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

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Supporting Information

ABSTRACT: Ti, Nb, and Ta atoms substituted into the framework of zeolite *BEA (M-BEA) or grafted onto mesoporous silica (M-SiO2) irreversibly activate hydrogen peroxide (H2O2) to form pools of metal-hydroperoxide (M-OOH) and peroxide (M-(η2-O2)) species for alkene epoxidation. The product distributions from reactions with Z-stilbene, in combination with time-resolved UV–vis spectra of the reaction between H2O2-activated materials and cyclohexene, show that M-OOH surface intermediates epoxidize alkenes on Ti-based catalysts, while M-(η2-O2) moieties epoxidize substrates on the Nb- and Ta-containing materials. Kinetic measurements of styrene (C8H8) epoxidation reveal that these materials first adsorb and then irreversibly activate H2O2 to form pools of interconverting M-OOH and M-(η2-O2) intermediates, which then react with styrene or H2O2 to form either styrene oxide or H2O2 decomposition products, respectively. Activation enthalpies (ΔHf) for C8H8 epoxidation and H2O2 decomposition decrease linearly with increasing heats of adsorption for pyridine or deuterated acetonitrile coordinated to Lewis acid sites, which suggests that materials with greater electron affinities (i.e., stronger Lewis acids) are more active for C8H8 epoxidation. Values of ΔHf for C8H8 epoxidation and H2O2 decomposition also decrease linearly with the ligand-to-metal charge-transfer (LMCT) band energies for the reactive intermediates, which is a more relevant measure of the requirements for the active sites in these catalytic cycles. Epoxidation rates depend more strongly on the LMCT band energy than H2O2 decomposition rates, which shows that more electrophilic M-OOH and M-(η2-O2) species (i.e., those formed at stronger Lewis acid sites) give both greater rates and greater selectivities for epoxidations. Thermochemical analysis of ΔHf for C8H8 epoxidation and adsorption enthalpies for C8H8 within the pores of *BEA and SiO2 reveal that the 0.7 nm pores within M-BEA preferentially stabilize transition states for C8H8 epoxidation with respect to the 5.4 nm pores of M-SiO2, while H2O2 decomposition is unaffected by the differences between these pore diameters due to the small Stokes diameter of H2O2. Thus, the differences in reactivity and selectivity between M-BEA and M-SiO2 materials is solely attributed to confinement of the transition state and not differences in the identity of the reactive intermediates, mechanism for alkene epoxidation, or intrinsic activation barriers. Consequently, the rates and selectivities for alkene epoxidation reflect at least two orthogonal catalyst design criteria—the electronegativities of the transition metal atoms that determine the electronic structure of the active complex and the mean diameters of the transition states that can selectively stabilize transition states for specific reaction pathways.

KEYWORDS: titanium, niobium, tantalum, epoxidation, hydrogen peroxide, reactive intermediates, solvation

1. INTRODUCTION

Highly dispersed metal oxides are ubiquitous in the selective oxidation of various alkanes, alkenes, aromatics, alcohols, and aldehydes to produce both commodity and fine chemicals.1–3 The production of epoxides from alkenes is important, because epoxides are precursors for the manufacture of plastics, fragrances, and pharmaceuticals.4–6 In recent years, a number of studies have investigated the use of highly dispersed group 4 and 5 metal oxides (e.g., grafted onto mesoporous silica7,8 or incorporated into a zeolite framework9,10) to activate hydrogen peroxide (H2O2) for epoxidation reactions.11 The interest in H2O2 is motivated, in part, by the lower environmental impact for the use of this oxidant in comparison to Cl2 (e.g., used in the chlorohydrin process)12 and organic oxidizers (e.g., tert-butyl hydroperoxide and ethylbenzene hydroperoxide).13 Epoxidations that utilize H2O2 form only H2O as a byproduct.
and, hence, do not require the regeneration or sale of organic co-products nor the remediation of environmentally impactful waste streams.

Large amounts of titanium silicate (TS-1) are used in the hydrogen peroxide-propylene oxide process to catalyze the activation of \( \text{H}_2\text{O}_2 \) and the epoxidation of propylene.\(^{14,15} \) However, many other monomeric metal centers and small oligomers of metal oxides (\( \text{e.g., } \text{Al},^{16,17} \text{Ti},^{18,20} \text{Zr},^{21} \text{Nb},^{22,23} \) and \( \text{Ta}^{24-26} \)) activate \( \text{H}_2\text{O}_2 \) and catalyze alkene epoxidations as well. Recent reports from our group show that the rates and selectivities for cyclohexene epoxidation increase with increasing heat of adsorption for Lewis acid bound deuterated acetonitrile, which suggests that materials that possess greater electron affinities (\( \text{i.e.,} \) stronger Lewis acids) are more productive catalysts for this chemistry.\(^{27,28} \) Despite the plethora of literature on the epoxidation of alkenes with \( \text{H}_2\text{O}_2,^{22,28} \) the changes in rates and selectivities that result from differences in the electronic structure due to changing pore environment (\( \text{e.g.,} \) type or morphology of support) and changes in the solvating environment (\( \text{i.e.,} \) catalyst pore diameter) have not been fully described in the open literature, to the best of our knowledge.

Here, we seek to establish and explain the relationships that exist between the rates and selectivities for alkene epoxidation and the electronic structure of the reactive intermediates and morphological properties (\( \text{e.g.,} \) metal atom coordination and mean pore diameters) of two series of catalysts that contain monomeric Ti, Nb, or Ta atoms on siliceous supports. The two categories of materials consist of transition metal atoms (Ti, Nb, or Ta) incorporated into the framework of zeolite *BEA (M-BEA)\(^{10} \) or those same atoms grafted onto mesoporous silica (M-SiO\(_2\)).\(^{7,10,27} \) UV–vis spectra obtained in situ suggest that all materials irreversibly activate \( \text{H}_2\text{O}_2 \) to form pools of M-OOH and M-(\( \eta^2\)-O\(_2\)) intermediates. Transient in situ UV–vis spectra obtained during reaction of these species with cyclohexene, in conjunction with the isomeric distribution of the products from Z-stilbene epoxidation, show that Ti-BEA and Ti-SiO\(_2\) catalysts react through M-OOH, while Nb and Ta materials epoxidize cyclohexene through M-(\( \eta^2\)-O\(_2\)).\(^{7} \) Changes in the rates of styrene (C\(_8\)H\(_8\)) epoxidation and \( \text{H}_2\text{O}_2 \) decomposition as functions of reactant concentrations show that the active M-OOH and M-(\( \eta^2\)-O\(_2\)) intermediates form following adsorption and irreversible activation of \( \text{H}_2\text{O}_2 \) after which these species react with C\(_8\)H\(_8\) or \( \text{H}_2\text{O}_2 \) to form the epoxidation or decomposition products, respectively. Epoxidation and \( \text{H}_2\text{O}_2 \) decomposition rates and selectivities depend exponentially on the extent of electron exchange between the reactive intermediate and the metal atom, as assessed by the ligand-to-metal charge-transfer (LMCT) energy measured via UV–vis. Activation enthalpies (\( \Delta H^f \)) for C\(_8\)H\(_8\) epoxidation are systematically lower on M-BEA materials than M-SiO\(_2\), by \( \sim 20 \) kJ mol\(^{-1}\), while \( \Delta H^f \) for \( \text{H}_2\text{O}_2 \) decomposition do not depend on the type of silica support used. Thermochromical analysis of the values of \( \Delta H^f \) for C\(_8\)H\(_8\) epoxidation and the adsorption enthalpies for C\(_8\)H\(_8\) adsorption into the purely siliceous materials show that transition states for C\(_8\)H\(_8\) epoxidation are preferentially stabilized within the microporous *BEA framework relative to those in mesoporous SiO\(_2\) while transition states for \( \text{H}_2\text{O}_2 \) decomposition are not affected because the Stokes diameter of \( \text{H}_2\text{O}_2 \) \( (\sim 0.24 \text{ nm}) \) is too small to be significantly stabilized by dispersive interactions with the pore walls of these materials. Consequently, the design of materials that maximize the extent of solvation of the desired alkene reactant in the microporous voids will result in a catalyst with increased rates and selectivities for this chemistry.

2. MATERIALS AND METHODS

2.1. Catalyst Synthesis. All M-BEA and M-SiO\(_2\) catalysts used in this study have been synthesized and characterized by the authors within previous reports.\(^7-10 \) The most relevant results are summarized here, with additional characterization data and interpretation provided in the Supporting Information (SI), section SI.

