HYDROGENATION OF TOLUENE OVER METAL-INCORPORATED SWELLABLE ORGANICALLY-MODIFIED SILICA

Research Proposal Submitted by

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I. BACKGROUND AND MOTIVATION

The production of oil, natural gas, and other industrial products may lead to contaminated water. More specifically, contaminants like benzene, toluene, ethylbenzene, and xylene (BTEX) are among the most abundantly produced chemicals, with worldwide annual production of 5-15 million tons each, and are often found in groundwater because of their use in various industries such as petroleum, pharmaceuticals, and everyday consumer products like synthetic rubber, plastics, and paints [1]. These compounds enter groundwater supplies through leaking tanks and pipelines and are especially problematic because they are more water-soluble and toxic than hydrocarbons [2]. For example, toluene has narcotic and neurotoxic properties and can affect the blood, liver, heart, and central nervous system [3]. Toluene detected in groundwater is generally below 3 ppb, but can go as high as 3,500 ppb in groundwater from industrially-polluted sites [1]. However, according to the World Health Drinking Water Guidelines, the acceptable toluene concentration in groundwater is 700 ppb. This is why development of remediation systems for BTEX removal from contaminated groundwater is of absolute importance.

This research project focuses on hydrogenation of aromatic ring containing contaminants in aqueous phase by using metal-incorporated swellable organically-modified silica (SOMS) materials as catalysts. Within the aromatic-ring containing contaminants, toluene, molecular make-up of which is shown in Figure 1, has been chosen as a model compound for this project. Toluene hydrogenation reaction is given in Figure 2, where toluene is reacted with hydrogen to reduce the double carbon bonds. It is believed that, if used as a support, metal-incorporated SOMS materials can face the challenges of aqueous-phase hydrogenation reactions due to the benign properties of the SOMS materials.
II. SIGNIFICANCE

Groundwater accounts for nearly one-third of the world’s freshwater resources, provides about 40% of the United State’s public water supply, and is used by more than 40 billion people [4, 5]. Groundwater remediation is of significant importance to prevent pollutants from spreading and increase the water availability, especially for drinking water. It is highly likely that a catalytic system that can hydrogenate toluene in the aqueous phase can also hydrogenate not only the remaining BTEX compounds, but also other aromatic ring compounds such as naphthalene, fluorene, and benzopyrene, which are among the most toxic contaminants created from coal processing [6].

III. METHODOLOGY AND RESEARCH PLAN

This section will address the shortcomings to the existing approach of groundwater remediation and then propose a plan for this specific research project.

A. SHORTCOMINGS WITH EXISTING METHODS

Currently, there are two types of remediation processes: recovery based and destruction based. Recovery based remediation is when contaminants are separated from groundwater and then treated further. However, this will require at least two processes and ultimately will only transfer contaminants from one phase to another. Adsorption is a popular recovery based technique in which activated carbon adsorbs the aromatic compounds. However, after a period of time, the activated adsorbent must be replaced or regenerated, which is a slow and expensive process [7].

In destruction-based remediation, the contaminants are treated directly in one step and eliminated via a chemical reaction, which avoids the transfer of the contaminant to another phase and additional treatments. The most common treatments are biodegradation and hydrogenation.
Many studies have analyzed the disappearance of benzene due to biodegradation mechanisms, in which microorganisms produce enzymes that degrade compounds to inorganic materials like CO$_2$ and H$_2$O. But, bioremediation does not give predictable, consistent, or complete results in removing indigenous contaminants [8, 9].

