$^*$ ($C</em>{2+}$oxy selectivity)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rh(111) MnO*/Rh</td>
<td>Rh(111) MnO*/Rh</td>
</tr>
<tr>
<td>Free Energy (eV)</td>
<td>1.18 1.16</td>
<td>1.02 0.78</td>
</tr>
</tbody>
</table>

DFT calculation by Jong Suk Yoo
Summary

- By controlling the catalyst structure on atomic level, we identified that Rh-MnO interface site is responsible for activity and selectivity enhancement for $C_{2+}$oxy production.
- MnO overlayer is not as effective, due to the instability upon CO adsorption.
- Similar strategy can be generalized to other heterogeneous catalyst systems to understand the active sites.
- Guide the rational design and enable highly controlled synthesis of heterogeneous catalysts.
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Thanks for your attention!