Supporting Information

Consequences of Confinement for Alkene Epoxidation with Hydrogen Peroxide on Highly Dispersed Group 4 and 5 Metal Oxide Catalysts

Daniel T. Bregante,¹ Nicholas E. Thornburg,² Justin M. Notestein,² and David W. Flaherty¹,*

¹Department of Chemical and Biomolecular Engineering
University of Illinois Urbana-Champaign, Urbana, IL 61801

²Department of Chemical and Biological Engineering
Northwestern University, Evanston, IL 60208

*Corresponding Author
Phone: (217) 244-2816
Email: dwflahrty@illinois.edu
S1.0 Additional Catalyst Characterization and Verification of Measuring True Kinetics

S1.1 Catalyst Characterization

Figure S1. X-ray diffractograms for Ti- (blue), Nb- (black), and Ta-BEA (orange) taken on a Siemens/Bruker D5000 X-ray diffractometer with Cu Kα radiation (0.15418 nm) at ambient conditions. Reproduced from ref [1]. Copyright 2017 American Chemical Society.
Figure S2. Diffuse reflectance UV-vis spectra for (a) M-BEA (solid lines) and (b) M-SiO$_2$ (dashed lines) catalysts. Colors represent: Ti (blue), Nb (black) and Ta (orange). (a) is reproduced with permissions from ref [1]. Copyright 2017 American Chemical Society.
Figure S3. IR absorbance intensities for the Lewis-acid bound pyridine (≈1450 cm\(^{-1}\) absorbance feature; Figure 1) on Ti-BEA (blue ▼, 1445 cm\(^{-1}\)), Nb-BEA (black ■, 1447 cm\(^{-1}\)), Ta-BEA (orange ◆, 1448 cm\(^{-1}\)), Ti-SiO\(_2\) (blue open ▼, 1445 cm\(^{-1}\)), Nb-SiO\(_2\) (black open ■, 1448 cm\(^{-1}\)), and Ta-SiO\(_2\) (orange open ◆, 1449 cm\(^{-1}\)) as a function of inverse temperature (0.1 kPa pyridine, 101 kPa He, 50 cm\(^3\) min\(^{-1}\)) after background subtraction. Dashed lines represent linear fits, where the slopes are proportional to the value of ΔH\(_{Py}\).
Figure S4. Styrene (C₈H₈) uptake (per gram of Si-BEA or SiO₂) into Si-BEA (solid symbols) and SiO₂ (open symbols) as a (a) function of [C₈H₈] (in CH₃CN, 313 K) and (b) inverse temperature (0.03 mM C₈H₈ for Si-BEA and 0.007 mM C₈H₈ for SiO₂ in CH₃CN). Dashed lines in Figure S4a are intended to guide the eye, while those in Figure S4b are linear fits where the slopes are proportional to ΔH_{Ads}.

Figure S4a shows two distinct regimes of C₈H₈ uptake into purely siliceous materials (i.e., Si-BEA and SiO₂), where at low [C₈H₈], uptake is proportional to the concentration of [C₈H₈] in the bulk solution and approaches a saturation value at relatively high [C₈H₈] (e.g., >0.03 mM for SiO₂). Adsorption enthalpies for C₈H₈ within a solution of CH₃CN (i.e., the solvent used for epoxidation in this study) are measured by van’t Hoff analysis (Figure S4b) for the uptake of C₈H₈ into these materials. The uptake or C₈H₈ must be measured under the linear regime for C₈H₈ uptake (i.e., low [C₈H₈]) as a function of [C₈H₈] to avoid any artifacts that arise from saturation of the micropores of *BEA or mesopores of SiO₂.
S1.2 Methylphosphonic Acid Titrations to Determine Fraction of Active Metal in M-BEA Catalysts

Figure S5. Turnover rates for \( \text{C}_6\text{H}_{10}\text{O} \) formation as a function of methylphosphonic acid-to-metal ratio ([MPA]:[M]; 0.01 M \( \text{C}_6\text{H}_{10} \), 0.01 M \( \text{H}_2\text{O}_2 \), 313 K) for (a) Ti-BEA, (b) Nb-BEA, and (c) Ta-BEA. Dashed lines represent linear regression fits with the y-intercept set to the turnover rate in the absence of the MPA titrant.

