

**Kinetic and Spectroscopic Evidence for Reaction Pathways and Intermediates  
for Olefin Epoxidation on Nb in \*BEA**

**Supporting Information**

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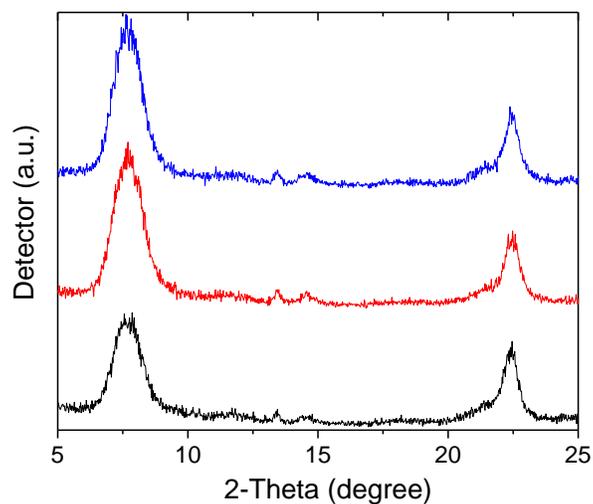
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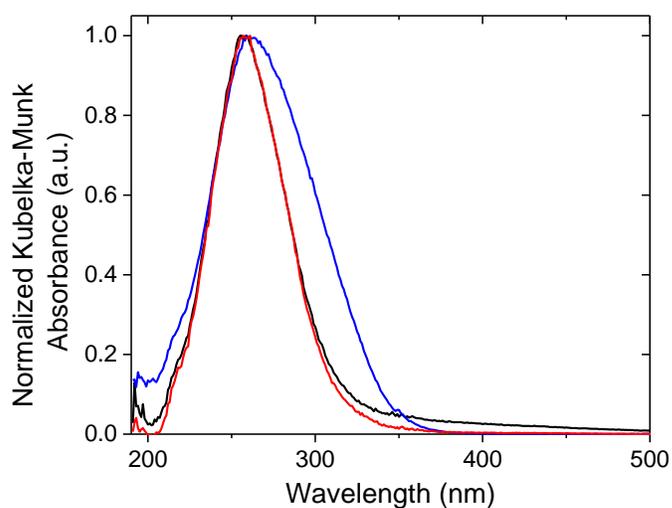
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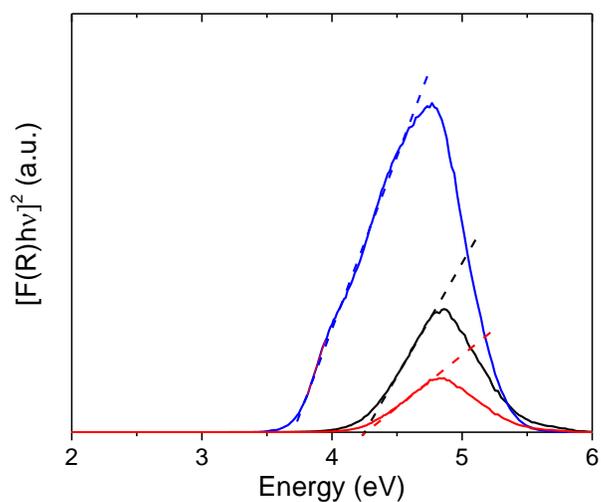
## S1. Catalyst Characterization



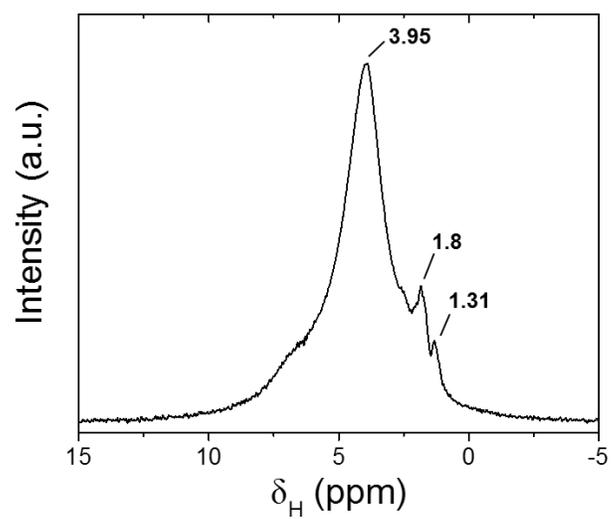
**Figure S1.** Powder X-ray diffractograms (p-XRD) for commercial Al-β (—, black), Si-β (—, red), and Nb<sub>1.5</sub>-β (—, blue). P-XRD spectra were recorded under an ambient atmosphere using Cu K-α radiation (0.15418 nm) with a step size of 0.02° at 1° min<sup>-1</sup>



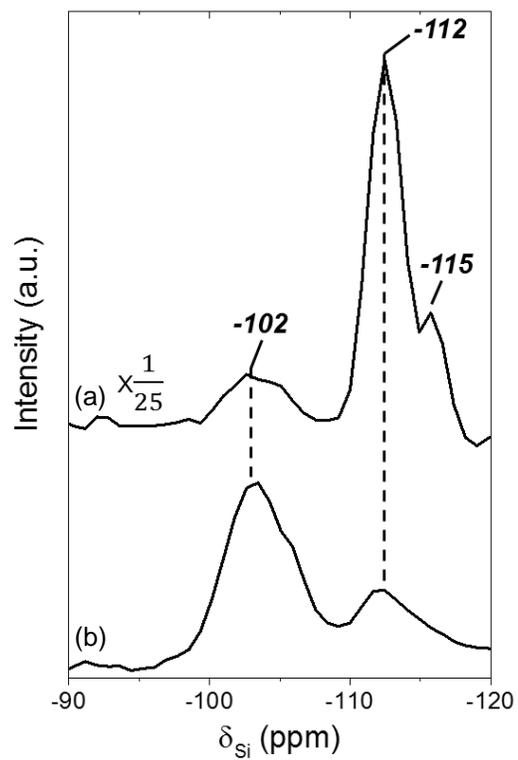
**Figure S2.** Diffuse reflectance UV-visible spectra for Nb<sub>0.7</sub>-β (—), Nb<sub>1.5</sub>-β (—), and 10 wt. % Nb-SiO<sub>2</sub> (—) normalized to the maximum feature. MgO was used as a reference to collect a total reflectance background spectrum. Nb<sub>0.15</sub>-β was omitted and did not have a band edge calculated because its low absorbance yielded a noisy signal.