M-BEA catalysts were prepared by the liquid-phase postsynthetic modification of commercially available NH\(_4\)-BEA (Zeolyst, CP814E)\(^{9,10,18,31-33} \). In short, NH\(_4\)-BEA (Si:Al \( \sim 12.5 \)) was dealuminated by reflux in concentrated HNO\(_3\) (Macron Chemicals, 68–70 wt%, 20 cm\(^3\) g\(^{-1}\)) for 18 h. The solids were recovered by vacuum filtration and washed thoroughly with \( \text{H}_2\text{O} \) (17.8 M\( \Omega\)-cm, 50 cm\(^3\) g\(^{-1}\)) and heated at 5 K min\(^{-1}\) to 823 K in flowing air (Airgas, Ultra-zero grade, 100 cm\(^3\) min\(^{-1}\)) and held for 6 h to produce Si-BEA (Si:Al \( >1200 \), determined by ICP-OES). The incorporation of Ti, Nb, or Ta atoms into the dealuminated framework involved stirring a suspension of Si-BEA in a solution of TiCl\(_4\) (Sigma-Aldrich, 99.99%); Caution! TiCl\(_4\) will violently react with the moisture in air to form TiO\(_2\) and HCl, and should be handled carefully in a fume hood. NbCl\(_5\) (Sigma-Aldrich, 99.9%), or TaCl\(_5\) (Sigma-Aldrich, 99%) in dichloromethane (Fisher Chemicals, Certified ACS stabilized) for TiCl\(_4\) or isopropanol (Fisher Chemicals, Certified ACS plus) for NbCl\(_5\) and TaCl\(_5\) at 333 K for 3 h. Volatile components were then removed by rotary evaporation. Recovered solids were heated at 5 K min\(^{-1}\) to 823 K in flowing air (Airgas, Ultra-zero grade, 100 cm\(^3\) min\(^{-1}\)) and held for 6 h to produce the corresponding M-BEA catalyst. The metal loading within the catalysts was varied by changing the concentration of the MCl\(_4\) solution used during the liquid-phase treatments.

All M-SiO\(_2\) materials were synthesized using standard glovebox and Schlenk techniques.\(^{34-37} \) TiCl\(_4\) (THF)\(_2\) (Strem Chemicals, >97% metals basis), NbCl\(_5\) (Strem Chemicals, >99%), and TaCl\(_5\) (Strem Chemicals, >99%) metal precursors were stored and weighed in an Ar glovebox. 1,3-Dimethoxy-calix[4]arene ("dmCalix") was prepared from p-tetralone and 4-arenecarboxylic acid ("Calix", Sigma-Aldrich, >95%) according to previous published procedures.\(^{38} \) Briefly, Ti-, Nb-, and Ta-calixarene complexes were synthesized by refluxing the metal chloride precursors with stoichiometric amounts of dmCalix (Ti) or Calix (Nb, Ta) in dry, degassed toluene under an N\(_2\) atmosphere for 14 h. Then, partially dehydroxylated SiO\(_2\) (Selecto Scientific, 32–62 \( \mu \)m particle size, 570 m\(^2\) g\(^{-1}\), 5.4 nm average pore diameter, treated at 573 K under dynamic vacuum (<5 Pa) for 10 h) was added to the flask, and the suspension was refluxed for an additional 24 h. Solids were vacuum-filtered and washed with fresh toluene, then Soxhlet-extracted with toluene, and dried under dynamic vacuum (<40 mTorr) to yield bright-orange (Calix-Ti-SiO\(_2\) and Calix-Nb-SiO\(_2\)) or light-brown (Calix-Ta-SiO\(_2\)) solids. Calix-M-SiO\(_2\) solids were then heated at 5 K min\(^{-1}\) to 823 K in flowing air (Airgas, Ultra-zero grade, 100 cm\(^3\) min\(^{-1}\)) and held for 6 h to remove the calixarene ligands and produce highly dispersed M-SiO\(_2\) materials (bleached white in appearance).

2.2. Catalyst Characterization. The metal contents (Table 1) of the M-BEA and M-SiO\(_2\) materials was quantified using inductively coupled plasma-optical emission spectroscopy (ICP-OES), which was calibrated against known dilution
Table 1. Band Edge Energies,$^a$ Metal Loadings,$^b$ Fraction of Active Metal,$^c$ and Enthalpies of Adsorption$^d$ for Pyridine ($\Delta H_{Py}$) and CD$_3$CN ($\Delta H_{CD3CN}$) Coordinated to Lewis Acid Sites on M-BEA and M-SiO$_2$ Catalysts

<table>
<thead>
<tr>
<th>sample</th>
<th>band edge (eV)</th>
<th>metal loading (mmol g$^{-1}$)</th>
<th>active metal (%)</th>
<th>$\Delta H_{Py}$ (kJ mol$^{-1}$)</th>
<th>$\Delta H_{CD3CN}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-BEA</td>
<td>4.0</td>
<td>0.22</td>
<td>96 ± 5</td>
<td>$-45 \pm 3$</td>
<td>$-31 \pm 2^c$</td>
</tr>
<tr>
<td>Nb-BEA</td>
<td>4.2</td>
<td>0.16</td>
<td>99 ± 8</td>
<td>$-25 \pm 3$</td>
<td>$-22 \pm 2^c$</td>
</tr>
<tr>
<td>Ta-BEA</td>
<td>4.8</td>
<td>0.16</td>
<td>99 ± 4</td>
<td>$-20 \pm 3$</td>
<td>$-17 \pm 1^c$</td>
</tr>
<tr>
<td>Ti-SiO$_2$</td>
<td>3.8</td>
<td>0.18</td>
<td>77 ± 10</td>
<td>$-34 \pm 4$</td>
<td>$-4$</td>
</tr>
<tr>
<td>Nb-SiO$_2$</td>
<td>4.0</td>
<td>0.18</td>
<td>60 ± 7$^c$</td>
<td>$-16 \pm 2$</td>
<td>$-4$</td>
</tr>
<tr>
<td>Ta-SiO$_2$</td>
<td>4.5</td>
<td>0.19</td>
<td>60 ± 7$^c$</td>
<td>$-11 \pm 2$</td>
<td>$-4$</td>
</tr>
</tbody>
</table>

$^a$Measured using DRUV-vis. $^b$Measured by ICP-OES. $^c$Determined by in situ methylphosphonic acid (for M-BEA) and phenylphosphonic acid (for M-SiO$_2$) titrations. $^d$Determined from adsorption isobars using FTIR. $^e$Not measured because CD$_3$CN readily coke on M-SiO$_2$ at temperatures >373 K. $^f$Reference 8. $^g$Reference 10.

The crystallinity of each M-BEA material was confirmed by powder X-ray diffraction using a diffractometer (Siemens/Bruker, D5000) with Cu Kα radiation (0.15418 nm) under ambient conditions. Figure S1 shows the X-ray diffractograms of all M-BEA. The similarities between the diffractograms for all M-BEA suggests that the *BEA framework is intact after postsynthetic modification.

Band edge energies ($E_f$) for each M-BEA and M-SiO$_2$ material were determined from extrapolation of the linear portion of the corresponding Tauc plot calculated from diffuse reflectance UV–vis spectra (DRUV–vis) (Figure S2). Total reflectance spectra were measured at ambient conditions with a UV–vis–NIR spectrophotometer (Agilent CARY 5 for M-BEA; Shimadzu UV-3600 for M-SiO$_2$) with magnesium oxide (MgO, Sigma-Aldrich, 99.995%, for M-BEA) or polytetrafluoroethylene powder (for M-SiO$_2$) as a solid diluent and background. The relatively large band gaps (Table 1), and lack of significant shoulders on the absorbance features suggests that the transition metal atoms in *BEA and on SiO$_2$ are highly disperse and contain little oligomeric or bulk oxide phases. The Ta-SiO$_2$ material is the sole exception and possesses a small shoulder on the UV–vis absorbance spectra (Figure S2), which suggests that small TaO$_x$ oligomers form upon oxidative heat treatments.$^{9}$ In this work, all reported rates were normalized by the fraction of active metal in the M-BEA and M-SiO$_2$ catalysts using in situ methylphosphonic acid (for M-BEA) or phenylphosphonic acid (for M-SiO$_2$) site titrations (see below).$^{5,39}$ Thus, the presence of TaO$_x$ oligomers does not significantly affect reported rates.

The presence of Lewis acid sites in M-BEA and M-SiO$_2$ was characterized by the infrared (IR) spectra of adsorbed pyridine (Sigma-Aldrich, >99%) using a custom-built transmission cell$^{40}$ coupled to a Fourier transform infrared (FTIR) spectrometer (Bruker, Tensor 37) with a liquid-N$_2$-cooled HgCdTe detector. Catalysts were pressed into self-supporting disks (~60 mg) and placed within the transmission cell, which was assembled using CaF$_2$ windows and connected to a gas manifold with lines heated to 423 K. All materials were first heated to 423 at 10 K min$^{-1}$ and held for 2 h under flowing He (50 cm$^3$ min$^{-1}$; Airgas, Ultra-zero grade), with the intent to desorb water and residual organics. Pyridine (0.1 kPa; Sigma-Aldrich, 99%) was introduced via a syringe pump (KD Scientific, Legato 100) and vaporized in the heated gas-transfer lines into a stream of flowing He (50 cm$^3$ min$^{-1}$). Steady-state IR spectra (128 scans, 1 cm$^{-1}$ resolution; Figure 1) of pyridine adsorbed to the M-BEA and M-SiO$_2$ samples were obtained while flowing the pyridine/He stream over the samples.

