In situ UV-visible assessment of extent of reduction during oxidation reactions on oxide catalysts

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The extent of reduction of active centers during oxidative alkane dehydrogenation on VO_x/Al_2O_3 was measured from pre-edge UV-visible spectral features and found to increase with increasing VO_x domain size and propane/O_2 ratio.

Oxidative dehydrogenation (ODH) of alkanes on VO_x and MoO_x domains involves Mars–van Krevelen redox cycles using lattice oxygen and reduced V^{3+} or V^{4+} and Mo^{4+} or Mo^{5+} as reactive intermediates.[1,2] Mechanistic studies suggest that reduced centers are minority species during steady-state catalysis,[1,2] a conclusion confirmed specifically for butane oxidation by *in situ* X-ray absorption spectroscopy.[3] Our efforts to detect reduced centers during propane ODH on supported VO_x and MoO_x catalysts by near-edge X-ray absorption spectra did not succeed because of the overlapping nature of near-edge features for various oxidation states of V and Mo absorbers and the low concentration of reduced centers. Similar difficulties arise for near-edge absorption features in the UV-visible spectrum of oxides. Here, we report the use of pre-edge spectral features in UV-visible spectra. These d–d transitions in reduced color centers become possible during reduction as electrons are placed within d-orbitals that are empty in oxides with cations in their highest valence state. These features appear in a spectral region devoid of strong absorption and provide more accurate measurements than previously used near-edge features in UV-visible and X-ray spectra.

Diffuse reflectance UV-visible spectroscopy probes the electronic structure of oxide domains commonly used as alkane ODH catalysts.[1,2,4,5] Edge energies depend sensitively on domain size; they reflect electron transfer in frontier orbitals that delocalize electron density during kinetically-relevant C–H bond activation steps.[1,2] Edge energies depend weakly on oxidation state, unless reduction leads to significant changes in coordination symmetry;[4,6] thus, edge energies are unreliable probes of reduced centers prevalent during steady-state oxidation catalysis (*e.g.* vacancies and OH groups). Yet, previous studies reported extents of reduction obtained from near-edge spectral changes using linear interpolation between spectra for stoichiometric oxides and structurally stable suboxides by reduction in H_2.[6–16]

Here, pre-edge absorption features in the UV-visible spectrum of VO_x oxides are used to measure extents of reduction using calibration curves obtained from independent measurements of stoichiometric oxygen deficiencies introduced by H_2 treatment at low temperatures (603 K). Two VO_x/Al_2O_3 samples[1] with 2.3 and 8.0 VO_x nm^{-2} surface densities were used. The intensity of pre-edge features (1.5–1.9 eV) was measured using a Cary 4 Varian spectrophotometer with a Harrick Scientific diffuse reflectance attachment (DRP-XXX), and a reaction chamber (DRA-2CR) modified to improve temperature and flow uniformity. Concurrent measurements of oxygen deficiency by on-line mass spectrometric analysis of effluent streams during H_2 reduction and re-oxidation in O_2/He

led to the relation between absorption intensity and number of electrons transferred to V centers depicted in Fig. 1. These reduced centers reflect vacancies, hydroxyls, or alkoxide species present as reactive intermediates during steady-state ODH reactions[2] and predominantly oxygen vacancies during H_2 reduction. In both cases, absorption intensities reflect the number of electrons present in metal d-orbitals.[9] The inset in Fig. 1 shows that these d–d transitions appear in a spectral region devoid of background absorption in fresh oxide catalysts in their highest oxidation state. Absorption at the edge arises from O-to-V ligand-to-metal charge transitions, which are less sensitive to d-orbital occupation than d–d transitions and appear in a much denser spectral region. The inset in Fig. 1 shows the relative magnitude of spectral changes in the pre-edge and edge region during propane ODH at 603 K on 10 wt% V_2O_5/Al_2O_3.

