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

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Graphical Abstract - TOC

Abstract

The selective epoxidation of olefins with hydrogen peroxide (H_2O_2) over transition metal substituted zeolites is less environmentally impactful than epoxidation schemes that use chlorinated or organic oxidants. The structure and reactivity of reactive intermediates derived from H_2O_2 and the mechanism for olefin epoxidation on such materials are debated. Here, cyclohexene oxide formation and H_2O_2 decomposition rates (measured as functions of reactant and product concentrations) and in situ infrared (IR) and UV-vis spectroscopy are used to probe the intervening elementary steps for cyclohexene (C_6H_{10}) epoxidation and the identity of the reactive intermediates on a Nb- β catalyst. IR and UV-vis spectra acquired in situ show that the reactive intermediates are predominantly superoxide species ($\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}^-$; observed also by X-ray photoelectron spectroscopy), which form by the irreversible activation of H_2O_2 over Nb centers. Similar $\text{M-(O}_2\text{)}^*$ ($\text{M} = \text{Ti or Ta}$) intermediates were previously assumed to form via reversible processes; however, in situ IR and UV-vis measurements directly show that $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}^-$ forms irreversibly in both H_2O and acetonitrile. Activation enthalpies ($\Delta H^\ddagger$) for C_6H_{10} epoxidation are 27 kJ mol^{-1} higher than for H_2O_2 decomposition, while activation entropies ($\Delta S^\ddagger$) for epoxidation are $56 \text{ J mol}^{-1} \text{ K}^{-1}$ lower than for H_2O_2 . These comparisons show that the selectivities for epoxidation, via primary reaction pathways, increase with increasing reaction temperatures. Collectively, these results provide a self-consistent mechanism for C_6H_{10} epoxidation that is also in agreement with previously published data. These findings will aid the rational design and study of alternative metal oxide catalysts for olefin oxidation reactions.

Keywords: olefin epoxidation, zeolites, niobium, in situ spectroscopy, metal oxide catalysis, green chemistry, hydrogen peroxide

1.0 Introduction

Epoxides are important precursors for the synthesis of epoxy resins, plastics, and complex molecules used to manufacture aircraft hulls, perfumes, and pharmaceuticals [1-3]. Currently, epoxides are produced primarily by the reaction of olefins with stoichiometric amounts of organic peroxy compounds [4] or through chlorohydrin intermediates followed by strong alkaline treatments to form oxiranes [5, 6]. These processes generate stoichiometric amounts of corrosive organic acids and alcohols [7] or chloride salts [5], respectively, that require subsequent energy-intensive separation, waste-treatment, and regeneration [8, 9]. More environmentally benign oxidants should be used; however, the costs of “green” oxidants that generate less waste are generally greater and the product selectivities may be lower than Cl-mediated pathways [10, 11]. Hydrogen peroxide (H_2O_2) is one such oxidant whose use only byproduct in epoxidation reactions is water (H_2O), which is easily separated from organic product streams by liquid-liquid extraction [12, 13]. Currently, the high relative cost of H_2O_2 (to that of Cl-based oxidizers) requires catalysts that selectively activate and utilize H_2O_2 for olefin epoxidation while minimizing non-productive H_2O_2 decomposition (i.e., $2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$) and epoxide decomposition.

Isolated metal centers and small oligomers of early transition metal oxides (e.g., Al^{III} [14, 15], Ti^{IV} [7, 16-18], Zr^{IV} [19, 20], Ta^{V} [21-23], and Nb^{V} [24, 25]) catalyze the epoxidation of olefins with H_2O_2 . Isolated Nb atoms grafted onto silica give greater rates and selectivities for olefin epoxidation compared to isolated Ti centers as well those of other group IV and V metals (i.e., Zr, Hf, V, and Ta) on silica, which was attributed to differences between the Lewis acidity (estimated from the ionic character of the M-O bond) of the different metal atoms [20]. Zeolite frameworks can stabilize relatively high loadings of isolated transition metal atoms [26-30],

which in some cases, are believed to possess higher turnover rates ((mol product)/(mol active site·s)⁻¹) and selectivities than their oligomeric- and bulk-oxide counterparts. For example, Ti centers in titania silicalite (TS-1) activate H₂O₂ to form intermediates that epoxidize propylene in one of few industrially practiced H₂O₂-based oxidation reactions [31-33]. TS-1, however, possesses relatively small diameter pores (~ 5 Å, due to the MFI framework) [34], which hinders the diffusion of larger olefins (e.g., cyclooctene, limonene, etc.) [31, 35] to Ti centers within the pores. Larger pore zeolite frameworks, such as the beta (*BEA) polymorph, possess pores with diameters of ~ 7 Å [34], which broadens the range of potential substrates for epoxidations [36]. Post-synthetic modification of *BEA and other zeolites provides a facile method to synthesize transition metal substituted catalysts using commercially-available zeolites as precursors [26, 27, 36, 37], which enables studies of how the elemental identity of isolated metal centers in similar coordination environments affects catalysis [38]. As such, the mechanism of olefin epoxidation on transition metal substituted *BEA (M-β) must be established before such periodic trends can be understood.

Here, we combine catalytic rate measurements with in situ UV-vis and Fourier transform-infrared (FTIR) spectra to determine the mechanism for cyclohexene epoxidation and the structure and reactivity of relevant reaction intermediates on Nb-β. In situ UV-vis and IR spectroscopy show Nb-bound superoxide (Nb^{IV}-(O₂)⁻) and hydroperoxide/peroxide (Nb^V-OOH and Nb^V-(O₂)²⁻) intermediates form by irreversible activation of H₂O₂ at Nb-atoms, which conflicts with proposed mechanisms for olefin epoxidation on similar catalysts (i.e., TS-1 [39], Ta-SBA-15 [21, 40], and Ta-SiO₂ [22, 23]) that assume reversible (and quasi-equilibrated) H₂O₂ activation. X-ray photoelectron spectroscopy of H₂O₂-activated Nb-β confirms the presence of Nb^{IV}-(O₂)⁻ surface species by showing that Nb atoms shift from a 5+ to 4+ oxidation state when

activated with H_2O_2 . A combination of transient in situ UV-vis and FTIR measurements demonstrate that the $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}^-$ specie is the active oxidizing intermediate for epoxidation and possesses a rate constant for epoxidation that is a factor of $2 \cdot 10^4$ larger than that for $\text{Nb}^{\text{V}}\text{-OOH/Nb}^{\text{V}}\text{-(O}_2\text{)}^{2-}$.

Turnover rates ((mol product)/(mol Nb atom·s) $^{-1}$) were measured as functions of the concentrations of C_6H_{10} (0.01 – 5 M), H_2O_2 (0.5 – 5 mM), and cyclohexene oxide ($\text{C}_6\text{H}_{10}\text{O}$, 1 – 5 mM). Formation rates of $\text{C}_6\text{H}_{10}\text{O}$ increase in proportion to $[\text{C}_6\text{H}_{10}]$ but become constant at high $[\text{C}_6\text{H}_{10}]$ values. The rate of epoxidation is independent of $[\text{H}_2\text{O}_2]$ when $[\text{C}_6\text{H}_{10}]$ is low, but becomes proportional to $[\text{H}_2\text{O}_2]$ at high $[\text{C}_6\text{H}_{10}]$. These results reflect the competitive adsorption of H_2O_2 - and C_6H_{10} -derived species, which results in a change in the most abundant reactive intermediate (MARI) on Nb-sites. Upon formation of $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}^-$, the intermediate reacts either with C_6H_{10} or H_2O_2 to form the epoxidation (i.e., cyclohexene oxide) or decomposition products (i.e., H_2O and O_2), respectively. Measured activation enthalpies ($\Delta H^\ddagger$) for epoxidation (72 kJ mol $^{-1}$) and H_2O_2 decomposition (45 kJ mol $^{-1}$) show that decomposition is enthalpically favorable, whereas activation entropies ($\Delta S^\ddagger$, -35 J mol $^{-1}$ K $^{-1}$ for $\text{C}_6\text{H}_{10}\text{O}$ formation and -91 J mol $^{-1}$ K $^{-1}$ for H_2O_2 decomposition) suggest that epoxidation is entropically favorable. Collectively, these data provide insight to the identity of the reactive surface species responsible for epoxidations and the mechanism for this reaction on transition metal substituted zeolites, which is needed to understand the underlying chemical reasons that lead to significant differences in rates and selectivities that reflect the elemental identity of the transition metal atoms that facilitate oxidation reactions.

2.0 Methods and Materials Characterization

2.1 Synthesis of Nb- β Catalysts

Niobium-substituted zeolite catalysts were prepared by the post-synthetic modification of commercial zeolite beta [26, 27]. Commercial *BEA (Zeolyst, Si:Al ~ 12.5, NH_4^+ cation, Al- β) was dealuminated by treatment with concentrated HNO_3 (Macron Chemicals, 69 – 70 wt. %, 20 cm^3 per gram of zeolite) at reflux (448 K) for 20 h. Slurries of Al- β and HNO_3 are initially a dark brown color, but the color of these suspensions change to a light tan after four hours at reflux. The dealuminated zeolite (Si- β , Si:Al > 1200 determined by inductively couple plasma – optical emission spectroscopy) was then recovered by filtration and washed with concentrated HNO_3 ($10 \text{ cm}^3 \text{ g}^{-1}$) followed by deionized (DI) water ($17.8 \text{ M}\Omega$, $20 \text{ cm}^3 \text{ g}^{-1}$). The wet recovered Si- β solids were dried in an oven within ambient air for 18 hours at 423 K. The dried solids were then heated to 823 K at 5 K min^{-1} and held at 823 K for 6 hours in flowing dry air (Airgas, Ultra-zero grade, $100 \text{ cm}^3 \text{ min}^{-1}$) with the intent to remove residual organics from the Si- β . Nb atoms were incorporated into the framework by liquid-phase adsorption (LPA), which involved stirring Si- β in a 0.35 – 3.5 mM solution of NbCl_5 (Sigma-Aldrich, 99%, $50 \text{ cm}^3 \text{ g}^{-1}$) in isopropyl alcohol (VWR Analytical, > 99.5%) for 6 hours at 343 K. Volatiles were then removed in vacuo at 6.6 kPa for 30 minutes followed by washing with $75 \text{ cm}^3 \text{ g}^{-1}$ DI water with the intent to remove any residual NbCl_5 not exchanged into defects within the framework. The recovered solids were heated to 723 K at 5 K min^{-1} and held at 723 K for 4 hours in flowing dry air (Airgas, Ultra-zero grade, $100 \text{ cm}^3 \text{ min}^{-1}$) to yield a white powder. Nb-substituted zeolites are referred to as $\text{Nb}_x\text{-}\beta$ where the subscript denotes the final wt. % of Nb (0.15 – 5.0 wt. %), which was controlled by changing the concentrations of NbCl_5 and Si- β in the LPA solution.