Table 1 contains the experimentally determined values for $\Delta H_{Py}$ on all M-BEA and M-SiO$_2$ materials. Table 1
also contains values for the enthalpy of adsorption for deuterated acetonitrile ($\Delta H_{\text{D,ACN}}$) coordinated to Lewis acid sites obtained using similar methodology by our group.\textsuperscript{10}

X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of transition metal atoms on bare and H$_2$O$_2$-activated Ti, Nb, and Ta-BEA and -SiO$_2$ materials. The XPS measurements were performed on a spectrometer (Kratos, AXIS Ultra) equipped with a monochromatic Al K$_\alpha$ (1486.6 eV) X-ray source. M-BEA and M-SiO$_2$ materials were activated with H$_2$O$_2$ by creating a slurry of catalyst (~60 mg) with a mixture of 2.5 cm$^3$ H$_2$O$_2$ (4.9 M; 30 wt% in H$_2$O; Fisher Scientific) in acetonitrile (CH$_3$CN; Macron Chemicals, >99.8%) and stirring at 333 K for 1 h. Volatile components were then removed in vacuo via a rotary evaporator (IKA, RV 10) and dried under dynamic vacuum for 12 h (~0.02 kPa). This treatment produced pale yellow solids from Ti and Nb materials and a cream colored solid for Ta materials and SiO$_2$ as a function of temperature within the linear regime (for Ti and Nb materials) and 1 cm$^3$ aliquots of 2.5 cm$^3$ H$_2$O$_2$ (4.9 M; 30 wt% in H$_2$O; Fisher Scientific) with 10 cm$^3$ CH$_3$CN (Sigma-Aldrich, thiophene-free, >99%) in CH$_3$CN was heated to a desired temperature while stirring in a 100 cm$^3$ three-neck round-bottom flask. An initial (solids-free) aliquot was taken and analyzed via gas chromatography (GC; HP 5890, Series A) to determine the initial concentration of C$_8$H$_8$. An appropriate amount of Si-BEA or SiO$_2$ was then added to the stirring solution of C$_8$H$_8$ and allowed to equilibrate at a given temperature. An aliquot of solution was then passed through a syringe filter (polypropylene, 0.22 μm) to remove the solids and was analyzed via GC. The difference in GC peak area between the aliquot after Si-BEA or SiO$_2$ introduction and the initial sample was assumed to be proportional to the amount of styrene adsorbed to the purely siliceous solids. Multiple concentrations of C$_8$H$_8$ were tested to determine a concentration that is well within the linear regime for the C$_8$H$_8$ adsorption isotherm (from $5 \times 10^{-6}$ to $10^{-3}$ M [C$_8$H$_8$]). The uptake of C$_8$H$_8$ was then measured as a function of temperature to determine the enthalpies for adsorption of styrene from the CH$_3$CN solution to the siliceous support ($\Delta H_{\text{ads}}$; Figure S4), and these values were found to be $-35 \pm 6$ and $-18 \pm 3$ for Si-BEA and SiO$_2$, respectively.

### 2.3. Measurement of Rates for Epoxide Formation and H$_2$O$_2$ Decomposition

Rates for C$_8$H$_8$ epoxidation and H$_2$O$_2$ decomposition were measured using batch reactors (100 cm$^3$, three-neck round-bottom flasks) equipped with reflux condensers to minimize evaporative losses. C$_8$H$_8$ and H$_2$O$_2$ (Fischer Chemicals, 30 wt% in H$_2$O) were added to a solution of CH$_3$CN and benzene (internal standard for GC analysis; Sigma-Aldrich, thiophene-free, >99%) and heated to the desired temperature (303–348 K) while stirring at 600 rpm. H$_2$O$_2$ (30% w/v) was distilled via rotary evaporation to produce ~90% w/v H$_2$O$_2$ and was combined with an appropriate amount of H$_2$O to quantify the effects of H$_2$O on styrene epoxidation rates. The reactions were initiated by addition of the M-BEA or M-SiO$_2$ catalysts and small aliquots (~300 μL) of the reaction solution were extracted as a function of time through a 0.22 μm syringe filter (to remove suspended catalyst and stop the reactions from proceeding). The concentrations of the organic components within these aliquots were quantified via a GC equipped with a flame-ionization detector. All species were identified and quantified by using standards of known concentration. The concentration of H$_2$O$_2$ in each aliquot was measured by colorimetric titration using an aqueous solution of CuSO$_4$ (8.3 mM, Fisher Chemicals, >98.6%), neocuproine (12 mM; Sigma-Aldrich, >98%), and ethanol (25% v/v; Decon Laboratories Inc., 100%). The concentration of H$_2$O$_2$ was calculated by comparison of the absorbance at 454 nm to calibrated standards, measured using a visible-light spectrophotometer (Spectronic, 20 Genesys). Test reactions using purely siliceous Si-BEA and SiO$_2$ materials (0.01 M C$_8$H$_8$, 1 mM H$_2$O$_2$, 313 K) reveal that no reaction (i.e., epoxidation or H$_2$O$_2$ decomposition) occurs in the absence of the metal atoms.

The number of catalytically active metal atoms in M-BEA samples were determined using in situ site titrations with methylphosphonic acid (MPA; Sigma-Aldrich, 99%) during the epoxidation of cyclohexene (C$_8$H$_{10}$; Sigma-Aldrich, 99%).\textsuperscript{9,39} Briefly, M-BEA was combined with a solution of MPA and C$_8$H$_8$ with the intent for MPA to irreversibly bind to the active sites and inhibit epoxidation catalysis. An appropriate amount of H$_2$O$_2$ was then spiked into the reactor to initiate the reaction. Reactions were run with varying ratios of MPA-to-metal (MPA:M) where the MPA:M ratios that correspond to extrapolated turnover rates of zero are taken to be the fraction of active metal in M-BEA (Table 1; see SI, section S1.2). Cyclohexene epoxidation on all M-BEA produced only cyclohexene oxide, as no other oxidation products (e.g., cyclohexeneone, 1-cyclohexen-3-ol, cyclohexanediol) were observed under differential conversion. Turnover rates were calculated by calculating the change in turnover number (the total amount of oxygenate product formed or amount of H$_2$O$_2$ consumed normalized by the total number of active M atoms used in a given reaction) as a function of time at differential conversion. In all reported data, the carbon balance closed within 98% and the standard uncertainty for measured reaction rates was <7%. Rates for the conversion of C$_8$H$_8$ and H$_2$O$_2$ were measured as functions of [H$_2$O$_2$] and [C$_8$H$_8$], and all reported results were obtained at differential conversion (i.e., <1% conversion of the limiting reagent for epoxide formation rates and <5% conversion of H$_2$O$_2$ for H$_2$O$_2$ consumption rates). Reported rates were measured in the absence of intra-pellet mass-transfer artifacts, as shown by satisfaction of the Madon–Boudart criterion\textsuperscript{44} for Ti-BEA (i.e., the catalyst with the smallest pore diameter and largest rates; see SI, section S1.3) by performing reactions under identical conditions with Ti-BEA samples containing different metal loadings (SI, section S1.3). Over the loadings tested, epoxidation rates do not depend on the metal content, which shows that concentration gradients do not exist within the reactor or catalyst particles.

Styrene oxidation results in the formation of styrene oxide (C$_8$H$_{10}$O), phenylacetaldehyde, and benzaldehyde (C$_7$H$_6$O). Extrapolation of the selectivity for each of these products to the limit of zero C$_8$H$_8$ conversion shows that phenylacetaldehyde forms by isomerization of C$_8$H$_{10}$O over Lewis acid sites\textsuperscript{45} and that both C$_8$H$_{10}$O and C$_7$H$_6$O form via primary reaction pathways (i.e., both give nonzero selectivities at nearly zero conversion). There are reports that benzaldehyde forms within the injection port of the gas chromatograph via oxidative decarboxylation of 1-phenyl-1,2-ethanediol.\textsuperscript{46} Control experiments where a solution of 1-phenyl-1,2-ethanediol (‘1,2-diol’; DOI: 10.1021/acscatal.7b03986
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Sigma-Aldrich, 97%) in CH$_3$CN (∼0.01 M) was injected into the GC injection port show that <1% of the diol is converted to benzaldehyde under the GC method used. Additionally, CH$_3$OH was not produced on any M-BEA materials and was produced with varying initial selectivities (30−50%) on all M-SiO$_2$ catalysts, which suggests that benzaldehyde forms catalytically and not within the GC. Here, the combined concentrations of CH$_3$OH and phenylacetaldehyde are used to calculate initial rates for epoxidation reactions, which are used to develop the relationships between catalyst structure and function for alkene epoxidation.

