Olefin Metathesis Using Methyltrioxorhenium (MTO) on a Novel Alumina Support

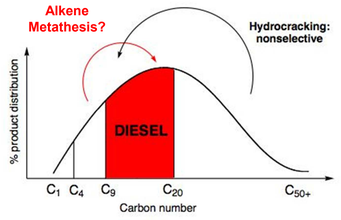
S. Michael Stewart,[1] **Trent M. Tovar**,[1] **Susannah L. Scott**[1,2]

[1]Department of Chemical Engineering, [2]Department of Chemistry and Biochemistry
University of California Santa Barbara, Santa Barbara, CA

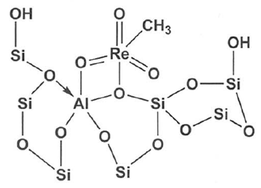
Introduction

Olefin Metathesis

- Olefin metathesis is the process of rearranging carbon double bonds
- To meet growing energy demands, olefin metathesis could potentially be used to convert undesirable high and low molecular weight olefins into more useful mid-range olefins, shown below



Typical carbon chain-length distribution from Fischer-Tropsch, where smaller olefins may be made into longer chain lengths using olefin metathesis



Structure of methyltrioxorhenium (MTO) supported on silica-alumina as determined by x-ray absorption spectroscopy

- Supported methyltrioxorhenium (MTO) shows promise as an olefin metathesis catalyst as it activates under mild conditions and is easy to recover

Goal

Identify the activation mechanism for supported MTO to improve activity

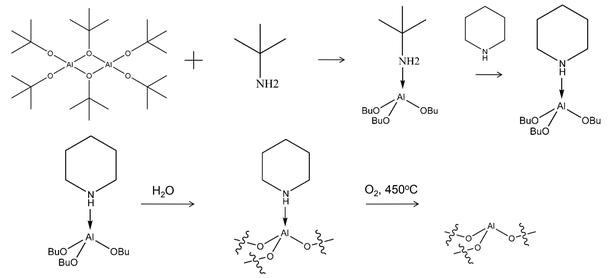
Focus

A recently reported high Lewis-acidity alumina by Kozlov, et al.,[1] has shown promise in elucidating the activation mechanism, due to its high Lewis acidity, which is known to be required for MTO activation. Characterization of this material was carried out, and comparison to γ-Al_2O_3 was made to show the improvement of the synthesized material to a traditional support.

[1]Kozlov, A. I.; Kung, M. C.; Xue, W. M.et al. *Angew. Chem. Int. Ed.* **2003**, 42, 2415.

Material Synthesis

Alumina Synthesis



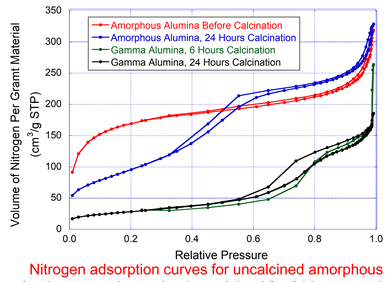
- A high Lewis-acidity, amorphous alumina was synthesized by hydrolyzing the product of piperidine bound to a tri(tert-butoxide)aluminum dimmer dissolved in toluene
- After synthesis, the alumina-piperidine material was calcined at 450ºC in flowing oxygen for 24 hours to remove bound amines, then evacuated for 12 hours at the same temperature

Catalyst Preparation

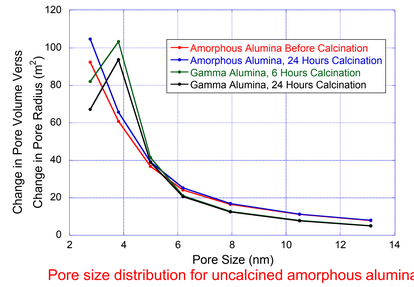
- Vapor transfer was used to adsorb controlled amounts of MTO onto the calcined amorphous alumina
- The supported MTO was then evacuated for 12 hours to remove any weakly bound MTO from the surface
- After evacuation, the supported MTO was sealed under vacuum via a glass side arm

Support Characterization

Nitrogen Adsorption



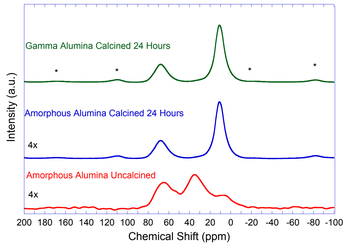
Nitrogen adsorption curves for uncalcined amorphous alumina, amorphous alumina calcined for 24 hours, and γ-Al_2O_3 calcined for 6 and 24 hours



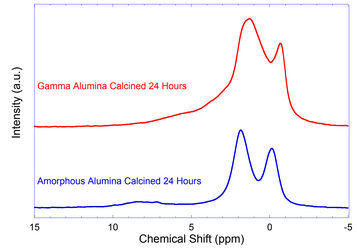
Pore size distribution for uncalcined amorphous alumina, amorphous alumina calcined for 24 h, and γ-Al_2O_3 calcined for 6 and 24 h

- BET surface areas of the amorphous alumina before and after calcination are 568±11 and 358±7 m^2/g, respectively, while γ-Al_2O_3 had a surface area of 100±7 m^2/g regardless of calcination time
- Loss of surface area for the amorphous alumina is attributed to loss of micropores
- From the desorption curves, the peak pore size of γ-Al_2O_3 was determined to be between 3 and 4 nm, while the amorphous alumina has pore sizes mostly less than 3 nm

Solid State NMR



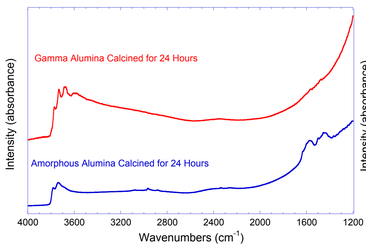
^{27}Al MAS NMR of uncalcined material, calcined amorphous alumina, and γ-Al_2O_3 calcined for 24 hours

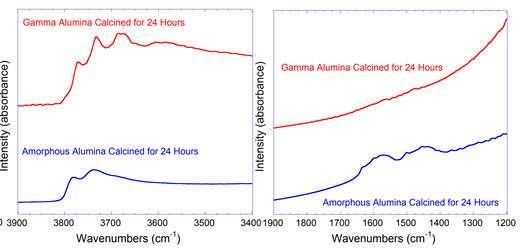


^{1}H MAS NMR of amorphous alumina and γ-Al_2O_3 calcined for 24 hours

- ^{27}Al NMR shows that 80% of the aluminum atoms in γ-Al_2O_3 are visible relative to AlN, while 22% of the aluminum atoms in the amorphous alumina are visible before calcination and only 8% are visible after calcination
- Using an external standard, the surface proton density of the γ-Al_2O_3 and the amorphous alumina were determined to be 5.1 and 2.0 H/nm^2, respectively

DRIFTS





Full DRIFTS spectra of the amorphous alumina and γ-Al_2O_3 for 24 hours of calcination showing the relative heights of all the spectra features

Left: Close-up of the hydroxyl region for amorphous alumina and γ-Al_2O_3 for 24 hours of calcination. Right: Close-up of the carbonate region for amorphous alumina and γ-Al_2O_3 for 24 hours of calcination

- DRIFTS spectra of γ-Al_2O_3 show that the alumina contains both tetrahedral and octahedral basic Al-OH groups (beneath 3770 cm^{-1}) and both isolated (ca. 3750 cm^{-1}) and associated (less than 3700 cm^{-1}) acidic Al-OH groups
- DRIFTS spectra of the amorphous alumina show only tetrahedral basic Al-OH groups and isolated acidic Al-OH groups
- For the amorphous alumina, bidentate carbonates on the surface could not be removed after 24 hours of calcination (ca. 1550 and 1450 cm^{-1})

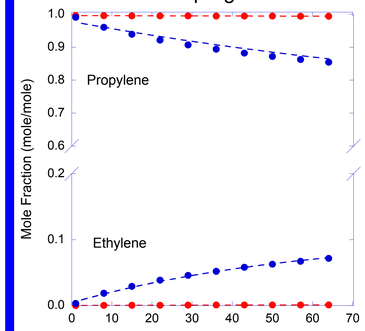
Catalytic Activity

Propylene Metathesis

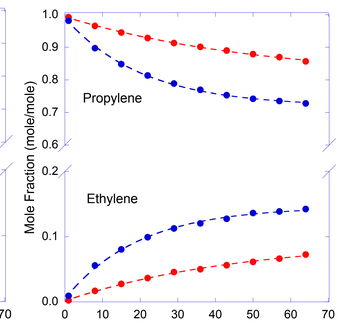
- Catalytic activity was determined by fitting the mole fraction versus time to an exponential decay, shown below

$$X_{Propyplene}(t) = X^{EQ}_{Propylene} + \left(X^{0}_{Propylene} - X^{EQ}_{Propylene}\right) e^{-k_{obs}t}$$

- For catalyst testing, 10 mg of supported catalyst was placed in a 120 mL round bottom flask and exposed to 45 torr of propylene
- The reaction progress was monitored using GC-FID



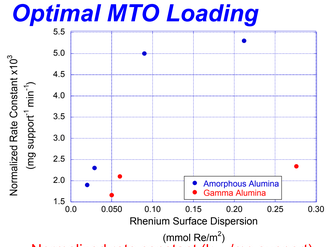
Propylene metathesis over γ-Al_2O_3 for 0.6 wt% loading (red) and 2.7 wt% loading (blue)



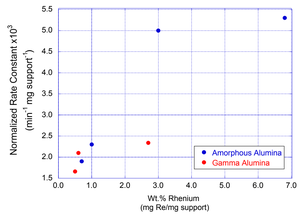
Propylene metathesis over amorphous alumina for 0.6 wt% loading (red) and 6.8 wt% loading (blue)

- Even after 64 minutes, γ-Al_2O_3 was unable to come to equilibrium
- For the amorphous alumina, equilibrium could be obtained after 50 minutes

Optimal MTO Loading



Normalized rate constant (k_{obs}/mg support) versus Re dispersion (mmol Re/area of support)



Normalized rate constant (k_{obs}/mg support) versus wt% Re (mg Re/mg support])

- Even for similar surface dispersion, the amorphous alumina gives better activity
- In comparing the rate versus weight loading, it was found that the amorphous alumina shows an optimal loading much above γ-Al_2O_3

Conclusions and Future Directions

Isotopic Labeling for Mechanism Determination

- This material shows good activity at high Re loadings with no side products, which makes identifying the carbene source possible via ^{13}C labeling of MTO
- GC-MS can be used to identify the number of active sites by determining extent of isotopic exchange with propylene

Acknowledgements:

This work was made possible by funding from the Department of Energy and the National Science Foundation Graduate Fellowship Program. Special thanks to Ramzy Shayib for his help with NMR