

1. PRF#: 59051-ND5

2. Project Title: The Role of Supercritical Ethylene on Heterogeneous Oligomerization Reactions

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Narrative Progress Report

Impact of research:

The overall goal of the present project is to pursue a new research direction focused on the use of supercritical fluids on heterogeneous catalysis. Specifically, we are proposing a novel, environmentally friendly route for production of alpha olefins via oligomerization of ethylene. This route: 1) uses heterogeneous catalysts, thereby not requiring organic solvents; 2) takes advantage of the low critical point of ethylene (9.4 °C and 50.6 bar) to carry out oligomerization of ethylene at supercritical conditions, 3) uses properties of supercritical ethylene as a reaction medium to enhance reaction rates and remove coke from the catalysts. The new process proposed involves temperatures around 120-200°C to promote the reaction kinetics of oligomerization, and pressures above 50.6 bar to ensure supercritical conditions, which promote the desorption of long chain oligomers from the catalyst surface, preventing catalyst deactivation. This new process is unique because it allows catalyst regeneration in-situ, building on kinetic and thermodynamic fundamental concepts to develop an application for heterogeneous catalysis in supercritical fluids.

In preliminary work performed prior to this grant, we had provided evidence of the benefits of using supercritical ethylene as both reactant and solvent, to increase the production rates of heavier olefins, simultaneously removing carbon deposits from the catalyst surface via solvation effect of the supercritical fluid. In accordance to the original plan of study, the work performed during the period covered by this report can be divided in two components: (1) a solubility study of heavy paraffins in subcritical and supercritical ethylene conditions, and (2) a kinetic study for the ethylene oligomerization (under subcritical conditions). The main accomplishments and findings for each component are described as follows:

Solubility study:

We performed a solubility study, which is intended to provide insights on how the supercritical ethylene affects the dissolution of coke from the solid catalyst during the reaction (ethylene oligomerization), assessing the contribution the influence of the supercritical fluid in the reaction kinetics. For this purpose, we developed a thermodynamic model to fit the experimental solubility data using Virial and Peng-Robinson equations of state (EOS) and calculated the binary interaction parameters for both EOS. For the catalytic reaction, we employed the Ni-H-Beta catalyst reported in several publications from our research group and reported kinetic data (yield, conversion, and product selectivity) for the ethylene oligomerization under supercritical conditions for temperatures ranging from 30 to 75°C and pressures between 50.1 and 68 bar. This work is unique because it employs thermodynamic principles to explain the physicochemical behavior of the catalytic system during the ethylene oligomerization over heterogeneous catalysts

Study of kinetics/overall reaction pathways: We developed a kinetic model based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics for the ethylene oligomerization over a Ni-H-Beta catalyst. We calculated an apparent activation energy (E_{app}) for the production of C₄, C₆ and C₈ products of 33.9, 72.4, and 77.5 kJ/ mol, respectively. The activation energy for the production of butene is lower than those obtained for hexene and octene, which suggests that desorbed butene produced participate in the chain growth process. Our results also show that ethylene dissociates upon adsorption on the Ni-H-Beta catalyst and we found evidence of the involvement of two distinct active sites in the ethylene adsorption process. Furthermore, we found that catalyst activity is a function of the Si/Al ratio, which suggests that the density of Brønsted sites affects catalyst activity. Based on these findings, we suggest that ethylene adsorbs dissociatively over Ni⁺-H sites. Additionally, our results indicate the involvement of an alternative pathway parallel to the well-known “*true-oligomerization*” pathway, which involves a desorption/re-adsorption mechanism of the butene products on the catalyst surface. This result validates our initial hypothesis that

desorbed butene products may re-adsorb and be consumed by reaction. Figure 1 shows the reaction network proposed, and the data obtained were used to evaluate the contribution of the several pathways involved in the ethylene oligomerization over the Ni-H-Beta catalyst. Finally, we modelled the selectivity for C₄, C₆, C₈, C₁₀, and C₁₂ products based on a Schultz-Flory distribution. We found that increasing pressure and temperature increases propagation probability and decreases termination probability.

Impact on career:

The ACS PFR grant is allowing the PI Dr. Resende to expand his research interests, adding supercritical fluids for catalysis to his areas of expertise. Prior to this grant, the work performed for oligomerization of ethylene in Dr. Resende's group was mostly applied. This project is adding another layer to the capabilities of the lab and allowing Dr. Resende and his students to investigate the interactions between supercritical fluids and heterogeneous catalysts in a molecular level.

Impact on students participating on project:

The graduate student working on this pt is pursuing his PhD degree in Bioresource Engineering at the University of Washington. The project is providing Gabriel with significant training on Reaction Engineering and also in Catalysis and Surface Science, via the determination of reaction pathways, kinetic models, and solubility studies. The work has inspired Gabriel to decide to pursue an academic career as a University Professor after he graduates. He will be presenting the results of this work in the next AIChE meeting in Orlando.

Future work:

For the next year of the project, we are planning to expand the kinetic studies for supercritical conditions. This will allow our team to connect the results of the solubility studies and kinetic model, to provide additional insights on how the supercritical ethylene affects the reaction kinetics. We also plan to expand the study to include another catalysts, such as Ni-MCM-41, Ni-SBA-15, and Ni-Siral30.

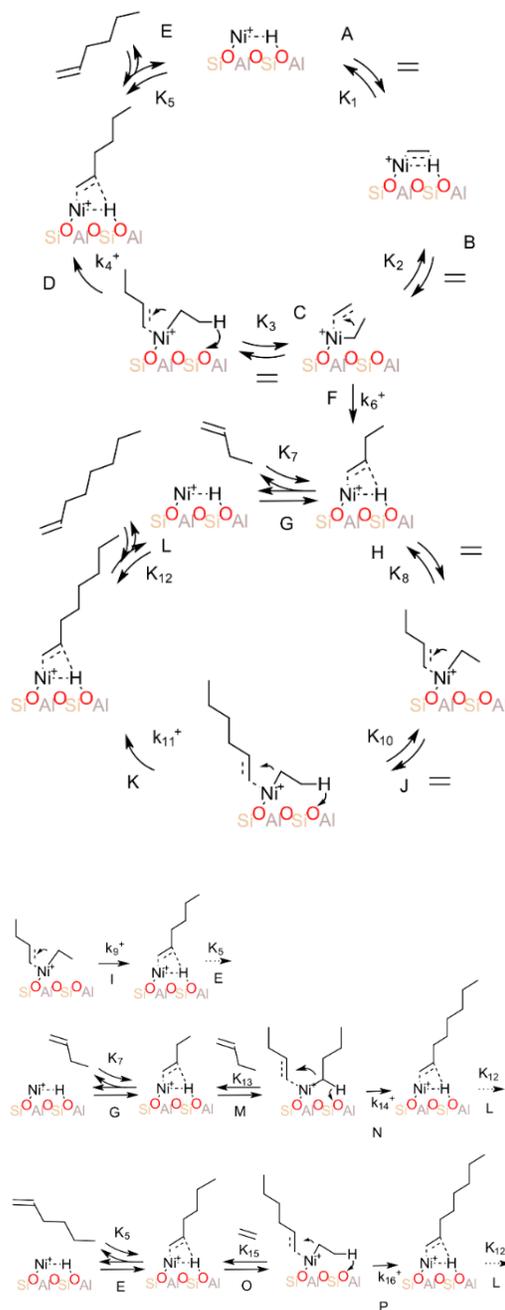


Figure 1: Proposed Reaction Pathway for oligomerization of ethylene