Nanomaterials design, synthesis and application for Energy Production and Storage

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Stavanger: 4th largest city; Norway’s oil/Energy capital.
The co-operation between UiS and the local industry has given the petroleum activities at the University of Stavanger an unique national and international position.

There is a need for transition from fossil fuel to renewable energy.
Department of Petroleum Engineering - Department of Energy and Petroleum Engineering

- Department of Petroleum Engineering has developed parallel to the growth of Stavanger as an oil capital.
- In view of the development of sustainable energies, IPT has been spitted into Department of Energy and Petroleum Engineering and Department of Energy Resources.
Nanomaterial for energy production: design, synthesis, characterization and applications

I was the leader of the prioritized research program “Clean Fuel and Petroleum Production by Application of Nanomaterials and Nanotechnology” at UiS during 2015-2017.
CO\textsubscript{2} to fuels: background

Press release

Ingolstadt/Berlin, 2015-04-21

Fuel of the future: Research facility in Dresden produces first batch of Audi e-diesel

- The verdict: Pilot plant produces high-quality diesel fuel
- No need for mineral oil: e-diesel made from water, CO\textsubscript{2} and green power
- Minister Wanka: “Synthetic diesel using CO\textsubscript{2} is a huge success”

1. Ecological power generation

The electricity used for the production of e-diesel comes entirely from renewable energy sources such as wind or solar.

2. Conversion

Blue Crude is then created from carbon dioxide and hydrogen in a two-stage process (crude oil equivalent):

- Carbon monoxide, hydrogen and water are created from hydrogen and carbon dioxide.
- The synthesis gas (consisting of CO and H\textsubscript{2}) reacts to form a liquid energy carrier (Blue Crude) comparable with crude oil.

Source: Audi
CO₂ to fuels: overview

More Oxidized → Different energetics → More Reduced

CO₂ → Oxalic acid → Glyoxal → Ethanol → Ethylene → Oil, Gas (CHₓ)

Formic acid → Formaldehyde → Methanol → Syngas

Acetone → Isopropanol → Propylene

2-Butanol
CO$_2$ reforming to methane

\[
\begin{align*}
\text{CH}_4 + \text{CO}_2 & \leftrightarrow 2\text{CO} + 2\text{H}_2 & \Delta H^\circ = 247 \text{ kJ/mol} \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 & \Delta H^\circ = -41 \text{ kJ/mol}
\end{align*}
\]

- The key to a cost-effective process is a breakthrough, methane dry reforming catalyst!
- A PhD student started the project Feb 2015.

Methanol synthesis: carbon-neutral fuels

- The key to the process is to develop effective nanostructured catalysts

- A PhD student started the project Oct 2016.

\[ \text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H^0 = -49.5 \text{ kJ/mol} \]

K. stangerland, H. Li, and Z. Yu: Thermodynamic analysis of chemical and phase equilibria in CO2 hydrogenation to methanol, dimethyl ether and higher alcohols; *Industrial & Engineering Chemistry Research*, under revision.
CO₂ to methane: power to gas

CO₂ + 4H₂ ↔ CH₄ + 2H₂O  \( \Delta H^o = -252.9 \text{ kJ/mol} \)

- Storage capacity of the electricity grid last for only 0.6 h; storage capacity of the natural gas grid lasts for 2000 h.
- The key to the process is to develop active catalysts and effective structured reactors.
- A PhD student is to start the project in 2018.

**H₂ production: hydrolysis of ammonia borane**

\[ \text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{BO}_2^- + 3\text{H}_2 \]

- Industrial H₂ production: steam methane reforming; \( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2, \Delta H^o = 206 \text{ kJ/mol.} \)
- Ammonia borane (AB) is a potential H₂ carrier due to its high H₂ content (19.6 wt. %) and high stability under moderate conditions.
- The hydrolysis of AB can proceed efficiently at room temperature with 100% H₂ yield in the presence of an active and durable catalyst.
- Nobel metals, e.g, Pt, Ru, Rh, have demonstrated high TOFs and low activation energy.
- Ni, Fe, Co, and Cu based nanomaterials have been investigated and reported to have good activities.
Ni NPs with different sizes: TEM

- All five Ni NPs are monodispersed except that the 27.4 nm Ni NPs are slightly agglomerated.
Activity test: The influence of Ni NP sizes

Time course of H₂ production with differently sized Ni NPs and the corresponding TOFs

NiCu NPs with different compositions: TEM

Ni

Ni_{0.75}Cu_{0.25}

Ni_{0.5}Cu_{0.5}

Ni_{0.25}Cu_{0.75}

Cu

Average Size=10.0 nm

Average Size=9.9 nm

Average Size=13.5 nm

Average Size=11.8 nm

Average Size=19.7 nm
NiCu: HAADE-STEM

$\text{Ni}_{0.75}\text{Cu}_{0.25}$

HAADF-STEM, elemental mapping and HRTEM images. 
Ni(111): 2.034 Å, Cu(111): 2.088 Å
Activity test: The effect of alloying with Cu

Time course of H₂ production with different NiCu and corresponding TOFs

K. Guo, Y. Ding, J. Luo, and Z. Yu: NiCu bimetallic nanoparticles on silica support for catalytic hydrolysis of ammonia borane: composition-dependent activity and support size effect. To be submitted.
Summary

• Ni NPs can be synthesized with controlled sizes, they are effective catalysts for hydrolysis of ammonia borane and their activity are found to be size-dependent.

• NiCu NPs can be synthesized with controlled sizes and compositions; By alloying with Cu, the activity of NiCu alloy NPs are found to be composition-dependent with Ni$_{0.75}$Cu$_{0.25}$ showing the best catalytic performance.
**In-situ and ex-situ catalytic upgrading of heavy crude oil: Rational design and synthesis of nanocatalysts**

TEM images and corresponding lateral size distribution curves with Gaussian fits of the MoS$_2$ (a, d), MoNiS (b, e) and MoCoS (c, f).

Application of nanomaterials for Enhanced oil recovery (EOR)

- Nanoparticles in the contact region tends to create a wedge like structure. A disjoining pressure is created and the wedge film spreads along the solid surface as monolayer, therefore enhancing the separation of oil or paraffin from the solid surface.

M.N. Agista, and Z. Yu: A state-of-the-art review of nanoparticles application in petroleum with focus on enhanced oil recovery; under review.
M.N. Agista, P.Ø. Andersen, and Z. Yu: Nanoparticle transport in porous media: simulation and comparison with experimental data; To be submitted.
Thank you for your attention!

I am interested in collaboration on nanomaterials synthesis and applications on energy production!

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