The calibration curve (Fig. 1) was obtained from the amount of O_2 required to restore the initial spectra after reduction in H_2 at 603 K for time increments of 300 s. This curve was used to measure the extent of reduction during alkane ODH from similar pre-edge intensity measurements at various reactant compositions. The calibration and *in situ* measurements were made in the same range of pre-edge intensities; the small extents of reduction measured during catalysis are consistent with those expected from reported ODH kinetics and mechanism in which surface oxygen appears as the most abundant reactive intermediate.[2] We note that the local nature and small number of reduced centers in these oxide domains makes absorption cross-
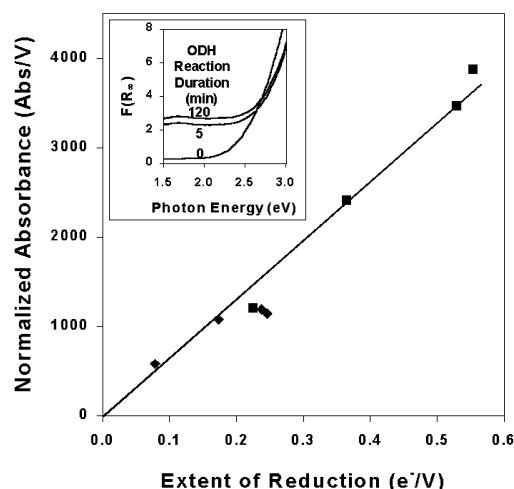

Fig. 1 UV-visible reduction response calibration curve for VO_x/Al_2O_3 catalysts [20 kPa H_2, balance He, 603 K reduction followed by 5 kPa O_2, balance He, 298–773 K reoxidation]; ◆: 3.5 wt% V_2O_5/Al_2O_3, ■: 10 wt% V_2O_5/Al_2O_3. Inset: UV-visible spectra for 10 wt% V_2O_5/Al_2O_3 [603 K, 14 kPa C_3H_8, 1.7 kPa O_2, balance He].

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sections proportional to the number of electrons transferred and largely insensitive to the identity of the reduced species (*e.g.*, vacancies, OH, alkoxides).[2]

Spectra were referenced to MgO and converted to difference spectra by dividing by R_∞ for stoichiometric oxides (Eqn. (1)). Normalized reflectances were converted to absorbance using the Kubelka–Munk formalism (Eqn. (2)), where K and S are proportional to the absorption and scattering coefficients, respectively.[17,18]

$$R_\infty = \frac{R_{\text{sample}}}{R_{\text{reference}}} \quad (1) \qquad F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{S}{K} \quad (2)$$

This relation between measured reflectances and sample absorbance can lead to inaccurate extents of reduction from linear interpolations between stoichiometric V^{3+} sub-oxides, especially for minority reduced centers, because of the strong ligand-to-metal transitions and their weak dependence on d-electron densities. These factors lead to lower values of R_∞ to larger values of $F(R_\infty)$, and to much poorer signal to noise ratios than obtainable in the pre-edge region.

Transient experiments showed that 60–70% of reduced centers formed during contact with C_3H_8–O_2 were neither reversible during reaction nor catalytically relevant. These spectator reduced species appear to form *via* conversion of minority V_2O_5 clusters to stable suboxides, which reoxidize slowly by V_2O_5 nucleation at reaction conditions. These irreversible absorption changes include a fast initial transient upon contact with reactants (~ 60 s), which is not fully reversed even after 4 h in 4 kPa O_2 at 603 K. Reversible and catalytically-relevant changes in pre-edge intensity were measured during exposure to 0–16 kPa C_3H_8 or O_2 at constant O_2 or C_3H_8 pressure (4 kPa) for 300 s. This time interval was chosen because absorption transients were accurately described as a single first-order relaxation process. Absorbances for these catalytically-relevant reduced centers were converted to extents of reduction using the data in Fig. 1 and the results are shown in Fig. 2 and Table 1. We note that total pre-edge absorption changes give much higher extents of reduction because they include irreversible reduction processes unrelated to catalytic redox turnovers, *e.g.*, total absorption changes give 0.060 and 0.31 e⁻ V⁻¹ for the 2.3 and 8.0 V nm⁻² catalysts, respectively, at the conditions listed in Table 1.

