

# EXAFS and *in Situ* XANES Studies of V/MgO Nanocrystals

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## Introduction

Vanadium-containing metal oxide catalysts are among the most active and selective oxidation catalysts for converting light hydrocarbons to more valuable products such as alkenes, anhydrides, and aldehydes. However, with the exception of vanadyl pyrophosphate, none of these catalysts have proven to be industrially viable. The limitation has been to develop a catalyst that is both active for oxidation and selective to the desired product. Development of active and selective oxidation catalysts could provide significant energy savings by replacing the energy-intensive processes currently used to upgrade light hydrocarbons.

Vanadium supported on magnesium oxide is one of the most active and selective catalysts for oxidative dehydrogenation of light alkanes. The interaction of highly acidic vanadium oxide with basic magnesium oxide leads to a strong interaction and the formation of magnesium-vanadium phases, such as magnesium ortho-vanadate [ $\text{Mg}(\text{VO}_4)_2$ ] and magnesium pyrovanadate [ $\text{Mg}(\text{V}_2\text{O}_7)$ ]. There has been much discussion in the literature on which phases are more selective for oxidative dehydrogenation [1, 2]. Kung and coworkers suggested that the ortho-vanadate phase is more selective for butane oxidative dehydrogenation, since the isolated nature of the  $\text{VO}_4$  groups in this structure means that adsorbed butane can only interact with one  $\text{VO}_4$ , preventing overoxidation [1]. Others have proposed that there can be a synergistic interaction between the vanadium phase or phases and MgO that leads to better performance than that achieved with pure V/MgO phases [2].

Use of nanoscale magnesium oxide offers significant potential for preparing more active and selective V/MgO catalysts. Nanoscale magnesium oxide can be prepared with a crystal size that is half that of conventional MgO and a surface area that is ten times larger. The smaller crystal size leads to different chemical properties, such as increased affinity for adsorbing acidic compounds, increased basicity, and more dispersed OH groups [3]. These properties could lead to different V/MgO phases; for example, OH groups isolated on the many corners and edges of the MgO nanocrystals may result in the production of isolated  $\text{VO}_4$  groups when vanadium is supported on the nanocrystals. In addition, the increased basicity of the MgO nanocrystals relative to conventional MgO could result in different catalytic behavior for oxidative dehydrogenation. Hohn has found that V/MgO

nanocrystals give higher selectivity to butene in the oxidative dehydrogenation of butane and suggested that the different chemical nature of MgO nanocrystals is responsible for the difference in catalytic behavior [4].

An important consideration in understanding the catalytic behavior of V/MgO nanocrystals is to characterize the structure of vanadium. Conventional techniques, such as x-ray diffraction and Raman spectroscopy, can provide valuable information on the identity of V/MgO phases [5, 6]. However, x-ray absorption spectroscopy can also play a key role in characterizing V/MgO nanocrystals, providing direct information on the bonding geometry around vanadium. In addition, *in situ* measurements, in which V/MgO nanocrystals are successively oxidized and reduced, can provide information on redox properties of the catalysts. This report details experiments conducted at the BESSRC beamline at the APS to characterize V/MgO nanocrystals by using extended x-ray absorption fine structure (EXAFS) and *in situ* x-ray absorption near-edge structure (XANES).

## Methods and Materials

MgO nanocrystals (AP MgO) were synthesized through a modified aerogel method. Briefly, Mg ribbon was reacted with methanol to form the methoxide. Hydrolysis was performed in toluene to yield a hydroxide gel. This gel was dehydrated through hypercritical drying in an autoclave to form a fine, white, magnesium hydroxide powder. This powder was calcined at 500°C under vacuum to yield nanocrystalline MgO. MgO microcrystals (CP MgO) were prepared from commercially purchased MgO (Aldrich, 99+% purity) by boiling it in distilled water, filtering it, and drying it at 500°C under vacuum.

Supported vanadium nanocrystals (AP V/MgO) and microcrystals (CP V/MgO) were prepared by using the same procedure, with the only difference being the MgO starting material. Freshly obtained MgO was impregnated with a solution of  $\text{V}(\text{acac})_3$  in tetrahydrofuran (THF) overnight at ambient temperature. After filtration, the slurry was washed with dry THF, heated to 500°C under a flow of air, and calcined overnight.

X-ray absorption spectra were collected at BESSRC beamline station 12-BM-B at the APS. The monochromator, equipped with Si(111) crystals, was calibrated by setting the inflection point of the first derivative from the V K edge to 5465 eV. Fluorescence

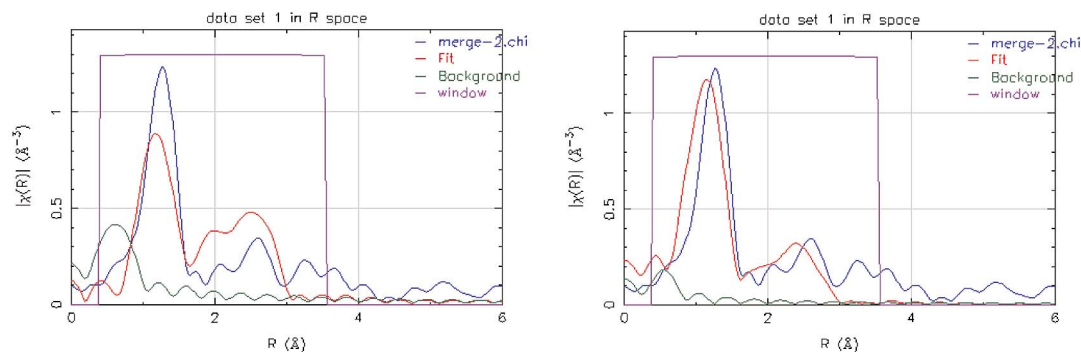


FIG. 1. FEFF fit of experimental EXAFS data for 3-wt% V/MgO nanocrystals. Chi is plotted as a function of  $R$  when the theoretical scattering function is used for ortho-vanadate (left) and pyro-vanadate (right). The blue curve is the experimental data, while the red curve is the FEFF fit.

