

ED-XAS Data Reveal *In-situ* Time-Resolved Adsorbate Coverage on Supported Molybdenum Oxide Catalysts during Propane Dehydrogenation

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Abstract. Energy-Dispersive X-ray Absorption Spectroscopy (ED-XAS) data combined with UV/Vis, Raman, and mass spectrometry data on alumina- and silica-supported molybdenum oxide catalysts under propane dehydrogenation conditions have been previously reported. A novel $\Delta\mu$ adsorbate isolation technique was applied here to the time-resolved (0.1 min) Mo K-edge ED-XAS data by taking the difference of absorption, μ , at $t > 1$ against the initial time, $t = 0$. Further, full multiple scattering calculations using the FEFF 8.0 code are performed to interpret the $\Delta\mu$ signatures. The resulting difference spectra and interpretation provide real time propane coverage and O depletion at the MoO_n surface. The propane coverage is seen to correlate with the propene and/or coke production, with the maximum coke formation occurring when the propane coverage is the largest. Combined, these data give unprecedented insight into the complicated dynamics for propane dehydrogenation.

Keywords: ED-XAS, catalysis, dehydrogenation, supported metal oxide catalysts, propane, *in situ* spectroscopy

PACS: 78.70Dm, 82.75Qt, 82.40Np, 82.65+r

INTRODUCTION

Recently Beale et al. [1] reported combined *in situ*, time-resolved, UV/Vis, Raman, and ED-XAS data along with MS (mass spectrometry) data on silica- and alumina-supported molybdenum oxide catalysts under propane dehydrogenation conditions. These data couple three spectroscopic techniques in one reactor, focused on the same spot of a metal oxide catalyst, under true reaction conditions with the capability for sub-second time resolution. The UV/Vis and Raman data provide information on the formation of coke on the catalysts, the MS on the products and reactants (propene and propane; hereafter referred to as A and H_2A) in the gas phase, and the EDXAS data on the change of oxidation state of the Mo for the dehydrogenation of propane (5% in He) over supported 13 wt% $\text{MoO}_n/\text{Al}_2\text{O}_3$ and $\text{MoO}_n/\text{SiO}_2$ catalyst at 550°C.

Although these data are quite remarkable even with straight forward interpretation, much more information can be obtained from the ED-XAS data using the novel ΔXANES technique [2], which isolates the relatively small effect in the XAS absorption (A_d) coefficient, μ , due to adsorption on a metal (M) atom by taking the difference, $\Delta\mu = \mu(A_d/M) - \mu(M)$. This

difference is then compared to FEFF8 [3] calculated $\Delta\mu$ signatures, which often reveal strong adsorbate binding site dependence. The ΔXANES technique has previously provided both binding site and coverage information for H (H_{opd} and H_{upd} in ontop and fcc sites, respectively), O, OH, and CO on supported Pt/C in electrochemical and operating fuel cells [4].

All of the previous applications of the ΔXANES technique varied the adsorbate coverage by either varying the potential or current in an electrochemical or fuel cell, or pumping off the adsorbate in vacuum in the gas phase. The current data allow for the ΔXANES technique to be applied using $\Delta\mu = \mu(t) - \mu(t_0)$, where t_0 is some initial time when presumably the adsorbate coverage is small. To the best of our knowledge, this is the first report of time resolved ΔXANES data for adsorbates on a metal oxide in operating catalysts.

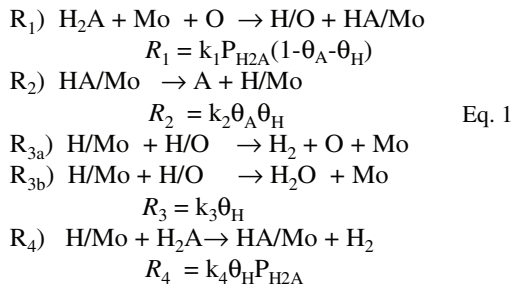
EDXAS DATA ANALYSIS

Figures 1 and 2 show the $\Delta\mu$ difference spectra for the indicated time increments ($\Delta t = 0.1$ min). We have determined that actually two spectral lineshapes are present, the one increasing with time corresponding to