A 10 wt. % Nb- SiO_2 ($\text{Nb}_{10}\text{-SiO}_2$) catalyst was prepared by incipient wetness impregnation of washed SiO_2 (1 g, Sigma-Aldrich, Davisil 646, 35–60 mesh) with 1.2 cm^3 of 0.898 M NbCl_5 dissolved in isopropyl alcohol. The catalyst was dried under ambient conditions for 4 h by

ramping to 823 K (5 K min⁻¹) for 6 hours under flowing dry air (Airgas, Ultra-zero grade, 100 cm³ min⁻¹).

2.2 Catalyst Characterization

Catalyst metal loadings were quantified using inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer 2000DV), calibrated against known dilution standards. The reported Nb_x-β subscript corresponds to values measured by ICP-OES.

Catalyst crystallinity was confirmed by powder X-ray diffraction (p-XRD). X-ray diffractograms were obtained using a powder X-ray diffractometer (Siemens/Bruker D-5000) with Cu K-α radiation (0.15418 nm) using a step size of 0.02° at 1° min⁻¹ in an ambient atmosphere. X-ray diffractograms for commercial NH₄⁺-β, the dealuminated Si-β, and prepared Nb-β catalysts are effectively indistinguishable (Figure S1). These comparisons show that the post-synthetic modification method does not affect the crystalline structure of the zeolites, and that framework crystallinity is maintained.

Diffuse reflectance UV-vis (DRUV-vis) spectra were measured from 700 to 175 nm using a spectrophotometer (Agilent CARY 5 UV-Vis-NIR) equipped with a diffuse-reflectance accessory (Harrick Cricket®). Spectra were recorded in absolute reflectance (R) mode at ambient pressure and temperature. Magnesium oxide powder (MgO, Sigma Aldrich, 99.995% trace metals basis) or a polished gallium mirror (Harrick Cricket®) was used to collect a total reflectance spectrum for use as a baseline for Kubelka-Munk pseudo absorbances (Fig. S2). Nb-β and Nb-SiO₂ samples were ground with MgO (10% sample by weight) prior to measurement. Optical band gaps (E_g) were calculated from the x-intercept of the linear portion of a Tauc plot (Fig. S3) [20, 41]. Table 1 summarizes the optical band edges of Nb-β, Nb₁₀-SiO₂, bulk Nb₂O₅

[42], and calixarene-assisted Nb grafted onto silica (Calix-Nb_{1.7}-SiO₂) [20]. Nb₁₀-SiO₂ has a band edge (3.7 eV) that is similar to that of bulk Nb₂O₅ (3.4 eV) [42], which indicates that this material contains metal-oxide clusters with bulk-like electronic properties and sizes of at least several nanometers. All Nb- β catalysts have band edge energies (4.2 eV) that are much larger than that of bulk Nb₂O₅ and similar to those previously reported (4.0 eV) for isolated atoms grafted onto mesoporous silica [20]. The similarity between the band gaps for Nb_{0.7}- β and Nb_{1.5}- β strongly suggests that Nb atoms are incorporated into the zeolite framework as single isolated sites (i.e., the samples contain immeasurable extents of Nb-O-Nb connectivity). If the Nb atoms were not incorporated into the zeolite framework, but rather forming small clusters, the NbO_x clusters would become larger with increasing loadings, which would result in a decreasing band gap. Additionally, Fig. S2 shows the Kubelka-Munk absorbance as a function of wavelength for Nb_{0.7}- β , Nb_{1.5}- β , and Nb₁₀-SiO₂. Both Nb- β samples show no distinct absorbance feature beyond ~300 nm, which suggests that no extra-framework Nb^V species exist either as bulk or oligomeric niobia-like phases [26, 43].

Table 1. Optical band edges and wavelengths of maximum absorption obtained from diffuse-reflectance UV-vis spectroscopy Nb-based catalysts. Catalysts were mixed with MgO in a 1:10 ratio by weight prior to measurement under ambient conditions. Pure MgO was used as the reference material.

Sample	Band Edge (eV)	Maximum Absorption (nm)
Bulk Nb ₂ O ₅	3.4 [42]	-
Nb _{10.0} -SiO ₂	3.7	-
Calix-Nb _{1.7} -SiO ₂	4.0 [20]	240
Nb _{0.7} - β	4.2	255
Nb _{1.5} - β	4.2	255

Solid-state magic angle spinning-nuclear magnetic resonance (MAS NMR) spectroscopy was performed on a spectrometer (Varian, Unity Inova 300 MHz) equipped with a 4 mm MAS probe (Varian-Chemmagetics, double resonance APEX HX). Approximately 36.4 mg of Nb_{1.5}- β was packed into a 4 mm zirconia rotor, which was spun at 10 kHz in the spectrometer for MAS-NMR. Powdered octakis(dimethylsilyloxy)silsesquioxane (Q₈M₈) was used for pulse calibration and ²⁹Si chemical shift referencing (Q₈M₈ has a chemical shift of 11.45 ppm, relative to the primary standard, tetramethylsilane at 0 ppm). ¹H direct polarization (DP-MAS NMR) was performed with a 10 sec recycle delay with the averaging of 32 scans. ¹H→²⁹Si cross polarization (CP-MAS NMR) was performed with a 5 sec recycle delay using an 8 msec contact time with the averaging of 6000 scans. ²⁹Si DP-MAS NMR was performed with a 10 sec recycle delay with the averaging of 6000 scans. ⁹³Nb MAS NMR experiments were unsuccessful due to low signal to noise levels even with 69,000 scans with a 1 sec recycle delay.

Figure S4 shows ¹H MAS-NMR spectra for Nb_{1.5}- β . The lack of a distinct feature located at 5.4 ppm is consistent with the incorporation of Nb atoms into silanol pockets during post-synthetic modification [43]. Figure S5a shows the ²⁹Si DP-MAS NMR spectra for Nb_{1.5}- β , which shows three distinct features at -102, -112, and -115 ppm. The feature at -102 ppm is attributed to

Si atoms in a Si(OH)(OSi)_3 environment [43-45], while the features at -112 and -115 ppm are assigned to Si atoms in a Si(OM)_4 environment, where $M = \text{Si}$ or Nb , which are similar to features seen in Nb- β [43], Ta- β [45], and Zr- β [44]. Figure S5b shows the $^1\text{H} \rightarrow ^{29}\text{Si}$ CP-MAS NMR spectra with an 8 msec contact time, which is used to selectively enhance the excitation of Si atoms that are near ^1H atoms. Figure S5b clearly shows the enhancement of the feature located at -102 ppm during cross polarization, which confirms the assignment of this feature to Si(OH)(OSi)_3 atoms. In short, the appearance of the -112 and -115 ppm features in Fig. S5a suggest that the Nb atoms are incorporated into the framework as there are two distinct type of Q4 Si atoms (i.e., Si(OM)_4), and these features are similar to those observed in related framework-substituted *BEA (i.e., Nb- β [43], Ta- β [45], and Zr- β [44]).

Nb-atom incorporation was also characterized by attenuated total reflectance IR spectroscopy (ATR-IR, Bruker Alpha). Nb_{1.5}- β and Si- β samples (~10 mg) were pressed onto a diamond ATR-IR internal reflection element and IR spectra were recorded (32 scans, 2 cm^{-1} resolution) at ambient conditions. Figure S6a shows IR spectra for Si- β and Nb_{1.5}- β samples just after heating to 823 K for 6 h in flowing air (100 $\text{cm}^3 \text{min}^{-1}$, Praxair, Ultra-zero grade), both of which exhibit absorbance features centered at 1234, 1075, and 803 cm^{-1} , which correspond to the SiO_4 internal tetrahedral stretch, the $\nu_{\text{as}}(\text{Si-O})$, and the $\nu_{\text{s}}(\text{Si-O})$ features, respectively [46]. Nb_{1.5}- β also possesses an additional feature in the ATR-IR spectra that is centered at 950 cm^{-1} (Fig. S6c), which corresponds to $\nu(\text{Si-O-Nb})$ [43, 47]. Additionally, extra-framework Nb atoms would result in a distinct absorbance feature at ~835 cm^{-1} which is assigned to $\nu_{\text{s}}(\text{O-Nb-O})$ of oligomeric or polymeric niobia [48]. Figure S6d shows the difference spectra for Nb_{10.0}- SiO_2 with respect to SiO_2 , and possesses a distinct absorbance feature at 831 cm^{-1} , which suggests that Nb_{10.0}- SiO_2 contained oligomeric or bulk-like clusters of niobia on the surface. Notably, the lack of an

additional IR absorbance feature (Fig. S6c) near 835 cm^{-1} suggests that these Nb- β samples do not contain oligomeric or bulk forms of NbO_x . These data, in conjunction with DRUV-vis and solid-state NMR, strongly suggest that Nb atoms have been incorporated into the *BEA framework and that no extra-framework Nb^{V} is formed after the post-synthetic modification of *BEA.

The presence of Lewis acid sites was characterized by the FTIR spectroscopy of deuterated acetonitrile (CD_3CN , Cambridge Isotope Laboratories, 99.8% D atom) [49, 50] coordinated to Nb_{1.5}- β and Si- β using a custom-made transmission cell, the design of which was described previously [51]. The transmission cell was mounted within an FTIR spectrometer (Bruker, Tensor 37) equipped with a liquid-N₂ cooled HgCeTe detector. Catalysts were pressed into self-supporting wafers ($\sim 80\text{ mg}$) and placed within the stainless-steel cell, which was equipped with CaF_2 windows and connected to a gas manifold by gas-transfer lines that were heated to 423 K via electrical heating tape (Omega, FGH Series). The catalyst temperature was measured using a K-type thermocouple (Omega) located within the cell. Catalysts were heated to 423 K at 10 K min^{-1} and held at 423 K for 1.5 h under flowing He ($50\text{ cm}^3\text{ min}^{-1}$, Airgas, Ultra High Purity) to remove H_2O and then allowed to cool to 298 K. Liquid CD_3CN ($1\text{ }\mu\text{L min}^{-1}$) was fed via a syringe pump (Legato 100, KD Scientific) and vaporized inside the heated gas-transfer lines into a stream of flowing He ($50\text{ cm}^3\text{ min}^{-1}$) to generate a mixture (1.2 kPa CD_3CN , 100 kPa He). Each catalyst was then contacted with the $\text{CD}_3\text{CN}/\text{He}$ stream until reaching the saturation coverage of CD_3CN (determined by constant absorbance intensities in FTIR spectra, $\sim 15\text{ min}$) at which point the CD_3CN flow was stopped. . The sample was then heated at 10 K min^{-1} to increasing temperatures in 20 K increments to a maximum temperature of 423 K, and steady-state FTIR spectra (128 scans, 1 cm^{-1} resolution) were acquired continuously.

