

# Fundamentals of Catalysis -Characterization of working catalysts (Understanding the Functioning of Supported Metal Oxide Catalysts using a combination of Ethanol Oxidation and X-ray Absorption Spectroscopy)

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## Introduction

Supported mixed transition metal oxide catalysts have been shown to be extremely promising as tunable catalysts for selective hydrocarbon oxidation reactions<sup>1</sup>. The acidic and redox properties of these catalysts can be probed using a reaction such as ethanol oxidation<sup>2</sup>. However, the catalytic properties that determine their turnover frequency and product selectivity are still not well understood.

In this work, ethanol oxidation is used as a probe reaction and combined with in-situ X-ray Absorption Spectroscopy (XAS) to gain insight into effect of domain size, composition and dispersion on the functioning of Alumina –supported Molybdenum Oxide (MoOx), Tungsten oxide (WOx) and Vanadium Oxide (VOx) catalysts.

## Materials and Methods

All catalysts were prepared using incipient wetness impregnation of gamma-alumina using aqueous solutions of appropriate precursors (ammonium heptamolybdate, ammonium vanadium oxide and ammonium metatungstate).

Ethanol oxidation reactions were performed over a bed of catalyst placed on a quartz frit in a quartz U-tube reactor at 180 °C. Product analysis was done using an Agilent 6890 Gas Chromatograph and a Hiden HPR20 mass spectrometer.

X-ray absorption studies were carried out at the Advance Photon Source, Argonne National Labs, IL. Spectra were collected at the Mo K-edge (19.9995 keV) and W-L III edge (10.2068 keV).

## Results and Discussion

The major highlights of this work are summarized below.

- It is shown that XAS can be used to measure oxide domain size on supported metal oxide catalysts. The XANES white-line at the W-LIII absorption edge (Figure 1) and at the Mo L absorption edge are dependent on the average coordination of the metal species in the oxide catalysts and hence correlate to the domain size.

- A mechanism is presented with supporting evidence for the formation of Acetaldehyde and Diethyl Ether from Ethanol on metal oxide catalysts. The Acetaldehyde mechanism involves a Mars-van Krevelen oxidation mechanism with catalyst reoxidation using oxygen from the gas-phase. The ether mechanism involves the interaction of multiple ethoxy to form the The mechanism is used to gain insight into properties of the catalyst that affect its performance.

- Based on the mechanism of acetaldehyde formation, a novel anaerobic titration method for counting *only active redox sites* is demonstrated<sup>3</sup>. This method is used to quantify active redox site densities and redox turnover frequencies on metal oxide catalysts with varying composition and domain size. It is found that the intrinsic Acetaldehyde production rate is independent of both the nature of the metal oxide and the metal oxide surface density<sup>3</sup> (Figure 2).

- XAS studies were used to study the structure of catalysts during reaction and anaerobic titration. XANES spectra indicate small reduction of the catalyst during reaction and further reduction during anaerobic titrations with ethanol. Variations in the metal oxidation state with time during titration are found to mirror the redox ability of the catalyst. Additionally, difference spectra calculated between reaction and titration conditions strongly suggest that bridging O atoms (M-O-M) are used during the oxidation of ethanol to acetaldehyde.

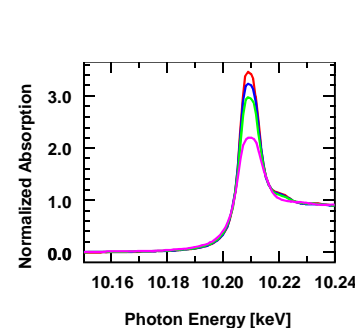


Figure 1: W L<sub>III</sub> XANES from 10.15 – 10.24 keV for W on Alumina Catalysts. **Red:** 2 W/nm<sup>2</sup> **Blue:** 4 W/nm<sup>2</sup> **Green:** 6 W/nm<sup>2</sup> **Pink:** WO<sub>3</sub>

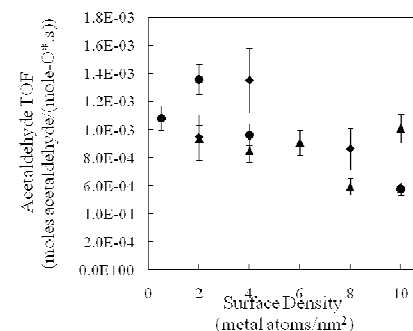


Figure 2: Number of active redox sites at 453 K as a function of surface density for MoO<sub>x</sub>-Al<sub>2</sub>O<sub>3</sub> (●), WO<sub>x</sub>-Al<sub>2</sub>O<sub>3</sub> (◆) and VO<sub>x</sub>-Al<sub>2</sub>O<sub>3</sub> (▲).

## Significance

This work demonstrates an accurate and simple technique to measure active site density on metal oxide catalysts, a problem that has existed in this area for years, and that neither metal oxide surface density nor metal identity affect intrinsic acetaldehyde formation rates. We show also for the first time how the white line at the L absorption edge is a good indicator of domain size.

## References

1. Fierro, J. G. L. *Metal oxides: Chemistry and Applications*; CRC Taylor & Francis: Boca Raton, FL.
2. Burckham, L. J.; Briand, L. E.; Wachs, I. E. *Langmuir* **2001**, *17*, 6164.
3. Nair, H. and Baertsch C.D. *Journal of Catalysis* **2008**, *258*, 1-4.