2.4. Detection of Reactive Intermediates via In Situ UV−Vis and Raman Spectroscopy. In situ UV−vis spectroscopy was used to identify the intermediates formed upon H$_2$O$_2$ activation and confirm which among those intermediates are active for alkene epoxidation on M-BEA and M-SiO$_2$ materials. Samples were pressed into 7 mm diameter pellets (∼5 mg) and loaded into a custom built temperature-controlled UV−vis liquid flow cell. UV−vis spectra (100 scans, 600 ms integration time) were collected using a 45-degree diffuse reflection probe (Avantes, solarization-resistant fibers) coupled to a fiber-optic spectrometer (Avantes, AvaDSC 2048) equipped with a compact deuterium-halogen light source (Avantes, AvaLight-DHc). Reactant and solvent solutions were introduced using a high-performance liquid chromatography pump (HPLC; Waters, 515). Background UV−vis spectra were obtained for each material by exposing the sample to a flowing CH$_3$CN solution (0.4 M H$_2$O, 1 cm$^3$ min$^{-1}$) at 313 K for 1 h. Samples were then activated with H$_2$O$_2$ by changing to a flowing solution 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$^{-1}$) at 313 K and continuing until the UV−vis spectra became constant (i.e., implying a steady-state coverage of surface intermediates). Samples were then flushed with pure CH$_3$CN (1 cm$^3$ min$^{-1}$) at 313 K for 10 min to remove residual H$_2$O$_2$ that had not been activated. Experiments to assign UV−vis features to specific surface intermediates (e.g., M-OOH or M-(η$^2$-O$_2$)) were performed by collecting UV−vis spectra at steady state while contacting M-BEA pellets with a solution of NH$_4$OH (Macron Chemicals, 28−30%; 0.01 M NH$_4$OH, 0.1 M H$_2$O$_2$, 0.4 M H$_2$O in CH$_3$CN, 313 K) and HCl (Rica, 10 M; 0.01 M HCl, 0.1 M H$_2$O$_2$, 0.4 M H$_2$O in CH$_3$CN, 313 K) to shift the equilibrium between M-OOH and M-(η$^2$-O$_2$) intermediates (see section 3.1).

The reactivities of the surface intermediates observed in the UV−vis spectra were determined by continuously acquiring UV−vis spectra as a function of time while flowing a solution of cyclohexene (C$_6$H$_{10}$; Sigma-Aldrich, 99%) in CH$_3$CN (0.1 M C$_6$H$_{10}$, 0.4 M H$_2$O, 1 cm$^3$ min$^{-1}$) over H$_2$O$_2$-activated M-BEA and M-SiO$_2$ catalysts. Cyclohexene was used for these experiments to avoid complexities related to the secondary reactions that occur during styrene epoxidation. Specifically, the epoxidation of C$_6$H$_{10}$ resulted in the parallel reaction pathway that produced benzaldehyde on M-SiO$_2$ (see above), which prohibits detection of the reactive intermediate implicated in alkene epoxidation on M-SiO$_2$ materials. Rate constants for the consumption of these surface species via epoxidation and isomerization reaction were calculated by mathematically modeling the rates of peak attenuation (SI, section S2). Notably, independent experiments showed that the UV−vis absorbance features for H$_2$O$_2$-activated materials do not change or attenuate (within a period of 2 h) under a flowing stream of either CH$_3$CN (0.4 M H$_2$O, 1 cm$^3$ min$^{-1}$) or pure H$_2$O (1 cm$^3$ min$^{-1}$) at 313 K. Processes for peak smoothing, background subtraction, and peak fitting are described in the SI, section S2.

In situ Raman spectra were collected on a Raman microscopy (Renishaw, inVia) equipped with a 442 nm laser (Kimmon, IK3). Samples were pressed into 7 mm diameter pellets and were loaded into a custom Raman flow cell with a quartz window for spectral acquisition. Spectra were obtained using a long 50X objective with line-scan mode (∼2.5 μm$^2$) and a laser power of 90 mW with 0.1 s acquisition times (300 co-averaged spectra). Reaction solutions were introduced via a HPLC pump and steady-state conditions were reached (i.e., where the spectra were unchanged with time) before acquiring spectra. Titanium oxysulfate (50 μL; Sigma, in 27−31% H$_2$SO$_4$) was combined with 1 μL of H$_2$O$_2$ (30% in H$_2$O) and was used to produce Ti(η$^2$-O$_2$)SO$_4$ for use as a reference compound.

3. RESULTS AND DISCUSSION

3.1. Intermediates Formed upon Activation of H$_2$O$_2$.

Figure 2 shows the UV−vis spectra of H$_2$O$_2$-activated M-BEA and M-SiO$_2$ materials acquired in situ (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. Spectra for M-BEA materials are adapted from ref 10.

![Figure 2. 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.](image-url)

and M-SiO$_2$ materials acquired in situ (0.1 M H$_2$O$_2$, 0.4 M H$_2$O in CH$_3$CN, 1 cm$^3$ min$^{-1}$). In all cases, UV−vis spectra possess two overlapping absorbance features, whose intensities are assumed to be proportional to the surface coverage of each UV−vis-active species. Previous reports from our laboratory mistakenly assigned the higher wavelength feature to hydroperoxide/peroxide (M-OOH/(η$^2$-O$_2$)) intermediates and the lower wavelength feature to the superoxide (M-(O$_2$)$^{−}$) moieties. These assignments were based on published peak assignments that used a combination of in situ EPR and UV−vis spectroscopy to identify similar overlapping features on TS-1 to Ti-OOH and Ti-(O$_2$)$^{−}$ features. Studies of amorphous Nb$_2$O$_5$ and Ta$_2$O$_5$, bulk oxides that assigned similar overlapping features on Nb and Ta contacting with H$_2$O$_2$ to the Nb-OOH (380 nm) and Nb-(O$_2$)$^{−}$ (320 nm) features. Moreover, X-ray photoelectron spectra of H$_2$O$_2$-activated M-BEA (SI, section S1.3) show that Nb and Ta atoms reduce from $M^{4+}$ to $M^{3+}$; however, it appears that the X-ray radiation caused photo-reduction of the reactive complexes. These data and literature precedents can lead to the incorrect conclusion that...
the UV–vis spectra contain features corresponding to M-(O$_2$)$_2$•

M-OOH intermediates are commonly invoked as the reactive intermediates on Ti-based heterogeneous catalysts for alkene epoxidation,$^{55-58}$ while both M-OOH and M-(η$_2$-O$_2$) have been observed spectroscopically on a various Ti, Nb, and Ta catalysts.$^{59-61}$ Yet much less is known about the identity of the reactive species involved in alkene epoxidation on Nb- and Ta-based heterogeneous catalysts, particularly in comparison to Ti-based catalysts (especially TS-1).

Figure 3 shows steady-state UV–vis spectra (0.1 M H$_2$O$_2$, 0.4 M H$_2$O in CH$_3$CN, 313 K) taken under basic (0.01 M NH$_4$OH), neutral, and acidic (0.01 M HCl) conditions for all M-BEA catalysts. For all Ti-, Nb-, and Ta-BEA catalysts, the ratio of the intensities of the absorbance feature at higher wavelengths to that of lower wavelength increases with the concentration of protons, which is determined by the water and NH$_4$OH or HCl present in the solvent. This suggests that the chemical species that is responsible for the UV–vis feature at higher wavelengths possesses an acidic proton and can be reversibly deprotonated to form a chemical species responsible for the lower wavelength feature. Scheme 1 shows that M-OOH forms M-(η$_2$-O$_2$) via reversible deprotonation, and the equilibrium between the two depends on the concentration of protons in the solvent.$^{54,55}$ Figure S10a shows Raman spectra collected in situ on Ti-BEA taken under identical neutral (0.1 M H$_2$O$_2$, 0.4 M H$_2$O, in CH$_3$Cl, 313 K), basic (0.01 M NH$_4$OH), and acidic (0.01 M HCl) solutions as those used in Figure 3. The Raman features at 491 and 750 cm$^{-1}$ correspond to vibrations of the zeolite framework (e.g., O atom vibration perpendicular to M-O-M moieties).$^{62}$ The peak area of this peak at 621 cm$^{-1}$ feature increases upon adding NH$_4$OH and decreases upon adding HCl, which qualitatively corroborates the phenomena observed in Figure 3. Figure S10b shows the peak area of the 380 nm UV–vis feature correlates to the peak area of the 621 cm$^{-1}$ Raman feature of Ti-(η$_2$-O$_2$).$^{54,55}$ The peak area of this 621 cm$^{-1}$ feature increases upon adding NH$_4$OH and decreases upon adding HCl, which qualitatively corroborates the phenomena observed in Figure 3. These in situ UV–vis and Raman spectra together with reports of Tilley and co-workers$^{52}$ and Ivanchikova et al.$^{53}$ show that the higher wavelength species must be a M-OOH intermediate and the lower wavelength species should be a M-(η$_2$-O$_2$) on each M-BEA and M-SiO$_2$ catalyst.