Figure 1. Infrared spectra of adsorbed CD_3CN on the (a) $\text{Si-}\beta$ and (b) $\text{Nb}_{1.5}\text{-}\beta$ samples at the indicated temperatures within a steam of flowing He (101 kPa). Prior to the acquisition of these spectra, the samples were saturated with CD_3CN at 298 K (1.2 kPa CD_3CN , 100 kPa He, $50 \text{ cm}^3 \text{ min}^{-1}$), after which CD_3CN flow was stopped.

Figure 1 shows representative FTIR spectra for CD_3CN adsorbed on $\text{Si-}\beta$ (Fig. 1a) and $\text{Nb}_{1.5}\text{-}\beta$ (Fig. 1b). Absorption features between $2260 - 2340 \text{ cm}^{-1}$ correspond to the $\nu(\text{C}\equiv\text{N})$ mode, while the band near 2115 cm^{-1} arises from the $\delta_s(\text{CD}_3)$ mode [50]. The absorbance peak located at 2275 cm^{-1} (Fig. 1a) is associated with CD_3CN hydrogen bonded to silanol groups located within the zeolite, while the shoulder located at 2265 cm^{-1} is attributed to physisorbed CD_3CN , which weakly interacts with the pore walls [50]. As the temperature of the $\text{Si-}\beta$ sample increases, hydrogen-bonded CD_3CN species (2275 cm^{-1}) persist on the surface, while the physisorbed

CD₃CN (2265 cm⁻¹) desorb. Spectra of CD₃CN on Nb_{1.5}-β (Fig. 1b, 298 K) largely resemble those of Si-β but possess an additional absorption feature at 2306 cm⁻¹ that can be attributed to Lewis acid sites associated with adsorption on Nb atoms, similar to CD₃CN features on Sn-β [49]. Yet these spectra on Nb_{1.5}-β show only a single new feature, in contrast to FTIR spectra of CD₃CN on Sn-β, which show features at both 2308 and 2316 cm⁻¹ and reflect the presence of both open and closed Lewis acid sites [49]. Consequently, we conclude that Nb_{1.5}-β possesses predominantly one type of Lewis acid site, because additional types of Lewis acid sites would result in multiple absorbance peaks in the 2300 cm⁻¹ region [52]. These results (Fig. 1) taken together with NMR spectra (Fig. S4 and S5) strongly suggest that the Lewis acid sites are Nb-atoms tetra-coordinated within the zeolite framework [52].

The UV-vis (Fig. S2 and S3), solid-state NMR (Fig. S4 and S5), and ATR-IR (Fig. S6) data show that Nb atoms are incorporated into the *BEA framework and do not exist as extra-framework bulk or oligomeric niobia. Additionally, the IR spectra of adsorbed CD₃CN (Fig. 1b) show a single absorbance feature associated with Lewis acidic sites. It is possible that multiple types of Nb sites exist in Nb-β, that have similar IR absorption features for adsorbed CD₃CN and also possess similar heats of adsorption that preclude their detection; however, this seems to be unlikely due to the significant shift in wavenumbers (2308 and 2316 cm⁻¹) and different heats of adsorption seen in Sn-β for open and closed sites [49]. These Lewis acid sites are most likely to be Nb atoms tetra-coordinated to the framework of β and to possess a single pendant –OH (i.e., Nb(OSi)₄(OH)) based on the characterization here, together with previous results that combined experiments (i.e., solid-state NMR, powder XRD, UV-vis, XPS, and IR spectroscopy) and theory (i.e., ab initio DFT calculations) to show that the most energetically stable form of Nb in Nb-β is the Nb(OSi)₄(OH) unit [26, 43].

X-ray photoelectron spectroscopy (XPS) measurements were used to measure the oxidation state of Nb atoms in Nb_{5.0}- β and H₂O₂-activated Nb_{5.0}- β (Section 2.4) and were performed on a Kratos AXIS Ultra spectrometer with a monochromatic Al-K α (1486.6 eV) X-ray source. High-resolution spectra were collected with 40 eV pass energy, and the binding-energy scales were referenced with respect to the aliphatic C 1s absorbance feature at 284.8 eV. Peak fittings were done in CasaXPS© via the method of Shirley.

2.3 Epoxide Formation and H₂O₂ Consumption Rate Measurements

Reaction rates for epoxidation were measured using a batch reactor (100 cm³, three-neck round bottom flask) equipped with a reflux condenser to minimize evaporative losses. For typical reaction conditions, the reactor was filled with a solvent mixture of ~30 cm³ acetonitrile (CH₃CN, Macron Chemicals, >99.8%) and 30 μ L benzene (Sigma-Aldrich, thiophene free, >99%) as an internal standard. The reagents, C₆H₁₀ (Sigma-Aldrich, >99%) or cis-stilbene (Sigma-Aldrich, >96%) and H₂O₂ (Fischer Chemicals, 30 wt. % in H₂O), were added and the reaction mixture was heated to the desired temperature (303 – 333 K) while stirring at 450 rpm. The epoxidation of C₆H₁₀ was initiated by introducing ~30 mg of the Nb- β catalyst. Small aliquots (~300 μ L) were extracted through a 0.22 μ m filter (GS-Tek, PVDF filter) to remove suspended catalyst, and thus quench C₆H₁₀ epoxidation and H₂O₂ decomposition. All reactants and solvents used were miscible under the conditions tested in this study. The concentrations of C₆H₁₀O and other potential reaction products (e.g., cyclohexane diol and cyclohexanol) were determined as a function of time with a gas chromatograph (HP-5890 Series A) equipped with a non-polar dimethylpolysiloxane capillary column (Agilent, HP-1, 30 m length, 1.05 μ m) and a flame ionization detector. All species were identified and response factors were calculated using calibrated mixtures of known standards. The change in the concentration of H₂O₂ was

determined by colorimetric titrations using a solution of Cu-based indicator (12 mM neocuproine (Sigma-Aldrich, >98%); 8.3 mM CuSO₄ (Fisher Chemicals, >98.6%); 25% v/v ethanol (Decon Laboratories Inc., 100%)) [53, 54]. The concentrations of H₂O₂ in each aliquot was determined from the absorbance at 454 nm, measured using a visible-light spectrophotometer (Spectronic, 20 Genesys), and by comparison to calibrated standards. In all reported data, the selectivity towards C₆H₁₀O formation was > 99% (e.g., no common byproducts were detected, such as cyclohexanol or cyclohexane diol) upon reaction of C₆H₁₀ with H₂O₂ over Nb-β. The carbon balance closed to within 98% for all reactions reported, which shows all significant reaction products were detected. The calculated uncertainties for all turnover rate measurements are less than 7%, as determined by comparison of repeated measurements.

Figure 2. Concentration profiles for the formation of C₆H₁₀O (black) and for the consumption of H₂O₂ (red) as a function of time expressed as (a) Relative Change in Concentration (given in mol (g_{cat})⁻¹) for direct comparison between catalysts, as there is no Nb present in Si-β, and (b) conversion of C₆H₁₀ (taken as $(\text{mol}_{\text{C}_6\text{H}_{10}\text{O}})(\text{mol}_{\text{C}_6\text{H}_{10},\text{initial}})^{-1}$) or H₂O₂ (10 mM C₆H₁₀, 1 mM H₂O₂, Nb_{1.5}-β (■) or Si-β (▲) in CH₃CN, 313 K) with hot filtration at 22 minutes. Lines are intended to guide the eye.

Control experiments were performed using Si-β and Nb_{1.5}-β to demonstrate that the metal centers contained within the zeolite were responsible for C₆H₁₀ epoxidation and H₂O₂

consumption. Figure 2 shows that turnover numbers (TON) for C_6H_{10} epoxidation and H_2O_2 consumption are undetectable on Si- β but increase with time on Nb_{1.5}- β , which shows that the Nb atoms in the framework catalyze epoxidation and H_2O_2 conversion. The values of the TON become constant (i.e., turnover rates are zero) after hot filtration, suggesting that Nb-atoms do not leach into solution and homogeneously catalyze epoxidation. Additionally, ICP-OES analyses of the reaction solution (after 1 h of reaction) and of the spent Nb_{1.5}- β show no discernible changes in the Nb content of either the liquid phase or the solid catalyst. The ICP-OES analysis performed has an experimental error of ± 0.01 wt. %, which correlates to a sensitivity of <1 % of the total Nb content of the catalyst. Turnover rates reported in all subsequent sections were obtained in the linear region (i.e., first 5 min) of olefin epoxidation at differential conversion (i.e., $< 5\%$ conversion of C_6H_{10} and H_2O_2).

Reported rates of C_6H_{10} epoxidation and H_2O_2 consumption were measured in the absence of mass-transfer limitations. To ensure that the Madon-Boudart criterion [55] was satisfied, reactions were performed with Nb- β catalysts with different metal loadings (0.15 – 1.5 wt. % Nb) at constant H_2O_2 concentrations over a range of C_6H_{10} concentrations (Section S2, Fig. S8). Epoxidation turnover rates did not depend on the Nb content over this range of weight loadings, which shows that intra-pellet mass-transfer limitations were insignificant. Reported turnover rates and kinetic analyses are taken from experiments using Nb_{1.5}- β .

2.4 Activation of Nb- β with H_2O_2 for XPS Analysis

Nb_{5.0}- β (200 mg) was combined with a mixture of 2.5 cm³ CH_3CN and 2.5 cm³ H_2O_2 (30 wt. % in H_2O) to produce H_2O_2 -activated Nb_{5.0}- β for XPS analysis of the Nb oxidation states. The Nb_{5.0}- β changed from bleached white to pale yellow in color upon addition of the H_2O_2 - CH_3CN mixture. This slurry was then heated to 333 K for 1 h with the intent of reacting all of the Nb

active sites with H_2O_2 in solution. The slurry was then dried under dynamic vacuum (5.3 kPa) at 333 K for 30 minutes followed by static vacuum (0.02 kPa) for 12 hours, which gave the final H_2O_2 -activated $\text{Nb}_{5.0}\text{-}\beta$ material (light yellow solid).