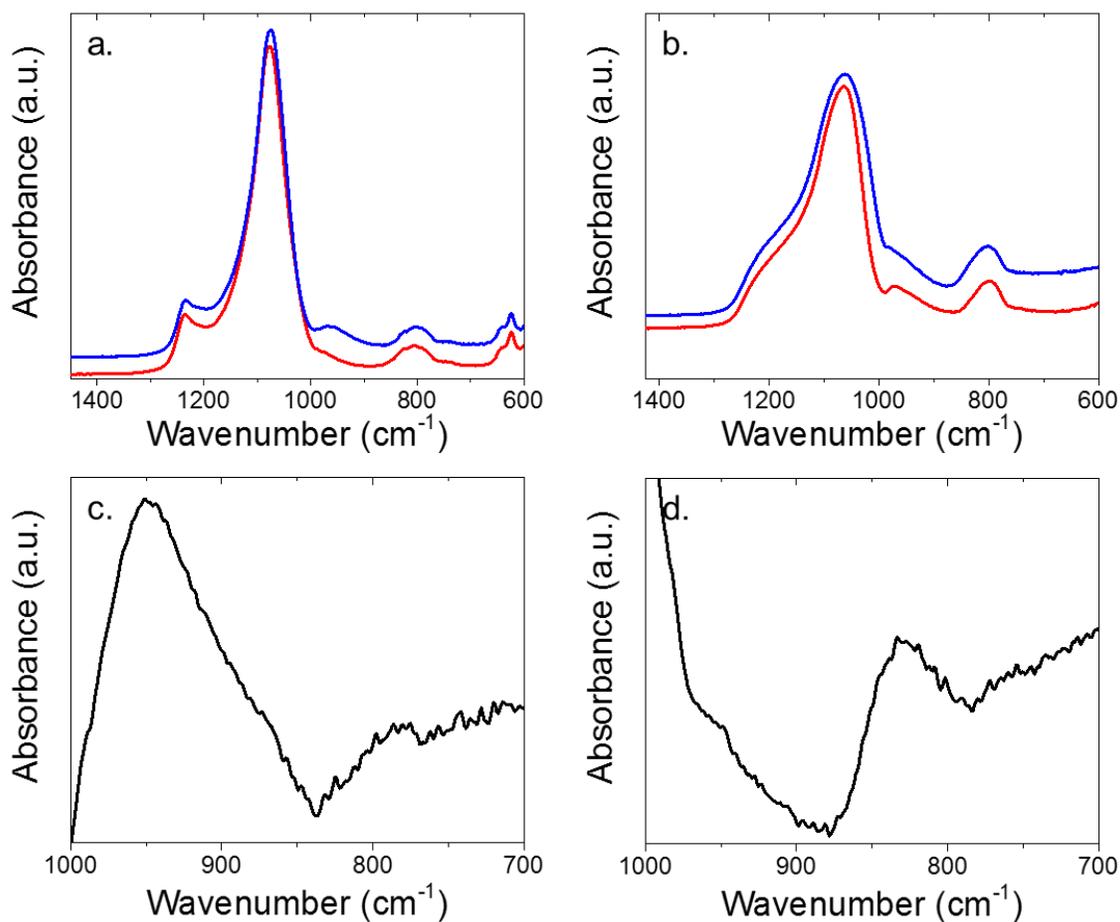
**Figure S3.** Tauc plots (where  $F(R)$  is the Kubelka-Munk absorbance function and  $h\nu$  is the energy of the photon) for  $Nb_{0.7-\beta}$  (—),  $Nb_{1.5-\beta}$  (—), and 10 wt % Nb-SiO<sub>2</sub> (—) using the DRUV-vis data from Figure S1.2. Dotted lines (with respective color) represents the fit to determine the band edge for each material.



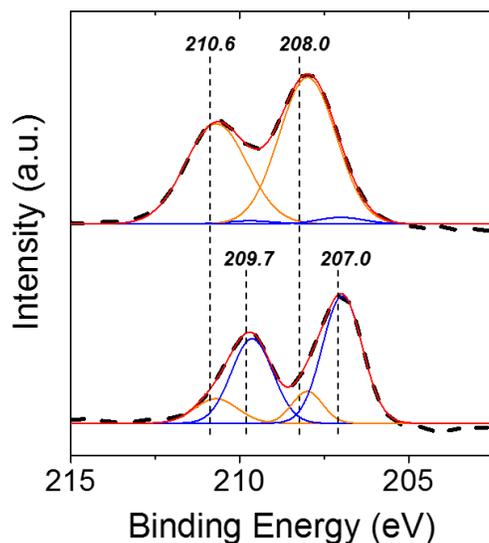
**Figure S4.**  $^1\text{H}$  MAS NMR spectra obtained for  $\text{Nb}_{1.5}\beta$ , recorded at ambient conditions in a 4 mm diameter zirconia rotor (10 kHz, 32 scans, 10 sec recycle delay).



**Figure S5.**  $^{29}\text{Si}$  MAS NMR spectra of  $\text{Nb}_{1.5}\text{-}\beta$  with (a)  $^1\text{H} \rightarrow ^{29}\text{Si}$  cross or (b)  $^{29}\text{Si}$  direct polarization recorded at ambient conditions in a 4 mm diameter zirconia rotor



**Figure S6.** Normalized ATR-IR spectra of (a) Si- $\beta$  (red, -) and Nb<sub>1.5</sub>- $\beta$  (blue, -), (b) SiO<sub>2</sub> (red, -) and Nb<sub>10.0</sub>-SiO<sub>2</sub> (blue, -), (c) difference spectra of Nb<sub>1.5</sub>- $\beta$  with respect to Si- $\beta$ , and (d) difference spectra of Nb<sub>10.0</sub>-SiO<sub>2</sub> with respect to SiO<sub>2</sub>. Spectra were acquired at ambient conditions with FTIR spectrometer (Bruker Alpha) equipped with a diamond ATR-IR accessory.