data were collected by using a Lytle detector. Energy resolution was approximately 1 eV. All reported spectra represent the average of three trials. XANES spectra were analyzed by first fitting the pre-edge baseline with a least-squares fit and then subtracting the baseline from the spectrum. The near-edge data were normalized by dividing by the height of the linear portion of the absorption spectrum  $\sim 100$  eV above the absorption edge.

EXAFS data were analyzed by the IFEFFIT (version 1.2.1) software package. The known crystal structures of magnesium ortho-vanadate and magnesium pyro-vanadate were input into ATOMS to generate the theoretical photoelectron scattering paths. The experimental data were normalized and converted to chi versus  $k$  data via ATHENA and then fit with the theoretical scattering paths via ARTEMIS. It was assumed that the crystal expanded and contracted isotropically with temperature. Different expansion coefficients were used for different atom-atom expansions and were varied to fit the data. Only single scattering paths with large amplitudes were used in the fit.

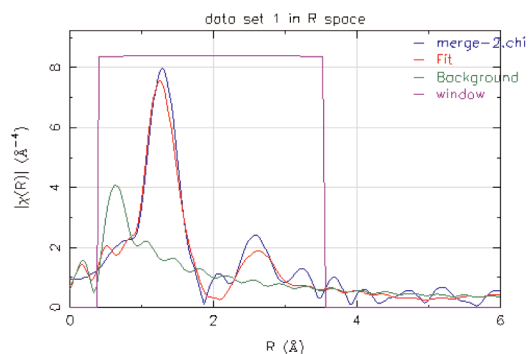


FIG. 2. FEFF fit of experimental EXAFS data for 3-wt% V/MgO nanocrystals. The blue curve is the experimental data, while the red curve is the FEFF fit.

## Results and Discussion

### EXAFS Studies of V/MgO Nanocrystals

EXAFS studies were conducted in an attempt to determine the relative concentrations of the ortho- and pyro-vanadate phases. EXAFS data for 3-wt% V/MgO nanocrystals were fit first with theoretical FEFF predictions for pure ortho- and pyro-vanadate phases. These fits take the single paths that have a half path length smaller than 3.5 Å and are shown in Fig. 1. Next, seven single paths for ortho-vanadate and eight paths for pyro-vanadate were used to fit the experimental EXAFS data. A weighting factor,  $x_1$ , representing the fraction of vanadium present as ortho-vanadate, was varied to fit the data. These results are shown in Fig. 2. The fit is better, but it is hoped that further analysis of pure vanadium phases will lead to a better fit of the data and better understanding of the vanadium phases present in V/MgO nanocrystals.

### In Situ XANES Studies

The XANES spectra for 5-wt% AP and CP V/MgO were measured during oxidation and reduction cycles at 500°C. Oxidation was carried out in a 10% oxygen/helium mixture, while reduction was carried out in 10% H<sub>2</sub> in helium. Scans were taken roughly every 4 minutes to give trends over time. The only noticeable difference in the XANES spectra was in the intensity of the pre-edge peak intensity. This intensity increased with oxidation and decreased with reduction. The intensity of this peak has been related to the coordination geometry of vanadium: the more intense the peak, the less the symmetry around vanadium [7]. The results indicate that the coordination becomes more symmetric as oxygen is added to the crystal lattice and less symmetric as it is removed.

Figure 3 shows the variation of the pre-edge intensity for both CP and AP V/MgO during oxidation. The same

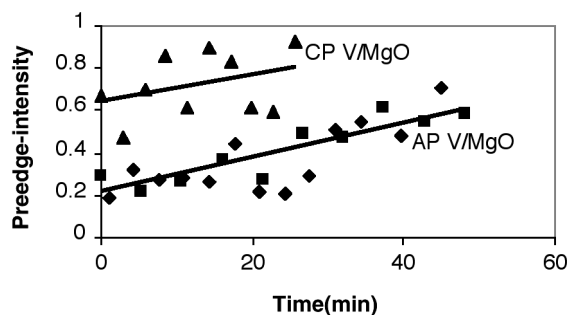


FIG. 3. Variation of pre-edge intensity for 5-wt% AP V/MgO and CP V/MgO during oxidation at 500°C.

AP V/MgO catalyst was oxidized twice, and the results for the two runs were similar. Interestingly, the initial intensity of the CP V/MgO was higher than that of the AP V/MgO, which may reflect differences in oxidation state before the experiment was run. While the scatter for CP V/MgO is large, it appears that the oxidation of AP V/MgO occurs more rapidly. Further studies are planned to further elucidate the differences in redox properties between the two samples.

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