2.5 In Situ UV-Vis and IR Spectroscopy

In situ UV-vis spectroscopy was used to measure the reactivity of the different intermediates for epoxidation on $\text{Nb-}\beta$. $\text{Nb}_{0.3}\text{-}\beta$ samples were pressed into 7 mm diameter self-supporting pellets (~5 mg) and loaded into a custom-built UV-vis liquid flow cell. Reactant and solvent solutions were introduced using a high-performance liquid chromatography (HPLC) pump (Waters, 515), and UV-vis spectra were collected using a 45-degree reflection probe (Avantes, solarization-resistant fibers) attached to an AvaFast fiber-optic spectrometer (Avantes 2048) with a compact deuterium-halogen light source (Avantes, 200 – 1700 nm). The $\text{Nb}_{0.3}\text{-}\beta$ samples were activated by flowing ($1\text{ cm}^3\text{ min}^{-1}$) a solution of H_2O_2 in CH_3CN (0.1 M H_2O_2 , 0.4 M H_2O) over the pellet at 313 K until the absorbance features at ~320 nm were unchanging (~ 15 min). A H_2O_2 -free solution of CH_3CN (0.4 M H_2O) then flowed through the reactor ($1\text{ cm}^3\text{ min}^{-1}$) to remove all liquid-phase and weakly adsorbed H_2O_2 from the system at 313 K. This treatment did not attenuate the UV-vis absorbance features, which shows that the surface species on H_2O_2 -activated $\text{Nb}_{0.3}\text{-}\beta$ were stable at 313 K under pure CH_3CN . The reactivity of the surface intermediates on $\text{Nb}_{0.3}\text{-}\beta$ was measured by continuously acquiring UV-vis spectra (600 msec integration time, co-adding 100 scans per spectrum) while flowing a solution of C_6H_{10} in CH_3CN (0.1 M C_6H_{10} , 0.4 M H_2O), similar to that used for rate measurements in the batch reactor. Reference spectra for all experiments were obtained using a $\text{Nb}_{0.3}\text{-}\beta$ pellet within a flowing CH_3CN solution (0.4 M H_2O) at 313 K. Peak smoothing, background subtraction, and spectral deconvolution were performed in OriginPro® (Section S3.1 for example spectra).

In situ attenuated total reflectance infrared (ATR-IR) spectroscopy was used to characterize the vibrational structure and chemical stability of the intermediates formed upon exposing Nb- β to H₂O₂. Untreated Nb_{1.5}- β was deposited onto a ZnSe cylindrical internal reflection element (IRE, International Crystal Labs) by dip coating. Briefly, 100 mg of Nb_{1.5}- β were suspended in ~10 cm³ of CH₃OH (Macron Chemicals, anhydrous) and the IRE was dipped into the suspension and subsequently dried at ambient temperature to retain the powdered catalyst on the IRE. A series of 10 cycles were typically used to accumulate a thin layer of Nb_{1.5}- β . The catalyst-coated IRE was then loaded into a customized ATR flow cell (Axiom TNL-120) equipped with two liquid inlets and one outlet with a cell volume of 40 μ L. The ATR cell was mounted within the sample compartment of a FTIR spectrometer (Bruker Vertex 70, RapidScan) and liquid streams were introduced at controlled flowrates using two high-pressure piston pumps (SSI Series 1), which were controlled using LabViewTM. Background scans were obtained at steady-state under pure flowing DI H₂O at 333 K after loading the ATR cell. Transient FTIR spectra showing changes upon introducing H₂O₂ were obtained while flowing aqueous H₂O₂ (0.03 M H₂O₂ in DI H₂O, 0.5 cm³ min⁻¹) over the Nb_{1.5}- β coated IRE for 2.5 h at 333 K. Subsequently, a stream of pure DI H₂O was pumped through the cell at 0.5 cm³ min⁻¹ for 1 h. Reported FTIR spectra for these experiments are the average of 1000 scans taken at a resolution of 4 cm⁻¹ and were acquired every 66 seconds. Deconvolution of steady-state FTIR spectra were performed in OriginPro[®] by fixing the centers of the known framework vibrations attributed to the BEA framework of Nb_{1.5}- β (950 cm⁻¹, 1090 cm⁻¹) [43, 46, 47, 56, 57] and fitting the residual absorbance features with Gaussian functions.

Modulation excitation spectroscopy (MES) is a powerful technique, in which a periodic stimulation is applied to the system while acquiring spectra as a function of time. The time

domain response is then converted to a phase domain response, and the spectral changes that occur at the frequency of the applied stimulation are extracted using a phase sensitive detection (PSD) method described by the following equation:

$$A_k(\varphi_k^{\text{PSD}}) = \frac{2}{T} \int_0^T A(t) \sin(k\omega t + \varphi_k^{\text{PSD}}) dt, \quad (1)$$

where $A(t)$ and $A_k(\varphi_k^{\text{PSD}})$ are time- and phase- domain response of the active species respectively, T is the length of a time period, ω is the demodulation index and φ_k^{PSD} is the user defined phase demodulation angle. The application of the MES-PSD technique to FTIR spectra of intermediates on catalytic surfaces greatly increases the signal to noise ratio, suppresses the spectral contributions of static (i.e., spectator) species, and reveals high quality spectra containing contributions only of intermediates that change with respect to our applied stimulus (i.e., changing reactant concentrations) [58].

MES-PSD was used with ATR-IR to confirm that the predominant surface intermediates that form upon exposing $\text{Nb}_{1.5}\text{-}\beta$ to aqueous H_2O_2 solutions (vide supra) are, in fact, active species for the epoxidation of olefins. MES-PSD experiments were performed by sinusoidally modulating the flowrates of two liquid streams (0.065 M H_2O_2 in CH_3CN , and 0.1 M C_6H_{10} in CH_3CN) from 0 to $0.5 \text{ cm}^3 \text{ min}^{-1}$ with a period of 0.5 h (which approximately corresponds to the turnover rate for epoxidation at these conditions), while maintaining a total flowrate of $0.5 \text{ cm}^3 \text{ min}^{-1}$. Spectra (128 scans, 4 cm^{-1}) were acquired every 8.5 sec over 3 h. Flowrates were sinusoidally modulated and controlled on the two piston pumps through use of a LabView program that changes the set point of the pump in a step-wise manner every 0.5 s to approximate a sine wave with the desired frequency. Verification of sinusoidal reactant modulation was done by monitoring and absorbance feature at 1630 cm^{-1} , that is assigned to the ν_2 bending mode of H_2O [59], as a

function of phase angle (Fig. S10) because H₂O was only present in the H₂O₂-containing stream. The recorded time domain spectra were resampled to a single period, and subsequently the spectra of the active species were extracted by PSD using equation 1. Details of the analysis method are described in Section S4.1.

3.1 Spectroscopic Evidence for an Irreversibly Formed Nb-(O₂)⁻ Active Intermediate

Metal-bound oxygen intermediates (i.e., superoxide (M-(O₂)⁻), peroxide (M-(O₂)²⁻), and hydroperoxide (M-OOH)), have been implicated in the epoxidation of olefins (e.g., propylene, cyclohexene, allylic alcohol) on metal-oxide catalysts (e.g., Ta-SBA-15 [21], TS-1 [60, 61], and peroxoniobate ionic liquids [62]). The primary distinction between superoxide and peroxide species is the charge of the -O₂ moiety bound to the metal (i.e., superoxide (-O₂⁻) and peroxide (-O₂)²⁻), and is, therefore, reflected in the oxidation state of the metal center (e.g., Ti^{III}-(O₂)⁻ vs. Ti^{IV}-(O₂)²⁻; or Nb^{IV}-(O₂)⁻ vs. Nb^V-(O₂)²⁻) [63, 64]. Zecchina [65] and Frei [60] used combinations of IR, Raman, and UV-vis spectroscopy to show that reactive Ti^{IV}-(O₂)²⁻ and/or Ti^{IV}-OOH species form by activation of H₂O₂ on TS-1. However, Ratnasamy et al. used in situ electron paramagnetic resonance (EPR) spectroscopy and determined that a paramagnetic Ti-superoxo (Ti^{III}-(O₂)⁻) species is created on TS-1 upon activation of H₂O₂ and is active and selective for the epoxidation of allylic alcohol [66], and the exact identity of the reactive intermediate on TS-1 (specifically the Ti^{IV}-OOH or Ti^{III}-(O₂)⁻) [63, 64, 67, 68] is still debated. Similar types of hydroperoxo, peroxo, and superoxo species (i.e., Nb^V-OOH, Nb^V-(O₂)²⁻, or Nb^{IV}-(O₂)⁻) likely form when H₂O₂ reacts with Nb-β, and the vibrational structure, electronic transitions, and oxidation states, of the reactive complexes may be determined with the combination of FTIR, UV-vis, and x-ray photoelectron spectroscopy.

Figure 3. In situ FTIR spectra obtained upon exposing Nb_{1.5}-β to H₂O₂ (0.03 M H₂O₂ in CH₃CN, 0.5 cm³ min⁻¹, 333 K) showing, a) changes in the infrared spectra of Nb-β upon first contact with flowing H₂O₂, and b) deconvoluted FTIR spectrum obtained at steady-state after flowing H₂O₂ for 2 hr. Vibrational frequencies and peak assignments are given in Table 2.

Table 2. Observed Vibrational Frequencies and Mode Assignments for the Deconvoluted FTIR Spectrum in Figure 3b.