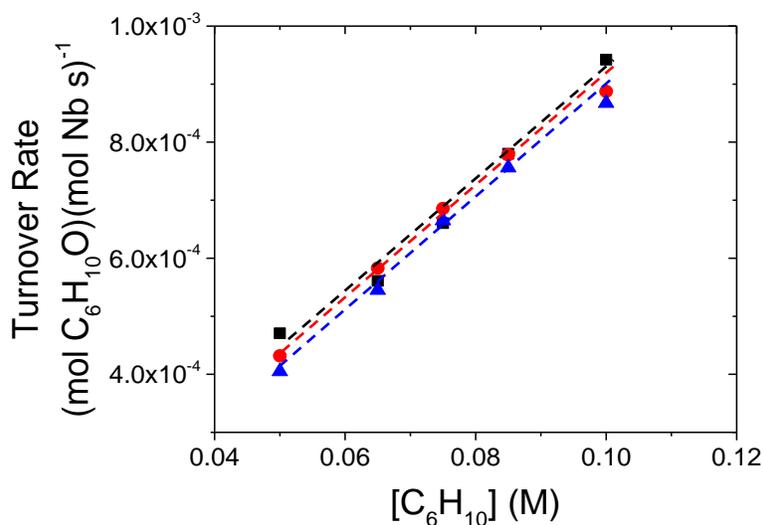


**Figure S7.** X-ray photoelectron spectra (black, dashed) of the Nb 3d region with peak fittings (colored, solid) for (a) untreated Nb<sub>5.0</sub>-β and (b) H<sub>2</sub>O<sub>2</sub>-treated Nb<sub>5.0</sub>-β. The peak fittings from the different oxidation states are color-coded for clarity: Nb<sup>IV</sup> (blue, -), Nb<sup>V</sup> (orange, -), and cumulative peak fit (red, -). Spectra are referenced to an aliphatic C 1s feature at 284.8 eV. The H<sub>2</sub>O<sub>2</sub> treatment procedure is described in section 2.4.

Figure S7a (top curve) contains two large features (orange curves) at 210.6 and 208 eV, which are attributed to the Nb 3d 3/2 and 5/2 electrons for Nb<sup>V</sup>, while the corresponding Nb<sup>IV</sup> features (blue curves) are negligible in magnitude. While in contrast, Fig. S7b (bottom curve), contains two doublet features that correspond to both Nb<sup>V</sup> and Nb<sup>IV</sup> features, which would be expected for the Nb<sup>V</sup>-OOH/Nb<sup>V</sup>-(O<sub>2</sub>)<sup>2-</sup> (i.e., hydroperoxide and peroxide) and Nb<sup>IV</sup>-(O<sub>2</sub>)<sup>-</sup> (i.e., superoxide) species, respectively.

## S2. Control Experiments to Test Importance of Mass-Transfer Restrictions

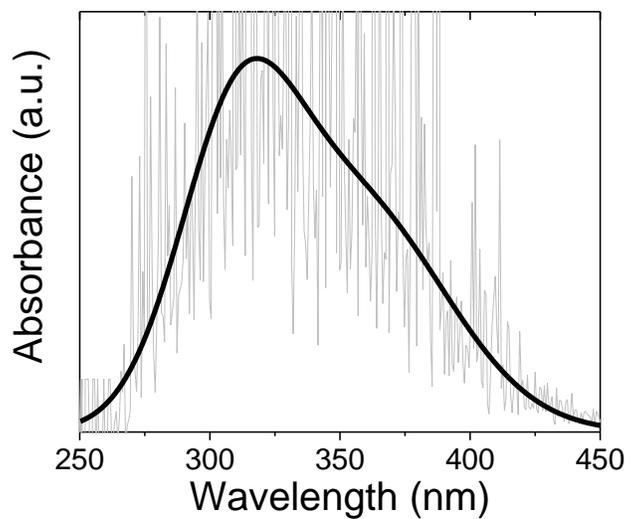
Figure S2.1 Shows cyclohexene oxide formation measured as a function of cyclohexene concentration for multiple metal loads of Nb in Nb- $\beta$ . The slope is independent of metal loading at all metal loadings tested (0.15, 0.7, 1.5 wt%), indicating that the Madon-Boudart criterion [1] is satisfied for Nb- $\beta$  catalysts used to determine the kinetics of the reaction. Within Figure S7, the maximum difference in turnover rate values ( $7.5 \cdot 10^{-5}$  (mol C<sub>6</sub>H<sub>10</sub>O)(mol Nb·s)<sup>-1</sup>) is within the maximum observed error for these reactions (< 7% error). Moreover, the differences between the turnover rates on these catalysts are not systematic across the range of cyclohexene concentrations, which indicates that these differences result from random error. Thus, we do not interpret any minute changes in turnover rates as an indicator about a change in the catalyst structure.



**Figure S8.** C<sub>6</sub>H<sub>10</sub>O turnover rates as a function of [C<sub>6</sub>H<sub>10</sub>] in 1mM H<sub>2</sub>O<sub>2</sub> with Nb<sub>1.5</sub>- $\beta$  (■), Nb<sub>0.7</sub>- $\beta$  (●) and Nb<sub>0.15</sub>- $\beta$  (▲) (30 mg catalyst, 30 cm<sup>3</sup> CH<sub>3</sub>CN, 313 K). Lines are intended to guide the eye.