The extent of reduction during steady-state propane ODH is much lower than for stoichiometric reduction of V^{5+} to V^{4+} or V^{3+}. These data confirm the conclusion from kinetic and isotopic studies[2] that lattice oxygen atoms are the most abundant reactive intermediates during propane ODH on VO_x domains, even at relatively high C_3H_8/O_2 reactant ratios. The extent of reduction was lower on the 2.3 V nm⁻² sample than on the 8.0 V nm⁻² sample, suggesting that the larger VO_x domains prevalent in the latter sample undergo faster redox cyles than isolated VO_x species,[1,2] consistent with the observed increase in ODH rates (per V or Mo) with increasing VO_x or MoO_x domain size[1,19] (Table 1). These higher rates parallel the measured higher extents of reduction because turnover rates are limited by reduction steps involving activation of methylene C–H bonds in propane using lattice oxygen atoms.[2] The extent of reduction increases with increasing C_3H_8 or decreasing O_2 pressure (Fig. 2), consistent with proposed ODH mechanistic steps. The data in Fig. 2 are in quantitative agreement with the expected dependence of reduced centers on C_3H_8:O_2 (dashed curves) when oxygen vacancies are the prevalent reduced centers.[2]

The extents of reduction reported here for catalytically relevant species on VO_x/Al_2O_3 are much lower than reported previously on VO_x/ZrO_2 for similar conditions and surface densities, but using total absorption edge intensity changes (*e.g.*, 0.10 e⁻ V⁻¹ on VO_x/Al_2O_3; 0.60 e⁻ V⁻¹ on VO_x/ZrO_2[6,9] 6:1 C_3H_8/O_2). Spectator reduced centers, perhaps in part on ZrO_2 supports,[9] may be responsible for these differences and also account for the higher CO_x selectivities on ZrO_2-supported samples.[1,6]
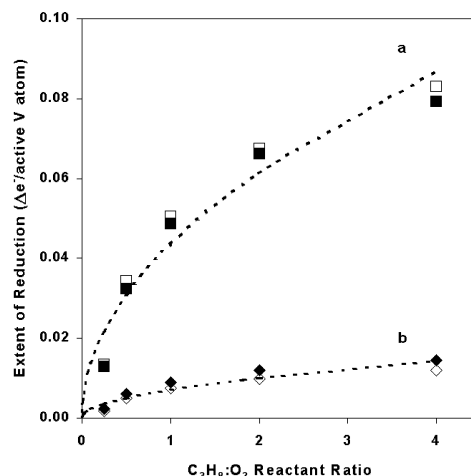

Fig. 2 Extent of reduction as a function of C_3H_8:O_2 reactant ratio, (a) 10 wt% (8.0 V nm⁻²), (b) 3.5 wt% (2.3 V nm⁻²) V_2O_5/Al_2O_3 [603 K, filled symbols: 1.0–16 kPa C_3H_8, 4.0 kPa O_2, open symbols: 1.0–16 kPa O_2, 4.0 kPa C_3H_8; dashed lines represent $(C_3H_8/O_2)^{0.5}$ dependence].

Table 1 Extent of vanadium reduction during propane ODH[a]

Catalyst (wt% V_2O_5 on Al_2O_3)	V surface density (V nm⁻²)	e⁻ transferred per active V	C_3H_6 Rate [*10⁻³ mol s⁻¹ (g-atom V)⁻¹]
3.5	2.3	0.020	0.33
10	8.0	0.12	1.0

[a] 603 K, 14 kPa C_3H_8, 1.7 kPa O_2, balance He.

We show here that the use of the pre-edge region in UV-visible spectra, the rigorous calibration of the intensity of these features, and the isolation of the dynamic processes relevant to catalysis from those of spectator species lead to accurate measurements of the number of reduced centers present at very low concentrations during alkane ODH catalysis.

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