M-BEA was stirred with cyclohexene (0.01 M), benzene (an internal standard), CH₃CN (solvent), and an appropriate amount of methylphosphonic acid (MPA) at 313 K for 30 min with the intent of irreversibly adsorbing MPA to the active metal atoms. Epoxidations were initiated by the introduction of \( \text{H}_2\text{O}_2 \), and cyclohexene oxide (\( \text{C}_6\text{H}_{10}\text{O} \)) formation rates were determined using a gas chromatograph and analyzing extracted aliquots of the reaction mixture as a function of time. Figure S5 shows that turnover rates on M-BEA (M = Ti, Nb, and Ta) decrease linearly with the ratio of MPA:M, which suggests that the MPA selectively titrates the active sites for epoxidation. The extrapolation of these data to the point where turnover rates approach zero gives the fraction of metal atoms that are active for epoxidation.²
S.1.3 Control Experiments to Test Importance of Mass Transfer

**Figure S6.** Turnover rates for the formation of C₆H₁₀ measured as a function of [C₆H₁₀] on Ti-BEA (blue solid ▼, 0.22 mmol Ti g⁻¹; 0.01 M H₂O₂, 313 K) and Ti-BEA (blue open ▼, 0.02 mmol Ti g⁻¹; 0.01 M H₂O₂, 313 K). Dashed line is intended to guide the eye.

Figure S5 shows rates for the formation of styrene oxide (C₈H₈O) via primary reaction pathways measured as a function of C₈H₈ concentration for multiple metal loadings of Ti (0.22 mmol g⁻¹ and 0.02 mmol g⁻¹) in Ti-BEA. The rate of C₈H₈O formation is invariant with metal loading, which indicates that the Madon-Boudart criterion is satisfied for Ti-BEA.³ Under the conditions tested, we see that the turnover rate for C₈H₈O formation is proportional to [C₈H₈] and independent of [H₂O₂], which corresponds to a simplified rate expression (Section 3.3 of main text) of:

\[
\frac{r_E}{[L]} = k_4[C_8H_8]
\]

(S1)

where \( r_E \) is the rate of C₆H₁₀O formation, [L] is the total number of metal atoms in the reactor, \( k_4 \) is the rate constant for step 4 of scheme 2, and [C₈H₈] is the concentration of C₈H₈. For a first-order reaction (such as in equation S1), an effective Thiele modulus for a spherical pellet³ can be defined as:

\[
\phi = \left(\frac{k_4 R^2 [C_8H_8]}{D_e}\right)^{1/2}
\]

(S2)

where \( \phi \) is the Thiele modulus, \( R \) is the radius of the spherical pellet, [C₈H₈] is the bulk concentration of C₈H₈, and \( D_e \) is the effective diffusivity of C₈H₈ through the spherical pellet. The Madon-Boudart criterion is an experimental way to determine the relative value of the Thiele
modulus, where the independence of turnover rates on metal loading signifies a relatively small Thiele modulus (i.e., $\phi \ll 1$). When the Thiele modulus is small, the rates of diffusion are much greater than those for the inherent kinetics of the reaction (at reactant concentrations equal to that in the bulk fluid phase), which shows that the measured reaction rates are not convoluted by diffusion restrictions within the catalyst particles.

In Figure 5 (main text), C$_8$H$_8$ formation rates are highest for Ti-BEA (of all M-BEA and M-SiO$_2$) under these conditions. Therefore all other M-BEA and M-SiO$_2$ give values of $k_3$ that are much smaller than for Ti-BEA, which suggests that Thiele moduli on these materials are even smaller than that for Ti-BEA. Additionally, M-SiO$_2$ catalysts possess nominal pore diameters of 5.4 nm, which are significantly larger than those in M-BEA (~0.7 nm). This increases the effective diffusivity of C$_8$H$_8$ in M-SiO$_2$ materials relative to M-BEA and decreases the Thiele moduli further. Therefore, satisfaction of the Madon-Boudart criterion for Ti-BEA suggests that the other M-BEA and M-SiO$_2$ are also not mass-transfer limited and all measured reaction rates are reflective of only chemical kinetics.
S1.4 X-ray Photoelectron Spectroscopy of Untreated and H$_2$O$_2$-Treated M-BEA and M-SiO$_2$

**Figure S7.** X-ray photoelectron spectra (gray, bold) of the (a) Ti 2$p$, (b) Nb 3$d$, and (c) Ta 4$d$ regions from untreated and H$_2$O$_2$-treated (Section 2.2) Ti-, Nb-, and Ta- BEA and SiO$_2$. The peak fittings from the different oxidation states are color coded (blue and orange dashed curves) for clarity with the cumulative peak fit in red (solid). Table S1 contains peak center values and corresponding metal oxidation states. Spectra are references to an aliphatic C 1$s$ feature at 284.8 eV. Nb-BEA data is adapted from ref [6].