In summary, these in situ UV–vis and Raman spectra strongly suggest that M-OOH (higher wavelength) and M-(η$_2$-O$_2$) (lower wavelength) species form irreversibly upon activation of H$_2$O$_2$ in CH$_3$CN, and that these species are plausible surface intermediates for alkene epoxidation.

3.2. Identification of Intermediates Responsible for Alkene Epoxidation. The identification of the exact active
intermediate for alkene epoxidation among these M-BEA and M-SiO₂ materials is necessary in order to relate electronic structure of the reactive intermediates to epoxidation rates and selectivities. Figure 4 shows that the normalized intensities of the UV–vis absorbance features for M-OOH and M-(η²-O₂) intermediates attenuate exponentially with time upon contact with a flowing solution containing cyclohexene (C₆H₁₀) 0.1 M, 0.4 M H₂O₂ in CH₃CN, 313 K). Differences in the rate of attenuation for individual UV–vis absorbance features indicate that specific intermediates are more reactive than others on each catalyst. For example, on Ti-BEA and Ti-SiO₂ the UV–vis features corresponding to Ti-OOH attenuate at a greater rate than those for Ti-(η²-O₂), whereas the opposite trend is observed on Nb- and Ta-based catalysts.

Scheme 1 shows that H₂O₂ activates on M-BEA and M-SiO₂ materials to form a pool of M-OOH and M-(η²-O₂) intermediates which then either interconvert or react with alkenes to yield epoxides and to regenerate the active site. The interconversion of these two species (k_i and k⁻¹) must be accounted for in order to accurately estimate the values of the rate constants for the consumption of M-OOH (k_OOH) and M-(η²-O₂) (k_O₂) by reaction with cyclohexene. The relationship between k_i and k⁻¹ is constrained by the equilibrium coefficient (K_i; i.e., ratio of k_i to k⁻¹) that represents the ratio of M-OOH to M-(η²-O₂) species under reaction conditions. (SI, section S2.3, outlines the procedure for estimating K_i on the different M-BEA materials.)

Table 2 shows the ratio of the rate constants for the reaction between M-OOH with C₆H₁₀ to M-(η²-O₂) with C₆H₁₀ on all materials that are calculated by mathematically modeling the rate expressions derived from the mechanism in Scheme 1 (SI, section S2) and numerically determining the rate constants from the consumption of the species detected via in situ UV–vis (Figure 4). The differences between the rate constants for epoxidation by M-OOH and M-(η²-O₂) intermediates reveal distinct periodic trends in reactivity. Comparison of the ratio of calculated rate constants for M-OOH to M-(η²-O₂) consumption on Ti materials show that the rate constant for Ti-OOH to epoxidize cyclohexene is greater than that for epoxidation by M-(η²-O₂) (i.e., k_OOH > k_O₂), while the opposite is true for reactions on Nb and Ta catalysts (i.e., k_O₂ > k_OOH). The difference between values of k_OOH and k_O₂ on M-BEA and M-SiO₂ materials suggests that the active intermediate on Ti catalysts is Ti-OOH species, while Nb and Ta materials react through Nb-(η²-O₂) and Ta-(η²-O₂) complexes, respectively. The implication of these specific reactive intermediates on these materials was tested also by a complementary and independent method, described next.

Analysis of the isomeric distribution of epoxide products formed by the reaction of Z-stilbene with H₂O₂ on M-BEA and M-SiO₂ catalysts (0.003 M Z-stilbene, 0.005 M H₂O₂, in CH₃CN, 313 K) can provide direct evidence for the identity of the reactive surface species (i.e., the “radical clock” technique). Epoxidations of alkenes that involve M-OOH species proceed through a concerted O atom transfer step that retains the stereochemistry of the alkene reactant (i.e., through a “butterfly” transition state or Prilezhaev-type mechanism). Alternatively, epoxidations that occur via M-(η²-O₂) intermediates must react through a multi-step mechanism that involves the stepwise formation of the two C–O bonds that allows for rotation about the C–C bond to form the E-isomer. Examples of such mechanisms include those postulated for the stepwise formation of oxirane rings on homogeneous Mo complexes (later disproven) and a biradical mechanism for homogeneous vanadium complexes. Either mechanism could reproduce the mixture of isomers observed to form on the group 5 M-BEA and M-SiO₂ catalysts. Table 2 shows that Ti catalysts preferentially form Z-stilbene oxide, while Nb and Ta materials give nearly equimolar distributions of Z- and E-stilbene oxide products. Consequently, these selectivities indicate that epoxidations occur primarily through Ti-OOH.

Table 2. Ratio of the Rate Constants for the Consumption of M-OOH to That of M-(η²-O₂) by Reaction with C₆H₁₀ and Z:E (cis:trans) Product Ratios from the Epoxidation of Z-Stilbene (0.003 M Z-Stilbene, 0.005 M H₂O₂, in CH₃CN, 313 K)

<table>
<thead>
<tr>
<th>sample</th>
<th>k_OOH/k_O₂</th>
<th>Z:E ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-BEA</td>
<td>1.7</td>
<td>9.2 ± 0.3</td>
</tr>
<tr>
<td>Nb-BEA</td>
<td>0.6</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>Ta-BEA</td>
<td>0.6</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>Ti-SiO₂</td>
<td>11.1</td>
<td>10.1 ± 0.4</td>
</tr>
<tr>
<td>Nb-SiO₂</td>
<td>0.4</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>Ta-SiO₂</td>
<td>0.5</td>
<td>0.9 ± 0.1</td>
</tr>
</tbody>
</table>
on Ti-BEA and Ti-SiO₂ and via Nb-(η²-O₂) and Ta-(η²-O₂) on the Nb and Ta catalysts, which are consistent with the interpretation of the in situ UV–vis measurements (Figure 4). Previous studies have shown that the microporous nature of the *BEA framework does not inhibit the diffusion of Z-stilbene or influence the preference for Z- or E-isomer formation,¹⁰ which suggests also that the larger-pore SiO₂ supports do not influence the distribution among these epoxide products.

In summary, the independent estimates for the values of rate constants for specific elementary steps (Scheme 1) derived from the in situ UV–vis experiments (Figure 4) and the observed isomeric product distributions from reactions of Z-stilbene with H₂O₂ (Table 2) both indicate that all Ti-based materials in this study epoxidize alkenes through the Ti-OOH intermediate, while Nb- and Ta-based catalysts react through M-(η²-O₂) species. Notably, the difference in coordination environment (i.e., metal atoms incorporated into the *BEA framework compared to those grafted onto mesoporous SiO₂) does not significantly affect the electronic structure (Figure 2) of the intermediates formed upon H₂O₂ activation.

### 3.3. Mechanistic Interpretations of Styrene Epoxidation Rates

Figure 5 shows turnover rates for the formation of styrene oxide (C₈H₈O) via primary reaction pathways as a function of [C₈H₈] for (a) M-BEA (closed symbols), including Ti-BEA (blue ▼, 0.01 M H₂O₂), Nb-BEA (black ■, 1 mM H₂O₂), and Ta-BEA (orange ◆, 1 mM H₂O₂) and (b) M-SiO₂ (open symbols), including Ti-SiO₂ (blue ▼, 0.01 M H₂O₂), Nb-SiO₂ (black ■, 0.01 M H₂O₂), and Ta-SiO₂ (orange ◆, 0.01 M H₂O₂) in CH₃CN at 313 K. Dashed lines are intended to guide the eye.

