

2019「中技社科技獎學金

2019 CTCI Foundation Science and Technology Scholarship

境外生研究學等金

Research Scholarship for International Graduate Students



2019 CTCI Foundation Science and Technology Scholarship

Strategies for the Selective Hydrotreatment of Oleic Acid and Castor Oil to Biofuels via Hydrodeoxygenation

Saurav Bhattacharjee (Ph.D. 4th year), Chung-Sung Tan (Advisor)*

Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan 30013, ROC

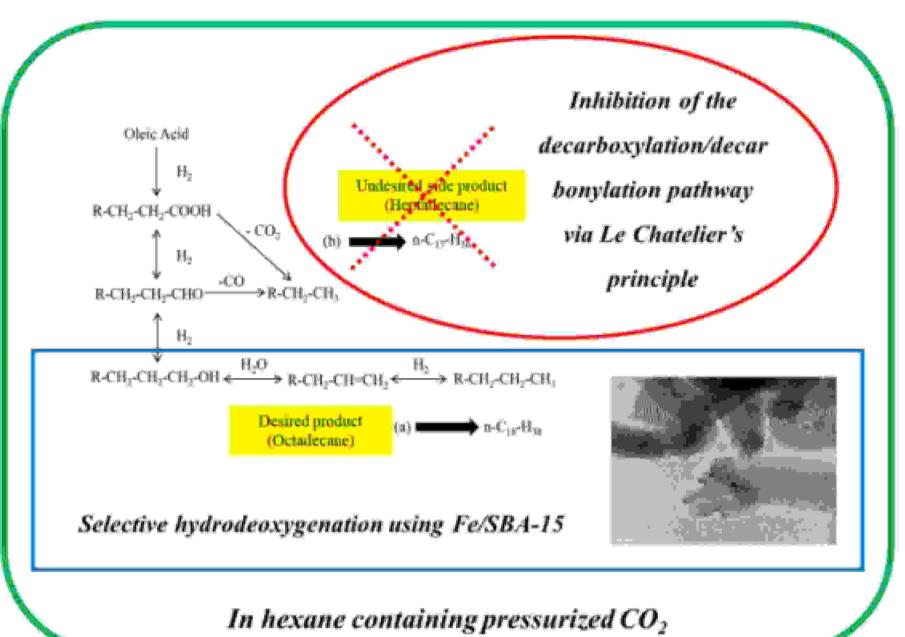


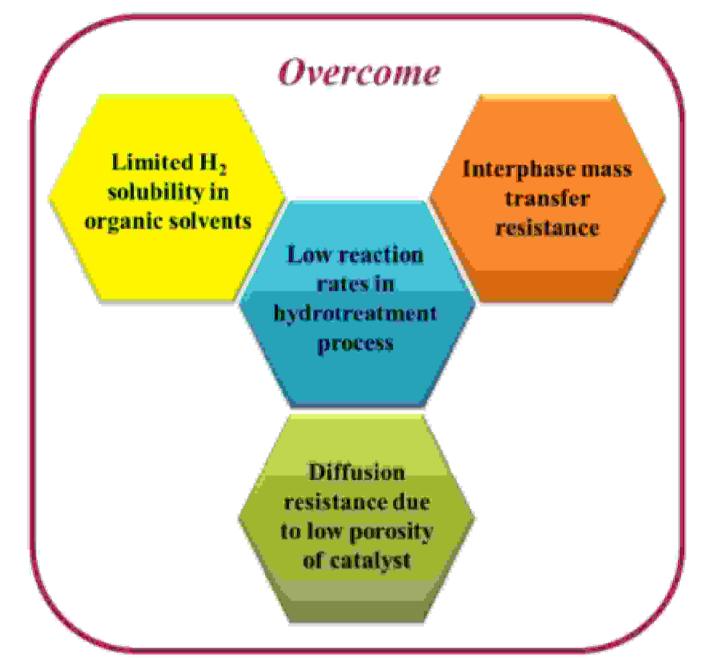
Abstract

Selective production of octadecane through the hydrodeoxygenation (HDO) of oleic acid and castor oil in hexane containing pressurized CO₂, a green reaction media, using a mesocellular foam (MCF) supported Fe-Pd-Ni/MCF catalyst was demonstrated in this study. Hexane containing pressurized CO₂ played a key role in directing the hydrotreatment of oleic acid towards HDO over decarboxylation/decarbonylation via Le Chatelier's principle. Negligible diffusion