Figure S7 shows X-ray photoelectron spectra that reveal the oxidation states of Ti, Nb, and Ta atoms in both untreated and H$_2$O$_2$-treated M-BEA and M-SiO$_2$. Untreated Ti-, Nb-, and Ta-materials possess doublet features that correspond to Ti$^{4+}$ (Ti 2$p_{1/2}$ and Ti 2$p_{3/2}$),$^{4,5}$ Nb$^{5+}$ (Nb 3$d_{3/2}$ and Nb 3$d_{5/2}$),$^{6,7}$ and Ta$^{5+}$ (Ta 4$d_{3/2}$ and Ta 4$d_{5/2}$)$^8$ species, respectively, both in the *BEA framework and grafted onto SiO$_2$. Table S1 summarizes the position of the peak centers and corresponding oxidation states. In the case of Ti-BEA and Ti-SiO$_2$, treatment with H$_2$O$_2$ creates two additional features with peak binding energies that are ~0.3 eV lower than those of the untreated Ti-BEA and Ti-SiO$_2$ materials. The red shift of ~0.3 eV indicates that a fraction of the Ti atoms are coordinated to electron rich substituents, such as for Ti-(η$^2$-O$_2$) and Ti-OOH, after treatment with H$_2$O$_2$. Notably, these shifts are not large enough, however, to suggest a full formal oxidation state change from Ti$^{4+}$ to Ti$^{3+}$. Nb and Ta materials show overlapping features with significant shifts (~1 eV) in electron binding energies that may indicate a fraction of the metal cations reduce from a +5 to +4 oxidation state upon reaction with H$_2$O$_2$, which may be due to the Haber-Weiss decomposition of M-OOH species to produce reduced metal centers, or result from X-ray induced photoreduction of Nb and Ta metal centers.$^{10}$
Table S1. Photoelectron Binding Energies (BE) and Corresponding Oxidation States of Metal Atoms in Untreated and H$_2$O$_2$-Activated M-BEA and M-SiO$_2$, as Determined by X-ray Photoelectron Spectroscopy.$^a$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Untreated Samples BE (eV)</th>
<th>Untreated Samples Oxidation States</th>
<th>H$_2$O$_2$-activated Samples BE (eV)</th>
<th>H$_2$O$_2$-activated Samples Oxidation State(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-BEA</td>
<td>464.7, 459.0</td>
<td>+4$^b$</td>
<td>464.7, 459.0</td>
<td>+4$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>464.3, 458.5</td>
<td></td>
</tr>
<tr>
<td>Nb-BEA</td>
<td>210.6, 208.0</td>
<td>+5$^c$</td>
<td>210.6, 208.0</td>
<td>+5$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>209.7, 207.0</td>
<td>+4$^c$</td>
</tr>
<tr>
<td>Ta-BEA</td>
<td>243.0, 231.3</td>
<td>+5$^d$</td>
<td>243.4, 231.0</td>
<td>+5$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>241.1, 229.7</td>
<td>+4$^d$</td>
</tr>
<tr>
<td>Ti-SiO$_2$</td>
<td>464.6, 458.9</td>
<td>+4$^b$</td>
<td>464.6, 458.9</td>
<td>+4$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>464.4, 458.6</td>
<td>+4$^b$</td>
</tr>
<tr>
<td>Nb-SiO$_2$</td>
<td>211.1, 208.3</td>
<td>+5$^c$</td>
<td>211.1, 208.3</td>
<td>+5$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>209.9, 207.1</td>
<td>+4$^c$</td>
</tr>
<tr>
<td>Ta-SiO$_2$</td>
<td>243.0, 231.6</td>
<td>+5$^d$</td>
<td>241.8, 231.1</td>
<td>+5$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>240.6, 229.8</td>
<td>+4$^d$</td>
</tr>
</tbody>
</table>

$^a$See Figure S7 for XP spectra; $^b$Refs [3, 4]; $^c$Refs [5, 6]; $^d$Ref [7]
S2. Identification of Active Intermediates via *In Situ* UV-Visible and Raman Spectroscopy

S2.1 Sample Raw UV-Vis Spectrum and Method for Processing Spectra

![UV-vis absorbance spectrum](image)

Figure S8. UV-vis absorbance spectrum (raw data, gray) of H$_2$O$_2$-treated (a) Ti-BEA, (b) Nb-BEA, (c) Ta-BEA, (d) Ti-SiO$_2$, (e) Nb-SiO$_2$, and (f) Ta-SiO$_2$ at 313 K in flowing CH$_3$CN (0.4 M H$_2$O) and smoothed data (bold black line) using a finite fourier transform (20 points of smoothing). Dashed curves represent peak fittings using a Gaussian function.
S2.2 Values of Ligand to Metal Charge Transfer Energies for H$_2$O$_2$-activated M-BEA and M-SiO$_2$

Table S2. Ligand to Metal Charge Transfer Energies ($h\nu$) for the M-OOH and M-(η$^2$-O$_2$) Intermediates as Detected via In Situ UV-vis Spectra (Figure 2).