### S3. In Situ UV-vis Spectroscopy

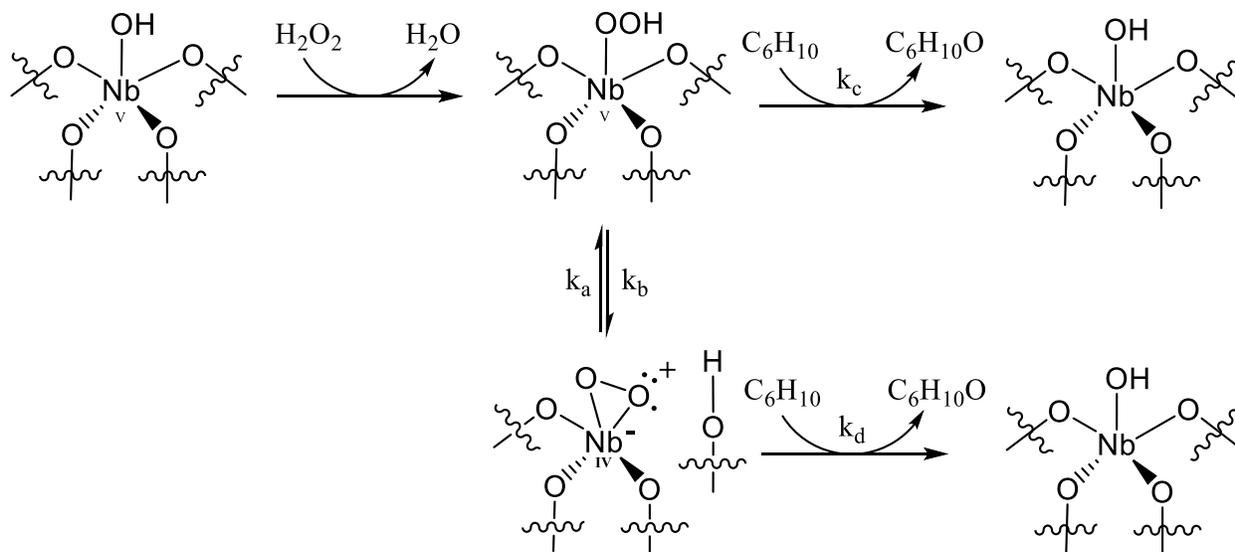
#### S3.1 Data Acquisition and Processing



**Figure S9.** UV-vis absorbance spectrum (raw data, -) of  $\text{H}_2\text{O}_2$ -treated  $\text{Nb}_{0.3}\beta$  at 313 K in flowing  $\text{CH}_3\text{CN}$  (0.4 M  $\text{H}_2\text{O}$ ) and smoothed data (—) using a finite fourier transform with 40 points of smoothing between 250 and 500 nm. Data smoothing performed in OriginPro®.

### S3.2 Kinetic Parameter Optimization

**Scheme 1.** Proposed mechanism for the formation of Nb-OOH and Nb-(O<sub>2</sub>)<sup>-</sup> with interconversion between the two proposed intermediates followed by epoxidation of C<sub>2</sub>H<sub>4</sub>.



<sup>a</sup>Formation of Nb-OOH and Nb-(O<sub>2</sub>)<sup>-</sup> occurs during the activation of H<sub>2</sub>O<sub>2</sub> over Nb<sub>1.5</sub>-β with subsequent drying steps to remove formed and adsorbed H<sub>2</sub>O (Section 2.4).

The ODE45 function in MATLAB<sup>TM</sup> was used to simultaneously solve equations 2 and 3 (from the main text) with an initial guess for the kinetic parameters (i.e., k<sub>a</sub>, k<sub>b</sub>, k<sub>c</sub>, and k<sub>d</sub>, Scheme S1). The sum of the square of the differences between the solution of the two coupled differential equation and the experimental data was used to calculate a residual value. The “fmincon” function was used with a lower bound of 0 for all parameters to optimize the k<sub>a</sub>, k<sub>b</sub>, k<sub>c</sub>, and k<sub>d</sub> values to minimize the residual between the simulated differential equations and our experimental data. The initial guess used was 0.01, 0.01, 0.001, and 0.001 for k<sub>a</sub>, k<sub>b</sub>, k<sub>c</sub>, and k<sub>d</sub>, respectively. Changes of each of the values by an order of magnitude (increasing and decreasing) led to the same optimized results, which suggests that the fit values for rate constants are not in a local minimum in solution space. As such, the unconstrained solution is presumed to be correct (Table 3), as there is no evidence for Nb-OOH being inactive for consumption by reaction with C<sub>6</sub>H<sub>10</sub>; while the high ratio of k<sub>d</sub> to k<sub>c</sub> (i.e., ~ 2 · 10<sup>4</sup>) strongly suggests that Nb-(O<sub>2</sub>)<sup>-</sup> is the active intermediate for olefin epoxidation.

## S4. In Situ FTIR Spectroscopy

### S4.1. MES-PSD Data Analysis

The raw time-resolved FTIR spectra is collected and processed through various mathematical steps before analysis. The time-domain raw spectra is first averaged onto a single period using:

$$A_{\text{average}}(t) = \frac{T}{T_{\text{total}}} \sum_{i=0}^{\frac{T_{\text{total}}}{T}} A(t + iT) \quad (\text{S4.1})$$

where  $A(t + iT)$  is the absorbance at each time point,  $A_{\text{average}}(t)$  is the absorbance after averaging into a single period,  $T$  is the time period of stimulation, and  $T_{\text{total}}$  is the total time for which the experiment was run. Hence,  $\frac{T_{\text{total}}}{T}$  represents the total number of periods of stimulations for which an experiment was run. The averaged spectra is then subjected to demodulation by phase sensitive detection (PSD) using:

$$A_k(\varphi_k^{\text{PSD}}) = \frac{2}{T} \int_0^T A_{\text{average}}(\vartheta, t) \sin(k\omega t + \varphi_k^{\text{PSD}}) dt, \quad (\text{S4.2})$$

Equation S4.2 is transformed into a Fourier series by Fourier's theorem for a periodic function:

$$A(\vartheta, t) = \sum_{i=1}^N A_{i,0}(\vartheta) + \sum_{i=1}^N \sum_{k=1}^{\infty} (A_{i,k}^{0^\circ}(\vartheta) \cos k\omega t + A_{i,k}^{90^\circ}(\vartheta) \sin k\omega t) \quad (\text{S4.3})$$