resistance aided by the 3-dimensional cage like structure and large pore opening of MCF, plus a better dispersion of the catalyst helped achieve higher selectivity for octadecane. An octadecane yield of 93% was achieved at 278 °C, a H₂ pressure of 40 bars and a CO₂ pressure of 20 bars for 4 h. The activation energy for the HDO of stearic acid to octadecane was observed to be a 43.6% reduction over existing literature. An increased spillover of H₂ onto the surface of Fe nanoparticles, triggered by an increased sticking capability of H₂ on Pd-Ni alloy patches formed on top Fe nanoparticles, was proposed as the major reason for this acceleration. Investigation on active one-pot single atom catalysts for hydrodeoxygenating castor oil is currently underway.

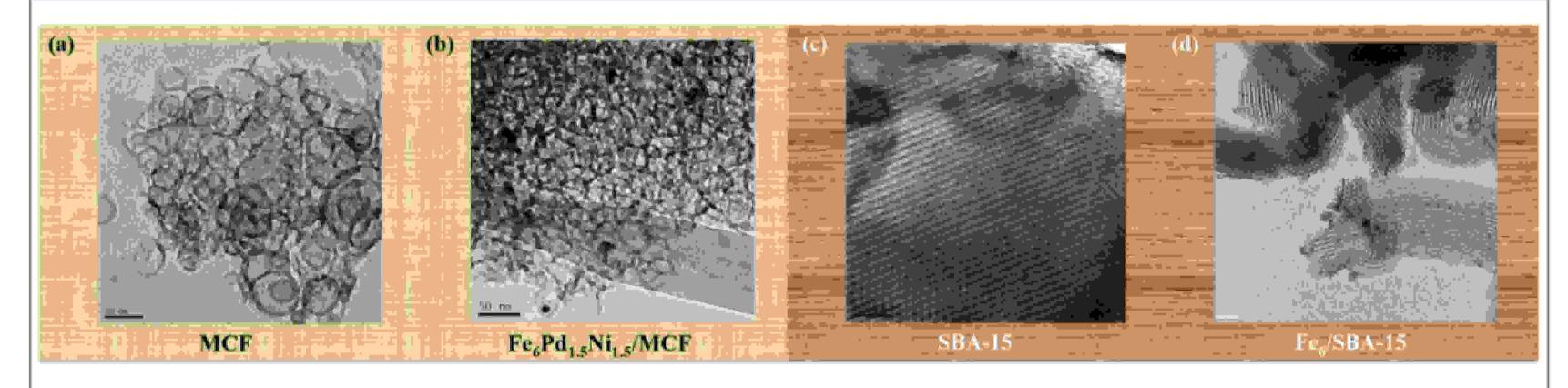
Additionally, the selective hydrogenation of aromatic rings in everyday chemicals by utilizing effective catalysts to produce environmentally friendly, high-value chemicals was reported.

