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$_2$O$_3$ 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$_x$/MoO$_3$ domains involves Mars–van Krevelen redox cycles using lattice oxygen and reduced V$^{3+}$ or V$^{4+}$ and Mo$^{6+}$ or Mo$^{5+}$ as reactive intermediates. Mechanistic studies suggest that reduced centers are minority species during steady-state catalysis, and a conclusion confirmed specifically for butane oxidation by in situ X-ray absorption spectroscopy. Our efforts to detect reduced centers during propane ODH on supported VO$_x$/MoO$_3$ 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. Edge energies depend sensitively on domain size; they reflect electron transfer in frontier orbitals and provide more accurate measurements than previously used near-edge features in UV-visible and X-ray spectra.

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. We note that the local nature and small number of reduced centers in these oxide domains makes absorption cross-sections and reaction kinetics significantly different from those of perovskite VO$_2$.$x$. A feature in the spectrum at 603 K for a sample with 3.5 wt% V$_2$O$_5$/Al$_2$O$_3$ is observed in the region devoid of strong absorption and provides more accurate measurements than previously used near-edge features in UV-visible and X-ray spectra.
sections proportional to the number of electrons transferred and largely insensitive to the identity of the reduced species (e.g., vacancies, OH, alkoxydes).17,18 Spectra were referenced to MgO and converted to difference spectra by dividing by $R_n$ 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

$$R_n = \frac{R_{\text{sample}}}{R_{\text{reference}}}$$ (1)

$$F(R_n) = \frac{(1 - R_n)^2}{2K_n} - \frac{S}{K}$$ (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 electron densities. These factors lead to lower values of $R_n$ to larger values of $F(R_n)$, 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 $C_3H_8$ 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 $V_2O_6$ 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 studies2 that lattice oxygen atoms are the most abundant reactive intermediates during propane ODH on VO$_x$ domains, even at relatively high $C_3H_6O_2$ 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 cycles 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.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 $C_3H_6$ 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 $C_3H_6O_2$ (dashed curves) when oxygen vacancies are the prevalent reduced centers.2

The extent of reduction reported here for catalytically relevant species on VO$_x$/Al$_2$O$_3$ 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$_2$O$_3$; 0.60 e$^{-}$ V$^{-1}$ on VO$_x$/ZrO$_2$6,9 6:1 C$_3$H$_6$/O$_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 selectivities on ZrO$_2$-supported samples.1,6

### Notes and references