Scheme 2. Proposed Elementary Steps for C₈H₈ Epoxidation and H₂O₂ Decomposition over M-BEA and M-SiO₂ Catalysts

For brevity, only group 4 catalysts (i.e., Ti) are shown. The oval superimposed over the equilibrium arrows represents a quasi-equilibrated step, while the carat (^) superimposed over the reaction arrow represents a kinetically relevant step. The depictions of M-OOH 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. Scheme S1 shows an analogous proposed set of elementary steps for group 5 (i.e., Nb and Ta) catalysts. The M-OOH intermediates drawn are intended to represent the pool of M-OOH and M-(η²-O₂) species that are present as shown by UV–vis (Figure 2).
[H$_2$O$_2$] suggest that the identity of the most abundant reactive intermediate (MARI) changes from a H$_2$O$_2$-derived species to one originating from C$_8$H$_8$. Scheme 2 depicts a series of elementary steps that account for the measured effects of [C$_8$H$_8$] (Figure 5) and [H$_2$O$_2$] (Figure S12) on the rates of C$_8$H$_8$ epoxidation. The catalytic cycle involves the quasi-equilibrated adsorption of C$_8$H$_8$ (step 1) and H$_2$O$_2$ (step 2), followed by the irreversible activation of H$_2$O$_2$ (step 3) to form a pool of M-OOH and M-(η$^2$-O$_2$) intermediates, which are collectively denoted as “M-(O$_2$)” for the subsequent development of rate expressions. The active M-(O$_2$) intermediates react either with C$_8$H$_8$ to form the epoxide (C$_8$H$_8$O) (step 4) or with H$_2$O$_2$ (step 5) to decompose nonproductively. The C$_8$H$_8$O product subsequently desorbs in a quasi-equilibrated manner (step 5). C$_8$H$_8$O formation rates represent the kinetically relevant reaction of M-(O$_2$) with C$_8$H$_8$.

\[ r_e = k_i[M-(O_2)][C_8H_8] \]  

(1)

where \( r_e \) is the rate of C$_8$H$_8$O formation, \( [M-(O_2)] \) is the number of the reactive M-OOH complexes (for Ti) or M-(η$^2$-O$_2$) species (for Nb and Ta), and \( k_i \) is the rate constant for step \( x \) in Scheme 2. The application of the pseudo-steady-state hypothesis on the M-(O$_2$) intermediates, in conjunction with a site balance to account for all possible surface intermediates allows eq 1 to be restated as

\[ \frac{r_e}{[L]} = \frac{k_i K_i[H_2O_2][C_8H_8]}{k_i[C_8H_8] + k_i[H_2O_2]} \]  

(2)

where \( [L] \) is the total number of active metal atoms present during the reaction, \( K_i \) is the equilibrium constant for step \( y \), and \( \beta \) describes the summation of the numbers of all potential surface intermediates,

\[ \beta = 1 + K_i[C_8H_8] + K_i[H_2O_2] + \frac{k_y K_i[H_2O_2][C_8H_8]}{k_i[C_8H_8] + k_i[H_2O_2]} + K_i[C_8H_8O] \]  

(3)

where the five terms in eq 3 correspond (in series) to catalytic sites occupied by CH$_3$CN (i.e., the reaction solvent), C$_8$H$_8$, H$_2$O$_2$, M-(O$_2$), or C$_8$H$_8$O (or phenylacetaldehyde), respectively. The complete derivation of the rate expression (eq 2) is shown in the SI, section S3.1.

Equation 2 reproduces the observed effects of [C$_8$H$_8$] (Figure 5) and [H$_2$O$_2$] (Figure S12) on epoxidation turnover rates. At low ratios of [C$_8$H$_8$] to [H$_2$O$_2$] (e.g., <5 on M-SiO$_2$ materials), M-(O$_2$) species are the MARI and eq 2 simplifies to the form

\[ \frac{r_e}{[L]} = k_i[C_8H_8] \]  

(4)

which is quantitatively consistent with turnover rates for styrene epoxidation that increase linearly with [C$_8$H$_8$] (Figure 5) and do not depend on [H$_2$O$_2$] (Figure S12a). Similarly, at higher [C$_8$H$_8$] (e.g., >0.1 M) the reaction products (e.g., C$_8$H$_8$O or phenylacetaldehyde) become the MARI as indicated by epoxidation rates that are independent of [C$_8$H$_8$] (Figure 5) and proportional to [H$_2$O$_2$] (Figure S12b). In this limit, the rate of epoxidation is much greater than the rate of H$_2$O$_2$ decomposition (i.e., \( k_i[C_8H_8] \gg k_i[H_2O_2]; \) Table S4), which simplifies eq 2 to yield

\[ \frac{r_e}{[L]} = \frac{k_i K_i[H_2O_2]}{k_i K_i[C_8H_8]} \]  

(5)

Equation 5 matches the ways in which \( r_e \) changes with variations in [C$_8$H$_8$] and [H$_2$O$_2$] at high [C$_8$H$_8$]. Notably, the dependence of styrene epoxidation rates on [C$_8$H$_8$] and [H$_2$O$_2$] resemble the changes in epoxidation turnover rates during cyclohexene epoxidation on M-BEA materials previously reported to occur through a perfectly analogous set of elementary steps.$^{9,10}$

Equitable comparisons of turnover rates and selectivities require that the reaction conditions result in comparable MARIs (e.g., M-(O$_2$) across all M-BEA and M-SiO$_2$ materials. Figure 6 shows that rates and selectivities for C$_8$H$_8$ epoxidation differ significantly among the M-BEA and M-SiO$_2$ catalysts at standard conditions that result in M-(O$_2$) MARI for all materials (0.01 M C$_8$H$_8$, 5 mM H$_2$O$_2$, 313 K). For example, epoxidation turnover rates on Ti-BEA are ~10 times greater than those for Ta-BEA. In addition, H$_2$O$_2$ selectivities vary by a factor of 30 among these catalysts. Overall, epoxidation rates and selectivities are systematically greater for M-BEA materials than for the M-SiO$_2$ counterparts (e.g., rates and selectivities for Ti-BEA are greater than those on Ti-SiO$_2$ by factors of 7 and 5, respectively).

The underlying reasons for these large differences in rates and selectivities between Ti, Nb, and Ta atoms coordinated to the *BEA framework and those grafted to mesoporous SiO$_2$ must be related to physical differences between the two forms of silica supports. Specifically, these differences do not arise from changes in the identity of the reactive intermediates (section 3.2), which are constant for a given metal atom nor from the reaction mechanisms, which are indistinguishable among the catalysts described here. Therefore, the differences among the performance of the catalysts must be caused by consequential differences in the apparent activation barriers for C$_8$H$_8$ epoxidation and H$_2$O$_2$ decomposition, respectively, that are associated with the crystallographic or morphological differences between the crystalline *BEA framework and the amorphous mesoporous silica support.

3.4. Influence of Metal Identity on Activation Barriers. Transition-state theory (TST) provides a theoretical founda-
tion to quantify the stabilities of the transition states for C\(_8\)H\(_8\) epoxidation (eq 6) and for H\(_2\)O\(_2\) decomposition (eq 7) relative to a known reference state in the catalytic cycle (e.g., the state free energy of the M-(O\(_2\)) reactive intermediates, and M-(O\(_2\))-H\(_2\)O\(_2\) apparent free energies of activation (\(\Delta S^*\)) for position transition states, respectively. Consequently, the apparent free energies of activation (\(\Delta G^\ddagger\)) represent the difference in the relative free energy between the transition state and reference states, as shown by

\[
\Delta G^\ddagger = G^\ddagger + G_{M-(O_2)} - G_X
\]

where \(G^\ddagger\) is the free energy of the relevant transition state (i.e., for C\(_8\)H\(_8\) epoxidation or H\(_2\)O\(_2\) decomposition), \(G_{M-(O_2)}\) is the free energy of the M-(O\(_2\)) reactive intermediates, and \(G_X\) is the free energy of fluid-phase C\(_8\)H\(_8\) or H\(_2\)O\(_2\). Equation 8 emphasizes the need to have a consistent MARI on all catalysts, in order to probe how differences in the identity of the transition metal atoms or type of silica support (i.e., M-BEA versus M-SiO\(_2\)) used influence activation barriers for epoxidation and H\(_2\)O\(_2\) decomposition. Values of the activation enthalpies (\(\Delta H^\ddagger\)) and entropies (\(\Delta S^\ddagger\)) for reactions shown in eqs 6 and 7 are obtained by analysis of transition state equilibrium constants measured as functions of inverse temperature (SI, Figure S13 and section S3.2) using the Eyring equation. 

Table 3 shows activation enthalpies and entropies for both C\(_8\)H\(_8\) epoxidation (\(\Delta H^\ddagger\)) and H\(_2\)O\(_2\) decomposition (\(\Delta H^\ddagger\)) obtained at reaction conditions that result in a M-(O\(_2\)) MARI on each M-BEA and M-SiO\(_2\) sample and in the absence of mass-transfer and diffusive limitations (SI, section S1.3). Table 3 shows that \(\Delta H^\ddagger\) values increase in the order of Ti < Nb < Ta for a given type of catalyst (i.e., M-BEA or M-SiO\(_2\)), which is consistent with the differences in turnover rates in Figure 5 and in agreement with previous findings for cyclohexene epoxidation on M-BEA (M = Ti, Nb, Ta, Zr, and Hf) catalysts.\(^{15}\) Values of \(\Delta H^\ddagger\) for M-BEA materials are, on average, \(\sim 20\) kJ mol\(^{-1}\) lower than the values for the corresponding M-SiO\(_2\) catalysts (e.g., 9 \(\pm\) 3 kJ mol\(^{-1}\) versus 30 \(\pm\) 4 kJ mol\(^{-1}\) for Ti-BEA and Ti-SiO\(_2\), respectively). 

