Controlled Metal@Metal Oxide Core-Shell Structures for Selective Hydrodeoxygenation Reaction of Biomass Derived Alcohols

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Opportunity and Significance
The efficiency of production of fuels or chemicals from biomass derived alcohols can benefit from proper design of multi-step reactions, such as hydrodeoxygenation (HDO): \[ R\text{O} + 2H_2 \rightarrow RH + 2 H_2O \]
A desirable path for sustainable production of fuels can be achieved through the improvement of activity, selectivity, and stability of the catalysts utilized in HDO. This study focuses on the synthesis of a core-shell nanorod structure consisting of Pd NPs encapsulated in TiO\(_2\), where:
- Core: Pd NPs (noble metal)
- Shell: TiO\(_2\) (reducible metal oxide)
- Provides hydrogenation sites
- Provides deoxygenation sites

Advantages of using a core-shell catalytic structure:
- Production of interface sites controlled by nanoporous shell
- Accessible conformations of aromatics are restricted
- Increase in HDO selectivity

Our goal is to control the encapsulation of Pd NPs through optimization of nanoporous TiO\(_2\) shell synthesis.

Related Work and State of Practice
The state-of-the-art for synthesis of core-shell catalysts involves a two-step seeded growth mechanism. The challenge in optimizing the synthesis of this approach arises from:
- Heat treatment required to achieve crystallinity:
  - Effects the metal/oxide interface
  - Decreases catalytic activity
  - Control of hydrolysis rate
  - Creates a compromise between crystallinity and porosity of the catalyst

Technical Objectives
To optimize the sol-gel synthesis for the two-step seeded growth mechanism to achieve crystalline Pd@TiO\(_2\) nanoporous shell by:
- Varying parameters such as precursors and solvents
- Running the reaction at room temperature

Technical Approach
Sol-Gel Synthesis Method:
- Tuning Pd@TiO\(_2\) shell structure at room temperature:
  - Pd nanoparticles are pre-synthesized prior to coating of the TiO\(_2\) shell
  - CTAB is used as hydrophilic ligand to modify the metal nanoparticle surfaces
  - Metal alkoxide precursors (Ti(OBu\(_2\))\(_n\) or Ti(OPr\(_i\))\(_n\)) are used to synthesize metal oxide-shell using alcohols (ethanol or isopropanol) as solvents
  - De-ionized water is used as an initiator to start sol-gel shell the reaction

Effect of Titanium Alkoxide Precursor (TAP) on Crystallinity and Porosity:
- Crystallinity:
  - Ti(OBu\(_2\))\(_n\) led to better crystallinity, while Ti(OPr\(_i\))\(_n\) led to an amorphous structure of the TiO\(_2\) shell.
- Porosity:
  - Use of Ti(OBu\(_2\))\(_n\) led to slightly larger amount of micropores when compared with Ti(OPr\(_i\))\(_n\)

Effect of Solvent on Crystallinity and Porosity:
- Crystallinity:
  - Changing the nature of the solvent did not show significant effect on crystallinity
  - Isopropanol led to larger pore size (>6nm), while ethanol led to smaller pores (<4nm)

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Catalytic Performance
Selective HDO of benzyl alcohol towards toluene:
- Temperature: 190 °C, gas flow rates: 140 ml/min (H\(_2\)=20%, benzyl alcohol=0.09%), conversion=6.1%

Selective HDO of furfural alcohol towards methyl furan:
- Temperature: 170 °C, gas flow rates: 70 ml/min (H\(_2\)=3%, furfural alcohol=0.3%), conversion=6.2%

Next Steps for Development and Test
Our main goals for future work include:
- To expand the metal/oxide core-shell synthesis method to other reducible metal oxides, such as CeO\(_2\) and ZrO\(_2\), by following a similar approach as the proposed sol-gel synthesis utilized in the formation of nanoporous Pd@TiO\(_2\) core-shell structures.
- To test the selectivity and stability of our metal/oxide core-shell catalysts in other multi-step reactions for a wider range of applications.

Commercialization Plan & Partners
- Partners: The testing portion of the project was completed by Dr. Jing Zhang, under the supervision of Prof. Will Medlin, at University of Colorado, Boulder. Commercialization Plan: Given the high selectivity achieved by our Pd@TiO\(_2\) catalyst in HDO for biomass derived alcohols, the feasibility of commercializing the catalyst could be discussed with companies, such as BioCatalytics and PetroSun.

- The main challenge in commercialization of Pd@TiO\(_2\) involves the generalization of such detailed procedure, which creates a compromise between large scale production and selective performance of the catalyst.

References

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