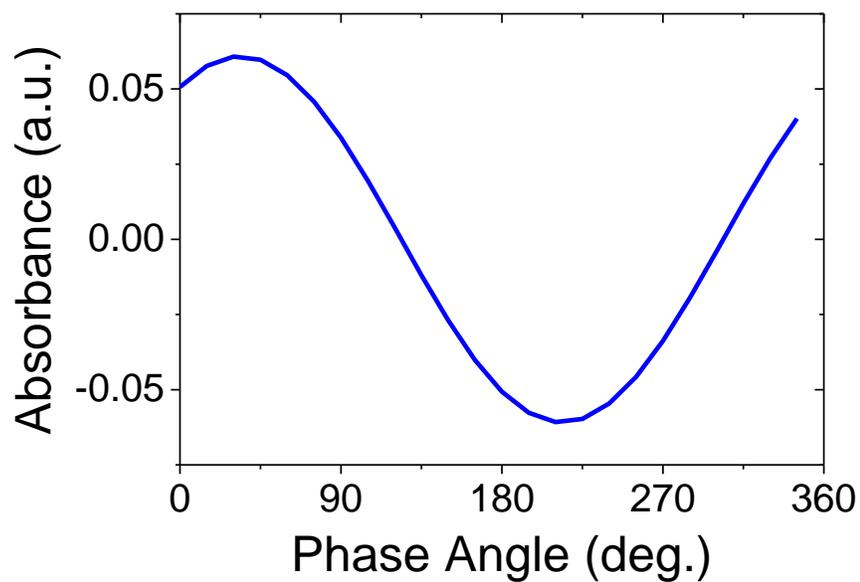
where  $A_{i,0}$  is the dc component, and  $A_{i,k}^{0^\circ}$  and  $A_{i,k}^{90^\circ}$  are the orthogonal components of the vector.

Each of the above terms in the integral is converted into a single equation using Simpson's Rule:

$$\int_0^T y(t) dt = \frac{\Delta t}{3} (y_0 + 4y_1 + 2y_2 + 4y_3 + \dots + 2y_{n-2} + 4y_{n-1} + y_n) = \frac{\Delta t}{3} \sum_{i=0}^n s_i y_i \quad (\text{S4.4})$$

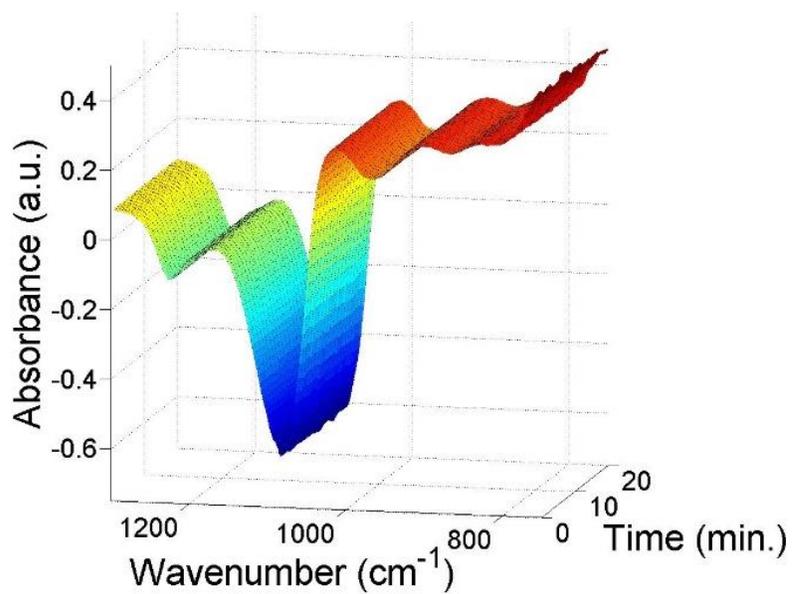
where  $s_i$ , is Simpson's coefficient (where  $n$  must be an even number). A detailed mathematical derivation and implications were discussed in details by Baurecht et. al. [2]. A self-developed code in MATLAB<sup>TM</sup> was used to resample the acquired spectra and perform the phase sensitive detection analysis using equations S4.1-S4.4.

## S4.2. Verification of Sinusoidal Reactant Modulation



**Figure S10.** Infrared absorbance value at  $1630\text{ cm}^{-1}$  (bending mode of liquid  $\text{H}_2\text{O}$ ) as a function of phase angle obtained while sinusoidally modulating the flowrates of  $\text{C}_6\text{H}_{10}$  (0.1 M  $\text{C}_6\text{H}_{10}$  in  $\text{CH}_3\text{CN}$ ) and  $\text{H}_2\text{O}_2$  (0.065 M  $\text{H}_2\text{O}_2$  in  $\text{CH}_3\text{CN}$ , i.e.,  $\text{H}_2\text{O}$ -free liquid stream) solutions ( $0.5\text{ cm}^3$  total volumetric flowrate, 333 K, Section 2.5)

