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

![Chemical reaction diagram]

Triglyceride + 3 [\(\text{H}_3\text{C} - \text{OH}\)] \(\xrightarrow{\text{Catalyst}}\) Methanol (3) + Glycerol + Methyl Esters (3)
European Directive of 2009/28/EC, proposed 10% renewable fuel by the end of 2020. ~ 35 mtoe biofuel (i.e. 22 mtoe biodiesel & 13 mtoe bioethanol)

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

Source of data: Renewable Energy Association

Neste oil, (2008)
Transesterification Process

15% MeOH

Thermo catalytic cracking

Oil

NaOH acid catalyst

11% MeOH

Washing

66% FAMEs

Catalyst removal

Catalyst NaOH Glycerol

Glycerol removal

Experimental

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FAMEs

FAME purification

Experimental

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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 $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$ for 5 hours at 600°C

- **Conventional method (cm)**
  - $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was hydrolysed with $\text{NH}_4\text{OH}$,
  - $\text{Zr(OH)}_4$ was impregnated with $\text{H}_2\text{SO}_4$
  - Calcination for 3 hours at 650°C.

- **Characterization of catalysts**
Catalyst synthesis

Conventional method “cm”

NH₄OH → ZrOCl₂·8H₂O → hydrolysis

H₂O → filtration

H₂O → drying

H₂SO₄ → sulphating

H₂SO₄ → drying

H₂O → calcination

S/Zr

Direct method “ds”

(NH₄)₂SO₄ → ZrOCl₂·8H₂O → mixing

→ calcination

→ S/Zr
Catalyst application

S/Zr → Catalytic Cracking → Analysis of liquid sample

Gases
Light olefins
Light paraffins
Biodiesel
Alcohol
Aromatics
Characterization results

XRD of “cm” and “ds” catalysts
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

Motivation
Objective
Experimental
Results
Characterization results

Effect of SA and SO\textsubscript{4}\textsuperscript{2-} loading on biodiesel (FAMEs) production

- **Properties**
  - DS
  - CM
  - BET surface area
    - 168.9 (m\textsuperscript{2}/g)
    - 107 (m\textsuperscript{2}/g)
  - Pore size
    - 0.41 (µm)
    - 0.32 (µm)
  - Particle size
    - 48.83 (µm)
    - 25.61 (µm)
  - Crystallite size
    - -
    - 17.51 (nm)
  - Nature of phases
    - A
    - T, M
Selectivity of the catalysts

FAMEs profile showing saturated, mono and poly unsaturated
## Summary

<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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</thead>
<tbody>
<tr>
<td>DS</td>
<td>0.70</td>
<td>168.9</td>
<td>0.41</td>
<td>48.83</td>
<td>-</td>
<td>A</td>
<td>47.43</td>
<td>51</td>
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<tr>
<td>CM</td>
<td>0.56</td>
<td>101</td>
<td>0.32</td>
<td>25.61</td>
<td>17.51</td>
<td>T, M</td>
<td>38.78</td>
<td>53</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
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Bioenergy III

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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
Vegetable Oil + catalyst

- Condensation
- Polymerization

Coke

Heavy hydrocarbons + Oxygenates

- Deoxygenation and cracking

- Deoxygenation and secondary cracking

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

- Oligomerization

Aromatic Hydrocarbons

- Alkylation, Isomerization and Aromatization

Olefins + paraffins (gasoline, biodiesel and kerosene)

Gases (light olefins, paraffins, CO, CO₂ + H₂O)