Vibrational Frequency (cm^{-1})	Vibrational Assignment	Parent Species
750	Libration [59]	Water
845	$\nu(\text{O-O})$ [67, 69]	$\text{Nb}^{\text{V}}\text{-OOH/}$ $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}^{2-}$
915	Internal tetrahedral – asymmetric stretch [46]	*BEA Framework
950	$\nu(\text{Si-O-Nb})$ [43, 47]	$\text{Nb-}\beta$
1040	$\nu(\text{O-O})$ [69-71]	$\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}^-$
1090	Internal tetrahedral – asymmetric stretch [46, 47, 56, 57]	*BEA Framework
1230	Internal tetrahedral – asymmetric stretch [46, 47, 56, 57]	*BEA Framework

Figure 3 shows FTIR spectra obtained upon exposing $\text{Nb}_{1.5}\text{-}\beta$ to a flowing solution of H_2O_2 (0.03 M H_2O_2 in CH_3CN , $0.5 \text{ cm}^3 \text{ min}^{-1}$, 333 K). Figure 3a shows that several new absorption features appear (i.e., 1040 cm^{-1} , 845 cm^{-1} , and 915 cm^{-1}), while existing absorption features attenuate (i.e., 950 cm^{-1} , 1090 cm^{-1} , and 1230 cm^{-1}) when $\text{Nb}_{1.5}\text{-}\beta$ contacts H_2O_2 , and Figure 3b shows a representative steady-state FTIR spectrum acquired $\sim 2 \text{ h}$ after initiating the flow of H_2O_2 . The steady-state spectrum (Fig. 3b) is comprised of seven individual components, which are listed in Table 2 along with the corresponding vibrational assignments. The negative absorbance features at 1090 and 1230 cm^{-1} and the positive feature at 915 cm^{-1} are attributed to the quenching and stimulation, respectively, of internal framework tetrahedral Si-O vibrational modes in the *BEA framework [46, 47, 56, 57]. The absorbance feature at 750 cm^{-1} corresponds to the libration band of liquid-phase H_2O [59]. The absorbance peak observed at 845 cm^{-1} closely matches previously reported features at 837 cm^{-1} ($\text{Ti}^{\text{IV}}\text{-OOH/Ti}^{\text{IV}}\text{-(O}_2\text{)}^{2-}$ moieties on TS-1 [60,

68]) and in the range of 850-888 cm^{-1} ($\text{Nb}^{\text{V}}\text{-OOH}$ and $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}^{2-}$) species on niobate ionic liquids [62] and bulk niobia [69], respectively. Consequently, we attribute this feature to $\text{Nb}^{\text{V}}\text{-OOH/Nb}^{\text{V}}\text{-(O}_2\text{)}^{2-}$ intermediate(s). The feature at 1040 cm^{-1} resembles that previously attributed to superoxide (O_2^-) moieties bound to Nb-centers of bulk Nb_2O_5 [69]. The formation of $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}^{2-}$ and $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}^-$ species must occur concomitantly with the cleavage of an Nb-O-Si linkage shown by the formation of the negative feature at 950 cm^{-1} [43]. Additionally, Corma [70] and Wan [71] observed spectral features with similar wavenumber (900 – 1150 cm^{-1}) upon activating O_2 over CeO_2 -based catalysts, which form superoxide species bound to differently coordinated metal cations (e.g., defect sites). Thus, the peak at 1040 cm^{-1} likely corresponds to an $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}^-$ (i.e., Nb-superoxide) intermediate. Finally, all of the spectral features (Table 2) persist when H_2O contacts the IRE (Fig. S11) after activation of H_2O_2 at 333 K, which shows that the $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}^-$ and $\text{Nb}^{\text{V}}\text{-OOH/Nb}^{\text{V}}\text{-(O}_2\text{)}^{2-}$ intermediates form irreversibly and do not spontaneously decompose in the presence of H_2O . This finding is also in agreement with results from DRUV-vis spectroscopy, discussed below, which are used to further identify and test the stability of these intermediates. The isomerization between hydroperoxide, peroxide, and superoxide intermediates has been proposed over TS-1 catalysts [65, 67], which suggests that interconversion between $\text{Nb}^{\text{V}}\text{-OOH}$, $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}^{2-}$, and $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}^-$ species may also occur upon the irreversible activation of H_2O_2 (Scheme 1). For the purpose of brevity, $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}^-$ will be referred to as $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ while $\text{Nb}^{\text{V}}\text{-OOH}$ and $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}^{2-}$ will be collectively referred to as $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}$.

Scheme 1. Activation of H_2O_2 to form $\text{Nb}^{\text{V}}\text{-OOH}$ with the interconversion of $\text{Nb}^{\text{V}}\text{-OOH}$, $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}^{2-}$, and $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}^-$. The oxidation state of each Nb center is depicted beneath the atom.

X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of Nb in both untreated and H_2O_2 -activated (Section 2.4) $\text{Nb}_{5.0}\text{-}\beta$ samples in order to verify the presence of Nb^{IV} species (i.e., $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$). Figure 4a shows the XPS spectra for untreated $\text{Nb}_{5.0}\text{-}\beta$ in the Nb 3d region (200 – 220 eV), which possesses a doublet with absorbance peaks centered at 210.6 and 208.0 eV that correspond to Nb^{V} 3d_{3/2} and 3d_{5/2}, respectively [72, 73] (fitting that demonstrates the absence of Nb^{IV} is provided in the SI, Fig. S7). These features shift to lower binding energies when the $\text{Nb}_{5.0}\text{-}\beta$ sample has been treated with H_2O_2 (details given in section 2.4). Figure 4b shows that XPS spectra of H_2O_2 -activated $\text{Nb}_{5.0}\text{-}\beta$ contains overlapping doublet features with doublets at 210.6 and 208.0 eV as well as at 209.7 and 207.0 eV, which resemble reported values for Nb^{V} and Nb^{IV} species [72], [73], and is consistent with the presence of the proposed $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}$ and $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ species, respectively. Under ultra-high vacuum conditions (i.e., 10^{-9} Torr), the preferred state of the H_2O_2 -activated $\text{Nb-}\beta$ is $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$, because the lack of free protons favors the formation of the superoxo species, as shown for H_2O_2 -activated TS-1 [66], which explains why the magnitude of the features for Nb^{IV} is much larger than for Nb^{V} on H_2O_2 -treated materials.

Figure 4. X-ray photoelectron spectra (black, dashed) of the Nb 3d region with peak fittings (colored, solid) for (a) untreated Nb_{5.0}-β and (b) H₂O₂-treated Nb_{5.0}-β. The peak fittings from the different oxidation states are color-coded for clarity: Nb^{IV} (blue, ▬), Nb^V (orange, ▬), and cumulative peak fit (red, ▬). Spectra are referenced to an aliphatic C 1s feature at 284.8 eV. The H₂O₂ treatment procedure is described in section 2.4.

Figure 5. (a) UV-vis spectra of H_2O_2 -treated $\text{Nb}_{0.3}\text{-}\beta$ in flowing CH_3CN (0.4 M H_2O) at 348 K (—, black), and deconvoluted peaks (dashed) centered at 301 (–, blue) and 365 nm (–, orange); and (b) changes in the normalized coverages of $[\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}]$ (330 nm, $\blacktriangle$) and $[\text{Nb}^{\text{V}}\text{-(O}_2\text{)}]$ (370 nm, $\bullet$) as a function of time after contact with C_6H_{10} in CH_3CN (0.1 M C_6H_{10} , 0.4 M H_2O , $1\text{ cm}^3\text{ min}^{-1}$, closed symbols) or pure DI H_2O ($1\text{ cm}^3\text{ min}^{-1}$, open symbols) at 313 K. Dashed lines are intended to guide the eye.

The surface intermediates (i.e., $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ and $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}$) generated by reacting $\text{Nb}_{0.3}\text{-}\beta$ with H_2O_2 appear as distinct absorption features in in situ DRUV-vis spectroscopy. Figure 5a shows a UV-vis spectrum of H_2O_2 -treated $\text{Nb}_{0.3}\text{-}\beta$ (section 2.5), which contains two distinct absorbance bands at 310 and 355 nm that are assigned to $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ and $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}$ moieties, respectively [67, 69]. Figure 5b shows that the normalized intensities of the $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ (310 nm) and $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}$ (355 nm) features decrease with an exponential dependence on time when the H_2O_2 -treated

Nb_{0.3}-β contacts a flowing solution of C₆H₁₀ in CH₃CN (0.1 M C₆H₁₀, 0.4 M H₂O, 1 cm³ min⁻¹). However, Figure 5b shows also that neither the 310 or 355 nm absorbance feature change noticeably even after one hr of contact with a flowing stream of pure DI H₂O (1 cm³ min⁻¹), which demonstrates further that these intermediates (i.e., Nb^{IV}-(O₂) or Nb^V-(O₂)) form irreversibly. These data, along with steady-state IR spectra obtained under a flow of H₂O (Fig. S11), strongly suggest that Nb-β activates H₂O₂ irreversibly to form both Nb^{IV}-(O₂) and Nb^V-(O₂) intermediates, in contrast to proposed mechanisms on similar Ti- and Ta-based catalysts, where H₂O₂ activation is proposed to occur reversibly (and often in a quasi-equilibrated fashion) [21-23, 39].

Scheme 2. Formation and consumption of active species on Nb-β. Nb^V-(O₂) (Nb^{IV}-OOH shown) and Nb^{IV}-(O₂) form upon reaction of H₂O₂ with Nb-β, and these species interconvert, and may be consumed by reaction with C₆H₁₀.

^aFormation of Nb^V-(O₂) and Nb^{IV}-(O₂) occurs during the activation of H₂O₂ over Nb_{0.3}-β by flow of H₂O₂ in CH₃CN (Section 2.5).

The intensity of these two UV-vis features (Fig. 5a, 310 and 355 nm, normalized by their initial intensities) attenuate with an exponential dependence on time at different rates when

H₂O₂-treated Nb_{0.3}-β contacts a solution of C₆H₁₀ in CH₃CN (0.1 M C₆H₁₀, 0.4 M H₂O, 1 cm³ min⁻¹), and the differences in the rates of consumption of these species reflect the nature of the elementary steps that consume Nb^{IV}-(O₂) and Nb^V-(O₂) (Scheme 2). Nb^{IV}-(O₂) and Nb^V-(O₂) species may be consumed by reaction with C₆H₁₀, but these species may also interconvert during the course of the reaction, as shown in Schemes 1 and 2 [65]. Consequently, the change in coverage of Nb^{IV}-(O₂) and Nb^V-(O₂) depends on the summed rates of formation and consumption of each species, which take the forms of:

$$\frac{d[Nb^{IV}-(O_2)]}{dt} = k_a[Nb^V-(O_2)] - k_b[Nb^{IV}-(O_2)] - k_d[Nb^{IV}-(O_2)][C_6H_{10}] \quad (2)$$

$$\frac{d[Nb^V-(O_2)]}{dt} = k_b[Nb^{IV}-(O_2)] - k_a[Nb^V-(O_2)] - k_c[Nb^V-(O_2)][C_6H_{10}] \quad (3)$$

where [Nb^{IV}-(O₂)] and [Nb^V-(O₂)] represents the coverage of Nb^{IV}-(O₂) and Nb^V-(O₂), [C₆H₁₀] is the concentration of C₆H₁₀, k_a is the rate constant for the interconversion of Nb^V-(O₂) to Nb^{IV}-(O₂), k_b is the rate constant for the interconversion of Nb^{IV}-(O₂) to Nb^V-(O₂), and k_c and k_d are the rate constants for the epoxidation of C₆H₁₀ with Nb^V-(O₂) and Nb^{IV}-(O₂), respectively. Pseudo first-order kinetics are assumed for the reaction of Nb^V-(O₂) and Nb^{IV}-(O₂) with C₆H₁₀, and [C₆H₁₀] is constant because C₆H₁₀ flows continuously through the reactor and conversion of C₆H₁₀ is negligible. MATLABTM is used to numerically solve these two coupled differential equations (equations 2 and 3), while iteratively optimizing the rate constants (i.e., k_i) to fit the experimental data (Section S3.2), and Table 3 shows the optimized rate constants for Scheme 2. The value of k_d is calculated to be ~2·10⁴ times that of k_c, which shows directly that Nb^{IV}-(O₂) is the reactive species that is responsible for all observed epoxidation rates and that this species is more than four orders of magnitude more reactive than the Nb^V-(O₂) species. The consumption of Nb^V-(O₂) is, therefore, attributed to its interconversion to reform additional Nb^{IV}-(O₂)

throughout the course of the reaction (i.e., value of k_b significantly greater than k_a). Collectively, these data show that both $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ and $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}$ are formed upon activation of H_2O_2 , but only $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ participates directly in the epoxidation of C_6H_{10} , while $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}$ simply interconverts to partially replenish $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ during reaction.