<table>
<thead>
<tr>
<th>Material</th>
<th>LMCT $h\nu$ (eV) for M-OOH</th>
<th>LMCT $h\nu$ (eV) for M-(η$^2$-O$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-BEA</td>
<td>2.95</td>
<td>3.25</td>
</tr>
<tr>
<td>Nb-BEA</td>
<td>3.48</td>
<td>3.99</td>
</tr>
<tr>
<td>Ta-BEA</td>
<td>4.21</td>
<td>4.54</td>
</tr>
<tr>
<td>Ti-SiO$_2$</td>
<td>2.81</td>
<td>3.25</td>
</tr>
<tr>
<td>Nb-SiO$_2$</td>
<td>3.36</td>
<td>3.65</td>
</tr>
<tr>
<td>Ta-SiO$_2$</td>
<td>4.11</td>
<td>4.38</td>
</tr>
</tbody>
</table>
S2.3 Time-Resolved *In Situ* UV-Vis Spectroscopy and Kinetic Parameter Optimization

Scheme 1 (copied from main text). Consumption and interconversion of M-OOH and M-(η²-O₂) species upon reaction with C₆H₁₀ on group 4 metals.
Figure 2 (copied from main text). UV-vis spectra of H$_2$O$_2$-activated M-SiO$_2$ (top) and M-BEA (bottom) materials. Spectra were acquired in situ in flowing H$_2$O$_2$ in CH$_3$CN (0.1 M H$_2$O$_2$, 0.4 M H$_2$O, 1 cm$^3$ min$^{-1}$) at 313 K. Different colors indicate: Ta (orange), Nb (black), and Ti (blue), and dashed lines represent deconvoluted Gaussian peaks for M-(η$^2$-O$_2$) and M-OOH species.
Figure 3 (copied from main text). UV-vis spectra of H$_2$O$_2$-activated (a) Ti-BEA, (b), Nb-BEA, and (c) Ta-BEA. Spectra were acquired in situ in flowing H$_2$O$_2$ in CH$_3$CN (0.1 M H$_2$O$_2$, 0.4 M H$_2$O, 1 cm$^3$ min$^{-1}$; black), with HCl (0.01 M HCl, 0.1 M H$_2$O$_2$, 0.4 M H$_2$O, 1 cm$^3$ min$^{-1}$; red) or NH$_4$OH (0.01 M NH$_4$OH, 0.1 M H$_2$O$_2$, 0.4 M H$_2$O, 1 cm$^3$ min$^{-1}$; green) at 313 K. Dashed lines represent Gaussian peak fits for M-(η$^2$-O$_2$) and M-OOH species.

The change in surface coverage of the M-OOH and M-(η$^2$-O$_2$) species depends on the summed rates of formation/consumption through interconversion and consumption by reaction with C$_6$H$_{10}$, which take the forms of:

\[
\frac{d[M - (\eta^2 - O_2)]}{dt} = k_{-I}[M - OOH] - k_I[M - (\eta^2 - O_2)] - k_{oI}[M - (\eta^2 - O_2)][C_6H_{10}] \\
\frac{d[M - OOH]}{dt} = k_I[M - (\eta^2 - O_2)] - k_{-I}[M - OOH] - k_{OOH}[M - OOH][C_6H_{10}] 
\]

where [M-OOH] and [M-(η$^2$-O$_2$)] represent the coverages (assumed to be proportional to UV-vis absorbance feature intensities) of M-OOH and M-(η$^2$-O$_2$), respectively, and $k_x$ is the rate constant for step x in scheme 1. Pseudo first-order kinetics are assumed for the reaction between M-(O$_2$) intermediates and C$_6$H$_{10}$, as throughout the experiment the ratio of [C$_6$H$_{10}$] to number of metal atoms exceeds 10$^5$ in all cases. Similarly, pseudo first-order kinetics are assumed for the interconversion (via protonation or deprotonation) of M-OOH and M-(η$^2$-O$_2$), as this process is likely mediated by nearby H$_2$O molecules (where [H$_2$O] was kept constant at 0.4 M).