Values of \(\Delta H^\ddagger\) however, do not depend on the identity of the support for a given metal atom (e.g., 45 \(\pm\) 5 kJ mol\(^{-1}\) versus 42 \(\pm\) 4 kJ mol\(^{-1}\) for Nb-BEA and Nb-SiO\(_2\), respectively). Additionally, \(\Delta S^\ddagger\) values do not change significantly within a given type of material (i.e., across M-SiO\(_2\)), within the uncertainty of measurements. \(\Delta S^\ddagger\) values reflect the loss of translational entropy that arises from coordination of C\(_8\)H\(_8\) to the active M-(O\(_2\)) species, which is not expected to depend on the identity of the metal. Notably, values of \(\Delta S^\ddagger\) for M-BEA are \(\sim 50\) J mol\(^{-1}\) K\(^{-1}\) more negative than M-SiO\(_2\) (i.e., a greater entropic loss on M-BEA), which likely arises from the smaller pores of the *BEA framework (0.7 nm for *BEA versus 5.4 nm for SiO\(_2\)) confining the epoxidation transition state to a greater extent than SiO\(_2\).

Interestingly, \(\Delta S^\ddagger\) values do not change when the identity of the metal or the type of silica support (i.e., M-BEA and M-SiO\(_2\)) are changed, which suggests that neither the difference in transition metal identity nor change in pore diameter significantly influences the transition state for H\(_2\)O\(_2\) decomposition.

Figure 7 shows that values of \(\Delta H^\ddagger\) for C\(_8\)H\(_8\) epoxidation correlate linearly with the enthalpies of adsorption for C\(_3\)CN or pyridine (Table 1, section 2.2) coordinated to Lewis acid sites among M-BEA and M-SiO\(_2\) catalysts. These values (i.e., \(\Delta H_{py}\) and \(\Delta H_{CD,CN}\)) are not measurements of Lewis acid strength and cannot be used to compare properties of Lewis acid sites on M-BEA to those on M-SiO\(_2\) because the

![Graph showing the relationship between \(\Delta H^\ddagger\) and \(\Delta H_{CD,CN}\)](image_url)

Figure 7. Comparisons between activation enthalpies for C\(_8\)H\(_8\) epoxidation (\(\Delta H^\ddagger\)) and the enthalpies of adsorption for pyridine (\(\Delta H_{py}\); solid and open symbols) or deuterated acetonitrile (\(\Delta H_{CD,CN}\) symbols with cross (\(\times\)) through them) bound to Lewis acid sites over M-BEA (solid and crossed symbols) or M-SiO\(_2\) (open symbols) measured on a M-(O\(_2\)) saturated surface. Color symbols represent: Ti (blue ▼), Nb (black ■), and Ta (orange ◆). Dashed lines are intended to guide the eye.

<table>
<thead>
<tr>
<th>sample</th>
<th>(\Delta H^\ddagger) (kJ mol(^{-1}))</th>
<th>(\Delta S^\ddagger) (J mol(^{-1}) K(^{-1}))</th>
<th>(\Delta H^\ddagger) (kJ mol(^{-1}))</th>
<th>(\Delta S^\ddagger) (J mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-BEA</td>
<td>9 (\pm) 3</td>
<td>-200 (\pm) 55</td>
<td>31 (\pm) 10</td>
<td>-104 (\pm) 40</td>
</tr>
<tr>
<td>Nb-BEA</td>
<td>39 (\pm) 5</td>
<td>-150 (\pm) 34</td>
<td>45 (\pm) 55</td>
<td>-89 (\pm) 30</td>
</tr>
<tr>
<td>Ta-BEA</td>
<td>50 (\pm) 6</td>
<td>-130 (\pm) 45</td>
<td>56 (\pm) 59</td>
<td>-61 (\pm) 25</td>
</tr>
<tr>
<td>Ti-SiO(_2)</td>
<td>30 (\pm) 4</td>
<td>-90 (\pm) 25</td>
<td>34 (\pm) 55</td>
<td>-110 (\pm) 25</td>
</tr>
<tr>
<td>Nb-SiO(_2)</td>
<td>57 (\pm) 5</td>
<td>-75 (\pm) 20</td>
<td>42 (\pm) 42</td>
<td>-99 (\pm) 18</td>
</tr>
<tr>
<td>Ta-SiO(_2)</td>
<td>71 (\pm) 8</td>
<td>-68 (\pm) 15</td>
<td>60 (\pm) 58</td>
<td>-75 (\pm) 20</td>
</tr>
</tbody>
</table>

*Reported values are calculated from transition state equilibrium constants for styrene epoxidation and H\(_2\)O\(_2\) decomposition determined as functions of inverse temperature (SI, Figure S13 and section S3.2). \(\Delta H^\ddagger\) and \(\Delta S^\ddagger\) values for M-BEA are adapted from ref 10.
values of $\Delta H_{\text{BEA}}$ and $\Delta H_{\text{CD, CN}}$ also depend on dispersive interactions (i.e., van der Waals forces) between the adsorbates and the surfaces of the microporous *BEA or the mesoporous SiO$_2$. These results (i.e., linear correlations in Figure 7) resemble the linear relationships reported between the activation enthalpies cyclohexene epoxidation and $\Delta H_{\text{CD, CN}}$ previously reported for M-BEA catalysts ($M = \text{Ti, Zr, Hf, Nb, and Ta}$),$^{10}$ for which the stabilization of cyclohexene epoxidation transition states by dispersive interactions was similar among all M-BEA.

The underlying causes of these observed trends (Figure 7) and the correlations shown for cyclohexene epoxidation$^{10}$ are nuanced and do not reflect a simple linear dependence on “Lewis acid strength,” which cannot be readily measured. $\Delta H_{\text{BEA}}^f$ values correlate to the adsorption enthalpies for pyridine and CD$_3$CN coordinated to Lewis acid sites for these materials, but these correlations may be fortuitous. Rather, values of $\Delta H_{\text{BEA}}^f$ (and thus, epoxidation rates) depend on the electrophilicity of the reactive intermediates ($-\text{O}_2$), which in turn are influenced by the tendency of the metal center to withdraw electron density from the $\text{−O}_2$ moiety. Figure 7 suggests that pyridine and CD$_3$CN donate electrons to these Lewis acidic sites in ways that happen to be similar to the distribution of charge at the transition state for epoxidation, and as a result, a linear correlation exists.

UV–vis spectra of H$_2$O$_2$-activated catalysts provide direct and quantitative measures of the electronic structure of the reactive M-OOH and M-(η$^2$-O$_2$) complexes in the form of ligand-to-metal charge transfer band energies (LMCT $h\nu$). These LMCT $h\nu$ values reflect the tendency of the metal atoms to accept electrons from these moieties (i.e., another functional measure of the Lewis acid strength).$^{10}$ Figure 8a shows that

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Figure 8. Activation enthalpies for (a) H$_2$O$_2$ decomposition ($\Delta H_{\text{BEA}}^f$, solid and open symbols for M-BEA and M-SiO$_2$, respectively) and (b) epoxidation of C$_8$H$_8$ ($\Delta H_{\text{CD, CN}}^f$, solid and open symbols for M-BEA and M-SiO$_2$, respectively) or C$_6$H$_{10}$ (open symbols with a cross (X) for M-BEA) epoxidation measured on M-(O$_2$) saturated surfaces as a function of ligand-to-metal charge transfer energy (LMCT $h\nu$) of the reactive intermediate identified via in situ UV–vis (section 3.1) and Z-stilbene epoxidation product distributions. Color symbols represent: Ti (blue ▼), Nb (black ■), and Ta (orange ◀). Dashed lines are intended to guide the eye. Values of $\Delta H_{\text{BEA}}^f$ for C$_6$H$_{10}$ epoxidation on M-BEA materials are adapted from ref 10.
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The LMCT $h\nu$, and moreover, the slopes for these dependencies are nearly equal on both M-BEA and M-SiO$_2$ catalysts. These comparisons suggest that more electrophilic M-OOH and M-(η$^2$-O$_2$) species are also more reactive for alkene epoxidation. However, $\Delta H_{\text{BEA}}^f$ depends more strongly on LMCT $h\nu$ in all cases (slope $\sim$28 kJ mol$^{-1}$ eV$^{-1}$; Figure 8b) than does $\Delta H_{\text{CD, CN}}^f$ (slope $\sim$15 kJ mol$^{-1}$ eV$^{-1}$; Figure 8a), which indicates that the selectivities for epoxidation also increase with the electrophilicity of the reactive M-OOH and M-(η$^2$-O$_2$) intermediates. The greater dependence of $\Delta H_{\text{BEA}}^f$ on LMCT $h\nu$ than $\Delta H_{\text{CD, CN}}^f$ may be attributed to the inherent instability of the peroxide (i.e., O═O) bond in H$_2$O$_2$, as the decomposition of H$_2$O$_2$ by reaction with M-OOH intermediates in Ti-SBA-15 has been proposed to occur through a homolytic pathway (i.e., that involves the cleaving of the HO−OH bond).$^{35}$ Finally, the correlation of $\Delta H_{\text{BEA}}^f$ for C$_6$H$_8$ epoxidation to the values of LMCT $h\nu$ (Figure 8b) show that $\Delta H_{\text{BEA}}^f$ are consistently $\sim$20 kJ mol$^{-1}$ greater for M-SiO$_2$ catalysts in comparison to M-BEA materials with similar LMCT $h\nu$.

