



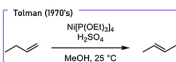
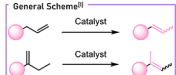
# Monometallic Alkene Isomerization Catalysts from Nickel-Hydrides supported on Sulfated Metal Oxides

Quinn P. Valentine, Alison Sy-Min Chang, Rachel M. Thomas, Lily H. Granados, Melanie A. Kascoutas, Amanda K. Cook\*



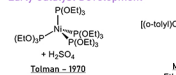
## ALKENE ISOMERIZATION

### Isomerization Reaction



Alkene isomerization moves the double bond through the molecule across C-C bonds. This allows for functionalization at previously inaccessible parts of the molecule.

### Early Catalyst Development



### Heterogeneous $\pi$ - $\pi$

KF/Al<sub>2</sub>O<sub>3</sub>  
Dius - 2009

Amino-grafted SiO<sub>2</sub> (MCM-41)  
Martin-Aranda - 2012

PA/SS (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, C, BaSO<sub>4</sub>)  
Lipinska - 2017

PF<sub>6</sub>  
Schoenebeck - 2019

X = CH<sub>3</sub> or (CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>  
Grothahn - 2014

Fragrance and Food Additives

10% KOH/Alumina

Nylon 6,6 Precursors

2 eq. HCN

isomerization step

Pharmaceutical Precursors

KOH

75 min, 80 °C

Nickel-hydrides as isomerization catalysts were thoroughly studied in the 1970's using nickel(0) complexes activated with acids.<sup>[1]</sup> Miller's work with ethylene bis(dipr-1-yl phosphine)nickel(0) highlighted how effective they are as catalysts, even isomerizing substrates that commonly poison metal complexes<sup>[2]</sup>

Miller - 1976  
Ethyl pentanoate

State-of-the-Art Examples

CoBz<sub>2</sub>RbONa/BH<sub>3</sub>·NH<sub>3</sub>

Finclater - 2022

HSiPh<sub>3</sub>

Cook - 2022

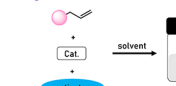
Development of homogeneous isomerization catalysts has expanded across late-transition metals. Nickel based complexes are still very prevalent in this area however, due to its effectiveness, both in catalysts and cost.

Skyrdrup - 2010

Grothahn - 2012

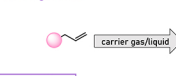
## HOMOGENEOUS VS. HETEROGENEOUS

### Homogeneous



In a homogeneous system, all components are in the same phase (in solution typically).

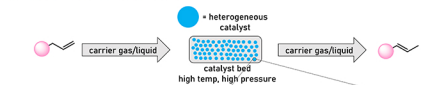
### Heterogeneous



In heterogeneous systems, the catalyst is present in a different phase than the substrate or interest. Often, high temperatures and high pressure conditions are required. These conditions are less favorable for catalysts - sensitive molecules.

## CATIONIC NICKEL-HYDRIDES ON SULFATED METAL OXIDES

### Issues with oxide supported catalysts



Catalysts supported on metal oxide surfaces often suffer from a lack of definition and understanding of the catalyst structure. Nanoparticles, monodentate, bidentate, metal oxides or single atoms are examples of possible metal-support interactions that are difficult to isolate and discern.

• heterogeneous catalyst

carrier gas/liquid

catalyst bed

high temp, high pressure

Active site?

Are all M sites active?

Our system

The development of our system was modeled after work done by Tolman in the late 60's/early 70's in order to investigate the role and activation of this complex in isomerization reactions. The role of the acid was shown to be of great importance in the catalyst activation and activity throughout the reaction.

Previously developed catalysts as our inspiration



Making the well-defined system heterogeneous

Solid Acid Support

Using solid acids that act as a proton source just like a liquid acid would, the nickel center is protonated, forming a nickel-hydride that is ionically tethered to the surface of the support.

Ni(P(OEt)3)4 (3 mol%)  
SZO<sub>300</sub> (3 mol%)  
Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

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Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

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Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

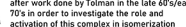
Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

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Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

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Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

Et<sub>2</sub>O, 30 °C, N<sub>2</sub>, 1 h

## SYSTEM INVESTIGATION

Catalyst (3 mol%)  
Acidic Support (3 mol% H<sup>+</sup>)

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

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Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

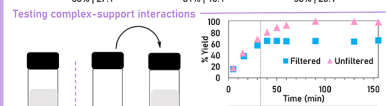
Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h



Two identical reactions were carried out, one being filtered halfway through the reaction's progress. The filtered solution was monitored, showing no further catalytic activity.

Catalyst recycle

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

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Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h

Et<sub>2</sub>O (0.12 M), 30 °C, N<sub>2</sub>, 2 h



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