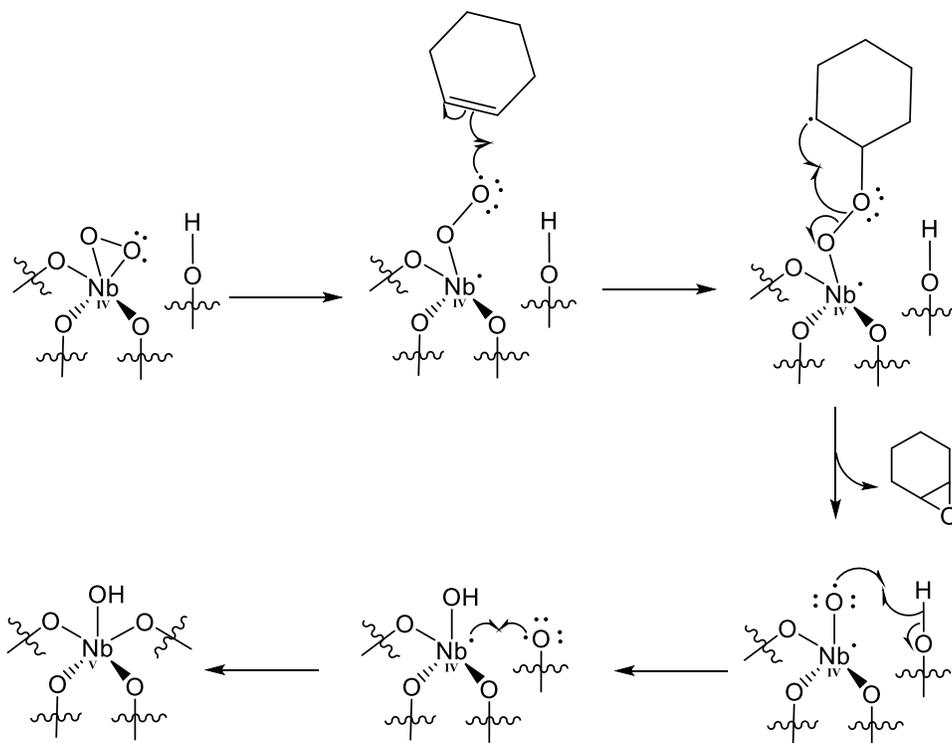
### S.4.3. Steady-State FTIR Spectra Showing Stability of Nb-(O<sub>2</sub>)\* Species



**Figure S11.** Time-resolved in situ IR spectra showing stability of Nb-(O<sub>2</sub>)<sup>-</sup> and Nb-OOH after contact with flowing H<sub>2</sub>O<sub>2</sub> (Fig. 3a), while DI H<sub>2</sub>O flow (0.5 cm<sup>3</sup> min<sup>-1</sup>) was initiated at 333 K.

### S.4.3. Proposed Mechanism for Olefin Epoxidation with Nb-(O<sub>2</sub>)<sup>•-</sup>

**Scheme S2.** Proposed bi-radical pathway for the epoxidation of cyclohexene by Nb-(O<sub>2</sub>)<sup>•-</sup>, similar to those proposed for epoxidation with homogeneous vanadium complexes [3, 4].



## S5. Previously Proposed Mechanisms for Olefin Epoxidation [5-7]

Previous models for olefin epoxidation on metal-oxide catalysts (i.e., TS-1 [7] and Ta [5, 6] grafted onto silica) are inconsistent with the experimental data obtained for C<sub>6</sub>H<sub>10</sub> epoxidation over Nb-β, specifically, these previous models assume quasi-equilibrated (QE) formation of a reactive intermediate (i.e., Ti- or Ta-(O<sub>2</sub>)\*) which does not encompass the observed dependence on epoxide concentration, likely because these studies did not test for oxygenate (e.g., epoxide) dependencies.

A reactive intermediate (Nb-(O<sub>2</sub>)<sup>-</sup>) reacts with C<sub>6</sub>H<sub>10</sub> in solution (Scheme 1, step 4) to yield the following rate expression:

$$r_E = k_4 [C_6H_{10}] [Nb - (O_2)^-] \quad (S5.1)$$

where  $r_E$  is the turnover rate of C<sub>6</sub>H<sub>10</sub>O formation,  $[Nb - (O_2)^-]$  is the number of Nb-(O<sub>2</sub>)<sup>-</sup>, and  $k_4$  is the rate constant for the epoxidation of C<sub>6</sub>H<sub>10</sub> with Nb-(O<sub>2</sub>)<sup>\*</sup>. When adsorption of the olefin, H<sub>2</sub>O<sub>2</sub>, epoxide, and the formation of a reactive intermediate are all assumed to be QE with olefin epoxidation being kinetically relevant (KR), the following rate equation emerges:

$$r_E = \frac{(k_4 K_2 K_3 K_5 [C_6H_{10}] [H_2O_2])}{[H_2O]} [*] \quad (S5.2)$$

where  $k_x$  and  $K_x$  are the rate and equilibrium constants, respectively, for each step  $x$  and  $[*]$  is the number of available Nb-OH moieties (i.e. active sites) that bind and react with species in solution. An expression for  $[*]$  is given from summing the number of likely surface intermediates:

$$[L] = [*] + [C_6H_{10}^*] + [H_2O_2^*] + [Nb - (O_2)^-] + [C_6H_{10}O^*] \quad (S5.3)$$

where  $[L]$  is the total number of active sites and  $[C_6H_{10}^*]$ ,  $[H_2O_2^*]$ , and  $[C_6H_{10}O^*]$  are adsorbed C<sub>6</sub>H<sub>10</sub>, H<sub>2</sub>O<sub>2</sub>, and C<sub>6</sub>H<sub>10</sub>O species, respectively, and  $[Nb - (O_2)^-]$  is the reactive intermediate. Equation S5.3 can then be re-expressed in terms of the rate and equilibrium constants as well as the reactant concentrations:

$$[L] = ([*] + K_1 [C_6H_{10}] [*] + K_2 K_3 [H_2O_2] [*] + K_5 [C_6H_{10}O] [*]) \quad (S5.4)$$

The combination of equations S5.2 and S5.4 yield the complete rate expression for C<sub>6</sub>H<sub>10</sub>O formation:

$$\frac{r_E}{[L]} = \frac{k_4 K_2 K_3 K_5 [C_6H_{10}] [H_2O_2]}{[H_2O] (1 + K_1 [C_6H_{10}] + K_2 K_3 [H_2O_2] + K_5 [C_6H_{10}O])} \quad (S5.5)$$

