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Computational Investigation of the preparation of hydroxylated amorphous silica substrates as supports for Ruthenium based metathesis catalysts for a heterogenous system

## B.Sc Hons project proposal and outline

A project that will be supervised by Dr. CGCE van Sittert was selected. This project will be conducted in the Catalysis and Synthesis Research group within the Chemical Resource Beneficiation Research Focus Area at the Potchefstroom Campus of the North West University.

## Scope of the Project

Metathesis reactions of alkenes and the catalysts for metathesis have become one of the most researched themes in chemistry in the recent past. The industrial applications for these reactions include pharmaceutical delivery systems and the synthesis of chemically resistant materials that find application in automotive and aeronautical fields.

The Grubbs group of Ru-based carbene catalysts have proven to be the most effective and widely used catalytic systems for metathesis reactions. Three generations of these catalysts have been developed to improve reactivity and selectivity of the catalysts.

The drawback of these catalysts however are that they are homogenous systems and recovery of the catalyst, post-reaction is a complex time consuming and costly process. A heterogenous system will eliminate these drawbacks and allow industry to benefit from the selectivity, reactivity and lifespan of the Grubbs catalyst systems.

Despite the decreased reactivity associated with heterogenization of catalysts, the cost and time benefits have been shown to outweigh the increased reactivity of the homogenous systems.

The heterogenization of the catalysts is accomplished by adsorbing or supporting the catalyst on a support material that does not significantly impact on the reactivity of the catalyst. For the purpose of this study an inorganic support, a hydroxylated amorphous silica surface, MCM-41 has been identified.

The project is a molecular modelling study of MCM-41 hydroxylated amorphous Silica surfaces. The goal will be to better understand the annealing process and characteristics of the surface. Furthermore the study will attempt to model the adsorption or bonding of the PUK-Grubbs-II catalyst to the surface of the support. Calculations will be focussed to determine the effect the coordination of the catalyst will have on the reactivity, selectivity and life span of the catalyst.

This project will also support and serve as background to a laboratory study to determine the bonding mechanism of the Ru-based PUK-Grubbs II metathesis catalyst to the surface of the MCM-41 amorphous silica surface.

The project will also support a parallel molecular modelling study of the structure and bonding of the Grubbs group of catalysts to the SBA-15 hydroxylated silica surfaces.

### Method

This study is a pure computational study. The software that will be used in this study is CASTEP in Materials Studio 2016. The approach in the study will be to

1. Retrieve the crystalline, bulk material structure of α-quartz from the database.
2. These structures will be simulating heating the bulk to liquid at various temperatures (4000, 5000 and 6000 K).
3. Quenching the melted bulk at 0K.
4. Annealing the bulk by modelling heating of the bulk structures from 1K-1000K in 500 steps of 2K/fs using DFT with a B3LYP functional. The bulk is then cooled to 300K in 500steps at a rate of 0.3K/fs using the same complexity of calculation
5. .After the bulk is annealed different Miller planes, with different slabs thicknesses and vacuums gap will be optimized to find a stable working system. This will be compared to experimental XRD results.
6. The Grubbs generation II catalyst as well as PUK Grubbs catalyst molecules will also be simulated using the same software package and complexity of calculation.
7. The coordination of the catalyst molecule to the amorphous silica surface will be investigated.
8. The influence of coordination on the reactivity and selectivity of the catalyst for the metathesis of 1-Octene will also be investigated.

### Planning

The proposed milestones and planning is outlined in Appendix 1

### Goal

The goal of the project is to establish a model to be able to determine the bonding interaction of the Ru-based catalyst to the silica surface and also determine how this binding effects the reactivity and regeneration characteristics of the catalyst.

* Modelling and optimization of the MCM-41 material using CASTEP.
* Modelling the PUK-Grubbs Catalyst within a periodic system.
* Modelling of the coorcination of the catalyst to the surface of the MCM-41 silica material.

Appendix 1: Gannt Chart