Table 3. Numerically optimized rate constants k_i for the interconversion of $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}$ and $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ and reaction with C_6H_{10} (Scheme 2). See Section S3.2 for a complete description of the procedure used to optimize parameters and fit the experimental data.

k_i	Numerically Optimized Value (min^{-1})
k_a	$2.3 \cdot 10^{-4}$
k_b	$2.0 \cdot 10^{-2}$
k_c	$1.3 \cdot 10^{-5}$
k_d	$2.7 \cdot 10^{-1}$

Figure 6. (a) Phase-angle resolved in situ FTIR spectra showing spectral contributions of active surface species for C_6H_{10} epoxidation on $\text{Nb}_{1.5}\beta$, and (b) Normalized $\text{Nb}^{\text{IV}}-(\text{O}_2)^-$ (1024 cm^{-1} , black, -) and C_6H_{10} (864 cm^{-1} , red, -) IR-feature absorbances as a function of phase angle. Spectra were obtained while sinusoidally modulating the flowrates of C_6H_{10} (0.1 M C_6H_{10} in CH_3CN) and H_2O_2 (0.065 H_2O_2 in CH_3CN) solutions (0.5 cm^3 total volumetric flowrate, 333 K, Section 2.5). Lines correspond to FTIR spectra obtained at 30° increments of the demodulation phase angle.

Modulation excitation spectroscopy (MES) experiments were employed to support the conclusion that $\text{Nb}^{\text{IV}}-(\text{O}_2)$ is the active intermediate for the epoxidation of C_6H_{10} . The flow rates H_2O_2 and cyclohexene in CH_3CN (Section 2.5) were modulated sinusoidally with the intent to periodically populate the catalyst surface with the active species (i.e., $\text{Nb}^{\text{IV}}-(\text{O}_2)$ and $\text{Nb}^{\text{V}}-(\text{O}_2)$)

and subsequently consume these species by cyclohexene epoxidation. Figure 6a displays phase domain spectra (obtained by resampling all spectra into a single period, converting to the phase domain, and employing phase sensitive detection, see Section S4.1), that show only the active surface species whose coverages change at frequencies comparable to the modulation (i.e., contributions from spectator species are suppressed). Figure 6 shows a broad feature at 864 cm^{-1} that is assigned to $\nu(\text{C-C})$ of a C_6 ring of either C_6H_{10} or $\text{C}_6\text{H}_{10}\text{O}$ [74]. Notably, this broad 864 cm^{-1} feature is perfectly out of phase (i.e., 180° phase shift) with the absorbance feature corresponding to the active $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ intermediate (1024 cm^{-1} , Fig. 6b), which supports the conclusion that $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ species are consumed by reaction with C_6H_{10} , which is followed by the replacement of $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ with C_6H_{10} or $\text{C}_6\text{H}_{10}\text{O}$ as the MARI on the catalyst surface. Unfortunately, the spectroscopic feature at 845 cm^{-1} attributed to $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}$ (Fig. 3b, $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}$) is overwhelmed by the broad feature at 864 cm^{-1} , which precludes clear analysis of how the coverage of $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}$ species vary with the changes in the concentrations of C_6H_{10} and H_2O_2 . However, the previous analysis of the in situ UV-vis spectra (Figure 5, Table 3) shows already that the $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}$ intermediates do not directly participate in epoxidation reactions. In summary, the combined in situ FTIR and UV-vis data (Figures 3, 5-6) suggest that H_2O_2 -activation over $\text{Nb}_{1.5}\text{-}\beta$ occurs irreversibly and that $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ (and not $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}$) is the active intermediate for C_6H_{10} epoxidation upon activation of H_2O_2 by $\text{Nb-}\beta$.

The conclusion that $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ is the active species for olefin epoxidation is not immediately intuitive, because superoxide species are typically thought to be one electron oxidants (or even reductants) and not two-electron ($2e^-$) oxidants. In order for $\text{Nb-(O}_2\text{)}$ to undergo a $2e^-$ oxidation (e.g., olefin epoxidation), the process must involve concomitant oxidation of the Nb-metal center from Nb^{IV} to Nb^{V} and the reformation of a Nb-O-Si framework bond. Similar processes have

been proposed to occur through a biradical, stepwise reaction on homogeneous vanadium complexes [75, 76], and Nb-(O₂)⁻ superoxide species may react in an analogous manner (Scheme S2). The epoxidation of cis-stilbene provides one method to test this hypothesis and to determine whether the epoxidation reaction proceeds through a concerted reaction or by a stepwise reaction, which would be consistent with the participation of Nb^{IV}-(O₂) as the active intermediate [77]. The reaction of cis-stilbene with Nb_{1.5}-β (0.01 M cis-stilbene, 0.01 M H₂O₂, in CH₃CN, 323 K) produces nearly equimolar quantities of cis- and trans-stilbene oxides (the exact ratio of cis- to trans-stilbene oxide is equal to 0.96). This equimolar ratio suggests that olefin epoxidation over Nb-β occurs through the biradical stepwise mechanism (e.g., Scheme S2), which provides sufficient time for the coordinated olefin intermediate to isomerize about the central C=C bond prior to oxirane cyclization. Collectively, these spectroscopic data and product selectivities provide compelling evidence that H₂O₂ irreversibly activates over Nb-β to form a pool of Nb^V-(O₂) and Nb^{IV}-(O₂) species that interconvert, and that from this pool, Nb^{IV}-(O₂) species participate directly in the epoxidation of olefins by a biradical, stepwise reaction pathway (Scheme S2).

3.2 Dependence of Turnover Rates on Reactant Concentrations and Mechanistic Interpretation

Figure 7. Turnover rates for the formation of $C_6H_{10}O$ as a function of (a) $[C_6H_{10}]$ ($\blacksquare$, 1 mM H_2O_2 , $Nb_{1.5}\beta$, 313 K) and $[C_6H_{10}O]$ ($\bullet$, 3 M C_6H_{10} , 1 mM H_2O_2 , $Nb_{1.5}\beta$, balance CH_3CN to 30 cm^3 , 313 K) and (b) as a function of $[H_2O_2]$ (50 mM C_6H_{10} ($\blacksquare$) or 3 M C_6H_{10} ($\bullet$), $Nb_{1.5}\beta$, 313 K). Error bars omitted for clarity, and lines are intended to guide the eye.

Figure 7a shows turnover rates for the formation of $C_6H_{10}O$ as a function of $[C_6H_{10}]$ (0.01 – 5 M C_6H_{10} , 1 mM H_2O_2 , 313 K) over $Nb_{1.5}\beta$, and Figure 7b shows turnover rates for $C_6H_{10}O$ formation as a function of $[H_2O_2]$ (0.5 – 5 mM H_2O_2 , 0.05 and 3 M C_6H_{10} , 313 K). Rates of epoxidation depend linearly on $[C_6H_{10}]$ and do not change with $[H_2O_2]$ (0.5 – 5 mM, 5 mM C_6H_{10}) at low $[C_6H_{10}]$ (0.01 – 0.1 M C_6H_{10}), which suggests that the active sites are saturated with an H_2O_2 -derived intermediate, such as adsorbed H_2O_2 or $Nb^{IV}-(O_2)/Nb^V-(O_2)$ (section 3.1). Rates of epoxidation become independent of $[C_6H_{10}]$ as $[C_6H_{10}]$ increases further (0.1 – 5 M C_6H_{10}), and this change indicates that the identity of the MARI changes to a C_6H_{10} -derived intermediate (e.g., C_6H_{10} or $C_6H_{10}O$). This is likely due to the increasing amount of C_6H_{10} -

derived species (i.e., C_6H_{10} or $C_6H_{10}O$) occupying additional Nb active sites which decreases the number of sites that exist as the active $Nb^{IV}-(O_2)^-$ species. Additionally, Figure 7b shows the turnover rates become proportional to $[H_2O_2]$ (0.5 – 3 mM) at higher $[C_6H_{10}]$ (3 M), which is consistent with a change in the MARI from an H_2O_2 -derived intermediate to a C_6H_{10} -derived MARI. Figure 7a shows that the rate of epoxidation depends inversely on the $C_6H_{10}O$ concentration (1 – 5 mM) within this same range of $[C_6H_{10}]$ (3 M) and $[H_2O_2]$ (1 mM), which implies that $C_6H_{10}O$ binds strongly to the active site and inhibits rates.

Previously proposed mechanisms for olefin epoxidation on metal-oxide catalysts (i.e., TS-1 [39] and Ta-SBA-15 [21, 22]) assume that steps for the adsorption of the olefin, H_2O_2 , epoxide, and the formation of the reactive intermediate (e.g., $M-OOH$ or $M-(O_2)^-$) are quasi-equilibrated (QE) and that the epoxidation of the olefin by the $M-(O_2)^-$ species is the sole kinetically relevant (KR) step. Such mechanisms give rate expressions (Section S5 contains the rate expressions based on these previous models) that predict epoxide formation rates that do not depend on $[H_2O_2]$ and increase linearly with $[C_6H_{10}]$ at low $[C_6H_{10}]$ (equation S5.6), and that reaction rates become constant with $[C_6H_{10}]$ but proportional to $[H_2O_2]$ at greater $[C_6H_{10}]$ (equation S5.7). The previously described mechanisms and rate expressions for cyclohexene and cyclooctene epoxidation on TS-1 [39] and Ta-SiO₂ [21, 22] are consistent with the rate data shown here (Fig. 7a and 7b) as a function of $[H_2O_2]$ and $[C_6H_{10}]$, but fail to predict the dependence on $[C_6H_{10}O]$. These previous studies did not report changes in rates as a function of the epoxide concentration. Several aspects of the previously proposed mechanisms are inconsistent with the results shown in this article (and perhaps with chemical intuition). The in situ FTIR and UV-vis spectra show that neither the $Nb^{IV}-(O_2)^-$ or the $Nb^V-(O_2)$ species decompose or reform H_2O_2 in the presence of H_2O (Section 3.1), which demonstrate that these intermediates form irreversibly (Scheme 3, step

3) when H_2O_2 reacts with the metal center (e.g., Nb). Notably, these results disagree with previous assumptions that $\text{M}-(\text{O}_2)$ species form on Ti- and Ta-based catalysts by QE processes [21, 22, 39]. Chemical intuition also suggests that H_2O_2 is not likely to reform from the $\text{Nb}^{\text{IV}}-(\text{O}_2)$ and Si-OH groups (created by hydroperoxidolysis of the Nb-O bond) when the sample is hydrated (Scheme 3, reverse step 3), because the formation of H_2O_2 from H_2O and the surface function is most likely endothermic and thermodynamically disfavored under these conditions. Therefore, the mechanism shown below (Scheme 3) differs from previous proposals in a few significant ways.

Scheme 3. Proposed mechanism for cyclohexene epoxidation with H_2O_2 over Nb- β . Subscripts for rate constants or equilibrium constants (k_x or K_x , respectively) denote the number of the elementary step. The proposal for an active $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ intermediate is supported by XPS (Fig. 4) and time-resolved in situ FTIR (Fig. 3 and 6) and UV-vis spectroscopy (Fig. 5).

Scheme 3 depicts our proposed mechanism for the epoxidation of C_6H_{10} with H_2O_2 over Nb- β . This scheme includes quasi-equilibrated adsorption and desorption of C_6H_{10} (step 1), H_2O_2 (step 2), and $\text{C}_6\text{H}_{10}\text{O}$ (step 5), and the irreversible formation of $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ (step 3). The epoxidation of C_6H_{10} (step 4) and the bimolecular decomposition of H_2O_2 (step 6) occur in kinetically relevant, irreversible steps that involve $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ and C_6H_{10} or H_2O_2 co-reactants, respectively. A Langmuir-Hinshelwood mechanism seems unlikely because the average distance between adjacent Nb atoms (2.64 nm [78]) is too large for interaction between adsorbates [79,

80]. Scheme 3 suggests net $C_6H_{10}O$ formation rates (r_E) that depend on the number of $Nb^{IV}-(O_2)$ intermediates and the concentration of C_6H_{10} in solution as:

$$r_E = k_4 [C_6H_{10}] \cdot [Nb^{IV}-(O_2)] \quad (4)$$

where $[Nb^{IV}-(O_2)]$ is the number of $Nb^{IV}-(O_2)$ species and k_4 is the rate constant for the epoxidation of C_6H_{10} with $Nb^{IV}-(O_2)$. Application of the pseudo-steady state hypothesis (PSSH) to the number of $Nb^{IV}-(O_2)$ complexes yields the following rate expression:

$$\frac{r_E}{[L]} = \frac{k_3 k_4 K_2 [C_6H_{10}] \cdot [H_2O_2] \cdot [*]}{(k_4 [C_6H_{10}] + k_6 [H_2O_2])} \quad (5)$$

where k_x and K_x are the rate and equilibrium constants, respectively, for each step x (Scheme 3) and $[*]$ is the number of available Nb-OH moieties (i.e., active sites) that can bind and react with species in solution (or weakly associate with silica near the active site). An expression for $[*]$ is given from the sum of all likely surface intermediates:

$$[L] = ([*] + [C_6H_{10}*] + [H_2O_2*] + [Nb-(O_2)] + [C_6H_{10}O*]) \quad (6)$$

where $[L]$ is the total number of active sites, $[Nb-(O_2)]$ is the pool of $Nb^{IV}-(O_2)$ and $Nb^V-(O_2)$ species, and $[C_6H_{10}*]$, $[H_2O_2*]$, and $[C_6H_{10}O*]$ are the number of adsorbed C_6H_{10} , H_2O_2 , and $C_6H_{10}O$ species, respectively. Equation 6 can then be re-stated in terms of the rate and equilibrium constants as well as the liquid-phase reactant concentrations by application of the PSSH to each specie:

$$[L] = \left([*] + K_1 [C_6H_{10}] \cdot [*] + K_2 [H_2O_2] \cdot [*] + \frac{k_3 K_2 [H_2O_2] \cdot [*]}{(k_4 [C_6H_{10}] + k_6 [H_2O_2])} + K_5 [C_6H_{10}O] \cdot [*] \right) \quad (7)$$

The combination of equations 5 and 7 yield a complete rate expression for C₆H₁₀O formation:

$$\frac{r_E}{[L]} = \frac{k_3 k_4 K_2 [C_6H_{10}] [H_2O_2]}{(k_4 [C_6H_{10}] + k_6 [H_2O_2]) \left(1 + K_1 [C_6H_{10}] + K_2 [H_2O_2] + \frac{k_3 K_2 [H_2O_2]}{(k_4 [C_6H_{10}] + k_6 [H_2O_2])} + K_5 [C_6H_{10}O] \right)} \quad (8)$$

The form of this full rate equation simplifies in the limit when active sites become saturated with H₂O₂-derived intermediates (i.e., Nb^{IV}-(O₂)/Nb^V-(O₂) are the MARI) as is expected in the limit of low [C₆H₁₀]:[H₂O₂] reactant ratios:

$$\frac{r_E}{[L]} = k_4 [C_6H_{10}] \quad (9)$$

Equation 9 is consistent with the C₆H₁₀O formation rates that increase in proportion to [C₆H₁₀] at low [C₆H₁₀] (Figure 7a, 0.01 – 0.1 M C₆H₁₀), and which do not depend on [H₂O₂] (Figure 8b, 0.5 – 5 mM H₂O₂, 5 mM C₆H₁₀). Turnover rates for epoxidation depend inversely on [C₆H₁₀O] at high [C₆H₁₀], because adsorbed C₆H₁₀O becomes the MARI at values of [C₆H₁₀] greater than 0.5 M. Intuitively, C₆H₁₀O becomes the MARI at high [C₆H₁₀] only when small amounts of epoxide (present as a reagent contaminant, or upon initial formation of C₆H₁₀O) are present. In this limit, equation 8 simplifies to:

$$\frac{r_E}{[L]} = \frac{k_3 k_4 K_2 [C_6H_{10}] [H_2O_2]}{(k_4 [C_6H_{10}] + k_6 [H_2O_2]) [C_6H_{10}O]} \quad (10)$$

The denominator in equation 10 shows that the rate of epoxidation when adsorbed C₆H₁₀O is the MARI depends on the propensity of Nb-(O₂)⁻ to epoxidize C₆H₁₀ ($k_4 [C_6H_{10}]$) relative to decompose by reaction with H₂O₂ ($k_6 [H_2O_2]$).

3.3 Mechanistic Interpretation for H₂O₂ Decomposition over Nb-β

Control experiments show that in the absence of Nb-β, no H₂O₂ decomposition is observed after 4 h at 333 K (data not shown). Values of [H₂O₂], however, decrease steadily with time when H₂O₂ contacts Nb-β. The unimolecular decomposition of H₂O₂ via a Nb^{IV}-(O₂) intermediate cannot account for H₂O₂ consumption, because FTIR (Fig. S11) and UV-vis spectra (Fig. 5b) show that the Nb^{IV}-(O₂) species are stable over multiple hours when they are isolated from liquid-phase C₆H₁₀ and H₂O₂. Therefore, H₂O₂ decomposition likely occurs through a bimolecular reaction between Nb^{IV}-(O₂) and a liquid-phase H₂O₂ molecule [22]. The rate of this reaction follows the form:

$$r_D = k_6 [H_2O_2] \cdot [Nb^{IV} - (O_2)] \quad (11)$$

where r_D is the rate of H₂O₂ consumption via decomposition over Nb-β and k_6 is the rate constant for the bimolecular reaction between Nb^{IV}-(O₂) and a H₂O₂ molecule in solution. The expression for total H₂O₂ consumption is obtained from the sum of equations 4 and 11 to yield:

$$r_{H_2O_2} = k_4 [C_6H_{10}] \cdot [Nb^{IV} - (O_2)] + k_6 [H_2O_2] \cdot [Nb^{IV} - (O_2)] \quad (12)$$

where $r_{H_2O_2}$ is the rate of total H₂O₂ consumption through epoxidation and decomposition processes. Application of the PSSH to Nb^{IV}-(O₂) (Section 3.2, algebraic manipulation omitted) allows equation 12 to be restated in terms of liquid concentrations as:

$$\frac{r_{H_2O_2}}{[L]} = \frac{k_3 K_2 [H_2O_2]}{\left(1 + K_1 [C_6H_{10}] + K_2 [H_2O_2] + \frac{k_3 K_2 [H_2O_2]}{(k_4 [C_6H_{10}] + k_6 [H_2O_2])} + K_5 [C_6H_{10}O] \right)} \quad (13)$$

Equation 13 shows that the rate of H_2O_2 consumption depends only on the rate of C_6H_{10} epoxidation ($k_4[C_6H_{10}]$) or H_2O_2 decomposition ($k_6[H_2O_2]$) when surfaces are saturated with $Nb^{IV}-(O_2)$. For all other identities of the MARI, H_2O_2 consumption is controlled by the rate of H_2O_2 activation at the reactive Nb-centers. This shows that the H_2O_2 selectivity for epoxidation can be controlled by reaction at conditions which solely maximize the turnover rate for $C_6H_{10}O$ formation.

3.4 H_2O_2 Selectivity for Epoxidation and Mechanistic Implications

The selective use of H_2O_2 for epoxidations is a necessary economic consideration before a catalyst can be adapted for industrial epoxidation chemistries, and consequently requires the ratio of the rates for epoxidation to H_2O_2 consumption (i.e., $r_E/r_{H_2O_2}$) to approach unity (i.e., 100% selectivity). From the combination of equations 8 and 13, the ratio of the rate of $C_6H_{10}O$ formation to that for H_2O_2 consumption (Fig. S12) yields the following expression:

$$\alpha = \frac{r_E}{r_{H_2O_2}} = \frac{k_4[C_6H_{10}]}{k_4[C_6H_{10}] + k_6[H_2O_2]} \quad (14)$$

Equation 14 may be linearized, with respect to inverse $[C_6H_{10}]$, by taking the inverse of α to give:

$$\alpha^{-1} = \frac{r_{H_2O_2}}{r_E} = 1 + \frac{k_6[H_2O_2]}{k_4[C_6H_{10}]} \quad (15)$$

Figure 8. Ratio of total H_2O_2 consumption to $C_6H_{10}O$ formation as a function of inverse C_6H_{10} concentration on $Nb_{1.5}\beta$ (1 mM H_2O_2 , 313 K). Dashed line represents linear fit to equation 15 with an r^2 of 0.995.