Active sites become saturated with H<sub>2</sub>O<sub>2</sub>-derived intermediates (i.e. H<sub>2</sub>O<sub>2</sub> or Nb-(O<sub>2</sub>)<sup>-</sup> is the MASI) in the limit of low [C<sub>6</sub>H<sub>10</sub>]:[H<sub>2</sub>O<sub>2</sub>], reducing the rate expression to

$$\frac{r_E}{[L]} = \frac{k_4 K_5 [C_6H_{10}]}{[H_2O]} \quad (S5.6)$$

Equation 6 is consistent with the C<sub>6</sub>H<sub>10</sub>O formation rates that increase in proportion to [C<sub>6</sub>H<sub>10</sub>] at low [C<sub>6</sub>H<sub>10</sub>]:[H<sub>2</sub>O<sub>2</sub>] (Figure 3a, 0.01 – 0.1 M C<sub>6</sub>H<sub>10</sub>), and which do not depend on [H<sub>2</sub>O<sub>2</sub>] (Figure 3b, 0.5 – 5 mM H<sub>2</sub>O<sub>2</sub>, 5 mM C<sub>6</sub>H<sub>10</sub>). The coverage of C<sub>6</sub>H<sub>10</sub> increases with [C<sub>6</sub>H<sub>10</sub>] such that C<sub>6</sub>H<sub>10</sub>\* becomes the MASI when [C<sub>6</sub>H<sub>10</sub>] is greater than 0.5 M (when [H<sub>2</sub>O<sub>2</sub>] is 1 mM), which causes equation S5.6 to take the form:

$$\frac{r_E}{[L]} = \frac{k_4 K_2 K_3 K_5 [H_2O_2]}{K_1 [H_2O]} \quad (S5.7)$$

This expression agrees with the C<sub>6</sub>H<sub>10</sub>O formation rates seen in Fig. 5a, in that the rate of reaction is independent of [C<sub>6</sub>H<sub>10</sub>]. Additionally, equation S5.7 is in agreement with the results shown in Fig. 5b, where the turnover rate for epoxidation is proportional to [H<sub>2</sub>O<sub>2</sub>] at high [C<sub>6</sub>H<sub>10</sub>]. Moreover, equations S5.5, S5.6, and S5.7 are identical to rate expressions derived previously for olefin epoxidations on similar metal-oxide catalysts.[5-7] However, the rate expressions obtained do not account for turnover rates for C<sub>6</sub>H<sub>10</sub>O formation being inversely proportional to C<sub>6</sub>H<sub>10</sub>O concentration. If C<sub>6</sub>H<sub>10</sub>O is assumed to become the MASI at high [C<sub>6</sub>H<sub>10</sub>], then equation S5.5 reduces to:

$$\frac{r_E}{[L]} = \frac{k_4 K_2 K_3 [C_6H_{10}] [H_2O_2]}{K_5 [H_2O] [C_6H_{10}O]} \quad (S5.8)$$

which possesses first-order dependence on [C<sub>6</sub>H<sub>10</sub>].

## S6. Rate Expression for H<sub>2</sub>O<sub>2</sub> Decomposition by Nb-β

When Nb-(O<sub>2</sub>)<sup>-</sup> undergoes a biomolecular reaction with H<sub>2</sub>O<sub>2</sub> (Scheme 1, Step 6) the following rate expression is given as:

$$r_D = k_4 [H_2O_2] [Nb - (O_2)^-] \quad (S6.1)$$

where  $r_D$  is the rate of H<sub>2</sub>O<sub>2</sub> decomposition,  $[Nb - (O_2)^-]$  is the concentration of Nb-(O<sub>2</sub>)<sup>-</sup>, and  $k_6$  is the rate constant for the decomposition of H<sub>2</sub>O<sub>2</sub> with Nb-(O<sub>2</sub>)<sup>-</sup>. When we apply the observation (Section 3.3) that Nb-(O<sub>2</sub>)<sup>-</sup> formation is irreversible, and all adsorption/desorption steps are QE we equation S6.1 becomes:

$$r_D = \frac{(k_6 K_2 K_3 K_5 [H_2O_2]^2) [*]}{(k_4 K_5 [C_6H_{10}] + k_6 [H_2O_2])} \quad (S6.2)$$

where  $k_x$  and  $K_x$  are the rate and equilibrium constants, respectively, for each step  $x$  and  $[*]$  is the number of available Nb-OH moieties (i.e. active sites) that bind and react with species in solution. An expression for  $[*]$  is given from summing the number of likely surface intermediates:

$$[L] = ([*] + [C_6H_{10}^*] + [H_2O_2^*] + [Nb - (O_2)^*] + [C_6H_{10}O^*]) \quad (S6.3)$$

where  $[L]$  is the total number of active sites and  $[C_6H_{10}^*]$ ,  $[H_2O_2^*]$ , and  $[C_6H_{10}O^*]$  are adsorbed C<sub>6</sub>H<sub>10</sub>, H<sub>2</sub>O<sub>2</sub>, and C<sub>6</sub>H<sub>10</sub>O species, respectively, and Nb-(O<sub>2</sub>)<sup>-</sup> is the reactive intermediate. Equation S6.3 can then be re-expressed in terms of the rate and equilibrium constants as well as the reactant concentrations:

$$[L] = \left( [*] + K_1 [C_6H_{10}] [*] + K_2 [H_2O_2] [*] + \frac{k_3 K_2 [H_2O_2] [*]}{(k_4 K_5 [C_6H_{10}] + k_6 [H_2O_2])} + K_5 [C_6H_{10}O] [*] \right) \quad (S6.4)$$

The combination of equations S6.2 and S6.4 yield the complete rate expression for H<sub>2</sub>O<sub>2</sub> decomposition:

$$\frac{r_D}{[L]} = \frac{k_3 k_6 K_2 [H_2O_2]^2}{(k_4 K_5 [C_6H_{10}] + k_6 [H_2O_2]) \left( 1 + K_1 [C_6H_{10}] + K_2 [H_2O_2] + \frac{k_3 K_2 [H_2O_2]}{(k_4 K_5 [C_6H_{10}] + k_6 [H_2O_2])} + K_5 [C_6H_{10}O] \right)} \quad (S6.5)$$

