Synthesis, Characterization and Evaluation of Sulphated Zirconias for Biodiesel Production by Triglyceride Cracking

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Outline

- Introduction
- Motivation of study
- Objective
- Experimental
- Results
- Conclusions
Introduction

- Biodiesel are mono-alkyl esters of fatty acids derived from natural oils. (FAMEs)
  - renewable,
  - Carbon neutral i.e. Not adding to the global warming crisis
  - it is sustainable

Conventional method

\[
\begin{align*}
\text{Triglyceride} & \quad + \quad 3 \left[ \text{H}_3\text{C} - \text{OH} \right] \quad \xrightarrow{\text{Catalyst}} \quad \text{Methanol (3)}
\end{align*}
\]

\[
\begin{align*}
\text{Glycerol} & \quad + \quad 3 \left[ \text{R} - \text{CO}_2 \right]
\end{align*}
\]

Methyl Esters (3)
Motivation

- European Directive of 2009/28/EC, proposes 10% renewable fuel by the end of 2020. ~ 35 mtoe biofuel (i.e. 22 mtoe biodiesel & 13 mtoe bioethanol)

Source of data: Renewable Energy Association

Global transport fuel demand is set to rise by 45% in 2030.

Source of data: Shell calculations based on IEA and PIRA data

Neste oil, (2008)
Transesterification Process

- Thermo catalytic cracking
- 
  - Oil
  - MeOH
  - NaOH
  - Acid catalyst

- Recovery
  - Solid

- FAME purification
- FAMEs

- Glycerol removal
  - Catalyst
  - NaOH

- Catalyst removal

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Sulphated zirconia is:
- super-acid catalyst with acidity $10^4$ times stronger than 100% sulphuric acid
- good for organic reactions

Drawbacks:
- a relatively small surface area
- rapid deactivation and
- sulphate leaching,
Objective

The main objective of our research is to improve the catalytic activity of sulphated zirconia for high activity and selectivity towards desired products.

Two different methods of Preparation

- **Direct method (ds)**, simple calcination of ZrOCl₂.8H₂O and (NH₄)₂SO₄ for 5 hours at 600°C

- **Conventional method (cm)**
  - ZrOCl₂.8H₂O was hydrolysed with NH₄OH,
  - Zr(OH)₄ was impregnated with H₂SO₄
  - Calcination for 3 hours at 650°C

- **Characterization of catalysts**
Catalyst synthesis

Conventional method “cm”

NH₄OH

ZrOCl₂·8H₂O

H₂O → hydrolysis → filtration → drying → sulphating → drying → calcination → S/Zr

H₂SO₄

H₂O

Direct method “ds”

(NH₄)₂SO₄

ZrOCl₂·8H₂O

mixing → calcination → S/Zr
Characterization results

XRD of “cm” and “ds” catalysts

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Characterization results

IR spectra of adsorbed pyridine on the catalysts

B = Bronsted site
L = Lewis site

XPS results for Oxygen on the surface of the catalysts
Characterization results

Effect of SA and SO$_4^{2-}$ loading on biodiesel (FAMEs) production

<table>
<thead>
<tr>
<th>Properties</th>
<th>DS</th>
<th>CM</th>
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<tr>
<td>BET surface area</td>
<td>168.9</td>
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<tr>
<td>(m$^2$/g)</td>
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<tr>
<td>Pore size</td>
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<td>(µm)</td>
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<tr>
<td>Particle size</td>
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<tr>
<td>(µm)</td>
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<td>Crystallite size</td>
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<tr>
<td>(nm)</td>
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<tr>
<td>Nature of phases</td>
<td>A T</td>
<td>M</td>
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</table>

Introduction  Motivation  Objective  Experimental  Results  Conclusions
Results

FAMEs profile showing saturated, mono and poly unsaturated
<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Conversion</th>
<th>BET surface area (m²/g)</th>
<th>Pore size (µm)</th>
<th>Particle size (µm)</th>
<th>Crystallite size (nm)</th>
<th>Nature of phases</th>
<th>FAMEs (%)</th>
<th>Acid sites (%)</th>
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<td>DS</td>
<td>0.70</td>
<td>168.9</td>
<td>0.41</td>
<td>48.83</td>
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<td>A</td>
<td>47.43</td>
<td>51 49</td>
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<tr>
<td>CM</td>
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<td>101</td>
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<td>25.61</td>
<td>17.51</td>
<td>T, M</td>
<td>38.78</td>
<td>53 47</td>
</tr>
</tbody>
</table>
Conclusions

- Both catalysts were active and contain "Bronsted sites" and Lewis sites.
- The morphology of “ds” contributed to it higher activity.
- Both catalysts were selective but “ds” exhibited higher selectivity, ~ 50% for FAMEs.
- However the cm exhibited a unique selectivity for saturated fatty acid methyl esters.

Overall

- The preparation method showed improved physical and chemical properties of the catalysts which influenced their activity observed in the yield of fatty acid methyl ester.
- Biodiesel (FAMEs) can be produced by thermocatalytic cracking of triglycerides using these catalyst from both method of preparation.
Future work

- Further improvement of the catalysts, for optimization of performance and more selectivity.
- The use of non-edible feedstock
Acknowledgements

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THANKS FOR LISTENING
First is deoxygenation by thermal cracking followed by catalytic cracking, oligomerization, alkylation etc of triglycerides.

Alcohol
2-cis-9-octadecenyloxy ethanol

E-14-Hexadecenal

1-Heptatriacotanol
Evidence of catalytic cracking
Catalysts leaching

% Transmittance vs. wave number (cm⁻¹)

- CM (used)
- CM (unused)
- DS (used)
- DS (unused)
Condensation

Vegetable Oil + catalyst

Deoxygenation and cracking

Coke

Light olefins + light paraffins (gasoline) + CO₂ + alcohol + CO + H₂O

Deoxygenation and secondary cracking

Heavy hydrocarbons + Oxygenates

Polymerization

Aromatic Hydrocarbons

Alkylation, Isomerization and Aromatization

Olefins + paraffins (gasoline, biodiesel and kerosene)

Oligomerization

Gases (light olefins, paraffins, CO, CO₂ + H₂O)
Kapilakarn and Peugtong (2007)
*International Energy Journal*