Figure 8 shows values of α^{-1} as a function of inverse $[C_6H_{10}]$ (1 mM $[H_2O_2]$, 313 K). The value of the slope (found to be 0.25) shows that $k_4[C_6H_{10}] \gg k_6[H_2O_2]$ at high $[C_6H_{10}]$ (1 – 5 M), which indicates that in the limit of high $[C_6H_{10}]:[H_2O_2]$, equation 10 can be approximated as follows:

$$\frac{r_E}{[L]} = \frac{k_3 K_2 [H_2O_2]}{[C_6H_{10}O]} \quad (16)$$

which qualitatively agrees with the trends observed in Figures 7a (i.e., $r_E \sim [C_6H_{10}]^0 \cdot [C_6H_{10}O]^{-1}$) and 7b ($r_E \sim [H_2O_2]^1$) when $[C_6H_{10}]:[H_2O_2]$ reactant ratios are large. Overall, the proposed mechanism (Scheme 3) agrees with the spectroscopic observations in Figures 3-6 and the rate data presented in Figures 7 and 8.

3.5 Epoxidation and Decomposition Activation Enthalpies ($\Delta H^\ddagger$) and Entropies ($\Delta S^\ddagger$)

Transition-state theory (TST) provides a theoretical foundation to relate the stability of a reference state (e.g., the most abundant reactive intermediate) to an activated complex that facilitates the reaction (i.e., the transition state) [4, 81]. Here, the values of apparent activation enthalpies ($\Delta H^\ddagger$) and entropies ($\Delta S^\ddagger$) can be used to compare the relative stability of the transition states that selectively activate H_2O_2 and epoxidize an olefin to those that facilitate non-selective H_2O_2 decomposition. TST, in conjunction with our proposed mechanism (Scheme 3), proposes that the reactant species (e.g., $\text{Nb}^{\text{IV}}-(\text{O}_2)$ and C_6H_{10}) exist in equilibrium with the transition state (i.e., $\text{Nb}^{\text{IV}}-(\text{O}_2)-\text{C}_6\text{H}_{10}^\ddagger$) for the elementary step for epoxidation (i.e., Scheme 3, step 4) [54].

Scheme 4. Thermochemical cycle depicting changes in free energy in the reaction sequence shown in Scheme 3, which forms transition states for epoxide formation and H_2O_2 decomposition through reaction with $\text{Nb}^{\text{IV}}-(\text{O}_2)$.

The combined equilibria are expressed as:

where $K_E^\ddagger$ and $K_D^\ddagger$ are the transition state equilibrium constants for $C_6H_{10}O$ formation and H_2O_2 decomposition, respectively. Expression of the rate of epoxidation and H_2O_2 decomposition in terms of the number of transition states (i.e., $[Nb^{IV}-(O_2)-C_6H_{10}^\ddagger]$ or $[Nb^{IV}-(O_2)-H_2O_2^\ddagger]$), yields:

$$\frac{r_E}{[L]} = \frac{k_B T}{h} [Nb^{IV}-(O_2)-C_6H_{10}^\ddagger] \quad (19)$$

$$\frac{r_D}{[L]} = \frac{k_B T}{h} [Nb^{IV}-(O_2)-H_2O_2^\ddagger] \quad (20)$$

where T is the temperature in Kelvin, and k_B and h are Boltzmann's and Planck's constant, respectively. When the rates of reaction are measured on $Nb^{IV}-(O_2)/Nb^V-(O_2)$ saturated surfaces, the equations 19 and 20 may be expressed in terms of reactant concentrations and transition-state equilibrium constants:

$$\frac{r_E}{[L]} = \frac{k_B T}{h} K_E^\ddagger [C_6H_{10}] \quad (21)$$

$$\frac{r_D}{[L]} = \frac{k_B T}{h} K_D^\ddagger [H_2O_2] \quad (22)$$

which allows the values of $K_E^\ddagger$ and $K_D^\ddagger$ to be determined by measuring the turnover rates for each reaction pathway at a given temperature. Values of $K_x^\ddagger$ may be expressed in terms of the

apparent free energy change of activation ($\Delta G^\ddagger$), and subsequently $\Delta H^\ddagger$ and $\Delta S^\ddagger$ (from the relationship $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$):

$$K_x^\ddagger = e^{-\Delta G_x^\ddagger / RT} = e^{-\Delta H_x^\ddagger / RT} e^{\Delta S_x^\ddagger / R} \quad (23)$$

where R is the ideal gas constant and the subscript x indicates that the associated variable corresponds to the formation of product x (i.e., epoxidation (E) for $C_6H_{10}O$ and decomposition (D) for H_2O). Figure S13 shows measured values for $K_E^\ddagger$ and $K_D^\ddagger$ as functions of inverse temperature, which are used to determine experimental values for $\Delta H_E^\ddagger$, $\Delta H_D^\ddagger$, $\Delta S_E^\ddagger$, and $\Delta S_D^\ddagger$ by combining equations 21-23.

Table 4. Catalyst Activation Enthalpies and Entropies for C_6H_{10} Epoxidation and H_2O_2 Decomposition on a $Nb^{IV}-(O_2)/Nb^V-(O_2)$ Covered Surface.^a

Catalyst	$\Delta H_E^\ddagger$ (kJ mol ⁻¹)	$\Delta S_E^\ddagger$ (J mol ⁻¹ K ⁻¹)	$\Delta H_D^\ddagger$ (kJ mol ⁻¹)	$\Delta S_D^\ddagger$ (J mol ⁻¹ K ⁻¹)
Nb _{1.5} -BEA	72 ± 3	-35 ± 21	45 ± 2	-91 ± 30

^aActivation enthalpies and entropies were calculated from measured transition-state equilibrium constants ($K^\ddagger$, Figure S13) and equation 23. Error in activation enthalpies and entropies was estimated by the linear regression analysis performed to fit the Eyring equation to the data in Fig. S13.

Table 4 shows values of $\Delta H_E^\ddagger$, $\Delta H_D^\ddagger$, $\Delta S_E^\ddagger$, and $\Delta S_D^\ddagger$ for Nb- β calculated from $K_E^\ddagger$ and $K_D^\ddagger$ (Fig. S13, equations 21 and 22). $\Delta H^\ddagger$ values for epoxidation (72 kJ mol⁻¹) are 27 kJ mol⁻¹ higher than for H_2O_2 decomposition (45 kJ mol⁻¹), which show that decomposition of H_2O_2 is enthalpically favored to that of C_6H_{10} epoxidation. Alternatively, $\Delta S^\ddagger$ values for H_2O_2 decomposition (-91 J mol⁻¹ K⁻¹) are significantly more negative than for C_6H_{10} epoxidation (-35 J

mol⁻¹ K⁻¹), which makes epoxidation entropically favored in comparison to H₂O₂ decomposition. Interestingly, epoxidation is entropically favored over H₂O₂ decomposition, which suggests H₂O₂ selectivity is maximized by running the reaction at higher temperatures. This finding is not immediately intuitive as H₂O₂ and H₂O₂-derived intermediates are generally thought to decompose rapidly (in comparison to many other species) at elevated temperatures. Besides the non-intuitive differences in $\Delta H^\ddagger$, the selectivities for H₂O₂ to epoxidize C₆H₁₀ reflect the ratio of the concentrations of the co-reactants (i.e., H₂O₂ or C₆H₁₀) for these bimolecular pathways, because the fate of the Nb^{IV}-(O₂) depends on the likelihood that this reactive intermediate first encounter liquid-phase C₆H₁₀ or H₂O₂.

4.0 Conclusions

Ex situ XPS and in situ UV-vis and FTIR spectra reveal two types of metal-bound oxygen species (i.e., $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ and $\text{Nb}^{\text{V}}\text{-(O}_2\text{)}$) that form upon the irreversible activation of H_2O_2 over Nb- β . Time-resolved UV-vis spectra acquired in situ reveal that $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$ (i.e., superoxide) species is responsible for olefin epoxidation, which is further confirmed by the isomeric distribution (cis:trans ~ 1) of the epoxide products from reaction with cis-stilbene. Collectively, these data, when combined with the observed dependencies of reaction rates on C_6H_{10} , H_2O_2 , and $\text{C}_6\text{H}_{10}\text{O}$ provide a complete mechanistic understanding of olefin epoxidation over Nb- β that is consistent with an Eley-Rideal mechanism and indicate that the reactive form of oxygen (i.e., $\text{Nb}^{\text{IV}}\text{-(O}_2\text{)}$) forms irreversibly under reaction conditions. Additionally, this mechanism also accurately describes the dependence of epoxidation rates on reactant concentrations observed in previous studies on similar Ti- and Ta-based catalysts, which had assumed the quasi-equilibrated formation of the reactive intermediate. Calculated values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for $\text{C}_6\text{H}_{10}\text{O}$ formation and H_2O_2 decomposition demonstrate that epoxide formation is enthalpically disfavored, which suggests that H_2O_2 selectivity towards epoxidation is maximized at higher temperatures. Overall, these results can aid in the rational design of increasingly selective catalysts for olefin epoxidation with H_2O_2 and provide methods to probe other metals to observe possible periodic trends in reactivity. Ongoing investigations in our group extend this mechanistic understanding of olefin epoxidation over M- β catalysts to the rational design of increasingly selective and active catalysts by probing periodic trends and the importance of the elemental identity of the substituted metal atom.

5.0 Supporting Information

Additional catalyst characterization (p-XRD, DRUV-vis, solid-state NMR), Madon-Boudart criterion, detection of metal-bound oxygen species (in situ DRUV-vis and FTIR), MES-PSD data analysis derivation, derivation of previously proposed epoxidation and H₂O₂-decomposition mechanisms, H₂O₂ selectivity data, temperature-dependence data

6.0 Acknowledgements

The authors acknowledge Ms. Megan Witzke and Mr. Neil Wilson for insightful discussions, feedback, and proofreading of the manuscript. We thank Dr. Damien Guironnet (UIUC) for use of equipment used in part for the synthesis of Nb- β , the preparation of H₂O₂-activated Nb- β , and ATR-IR for Nb- β and Si- β measurements. We thank Dr. Andre Sutrisno and the School of Chemical Sciences NMR lab for acquisition of the ¹H and ²⁹Si solid-state NMR spectra on Nb- β . We thank Dr. Rick Haasch for acquisition of the XPS spectra on Nb- β materials. This work was carried out in part in the Frederick Seitz Materials Research Laboratory Central Research Facilities, University of Illinois. DTB was supported in part by the National Defense Science and Engineering Graduate (NDSEG) Fellowship. This material is based upon work supported in part by, the U. S. Army Research Laboratory and the U. S. Army Research Office under grant number W911NF-16-1-0128, and upon work supported by the National Science Foundation grant number CBET-1553137.

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