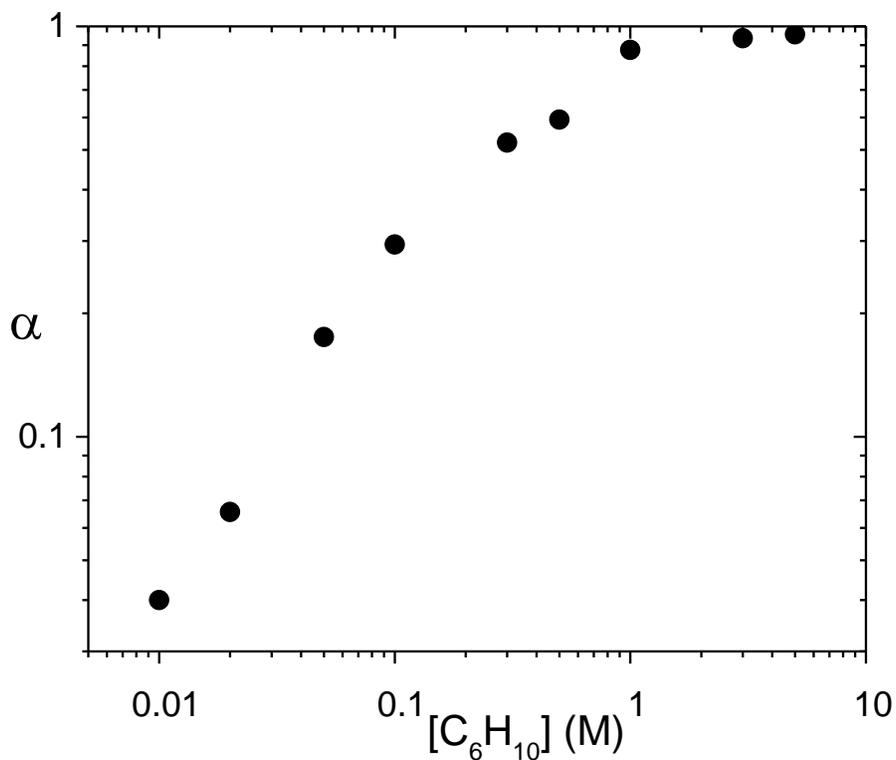
The form of this full rate equation simplifies in the limit when active sites become saturated with H<sub>2</sub>O<sub>2</sub>-derived intermediates (i.e. Nb-(O<sub>2</sub>)<sup>-</sup> is the MASI) as is expected in the limit of low [C<sub>6</sub>H<sub>10</sub>]:[H<sub>2</sub>O<sub>2</sub>]:

$$\frac{r_D}{[L]} = k_6 [H_2O_2] \quad (S6.6)$$

which shows that the apparent dependence on [H<sub>2</sub>O<sub>2</sub>] for H<sub>2</sub>O<sub>2</sub> decomposition is first order.

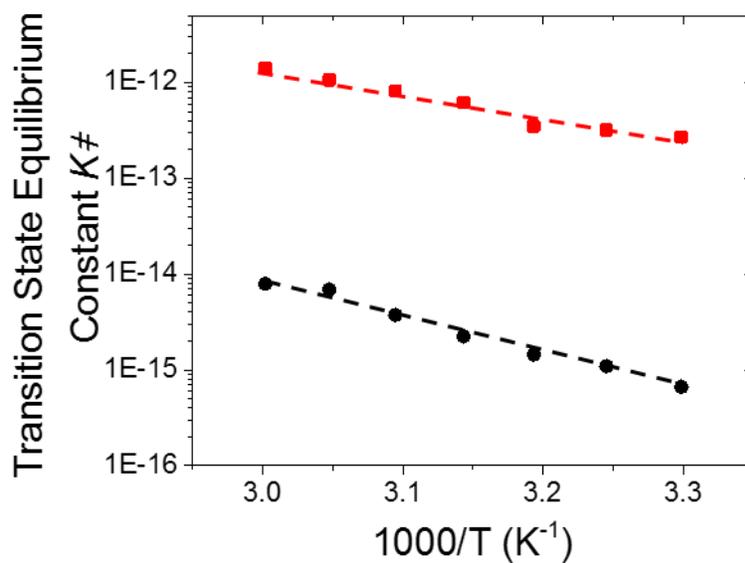
### S7. H<sub>2</sub>O<sub>2</sub> Selectivity as a Function of C<sub>6</sub>H<sub>10</sub> Concentration

H<sub>2</sub>O<sub>2</sub> selectivities expressed as  $\alpha$  values (the ratio of the turnover numbers for C<sub>6</sub>H<sub>10</sub>O formation to that of H<sub>2</sub>O<sub>2</sub> consumption) were calculated across the range of cyclohexene concentrations used in study. In general, H<sub>2</sub>O<sub>2</sub> is used more selectively to form C<sub>6</sub>H<sub>10</sub>O at the greatest C<sub>6</sub>H<sub>10</sub> to H<sub>2</sub>O<sub>2</sub> ratios.



**Figure S12.** H<sub>2</sub>O<sub>2</sub> selectivity ( $\alpha$ , Section 3.4) for epoxidation as a function of  $[C_6H_{10}]$  over Nb<sub>1.5</sub>- $\beta$  (1 mM H<sub>2</sub>O<sub>2</sub>, ~30 cm<sup>3</sup> CH<sub>3</sub>CN, 313 K)

## S8. Temperature Dependence of C<sub>6</sub>H<sub>10</sub>O Formation and H<sub>2</sub>O<sub>2</sub> Decomposition



**Figure S13.** Transition state equilibrium constants, ( $K^\ddagger$ ), for C<sub>6</sub>H<sub>10</sub> epoxidation (●) and H<sub>2</sub>O<sub>2</sub> decomposition (■) as functions of inverse temperature on Nb<sub>1.5</sub>-β (0.05 M C<sub>6</sub>H<sub>10</sub>, 1 mM H<sub>2</sub>O<sub>2</sub>) with a Nb-(O<sub>2</sub>)<sup>-</sup> MASI. Error bars were omitted for clarity. In all reported rate data, error was < 10%. Lines represent fits to the Eyring equation (equation 23).

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