The equilibrium coefficient ($K_I$) for the interconversion between M-OOH and M-(η$^2$-O$_2$) must be determined to constrain the ratio of $k_I$ to $k_{-I}$ and is defined as

\[
K_I = \frac{k_I}{k_{-I}} = \frac{[M - OOH]}{[M - (\eta^2 - O_2)]} = \frac{\varepsilon_{M-OOH}A_{M-OOH}}{\varepsilon_{M-(\eta^2-O_2)}A_{M-(\eta^2-O_2)}} 
\]
where $\varepsilon_{M-{\text{OOH}}}$ and $\varepsilon_{M-(\eta^2-O_2)}$ are the extinction coefficients (i.e., sensitivity factors) for M-OOH and M-(\eta^2-O_2), respectively, and $A_{M-{\text{OOH}}}$ and $A_{M-(\eta^2-O_2)}$ are the areas of the steady-state UV-vis features (Figure 2) that correspond to M-OOH and M-(\eta^2-O_2) species, respectively. Equation S5 shows that the ratio of $\varepsilon_{M-{\text{OOH}}}$ to $\varepsilon_{M-(\eta^2-O_2)}$ must be known to experimentally determine a value of $K_1$ for a given catalyst.

The area of the cumulative UV-vis feature ($A_{\text{Total}}$) for a given M-BEA or M-SiO$_2$ (Figure 2) is given by

$$A_{\text{Total}} = A_{M-{\text{OOH}}} + A_{M-(\eta^2-O_2)}$$

(S6)

The total number of metal atoms ([M]) that are detected by the UV-vis spectroscopy are given by

$$[M] = \varepsilon_{M-{\text{OOH}}} A_{M-{\text{OOH}}} + \varepsilon_{M-(\eta^2-O_2)} A_{M-(\eta^2-O_2)}$$

(S7)

such that [M] is equal to the sum of the number of M-OOH and M-(\eta^2-O_2) intermediates. Equations S6 and S7 are then combined to linearize the $A_{\text{Total}}$ as a function of $A_{M-(\eta^2-O_2)}$ to yield

$$A_{\text{Total}} = \frac{[M]}{\varepsilon_{M-{\text{OOH}}}} + \left(1 - \frac{\varepsilon_{M-(\eta^2-O_2)}}{\varepsilon_{M-{\text{OOH}}}} \right) A_{M-(\eta^2-O_2)}$$

(S8)

The peak areas within Figure 3 for the cumulative UV-vis feature and the UV-vis peak that is attributed to M-(\eta^2-O_2) can then be used to determine the ratio of $\varepsilon_{M-{\text{OOH}}}$ to $\varepsilon_{M-(\eta^2-O_2)}$. Collection of UV-vis features under varying conditions (e.g., different acid and base solutions) is necessary to estimate the ratio of $\varepsilon_{M-{\text{OOH}}}$ to $\varepsilon_{M-(\eta^2-O_2)}$ because this ratio depends on shifting the equilibrium between the M-OOH and M-(\eta^2-O_2) species while assuming that the total number of sites within the measurement is unchanged.
Figure S9. Total area ($A_{\text{Total}}$) as a function of $A_{M-(\eta^2-O_2)}$ for Ti- (blue ▼), Nb- (black ■), and Ta-BEA (orange ♦). Peak areas are from the steady-state UV-vis spectra (Figure 3) of these M-BEA materials when contacted with varying solutions of H$_2$O$_2$ with HCl and NH$_4$OH in CH$_3$CN (313 K). Dashed lines represent linear regression fits.

Figure S9 shows $A_{\text{Total}}$ as a function of $A_{M-(\eta^2-O_2)}$ for all M-BEA materials, where the slope of each line is given by -2.42, -2.47, and -2.04 for Ti-, Nb-, and Ta-BEA respectively. From these slopes, equation S8 shows that the ratio of $\varepsilon_{M-OOH}$ to $\varepsilon_{M-(\eta^2-O_2)}$ are 1.42, 1.47, and 1.04 for Ti-, Nb-, and Ta-BEA, respectively. These ratios of $\varepsilon_{M-OOH}$ to $\varepsilon_{M-(\eta^2-O_2)}$, in conjunction with equation S5, are then used to determine values of $k_I$ for each M-BEA and M-SiO$_2$ (Table S3).