Reaction pathway for HDO of oleic acid in hexane containing pressurized CO₂

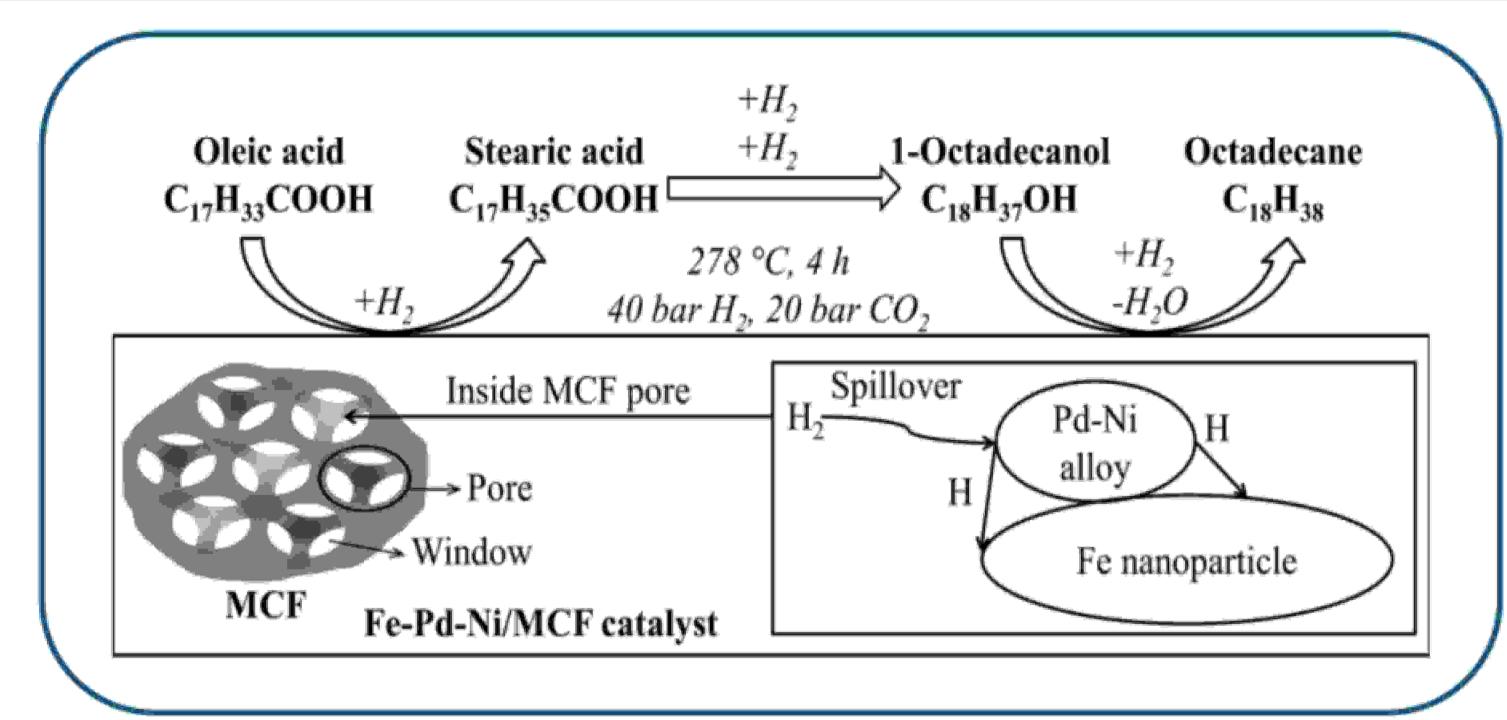




TEM imaging of synthesized supports and catalysts



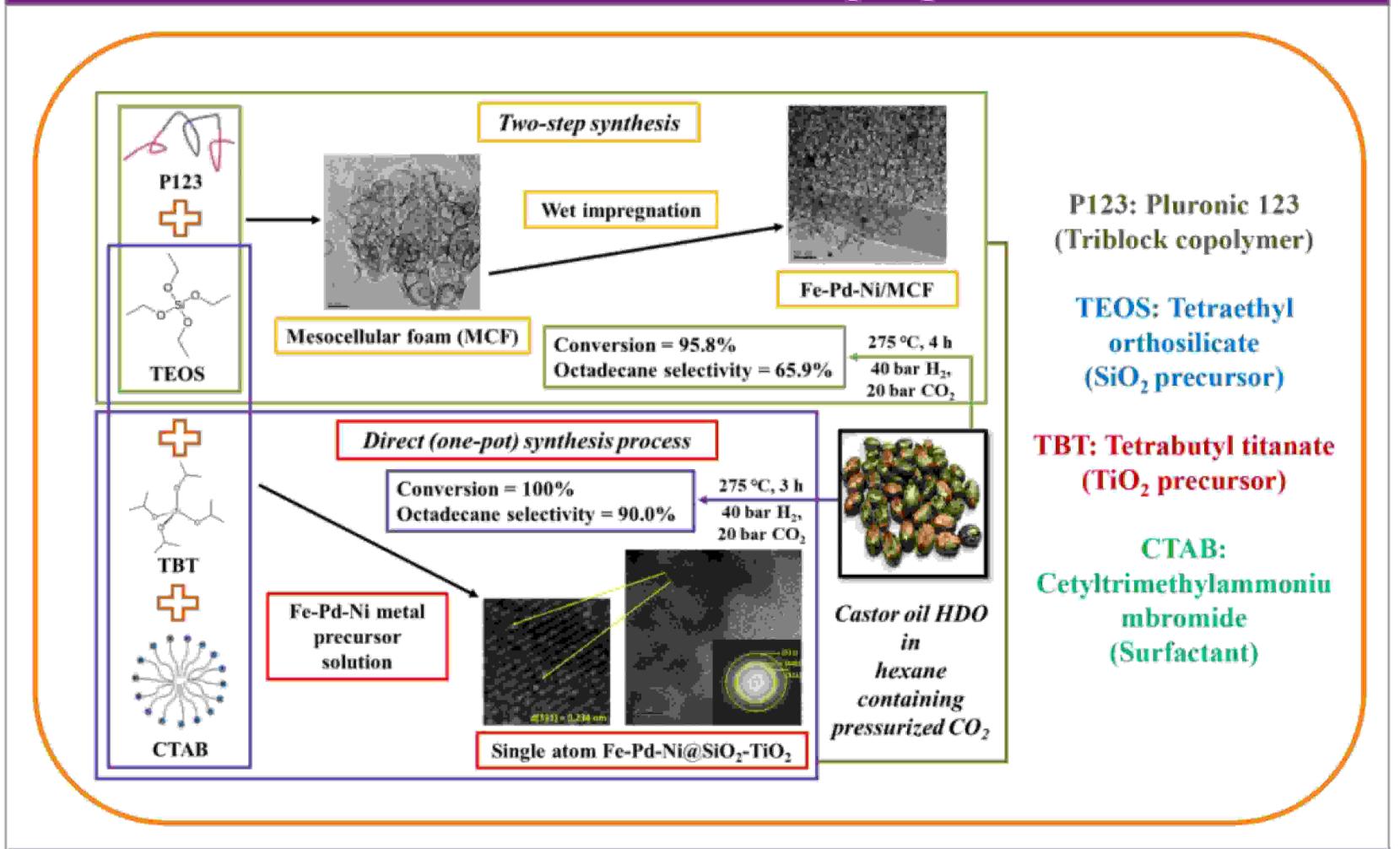
Catalysis mechanism of the Fe-Pd-Ni/MCF catalyst



The optimized reaction conditions of 278 °C, 40 bars H_2 and 20 bars CO_2 pressure giving an octadecane yield of 93.0% were obtained using the $Fe_6Pd_{1.5}Ni_{1.5}/MCF$ catalyst via a central composite design employing response surface methodology.

In comparison, the $Fe_6/SBA-15$ catalyst gave 83.3% yield of octadecane at 290 °C for 6 h of reaction with a H_2 pressure of 30 bars and CO_2 pressure of 40 bars.

