Designer Catalysts for Biofuels Synthesis

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Heterogeneous Catalysis
Homogeneous Catalysis

Surface Science
Biological Catalysis

£2.3M investment
19 academic staff

Chemical Engineering
Organic Synthesis

Prof Stan Golunski
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First Generation

- Dwindling fossil fuel reserves and global warming concerns.
  → Introduction of *First generation* biofuels from cultivated food crops.

- Sugars, starch.
- Plant oils.

Fermentation to Bio-ethanol

Conversion to Biodiesel

- Serious societal and environmental impacts.

Food shortages/price rises

Deforestation

- Cleaner, sustainable fuels & chemical are required to oil dependency
Non-food crops

- Renewable biomass should be derived from waste/non-food feedstocks.

Lignocellulosic feedstocks
- Non edible components of crops (stems, leaves and husks).
- Agricultural or forestry waste, or short rotation crops.

Oleo-feedstocks
- Jatropha → minimal cultivation.
- Aquatic biomass.

Jatropha

~ 2.2-2.7 tonne oil/ha (www.reuk.co.uk)

~180 x more oil/ha than Jatropha.

Renew & Sust En Rev, 2010, 14, 217
Routes to Renewable Fuels

- Fast pyrolysis to bio-oil not selective → unstable acidic mixtures.
- Transesterification offers a low energy route to fuel.
‘Well to Wheel’ Analysis

- Land-use changes affect the GHG mitigation potentials of biofuels.

\[ \text{CO}_2 \text{ emissions / g CO}_2 \text{ MJ}^{-1} \]

Land use in China

- Jatropha offers the best potential for reducing CO\(_2\) emissions.
  - Requires little cultivation

- Use of grassland further reduces CO\(_2\) emissions.

Deforestation is detrimental to improvements in CO\(_2\) emissions.

Biodiesel Synthesis

• Second-generation biofuels from sustainable bio-oils.

Jatropha

→ aqueous quench

→ stable emulsions

→ energy intensive separation

Bio-oil transesterification

Triglycerides

New Heterogeneous Catalysts

\[ \text{Triglyceride (TAG)} \rightarrow \text{Fatty acid esters} \]

3 \( \text{CH}_3\text{OH} \)

improved energy efficiency

Reduced smog & CO\(_2\)

Carbon neutral

3 \( \text{CH}_3\text{OH} \)

[\( \text{FAME} \)]

Biodiesel

Glycerol

Triglycerides

Renewable bio-oils

Jatropha

Algae

Oil

→ aqueous quench

→ stable emulsions

→ energy intensive separation

J. Biobased Mater. Bioenergy 2007, 1, 1
Cat. Sci. Techol., 2012, 2 (5), 884 - 897
1. Oil composition

Unsaturation & chain length

- Glyceryl trioleate $C_{18}$ unsaturated
- Glyceryl tripalmitate $C_{16}$ saturated

- Fatty acid content?
  - Fatty Acid (FFA)
  - $H^+ + CH_3OH$
  - FAME

2. Catalyst type

Solid acid vs Solid base

- Compatibility with oil?
- Acid/Base strength?
- Effect of porosity?

3. Reactor Design

Batch vs Flow

- Oscillatory Baffled Reactor

*Ind Eng Chem Res (2001), 40, 5371*
Solid Acids: Heteropolyacids

- Heteropolyacids are a versatile class of acid catalyst.
- Forms a secondary structure which is highly acidic.

But:
Soluble in polar media!

- Ion exchanged Heteropolyacids are insoluble in methanol.
  e.g. ion exchanged \( \text{Cs}_x \text{H}_{(3-x)} \text{PW}_{12} \text{O}_{40} \).

\( \rightarrow \) Evaluate in triglyceride (TAG) transesterification.
Transesterification by heteropolyacids

- Titrate acid sites by NH$_3$ calorimetry.

- Whafs happening?

- However – overall activity of solid acid in transesterification is low.

Solid Bases: Mg-Al hydrotalcites

- Layered mixed oxides prepared by precipitation.

\[
\text{Mg(NO}_3\text{)}_2 \quad \text{Al(NO}_3\text{)}_3
\]

- Increased pK\text{B}_{\text{BH}+}.

\[
[Mg_{(1-x)}Al_x(OH)]^{x+}_{(OH)}^{x/2-} (CO_3)^{2-}_{x/2}
\]

- Vary Mg:Al → tune basicity.

- Base strength varies:
  \[11 < pK_{\text{BH}^+} < 26.5\]

- \(\text{Catalyst activity correlates with} \uparrow [\text{Mg}^{2+}]\)

Applied Catalysis A (2005), 287, 183.
Designing Porous Architectures

Alkyl ammonium $\rightarrow$ MCM

Alkyl amine $\rightarrow$ HMS

- SBA-15 pore structure

- Mesopore size is limited by the surfactant micelle ($<10$ nm)

- Slow in-pore TAG diffusion

- Can we improve pore structure?

Catalytic biodiesel production (1)

• SBA-15-RSO₃ solid acid catalysts:
  - conventional SBA-15 has ~5 nm pores → too constricted for bulky bio-oils
  - trimethyl benzene helps swells micelles → expanded silica pores

Pore-expansion enhances accessibility of in-pore acid sites
Impact of pore interconnectivity

- 2D pore network of SBA-15-SO$_3$H $\rightarrow$ poor interparticle accessibility
- Is acid site accessibility enhanced via 3D interconnected KIT-6?
- Relative enhancement as function of FFA

Pore interconnectivity and expansion enhances acid site accessibility
Improving diffusion in porous solids

- Oil triglycerides are viscous bulky molecules → poor in-pore diffusion

- Can we design improved bimodal hierarchical pore networks?

- Can macropores ↑ inter-particle diffusion?

- Effect of pore hydrophobicity?

J. Amer. Chem. Soc., (2009), 131, 12896
Green Chem. (2010), 12, 296
Hierarchical macro-mesoporous supports

Polystyrene nanospheres

Templated macro-mesoporous SiO$_2$

Calcine

Macro-mesoporous SiO$_2$

J. Amer. Chem. Soc., (2009), 131, 12896
Green Chem. (2010), 12, 296
Catalytic biodiesel production (2)

- Macroporous-mesoporous solid acid catalyst:

  ![Diagram showing macroporous-mesoporous solid acid catalyst]

  **Green Chem. 2010, 12, 296**

  **Macro-Meso SiO₂**

  Tricaprylin
  Palmitic acid

  ![Tricaprylin and Palmitic acid molecules]

  Hierarchical solids tune structure and promote biofuels synthesis

  ![Bar graph showing FFA esterification TOF/h⁻¹ and TAG transesterification TOF/h⁻¹ for different catalysts]

  ↑ Macroporosity
Catalytic biodiesel production (3)

- **Hydrotalcite solid base catalysts:**

  - Conventional HT
  - Macroporous HT

  ![Graph showing TOF enhancement vs. bio-oil chain length](Image)

  - Macropores enhance bulky bio-oil transformation

  *Energy Env. Sci. 5, (2012), 6145-6150*
Concluding Remarks

Rational design of new materials for biodiesel synthesis

Materials Chemistry

Surface Science

Hierarchical pore networks

Tunable acid catalysts

Tunable base strength

Chemical Engineering – alternative reactors?
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