# EXAFS Studies of Perrhenate and $SnMe_4$-Promoted Perrhenate on Silica-Alumina and Alumina

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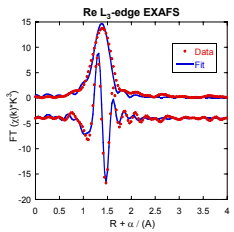
## Introduction

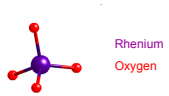
Although $Re_2O_7$ by itself is not a catalyst for olefin metathesis, heterogeneous olefin metathesis catalysts can be prepared by grafting $Re_2O_7$ onto acidic, high surface area oxides. The nature of the support determines whether or not the it can activate the perrhenate for olefin metathesis. For example, perrhenate-modified alumina and silica-alumina are both catalysts for olefin metathesis, however, perrhenate-modified silica is inactive for olefin metathesis. Treatment of these silica-alumina and alumina supported perrhenates with alkyltins The structures of perrhenate-modified silica-alumina and alumina were investigated by Extended X-Ray Adsorption Fine Structure (EXAFS) spectroscopy in order to identify the structure of the supported perrhenate in these catalysts.

## Rhenium EXAFS of Model Compounds

Two molecular compounds, ammonium perrhenate and trimethylsilylperrhenate (TMS perrhenate), were used as model compounds for supported perrhenate catalysts.

The **ammonium perrhenate** EXAFS fits a tetrahedral rhenium model with 4 equivalent oxygen paths.



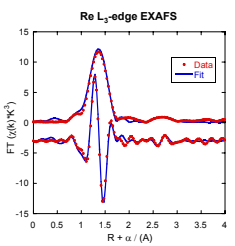

Ammonium perrhenate

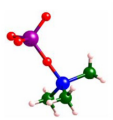
| path | N | R (Å) | $\sigma^2$ (Å$^2$) |
|---|---|---|---|
| Re=O | 4 | 1.74 | 0.0017 |

$E_0$ = 2.0 eV, $S_0^2$ = 0.90

The EXAFS of **TMS perrhenate** does not fit well to the 4 equivalent oxygen paths used in the ammonium perrhenate model. A new model was constructed from X-ray crystallography and DFT calculations of TMS perrhenate. This model includes 3 equivalent oxygen bonds plus one longer oxygen bond that bridges the rhenium and silicon atoms.

The EXAFS fits well to our model of TMS perrhenate, although the Re-Si distance is shorter than expected for the nearly linear Re-O-Si bond angle




Trimethylsilylperrhenate (pure, diluted to 2 wt% Re in BN)

| path | N | DFT-Calculated Distance (Å) | EXAFS Fit R (Å) | EXAFS Fit $\sigma^2$ (Å$^2$) |
|---|---|---|---|---|
| Re=O | 3 | 1.693 | 1.71 | 0.0010 |
| Re–O(Si) | 1 | 1.809 | 1.82 | 0.0033 |
| Re–Si | 1 | 3.522 | 3.08 | 0.0054 |

$E_0$ = 4.65 eV, $S_0^2$ = 0.923

Acknowledgements

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***SSRL***
***Cathy Knotts, Dr. Sam Webb, Dr. Erik Nelson, Dr. Allyson Aranda, Dr. Corwin Booth, Dr. Serena George***

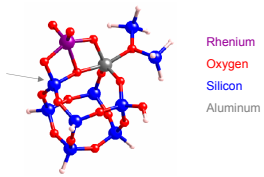
## Rhenium EXAFS of Catalytic Materials

Low quality fits result from fitting the tetrahedral perrhenate and TMS perrhenate models to both the perrhenate-modified silica-alumina and alumina samples.

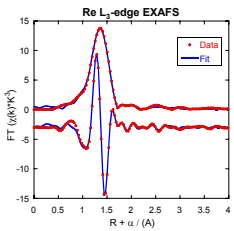
A computational model for perrhenate-modified silica-alumina was constructed using a silsesquioxane cube with an Al substituted into a silica site to represent the dehydrated silica-alumina surface.

After optimization through DFT calculations, the model includes interactions between rhenium and an oxygen from the support, as well as between two of the perrehante oxygens and either an aluminum or a silicon from the support. The model for **perrhenate-modified silica-alumina** is shown.