MATLAB™ is used to numerically estimate the kinetic parameters, by fitting the data (Figure 4) to the coupled differential equations (eqns. S3 and S4). The initial guesses used for the rate constants were 0.01, 0.001, 0.001 for $k_I$, $k_{OOH}$, and $k_{O_2}$, respectively. Values of $k_I$ are constrained by the relationship between $K_I$ and $k_1$ as shown in Equation S5. Changes of the initial values by an order of magnitude (increasing and decreasing) did not change the optimized parameter values.
Table S3. Numerically Optimized Rate Constants from Figure 4 (main text), $k_i$ (s$^{-1}$), and Equilibrium Constants for the Interconversion of M-OOH and M-(η$^2$-O$_2$) (Scheme 1) and the Ratio of Rate Constants for M-OOH to M-(η$^2$-O$_2$) Reaction with C$_6$H$_{10}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k_{-1}$ (s$^{-1}$)</th>
<th>$k_1$ (s$^{-1}$)</th>
<th>$k_{\text{OOH}} : k_{\text{O}_2}$</th>
<th>$K_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-BEA</td>
<td>$2.2 \times 10^{-4}$</td>
<td>$2.0 \times 10^{-4}$</td>
<td>1.7</td>
<td>0.9</td>
</tr>
<tr>
<td>Nb-BEA</td>
<td>$1.9 \times 10^{-4}$</td>
<td>$2.1 \times 10^{-4}$</td>
<td>0.6</td>
<td>1.1</td>
</tr>
<tr>
<td>Ta-BEA</td>
<td>$7.9 \times 10^{-5}$</td>
<td>$7.9 \times 10^{-5}$</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Ti-SiO$_2$</td>
<td>$1.3 \times 10^{-4}$</td>
<td>$2.2 \times 10^{-4}$</td>
<td>11.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Nb-SiO$_2$</td>
<td>$1.5 \times 10^{-4}$</td>
<td>$2.6 \times 10^{-4}$</td>
<td>0.4</td>
<td>1.7</td>
</tr>
<tr>
<td>Ta-SiO$_2$</td>
<td>$5.0 \times 10^{-4}$</td>
<td>$8.3 \times 10^{-4}$</td>
<td>0.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>
S2.4 Additional Raman Spectra of H₂O₂-Activated Ti-BEA

**Figure S10.** (a) Raman spectra of H₂O₂-activated Ti-BEA (top) and TiOSO₄ (to form Ti(η²-O₂)SO₄; bottom) (λₑₓ = 442 nm, 90 mW) and (b) correlation of the normalized 621 cm⁻¹ feature peak areas to the normalized area of the UV-vis feature corresponding to Ti-(η²-O₂) in Figure S9 when collected under identical reaction conditions. Ti-BEA Raman spectra were acquired in situ in flowing H₂O₂ in CH₃CN (0.1 M H₂O₂, 0.4 M H₂O, 1 cm³ min⁻¹; black), with HCl (0.01 M HCl, 0.1 M H₂O₂, 0.4 M H₂O, 1 cm³ min⁻¹; red) or NH₄OH (0.01 M NH₄OH, 0.1 M H₂O₂, 0.4 M H₂O, 1 cm³ min⁻¹; green) at 313 K). Dashed line in Figure S10b represents parity.
**Figure S11.** Steady-State peak intensities for the 621 cm$^{-1}$ Raman feature (Figure S10) as a function of cycle number while switching from a flow of H$_2$O$_2$ in CH$_3$CN (0.1 M H$_2$O$_2$, 0.4 M H$_2$O, 1 cm$^3$ min$^{-1}$; black) to HCl (0.01 M HCl, 0.1 M H$_2$O$_2$, 0.4 M H$_2$O, 1 cm$^3$ min$^{-1}$; red) and finally NH$_4$OH (0.01 M NH$_4$OH, 0.1 M H$_2$O$_2$, 0.4 M H$_2$O, 1 cm$^3$ min$^{-1}$; green) at 313 K. Dashed lines are intended to guide the eye.
S3.0 Additional Kinetic Data, Derivation of Relevant Rate Expressions and Transition State Theory

Figure S12. Turnover rates for the formation of styrene oxide via primary reaction pathways as a function of [H₂O₂] and [H₂O] for M-BEA (closed symbols) and M-SiO₂ (open symbols) at (a) 3 mM C₈H₈ (in CH₃CN, 313 K), (b) 0.5 M C₈H₈ (in CH₃CN, 313 K), and (c) 3 mM C₈H₈, 10 mM H₂O₂ (in CH₃CN, 313 K). Symbols and colors represent Ti- (blue ▼), Nb- (black ■) and Ta- (orange ♦) materials. Dashed lines are intended to guide the eye.
S3.1 Derivation of Full Rate Expression for C₈H₈ Epoxidation

Scheme S1. Proposed Elementary Steps for C₈H₈ Epoxidation and H₂O₂ Decomposition over group 5 M-BEA and M-SiO₂ Catalysts. The symbol \( \leftrightarrow \) represents a quasi-equilibrated step, while \( \rightarrow \) represents a kinetically relevant step. Note, the depiction of M-(\( \eta^2 \)-O₂) and adsorbed C₈H₈, H₂O₂, and C₈H₈O are meant to represent different types of surface species, rather than suggest a specific type of coordination to the active catalytic site. The M-(\( \eta^2 \)-O₂) intermediates drawn are intended to represent the pool of M-OOH and M-(\( \eta^2 \)-O₂) species that are present as shown by UV-vis (Figure 2).