**B. SHORTCOMINGS WITH EXISTING CATALYSTS**

In addition to the shortcomings of existing techniques, there are other problems with liquid phase catalytic hydrogenation. Kinetics of hydrogenation reactions suffer from the low concentrations of the BTEX compounds present in groundwater. Catalytic active sites of hydrogenation catalysts under such conditions are mostly covered with water, decreasing number of available active sites and slowing the kinetics. To enhance the kinetics, either large amounts of catalysts need to be used or hydrogenation reactions need to be conducted at higher temperatures. These solutions are not feasible because of two reasons: (i) Large amounts of catalysts and high energy inputs to conduct the reaction at high temperatures makes the treatment system expensive and unfeasible. (ii) At high temperatures, metals such as platinum, nickel, rhodium, and ruthenium, which are effective in hydrogenation of toluene, sinter and metal particle size increases [10, 11, 12, 13, and 14]. Increasing the size of the metal particles decreases the available surface area for reaction, which decreases the activity and kinetics for the reaction [10].

**IV. EXPECTED RESULTS**

The use of swellable organically-modified silica (SOMS) materials is expected to help resolve these issues since these materials are swellable and extremely hydrophobic. When placed inside the swollen matrix of SOMS, active metals will not be in contact with water during hydrogenation reactions since the SOMS materials only swell upon contact with organic
molecules. Hydrophobicity of these materials will become an additional barrier for water molecules, which will be repelled from the catalyst surface. Moreover, slow kinetics due to low concentration of toluene can be overcome by the swelling, which creates an additional volume for absorption of organics near the active sites, and by hydrophobicity, which will selectively concentrate organics near the active sites.

**B. RESEARCH PLAN AND TIMELINE**

In this project, different precious metals for hydrogenation of toluene on SOMS support will be tested and then the results will be compared with commercially available catalysts whenever available.

The first step will be to perform a thermodynamic analysis to determine the range of operating parameters of toluene hydrogenation. Since the experiments will be conducted in aqueous-phase, higher pressures may be needed to increase the solubility of hydrogen in water. Also, equilibrium calculations will be performed to distinguish kinetic control regime from thermodynamic control regime. The non-idealities will be taken into account by using corresponding equation of states.

Catalysts will be synthesized through incipient wetness impregnation method. Three different precious metals—palladium (Pd), platinum (Pt), and ruthenium (Ru)—will be used to synthesize metal incorporated catalysts using SOMS support in the lab. These materials will then be reduced with NaBH₄. Once these catalysts have been prepared, they will be placed in a batch reactor to start the hydrogenation reaction with toluene. Kinetic analysis will also be conducted and rate parameters will be obtained.

Infrared Spectroscopy (IR) experiments will be conducted to study the adsorption-desorption behavior of water on metal incorporated SOMS and alumina samples. It is expected that the
affinity of water to adsorb on the samples is going to be different. Since alumina is hydrophilic, water will strongly bind to the active sites. But, because SOMS is hydrophobic, it is expected that water will not cover the sample surface and the IR experiments will be help us to see this difference. Textural properties including surface area, pore volume, and pore diameter will be measured with nitrogen physisorption technique.

The projected timeline is shown in Figure 3.

V. PERSONAL STATEMENT

I have been part of the Heterogeneous Catalysis Research Group (HCRG) since November 2014. I joined because of my interests in sustainability and environmental projects. Since middle school and high school, I have delved in sustainable research projects like designing windmill blades to increase efficiency, competing to the State level in Science Fair competitions. In addition, through Green Engineering Scholars, Engineers Without Borders, and my internship with Marathon Petroleum, I have been able to implement sustainable solutions in various aspects from organizing speakers and events about sustainability, investigating a solution to the flooding problem in a community in the Dominican Republic, and working on a new membrane bioreactor in an industrial setting. Being a part of HCRG has been a platform in thinking about ways I could shape my career path in sustainable energy. I have been participating in a wide range of catalysis synthesis methods with impregnation techniques and catalytic activity testing and characterization. Through research, I have been able to connect with my chemical engineering curriculum better and learned several applications of my major. I know that whether I choose industry or academia, the knowledge I have gained on problem solving and innovating will play a pivotal role in the success of my career.
FIGURES

Figure 1: Toluene

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\text{Toluene} + 3 \text{H}_2 \rightarrow \text{Cyclohexane}
\]

Figure 2: Reaction Equation of Toluene

Figure 3: Timeline
REFERENCES


