Mechanisms and Catalyst Design for Heterogeneous Olefin Metathesis

Daniel Francis Consoli

Olefin metathesis offers a promising technology for on-purpose production of propylene and has been implemented in several industrial processes including the Lummus Olefin Conversion Technology. However, current metathesis technology cannot produce propylene cheaply and efficiently due to reliance on decades-old catalyst technology like tungsten oxide on silica. This poor performance can be attributed to a lack of understanding of heterogeneous metathesis reaction mechanisms and the catalysts involved.

Current understanding proposes that olefin metathesis follows the Chauvin mechanism in which olefins coordinate with catalytic metal carbenes to form metallacyclobutanes that then rearrange into metathesis products. While this mechanism has been proven for homogenous metathesis catalysts, for which the 2005 Nobel Prize was awarded, the mechanism over heterogeneous catalysts may be more complicated as metal carbenes do not necessarily exist over freshly prepared material.

In this work, we present a complete mechanistic cycle for heterogeneous olefin metathesis that accounts for the presence of *in situ* carbenes during steady state catalysis. We demonstrate why this expanded mechanism is necessary to explain certain characteristic behavior during propylene metathesis over industrial catalysts like WO_3/SiO_2. Furthermore, we leverage our knowledge of the mechanism to introduce new operating conditions that increase overall metathesis rates by an order of magnitude. Finally, we utilize our understanding to synthesize catalysts supported on tunable zeolite and metal organic framework materials that optimize metal-support interaction and metathesis rates. In sum, an improved understanding of the heterogeneous olefin metathesis mechanism has led to improvements in catalytic design, material characterization, and reactor operation.

Thesis Supervisor: Yuriy Román-Leshkov
Title: Professor of Chemical Engineering