Scheme 2 shows a series of elementary steps that account for the measured effects of [C₈H₈] (Figure 5) and [H₂O₂] (Figure S10) on both rates of C₈H₈ epoxidation. The catalytic cycle involves the quasi-equilibrated adsorption of H₂O₂ (step 2), followed by the irreversible activation of H₂O₂ (step 3) to form a pool of M-(\( \eta^2 \)-O₂) (Nb and Ta) and M-OOH (Ti) active intermediates (referred to collectively as M-(O₂)), which then react with C₈H₈ to form C₈H₈O (step 4), followed by C₈H₈O desorption (step 5) or decompose by reaction with H₂O₂ (step 6). Measured C₈H₈ epoxidation rates represent the kinetically relevant reaction of the active form of the oxidizing surface intermediate with a C₈H₈ molecule:
\[ r_E = k_x [M - (O_2)] [C_8 H_8] \]  
(\text{S9})

where \( r_E \) is the rate of \( C_6 H_{10} \) epoxidation, \([M-(O_2)]\) is the collective coverage of \( M-\text{OOH} \) (group IV) and \( M-(\eta^2-O_2) \) (group V) species, \( k_x \) is the rate constant for step \( x \) in Scheme 2, and \([C_8 H_8]\) is the concentration of \( C_8 H_8 \). Application of the pseudo-steady state hypothesis to the \( M-(O_2) \) intermediates, results in:

\[
r_E = \frac{k_x k_4 K_2 [C_8 H_8] [H_2 O_2][*]}{(k_4 [C_8 H_8] + k_6 [H_2 O_2])}\]
(\text{S10})

where \( K_x \) is the equilibrium constant for step \( x \) and \([*]\) is the total number of sites occupied by the solvent molecule (i.e., CH\textsubscript{3}CN). An expression for \([*]\) is given by the summation of all likely surface-bound intermediates:

\[
[L] = [*] + [C_8 H_8][*] + [H_2 O_2][*] + [M - (O_2)] + [C_8 H_8 O][*]
\]
(\text{S11})

where \([L]\) is the total number of \( M \) atoms, \([M-(O_2)]\) is the pool of \( M-\text{OOH} \) and \( M-(\eta^2-O_2) \) intermediates, and \([C_8 H_8][*], [H_2 O_2][*], \) and \([C_8 H_8 O][*]\) are surface-bound \( C_8 H_8, H_2 O_2, \) and \( C_8 H_8 O \) molecules, respectively. Equation S11 can then be restated in terms of the rate and equilibrium constants, as well as liquid-phase reactant concentrations and unoccupied \( M \) atoms by application of the PSSH to each surface specie to yield:

\[
[L] = [*] + K_1 [C_8 H_8][*] + K_2 [H_2 O_2][*] + \frac{k_3 K_2 [H_2 O_2][*]}{(k_4 [C_8 H_8] + k_6 [H_2 O_2])} + K_5 [C_8 H_8 O][*]
\]
(\text{S12})

Substitution of equation S12 into S10 yields the full rate expression for \( C_6 H_{10}O \) formation:

\[
\frac{r_E}{[L]} = \frac{k_x k_4 K_2 [C_8 H_8][H_2 O_2]}{(k_4 [C_8 H_8] + k_6 [H_2 O_2])}
\]
(\text{S13})

which is consistent with equation 2 from the main text.
Table S4. Calculated ratios of $k_4[C_8H_8]:k_6[H_2O_2]$ using interpolated values from Figure 5 and $H_2O_2$ decomposition rates at conditions that result in a $C_8H_8O$ MARI (i.e., 0.5 M $[C_8H_8]$ and values of $[H_2O_2]$ used in Figure 5).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k_4[C_8H_8]:k_6[H_2O_2]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-BEA</td>
<td>6.7</td>
</tr>
<tr>
<td>Nb-BEA</td>
<td>5.2</td>
</tr>
<tr>
<td>Ta-BEA</td>
<td>6.0</td>
</tr>
<tr>
<td>Ti-SiO$_2$</td>
<td>5.0</td>
</tr>
<tr>
<td>Nb-SiO$_2$</td>
<td>12.7</td>
</tr>
<tr>
<td>Ta-SiO$_2$</td>
<td>120.2</td>
</tr>
</tbody>
</table>
S3.2 Transition State Theory for Measurement of Activation Enthalpies and Entropies