O removal from the catalyst (catalyst reduction), and the other (reflecting HA/Mo) decreasing with time, because the catalyst is being poisoned with coke formation as indicated by the UV/Vis and Raman data, as shown in Figs. 3 and 4. FEFF8 calculations on the indicated clusters shown in Figs. 1 and 2 confirm that these signatures are representative of O depletion (Mo reduction) and propane adsorbed on MoO_n in a vertical type configuration as pictured. Fortunately, these two spectral line shapes have large magnitudes at different energies enabling the amount of each contribution to be observed as a function of time. The rectangle in each case (that at around 0 eV for the O depletion and that around 25 eV for the propane coverage) are utilized to record the relative $\Delta\mu$ magnitudes with time, which are plotted in Figs. 3 and 4 for the MoO_n/Al₂O₃ and MoO_n/SiO₂ catalysts respectively. The $\Delta\mu$ amplitudes with time have been smoothed with a 1 min. window to remove random and systematic noise. Negative $\Delta\mu$ amplitudes in Figs. 3 and 4 occur when the indicated $\Delta\mu$ is very small and the $\Delta\mu$ from the opposing component overlaps with a larger negative amplitude (e.g. the $\Delta\mu$ indicating O depletion for SiO₂ goes negative at $t < 2$ min. because the $\Delta\mu$ for propane is contributing a negative amplitude at 0 eV). Nevertheless, the $\Delta\mu$ amplitudes do qualitatively reflect the relative coverage of each component and can be compared with the UV/Vis and MS data as shown in Figs. 3 and 4. Note that the relative propane coverage with time roughly correlates with the product yield (propene and/or coke formation) and further the O depletion rate (Mo reduction) is greatest near or following the greatest rate of coke formation.

DISCUSSION

The mechanism for propane dehydrogenation has been indicated from the DFT calculations of Lillehaug et al. [5], which suggest a dual path mechanism as shown:



$$\begin{aligned}
 d\theta_{\text{A}}/dt &= R_1 - R_2 + R_4 \\
 d\theta_{\text{H}}/dt &= R_2 - R_3 - R_4
 \end{aligned}
 \tag{Eq. 2}$$

Here R_1 represents the initial adsorption of propane on Mo via a σ -bond metathesis, and R_2 a β -H transfer to the Mo atom with release of propene. R_3 represents catalyst regeneration, which either results in removal of H₂O (3b giving catalysts reduction) or just removal of H₂ (3a). R_4 represents an alternate reaction route with H₂A adsorption directly on the hydride complex yielding H₂ directly. Along with each reaction in Eq. 1, appropriate expressions for the rates are given.

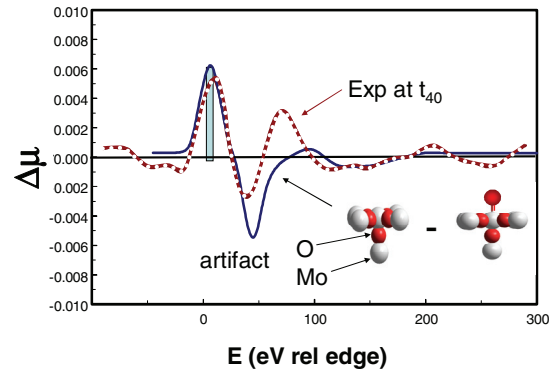


FIGURE 1. $\Delta\mu = \mu(t_{40}) - \mu(t_0)$ and comparison with FEFF8 results for the indicated clusters. FEFF8 calculations show that the spectral shape is representative of O depletion as pictured. The rectangle around 0 eV indicates the energy region utilized to determine the $\Delta\mu$ magnitude in Figs. 3 and 4. The large deviation above 50 eV results from a visible artifact in the data.

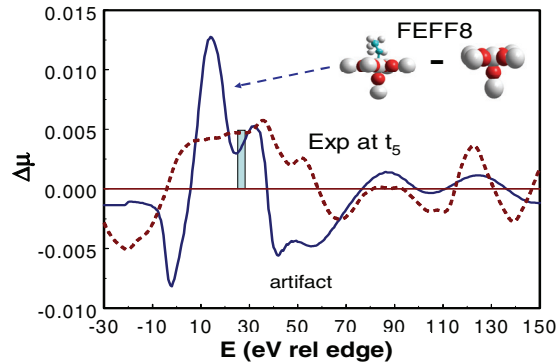


FIGURE 2. $\Delta\mu = \mu(t_5) - \mu(t_0)$ and comparison with FEFF8 results for the indicated clusters. FEFF8 calculations show that the spectral shape is representative of propane/Mo as pictured. The rectangle around 25 eV indicates the energy region utilized to determine the $\Delta\mu$ magnitude in Figs. 3 and 4. The large deviation around 50 eV results from a visible artifact in the data.

Eqs. 1 and 2 can be solved numerically with specified rate constants k_1 through k_4 ; these results will be reported elsewhere. The dual path mechanism of Lillehaug et al. suggests that either the 123 cycle or the 24 cycle could dominate in the dehydrogenation.

During the 123 cycle, Lillehaug et al. [5] indicate R_2 is the rate determining step, and R_2 is linearly dependent on the propane coverage, θ_A . During the 24 cycle, R_4 is the rate determining step, which depends instead on θ_H . The correlation of the propane coverage with the product yield (propene and/or coke formation) therefore suggests strongly that the 123 cycle dominates.

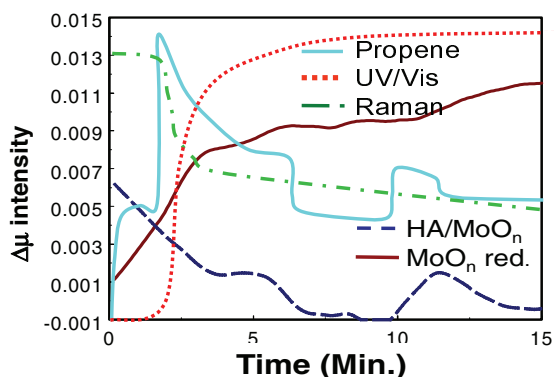


FIGURE 3. Plot of ED-XAS amplitude, $\Delta\mu = \mu(t) - \mu(t_0)$, and correlation with MS (propene), UV/Vis and Raman amplitudes (coke formation) (the latter 3 amplitudes on an arbitrary scale) for propane dehydrogenation on $\text{MoO}_n/\text{Al}_2\text{O}_3$.

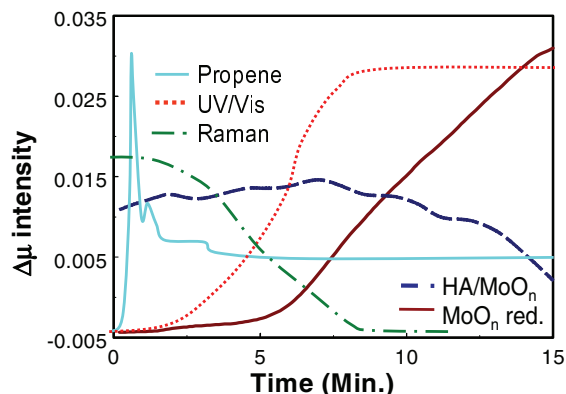


FIGURE 4. Same as Figure 3 but for $\text{MoO}_n/\text{SiO}_2$. Note the larger $\Delta\mu$ scale here compared with that in Fig. 3, showing larger O depletion in SiO_2 .

CONCLUSIONS

The following conclusions can be drawn from this work:

a) The ED-XAS data with the novel ΔXANES technique providing HA/Mo coverage information, along with the UV/Vis and Raman data providing coke formation and the MS providing propene formation, give unprecedented details into the complicated dynamics in a catalytic reactor.

b) The propene formation indicated in the MS data correlates in part with the HA/Mo coverage (Figs. 3 and 4), and strongly suggests that the Lillehaug et al. 123 kinetic cycle dominates.

c) The coke product appears predominately near the maximum coverage of propane (see Figs. 3 and 4) suggesting that coke appears when the propene partial pressure exceeds a certain threshold. Coke is not directly visible in the ED-XAS because it is not adsorbed in registry on the surface. Significant reduction of the supported molybdenum oxide occurs during or shortly after coke formation.

d) Mo K-edge EXAFS analysis (not shown) shows that the Mo atoms are surrounded by 6 O atoms on average, and that the MoO_n clusters are small (Mo-Mo coordination $\sim 1.0 \pm 0.2$). This Mo-Mo coordination number is consistent with that found in a more extensive EXAFS study by Keller et al. [6] for VO_n at similar loadings on Al_2O_3 , when both octahedral monomers and polymeric chains were indicated. The small Mo-O bond length found here in the EXAFS suggests that primarily Mo^{6+} is present, consistent with the presence of monomers and polymeric chains.

e) The rate of reduction of the MoO_n is 3-5 times greater in SiO_2 than in Al_2O_3 (Figs. 3 and 4). This can be attributed to the more acidic character of the SiO_2 support, which may increase the OH bond strength in $\text{HO/MoO}_n/\text{SiO}_2$ and thereby increase the rate of the R_{3b} step in eq. 1. However, the R_{3b} rate may also be larger in SiO_2 due a greater fraction of MnO_6 monomers, which may release O atoms easier. This latter point will be discussed elsewhere.

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