For the **perrhenate-modified alumina** model, the silicon atom connected to the perrhenate is replaced with an aluminum atom




Perrhenate-Modified Silica-Alumina

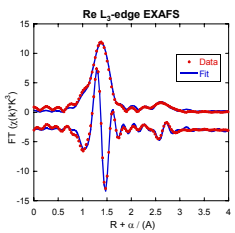



Perrhenate supported on Silica-Alumina (0.5 wt% Re)

| path | N | DFT-Calcualted Distance (Å) | EXAFS Fit R (Å) | EXAFS Fit $\sigma^2$ (Å$^2$) |
|---|---|---|---|---|
| Re=O | 2 | 1.680 | 1.68 | 0.0005 |
| Re–O | 2 | 1.799, 1.920 | 1.76 | 0.0006 |
| Re–O (support) | 1 | 2.078 | 2.14 | 0.0056 |
| Re–Si | 1 | 2.798 | 2.75 | 0.0157 |
| Re–Al | 1 | 3.053 | 3.06 | 0.0087 |

$E_0$ = 0.15 eV, $S_0^2$ = 0.908

Perrhenate-Modified Alumina

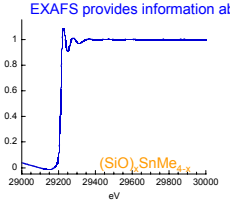


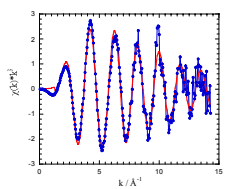

Perrhenate supported on Alumina (8 wt% Re)

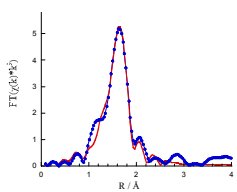
| path | N | R (Å) | $\sigma^2$ (Å$^2$) |
|---|---|---|---|
| Re=O | 2 | 1.69 | 0.0044 |
| Re–O | 2 | 1.74 | 0.0014 |
| Re–O (support) | 1 | 2.06 | 0.0079 |
| Re–Al | 2 | 3.04 | 0.0064 |

$E_0$ = -0.06 eV, $S_0^2$ = 0.88

EXAFS provides information about the tin's coordination environment



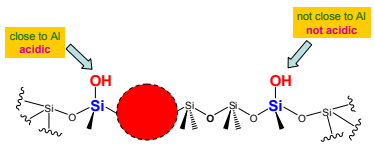



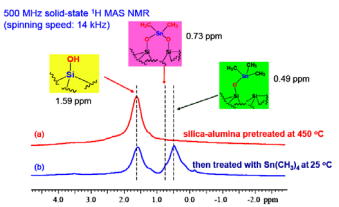

| path | CN | R (Å) | $\sigma^2$ |
|---|---|---|---|
| Sn-O | 2.51 | 2.06 | 0.037 |
| Sn-C | 1.49 | 2.13 | 0.004 |

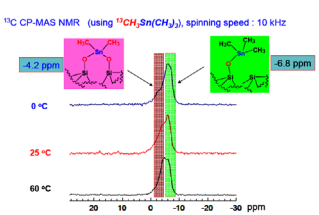
$S_0^2$ : 0.90, $\Delta E_0$ (eV) : 6.1

## Spectroscopic investigation of methyltin sites grafted onto silica-alumina

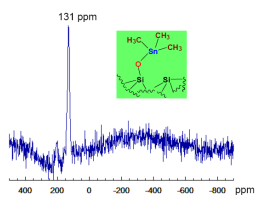
- Silica-alumina (13 wt% $Al_2O_3$) was calcined at 450 °C for 12 hr
  -- eliminates adsorbed water, and all hydrogen-bonding
- There are (at least) two types of hydroxyl groups remaining on dehydrated silica-alumina:
  -- acidic hydroxyl groups close to Al
  -- non-acidic silanols, not close to aluminum



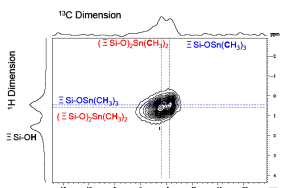




solid-state $^{119}$Sn MAS NMR




Two-dimensional $^1$H-$^{13}$C Heteronuclear Correlation (HETCOR) MAS NMR spectrum confirms two major Sn sites on silica-alumina support




**Conclusions**

**Ammonium perrehnate and TMS perrhenate are poor models for perrhenate-modified silica-alumina and alumina.**

**The proposed model, which includes interactions between the perrhenate and Lewis-acidic aluminum sites in the support, fits well to the silica-alumina and alumina samples. These perrhenate-support interactions are believed to be necessary for catalytic activity.**

**The 1H-13C HETCOR spectrum confirms that ≡SiOSnMe3 and (≡SiO)2SnMe2 sites have different chemical shifts.**
**The ratio of the two tin sites can be altered by changing the reaction temperature.**
**The 119Sn solid-state NMR spectrum provides clear evidence for a four-coordinate methyltin site on silica-alumina.**
**EXAFS provides information about the average number of Sn-C and Sn-O bonds in the grafted sites.**

**Funding**

**DOE**