Transition state theory (TST) is used to relate the stability of the reference state (e.g., the M-(O2) intermediates) to an activated complex that leads to reaction (i.e., the transition state). Transition state theory (TST), when combined with our proposed mechanism (Scheme 2), proposes that the reactant species (i.e., M-(O2), H2O2, and C8H8) exist in equilibrium with the transition state to yield:

\[
\frac{r_E}{[L]} = \frac{k_B T}{h} K_E^\dagger [C_8H_8]
\]

\[ (S14) \]

\[
\frac{r_E}{[L]} = \frac{k_B T}{h} K_D^\dagger [H_2O_2]
\]

\[ (S15) \]

where \( k_B \) is Boltzmann’s constant, \( h \) is Planck’s constant, \( T \) is the temperature in Kelvin, \( K_E^\dagger \) and \( K_D^\dagger \) are the Transition state equilibrium constants for epoxidation and H2O2 decomposition, respectively, and \([C_8H_8]\) is the concentration of C8H8. Values of \( K_E^\dagger \) and \( K_D^\dagger \) may be expressed in terms of changes in Gibbs free energy, via the Eyring equation, to result in:

\[
K_i^\dagger = e^{-\Delta G_i^\dagger / RT} = e^{-\Delta H_i^\dagger / RT} e^{\Delta S_i^\dagger / R}
\]

\[ (S16) \]

Where \( R \) is the ideal gas constant and \( \Delta G_i^\dagger \), \( \Delta H_i^\dagger \), and \( \Delta S_i^\dagger \) is the Gibb’s free energy, enthalpy, and entropy of activation, respectively. Figure S11 shows measured values for \( K_E^\dagger \) and \( K_D^\dagger \) as a function of inverse temperature for all M-BEA and M-SiO2.
Figure S13. Transition state equilibrium constants for (a) C₈H₈ epoxidation ($K_{E}^{\ddagger}$) and (b) H₂O₂ decomposition ($K_{D}^{\ddagger}$) as functions of inverse temperature on M-BEA (closed symbols) and M-SiO₂ (open symbols). Reactions conditions: Ti-BEA (3 mM C₈H₈, 0.01 M H₂O₂), Nb-BEA (3 mM C₈H₈, 1 mM H₂O₂), Ta-BEA (3 mM, 1 mM H₂O₂), Ti-SiO₂ (3 mM C₈H₈, 0.01 M H₂O₂), Nb-SiO₂ (3 mM C₈H₈, 0.01 M H₂O₂), and Ta-SiO₂ (3 mM C₈H₈, 0.01 M H₂O₂). Symbols and colors represent Ti- (blue ▼), Nb- (black ■) and Ta- (orange ♦) materials. Error bars were omitted for clarity. In all reported data, error was < 7%. Dashed lines represent fits to the Eyring equation (equation S16) whose slopes and intercepts are proportional to $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively.
Scheme S2. Changes in Enthalpies Due to the Intermediate Steps that Form the Transition State for C₈H₈ Epoxidation from a M-(O₂) Saturated Surface and Fluid-Phase C₈H₈, M-(η²-O₂) (M = Nb or Ta) is shown to illustrate the relationship between ΔH-slider, ΔH_ads, and ΔH-int. This thermochemical sequence for the epoxidation of C₈H₈ with a M-(η²-O₂) reference state (i.e., M-(η²-O₂) MASI) uses a transition state theory formalism that involves the quasi-equilibrated adsorption of C₈H₈ into the pores of *BEA or SiO₂, and the kinetically-relevant reaction of C₈H₈ with M-(η²-O₂).
S4.0 Calculated Reaction Constants for the Epoxidation of Para-substituted Styrene

Table S5. Reaction Constants ($\rho$) for the Epoxidation of $x$-C$_8$H$_7$ (x = -NO$_2$, -Br, -H, -Me, or -OMe) on M-BEA and M-SiO$_2$ Materials at Standard Reaction Conditions (3 mM $x$-C$_8$H$_8$, 0.01 M H$_2$O$_2$, in CH$_3$CN, 313 K). Values of $\rho$ Represent Least Squares Regression Fits of the Hammett Equation (Equation 9 in the main text) to Figure 9.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction constant ($\rho$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-BEA</td>
<td>-0.83</td>
</tr>
<tr>
<td>Nb-BEA</td>
<td>-0.80</td>
</tr>
<tr>
<td>Ta-BEA</td>
<td>-0.89</td>
</tr>
<tr>
<td>Ti-SiO$_2$</td>
<td>-0.91</td>
</tr>
<tr>
<td>Nb-SiO$_2$</td>
<td>-0.98</td>
</tr>
<tr>
<td>Ta-SiO$_2$</td>
<td>-0.93</td>
</tr>
</tbody>
</table>
References:


