Platinum nanoparticles in organic-metal framework:

Evaluating the catalytic performance in the selective hydrogenation of cinnamaldehyde

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Metal-Organic framework (MOF)

Metal-organic framework (MOF)
- UiO-66 versus UiO-66-NH$_2$
- Great potential in catalysis
  - Large surface area
  - High porosity


Synthesis of UiO-66-NH$_2$

\[ \text{Synthesis of UiO-66-NH}_2 \]
Platinum(Pt) nanoclusters in MOF

Platinum nanoclusters catalysts in MOF
- High activity due to high surface area and small size
- MOF can tune the catalyst properties by functionalizations

TEM image of 10.7%Pt@UiO-66-NH$_2$

Size distribution histogram of Pt nanoclusters
Hydrogenation of Cinnamaldehyde

Purpose
• Evaluate catalyst performance
• Obtain desired product (cinnamyl alcohol, C=O bond hydrogenated product)

Challenge
• The hydrogenation of C=C bond is more thermodynamically favorable
• Low selectivity (33%) obtained on commercial catalyst: Pt/C
The Conversion of CALD and the selectivity to CALC are optimized in ethanol and ethanol/water mixture solution (protic solvents).

Reaction condition: 5 mg catalyst, 10 mL solvent, 100 or 400 μL cinnamaldehyde, 40 bar H₂, room temperature, 800 rpm
Influence of Loading Amount

Higher Pt loading gave:

Higher Selectivity to CALC
Lower Selectivity to HCALD

Reaction condition: 5 mg catalyst, 10 mL methanol, 100 or 400 μL cinnamaldehyde, 1 mL triethylamine, 40 bar H₂, room temperature, 800 rpm
Influence of Reaction Time

Longer reaction time gave:

Higher conversion
Similar selectivity to CALC
Kinetic study during recycling experiments

Best results: 98.7% conv. 91.7% sel.

Recycle experiments: the catalyst is stable within 10 runs.

Kinetic study: the reaction rate of the catalyst kept the same during four runs, suggesting the catalyst did not deactivate.

Reaction condition: 5 mg catalyst, 10 mL methanol, 400 µL cinnamaldehyde, 1 mL triethylamine, 40 bar H₂, room temperature, 800 rpm, 44 hours (42 hours for first three cycles).
The END ADSORPTION of C=O group is preferred over the FLAT ADSORPTION of the C=C group, mainly due to the pore confinement effects.
Conclusion

1) The Conversion of CALD and the selectivity to desired product (CALC) is greatly influenced by the choice of solvents and loading amount of Pt nanoparticles

   Protic solvents and high Pt loading are preferred

2) The catalyst is reusable, and stable in recycling experiments
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^____^
Method

Liquid phase cinnamaldehyde hydrogenation: The hydrogenation of cinnamaldehyde was carried out in a 22mL Parr 4740 High Pressure/High Temperature Pressure Vessel

- 5mg of reduced catalyst added into a glass liner inserted in the autoclave
- Then 10mL of ethanol was added
- 40 bars H₂ @ 80°C for 12 hours with magnetic stirring at 800 rpm
- Cool to room temperature
- Then add 1mL triethylamine + 400 μL cinnamaldehyde + 20 μL mesitylene
- The Hydrogenation experiment was carried as the above condition
- After reaction, 0.1 mL of the solution and diluted with 0.7mL of EtOH
• The catalyst was separated after centrifugation at 8000 rpm for 10 minutes.

• The supernatant was then analyzed on a HP 5890 gas chromatograph equipped with a capillary column (HP-5, 30 m × 0.32 mm × 0.25 μm) with a flame ionization detector and SHIMADZU 505A GC-MS equipped with a capillary column (HP-5ms, 30 m × 0.32 mm × 0.25 μm).

• The response factors of each component were determined with standard samples, and were used to calculate the conversion and selectivity.