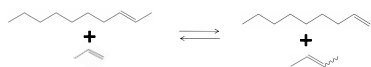


## Motivation

Olefin metathesis is a process which rearranges carbon-carbon double bonds to make new olefins, a method similar to cutting the carbon-carbon double bond of different olefins and reattaching the doubly-bound carbons together in different combinations.

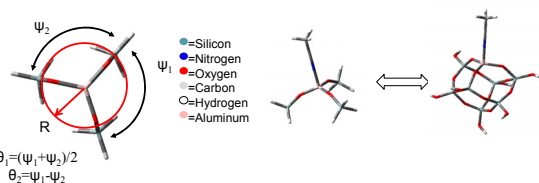


Olefin metathesis of 2-decene and propylene to form 1-nonene and a mixture of cis- and trans-butene

Olefin metathesis has already found industrial application in the production of propylene, neohexene, perfumes, pheromones, and fine chemicals. However, several olefin metathesis catalysts require high temperatures, which limit the types of olefins that can be produced, or are homogenous making them hard to recover from product streams. Olefin metathesis with methyltrioxorhenium (MTO) supported on silica-alumina is advantageous as the reaction occurs spontaneously under mild conditions and is easily recovered. Although it is known that the Lewis acidity of the support is important to the activity of MTO, the importance of this acidity is not well understood. Our goal is to examine the effects of changing the Lewis acidity of aluminum atoms in silica-alumina models on the formation of a carbene from MTO.

## Models of Silica-Alumina

Silica-alumina models were optimized using the Gaussian03 C.03 implementation of DFT and the B3LYP exchange correlation. All atoms were described using a triple-basis set. The Al(OSiH<sub>3</sub>)<sub>3</sub> were optimized by fixing the positions of the silicon atoms, while the -SiH<sub>3</sub> groups were held fixed for optimizations involving acetonitrile binding. The three coordinate aluminum model shown below was described by three parameters; R, which describes the radius of the circle containing the three silicon atoms, and  $\psi_1$  and  $\psi_2$ , which describe the symmetry and anti-symmetry of the molecule, respectively.



Description of the three-coordinate silica-alumina coordinate structure and a silsesquioxane cube of the anti-symmetry, and R describes the radius containing the three silicon atoms (left). The difference between acetonitrile binding to the three coordinate structure and a silsesquioxane cube of the same  $\theta_1$ ,  $\theta_2$ , and R parameters was than 1% of the total binding energy (right).

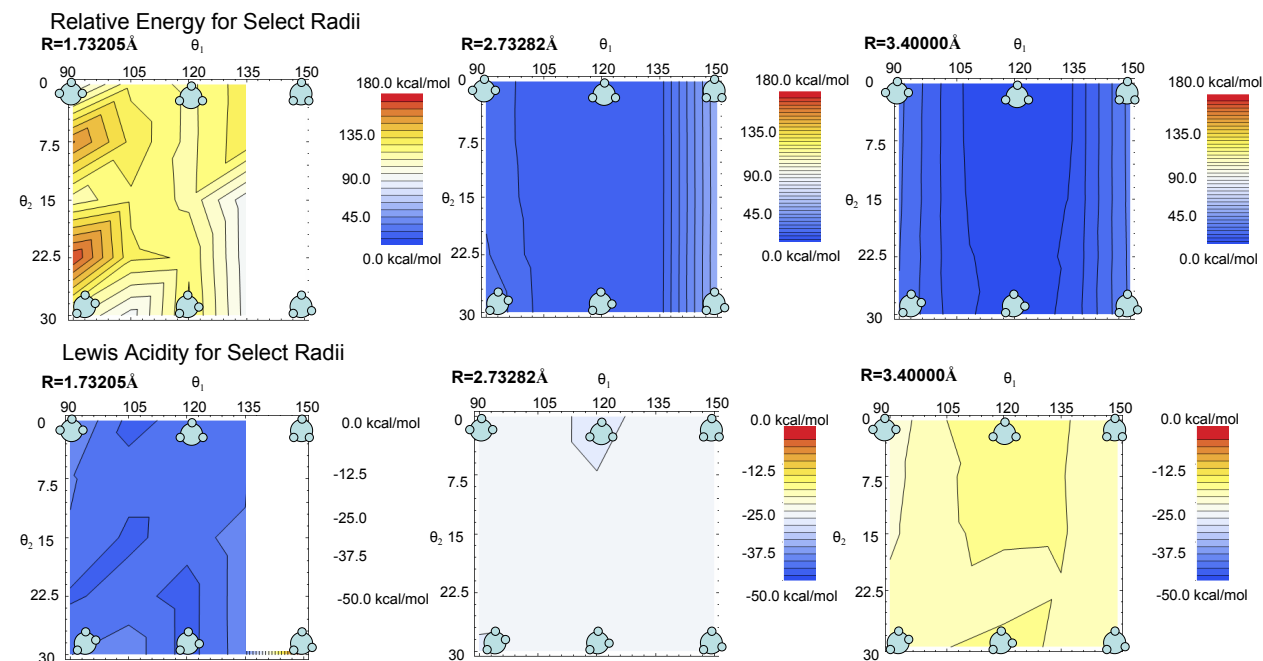
Computational models were then compared to experimental results. CD<sub>3</sub>CN (Sigma-Aldrich) degassed using a freeze-pump-thaw process and was stored over CaH<sub>2</sub>. Davicat-3113 silica-alumina was calcined at 450°C under flowing oxygen for six hours, then pumped under high vacuum (<100 mtorr) over night. A Shimadzu IRPrestige-21 Fourier Transform Infrared Spectrometer was used with 1 cm<sup>-1</sup> resolution. CD<sub>3</sub>CN was expanded into a closed IR cell and allowed to equilibrate for three minutes, then was pumped under high vacuum (<100 mtorr) for one hour. For each temperature, the sample was heated under vacuum for one hour then allowed to cool under vacuum for fifteen minutes.

