

# Investigation of Lewis Acidity in Silica-Alumina and Its Importance to Rhenium-based Metathesis Catalysts

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## Introduction

We employ a combined computational-experimental approach to probe the Lewis acidity of silica-alumina, and extend this study to the effect of Lewis acidity on the activation and activity of a supported methyltrioxorhenium (MTO) metathesis catalyst. Despite the widespread use of amorphous silica-alumina as a catalyst and a catalyst support, the structures of its Lewis acid sites remain elusive. Previous experimental studies have used probes such as acetonitrile and pyridine to quantify the number and strength of these sites, but unlike the extensive work on Brønsted acidity in zeolites, there have been few attempts to pair experimental probe studies with theory to assess the types of aluminum geometries required to generate the Lewis sites.

## Methods and Materials

Silica-alumina (Davicat 3113, 13 wt%  $\text{Al}_2\text{O}_3$ ) was calcined under flowing oxygen at 450 °C. MTO (Aldrich) was grafted onto silica-alumina using chemical vapor deposition. Propylene (Praxair, >99%) and butenes (Aldrich, >99%) for the metathesis reaction were dried and stored over molecular sieves. The metathesis reaction was studied in a batch reactor at 0 °C and 50 Torr total pressure. Aliquots were analyzed with a Shimadzu GC-2010 GC-FID. Calculations were performed using the DFT implementation in the Gaussian03 code, Revision C.02. Geometry optimizations were performed using the B3LYP density functional. Rhenium atoms were represented by the Stuttgart Effective Core Potential and the basis set proposed by Pietsch, et al.<sup>1</sup> This basis set was benchmarked against experimental work by Espenson<sup>2</sup> and Nabavizadeh.<sup>3</sup> Other atoms were represented using the 6-311g(d,p) basis set. Three-coordinate Lewis acid sites in silica-alumina were modeled using an  $\text{Al}(\text{OSiH}_3)_3$  cluster, while four-coordinate Lewis acid sites were investigated using an  $(\text{H}_2\text{O})\text{Al}(\text{OSiH}_3)_3$  cluster.

## Results and Discussion

Comparison of our  $\text{Al}(\text{OSiH}_3)_3$  model cluster with a silsesquioxane cube bearing a single aluminum substitution of silicon, both with  $R = 2.73 \text{ \AA}$ , showed comparable energies (<1% difference) for the binding of acetonitrile to the aluminum site, where  $R$  is the radius of the circle containing the three silicon atoms in the  $\text{Al}(\text{OSiH}_3)_3$  model. The more flexible  $\text{Al}(\text{OSiH}_3)_3$  model was used subsequently to investigate how Lewis acidity and catalytic properties depend on distortion of the local aluminum environment. 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 (Figure 1). When the coordination of aluminum is increased to four- or five-coordinate, the aluminum becomes less acidic. However, the acidity of these clusters still depend strongly on the geometry of the cluster.

Lewis acidity is essential to the catalytic activity of supported catalysts in alkene metathesis; thus grafted MTO is activated when supported on silica-alumina,<sup>4</sup> but not on silica, which lacks Lewis acidity. Interaction of one oxo ligand of MTO with the aluminum center facilitates reduction of  $\text{Re(VII)}$  by the olefin substrate. During the homometathesis of propylene over supported MTO, higher-molecular weight products such as 2,3-dimethyl-2-butene, which are not explained by the expected metathesis reaction or oligomerization side-reactions, are observed after long residence times over the catalyst. Alternative reaction

pathways to explain these products were explored. A pathway involving ring contraction of a rhenacyclopentane was investigated computationally. In addition, the transformation of the methylrhenium active site to a methoxorhenium complex by migration of the methyl group to an oxo ligand suggests a possible deactivation pathway.

## Significance

Our approach with careful benchmarking offers insight into the mechanism of initiation of olefin metathesis better than either calculations or experiments alone, by allowing easy manipulation of reaction pathway parameters, such as bond lengths, and simultaneously provides a picture of what the active site actually looks like. The combination of modeling and experiment allows us to probe the nature and effect of Lewis acidity, and furthermore to assess the range of geometries in the Lewis acid sites of silica-alumina.

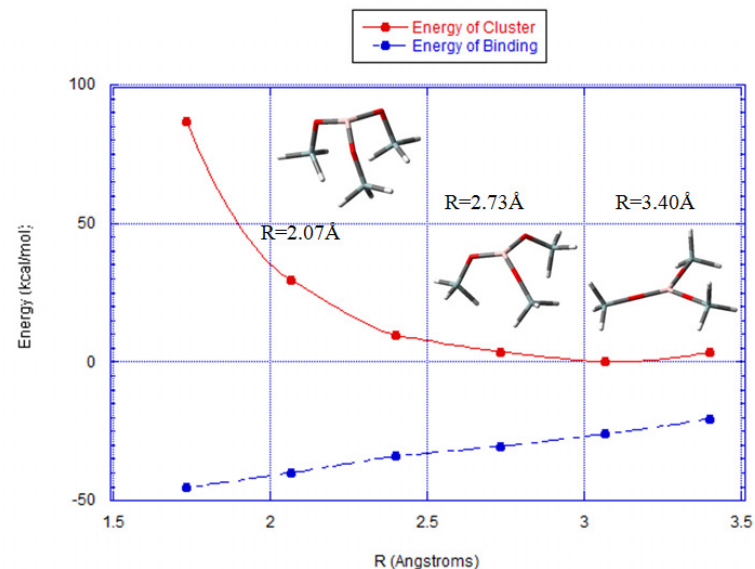


Figure 1: Cluster energy and binding energy for acetonitrile to aluminum as a function of the radius,  $R$ , of the circle containing the three silicon substituents, for three-coordinate aluminum. Pictures of the clusters illustrate the exposure of the aluminum atom at representative radii.

## References

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