HDO of castor oil and future perspectives



Conclusions

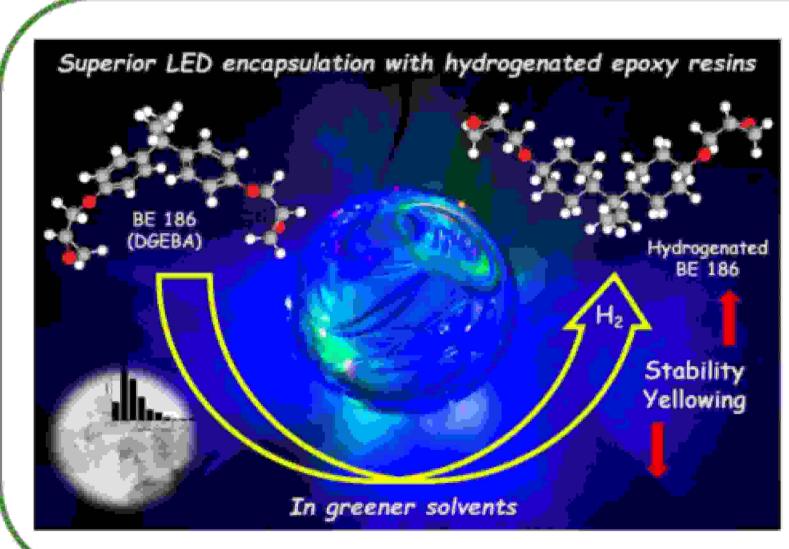
The role of CO₂

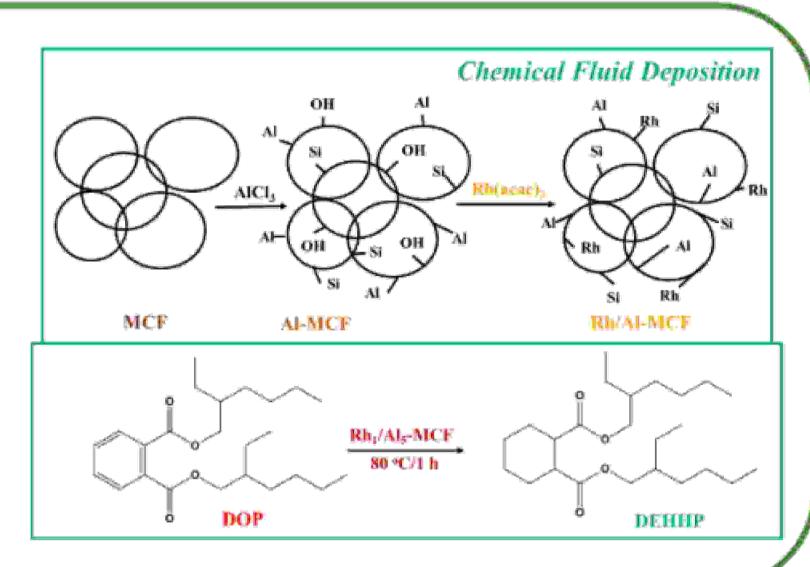
- Prevent decarboxylation/decarbonylation pathway following Le Chatelier's principle
- Reduce viscosity and diffusion resistance
- Increase mass transfer
- Increase H₂ solubility

The role of catalyst

- Large pore size and 3-D cage structure of MCF leads to negligible diffusion resistance
- 43.6% reduction in activation energy for HDO of stearic acid to octadecane
- Increased H₂ spillover caused by Pd-Ni patches on Fe nanoparticles
- Complete cut-off of heptadecane using the Fe-Pd-Ni/MCF trimetallic catalyst

Catalyst assisted selective aromatic ring hydrogenation of bisphenol A-type epoxy resin and dioctyl phthalate





The studies presented were supported by the ROC Ministry of Science and Technology (grant number MOST 106-2622-8-007-017) and National Tsing Hua University at Hsinchu, Taiwan, ROC.

Selected publications

[1] <u>Bhattacharjee</u>, S., Lu, W. -Y., Tan, C. -S. A cleaner route for hydrodeoxygenation of oleic acid in hexane containing pressurized CO₂ over a MCF supported Fe-Pd-Ni trimetallic catalyst. *Fuel*, 243, 210-220. (2019) [2] <u>Bhattacharjee</u>, S., Tan, C. -S. Hydrodeoxygenation of oleic acid in hexane containing pressurized CO₂ using Fe/SBA-15 as catalyst. *Journal of Cleaner Production*, 156, 203-213. (2017)

[3] Lende, A. B., Bhattacharjee, S., Lu, W. -Y., Tan, C. -S. Hydrogenation of dioctyl phthalate over a Rhsupported Al modified mesocellular foam catalyst. New Journal of Chemistry, 43, 5623-5631. (2019)

[4] Lu, W. -Y., Bhattacharjee, S., Lai, B. -X., Duh, A. -B., Wang, P. -C., Tan, C. -S. Hydrogenation of Bisphenol A-Type Epoxy Resin (BE186) over Vulcan XC72-Supported Rh and Rh-Pt Catalysts in Ethyl Acetate-Containing Water. Industrial & Engineering Chemistry Research, 58, 16326-16337. (2019)

[5] Yu, W., Bhattacharjee, S., Lu, W. -Y., Tan, C. -S. Synthesis of Al Modified SBA-15 Supported Ru Catalysts by Chemical Fluid Deposition for the Hydrogenation of Dimethyl Terephthalate in Water. ACS Sustainable Chemistry & Engineering, Under revision.