## Acknowledgements

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## Effects of Geometry on Structure Energy and Acidity

The plots below show the effect of geometry on the relative energy of the three-coordinate structures and the energy change for binding acetonitrile to the structure; each graph represents a different value of R, the radius containing the silicon atoms. Figures on the graphs show the general conformations of the structures, where the larger circle is the radius containing the silicon atoms and the smaller circles are -OSiH<sub>3</sub> groups around aluminum.



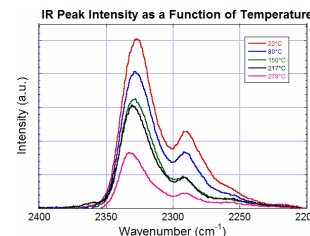
## FTIR of CD<sub>3</sub>CN on Silica-Alumina

CD<sub>3</sub>CN was used to prevent Fermi resonance of the  $\nu$ (CN) and  $\delta$ (CH<sub>3</sub>) +  $\nu$ (CC) peaks

Four peaks are associated with CD<sub>3</sub>CN adsorbed on silica-alumina

- 2283cm<sup>-1</sup> □ CD<sub>3</sub>CN interaction with S-OH groups
- 2330cm<sup>-1</sup> □ CD<sub>3</sub>CN interaction to 3-coordinate aluminum
- 2298cm<sup>-1</sup> □ CD<sub>3</sub>CN interaction with Al-O-Si oxygens
- 2323cm<sup>-1</sup> □ CD<sub>3</sub>CN interaction to 5-coordinate aluminum

Only the peaks at 2283cm<sup>-1</sup> and 2330cm<sup>-1</sup> were seen



### Peak Area Versus Temperature

Temperature	2330cm <sup>-1</sup>	2283cm <sup>-1</sup>
22°C	100.0	61.3
80°C	84.8	46.2
150°C	66.2	25.1
217°C	57.2	19.9
268°C	29.1	9.5

IR Peak heights as a function of temperature for acetonitrile adsorption on silica alumina (right). The table shows the relative area under the peaks for CD<sub>3</sub>CN adsorption to three coordinate aluminum (2330cm<sup>-1</sup>) and to coordination of Si-OH groups (2283cm<sup>-1</sup>) normalized relative to the 2330cm<sup>-1</sup> peak at 22°C (above).

## Conclusions

The results reveal that the more exposed an aluminum atom becomes, the more acidic it becomes, at the expense of becoming higher in energy. Surprisingly, the conformation in which the aluminum atom sits in the plane of the silicon atoms does not have the lowest energy. More work remains to correlate experimental results to predictions made by DFT, specifically the use of <sup>15</sup>N-<sup>27</sup>Al NMR to better resolve the distribution of Lewis acidic sites in silica alumina.