The clear correlations between $\Delta H^f$ and LMCT $h\nu$ values shown in Figure 8 are more relevant and meaningful than the correlations to $\Delta H_{\text{BEA}}$ and $\Delta H_{\text{CD, CN}}$ (Figure 7), because values of LMCT $h\nu$ report on the electronic structure of an intermediate directly involved in the kinetically relevant steps that dictate turnover rates and selectivities for epoxidations (Scheme 2, steps 4 and 6). Interpretation of the trends shown in Figure 8b reveal several important phenomena. First, the increasing rates and selectivities with decreasing LMCT $h\nu$ (i.e., more electrophilic M-OOH and M-(η$^2$-O$_2$) intermediates that are associated with lower-energy electronic transitions) suggests that these intermediates are electrophilic in nature, which results from the stronger electron-withdrawing nature of the Lewis acidic metal center. Second, the unchanging dependence of LMCT $h\nu$ on $\Delta H_{\text{BEA}}^f$ for both C$_6$H$_8$ and C$_6$H$_{10}$ epoxidation suggests that there may be little, if any, benefit (i.e., changes in selectivities differing from the trend observed in Figure 8) to changing the identity of the metal for different alkene substrates. Third, the constant vertical offset in $\Delta H_{\text{BEA}}^f$ for C$_6$H$_8$ epoxidation of M-BEA and M-SiO$_2$, and lack thereof for $\Delta H_{\text{CD, CN}}^f$ suggests that the pore size of the *BEA framework relative to SiO$_2$ primarily influences the rates of epoxidation, but not H$_2$O$_2$ decomposition. Each of these observations and suggested descriptions is discussed in detail in the following sections.

The electrophilic nature of the M-OOH and M-(η$^2$-O$_2$) species and the unchanging trend in epoxidation rates for C$_6$H$_8$ and C$_6$H$_{10}$ epoxidation on M-BEA can be probed further by measuring the changes in reactions rates that result from systematically changing the electronic structure of the C═C bond in styrene by incorporating different substituents at the para-position. Figure 9 shows that the ratio of the turnover rates for the epoxidation of para-substituted styrenes (x-C$_6$H$_{7}$, where x = -NO$_2$, -Br, -H, -Me, or -OME) to C$_6$H$_8$ (R$/R_0$) decreases exponentially with increasing values of the para Hammett substituent constant ($\sigma_{\text{para}}$) on all M-BEA and M-SiO$_2$ catalysts at a standard set of conditions (3 mM x-C$_6$H$_7$, 0.01 M H$_2$O$_2$ in CH$_3$CN, 313 K). These data strongly suggest that epoxidation rates increase with the electron-donating ability of the para substituent among these reactants. Values of R$/R_0$ depend similarly on $\sigma_{\text{para}}$ for all M-BEA and M-SiO$_2$, and are fit using the Hammett equation.
Figure 9. Ratio of the turnover rates for the epoxidation of para-substituted styrene (x-C6H7; x = -NO2, -Br, -H, -Me, or -OMe) to styrene (3 mM x-C6H7, 0.01 M H2O2 in CH3CN, 313 K) as a function of the Hammett constant (i.e., a Hammett plot) on M-BEA (solid symbols) and M-SiO2 (open symbols). Color symbols represent Ti (blue ▲), Nb (black ■), and Ta (orange ◆). The dashed line represents a fit of eq 9 to all data, which yields a reaction constant (ρ; Table S5 for all individual ρ values) of −0.9 ± 0.1.72

\[
\log \left( \frac{k_x}{k_H} \right) = \sigma_{\text{Ham}} \rho
\]  

(9)

where \( k_x \) and \( k_H \) are the rate constants for x-C6H7 epoxidation and ρ is the reaction constant (calculated ρ values for all M-BEA and M-SiO2 are in Table S4).

The turnover rates for x-C6H7 epoxidation (\( R_x \)) were used in place of \( k_x \) because all reactions were run at equivalent conditions. The average value of ρ (calculated by averaging all ρ for each M-BEA and M-SiO2 material; Table S5) is −0.9 ± 0.1, whose negative sign agrees with the loss of negative charge (i.e., reduction of M-OOH or M-(η2-O2) during epoxidation) that occurs during the 2-electron oxidation of x-C6H7 and shows that electrophilic intermediates possess lower activation barriers (i.e., higher rates) for the epoxidation of increasingly electron-rich C=C.72 Further, the invariance of ρ (i.e., the similarity among values of ρ; Table S5) between all M-BEA and M-SiO2 suggests that the rates of alkene epoxidation change similarly on all materials when the identity (and electronic properties) of the alkene is changed. This suggests that the chemoselectivity for alkene epoxidation (specifically for molecules with multiple C=C) may be independent of the type of metal atom used in these M-BEA or M-SiO2 materials.

3.5. Influence of the Average Pore Diameter of the Catalyst on Activation Barriers. Scheme 3 shows changes in enthalpies that correspond to a set of hypothetical elementary steps for the epoxidation of styrene on M-BEA and M-SiO2 catalysts that correspond to the proposed catalytic cycle (Scheme 2) and the prevalence of M-OOH and M-(η2-O2) species on the active sites at the conditions (i.e., the reference state) used to measure apparent \( \Delta H^\text{App} \) values (i.e., \( \Delta H^\text{App} \)) 71,73 Brieﬂy, styrene adsorbs from the fluid phase into the micro- or mesoporous environment near the active M-OOH or M-(η2-O2) complex, which corresponds to the enthalpy for adsorption into the porous environment (i.e., \( \Delta H^\text{ads} \)). Subsequently, adsorbed styrene and M-OOH or M-(η2-O2) combine to form the transition state for epoxidation and undergo an enthalpy change equal to the intrinsic activation enthalpy for the epoxidation reaction (\( \Delta H^\text{Int} \)).

Scheme 3. Changes in Enthalpies Due to the Intermediate Steps That Form the Transition State for C6H4 Epoxidation from a M-(O2) Saturated Surface and Fluid-Phase C6H4

\[\text{Ti-OOH is shown to illustrate the relationship between } \Delta H^\text{App}, \Delta H^\text{Ads}, \text{and } \Delta H^\text{Int} \text{ (see Scheme S2 for analogous scheme for group 5 catalysts). This thermochemical sequence for the epoxidation of C6H4 with a Ti-OOH reference state (i.e., Ti-OOH MASI) uses a transition-state theory formalism that involves the quasi-equilibrated desorption of C6H4 into the pores of M-BEA or SiO2 and the kinetically relevant reaction of C6H4 with Ti-OOH.} \]

\[\text{Scheme 3 shows that } \Delta H^\text{App} \text{ can be related to the other two enthalpy differences as follows} \]

\[\Delta H^\text{App} = \Delta H^\text{Int} - |\Delta H^\text{Ads}| \]  

(10)

In this sequence (Scheme 3), both the \( \Delta H^\text{Ads} \) into the porous voids and, by extension, \( \Delta H^\text{Int} \) depend on morphological properties of the catalyst (e.g., pore size) and the kinetic diameter of the alkene. Values for \( \Delta H^\text{Ads} \) are measured directly by applying van’t Hoff analysis to measurements of C6H4 uptake obtained at identical liquid-phase concentrations (0.03 mM for Si-BEA and 0.007 mM for SiO2). These \( \Delta H^\text{Ads} \) (35 ± 6 kJ mol\(^{-1}\) and 18 ± 3 kJ mol\(^{-1}\) for Si-BEA and SiO2, respectively) are measured in liquid CH3CN (the reaction solvent) to account for the displacement of CH3CN from the vicinity of the active site. The values of \( \Delta H^\text{Int} \) for each catalyst are calculated using eq 10 and measured values for \( \Delta H^\text{Ads} \) and \( \Delta H^\text{Int} \).

Figure 10 shows that \( \Delta H^\text{Int} \) for C6H4 epoxidation for all M-BEA and M-SiO2 materials correlate linearly with the LMCT among values of \( \eta \); Table S5) between all M-BEA and M-SiO2 materials when the identity (and electronic properties) of these M-OOH and M-(η2-O2) complexes on (Figure 10) suggest that the electronic structure and the vicinity of the active site. The values of \( \Delta H^\text{Int} \) on a given catalyst are calculated using eq 10 and measured values for \( \Delta H^\text{Ads} \) and \( \Delta H^\text{Int} \).

The combination of nearly equal values for \( \Delta H^\text{Int} \) on a given transition metal to crystalline *BEA or amorphous SiO2 do not change the relationship between \( \Delta H^\text{Int} \) and the electronic structure (i.e., LMCT \( h_v \)) of the reactive M-OOH or M-(η2-O2) intermediates (section 3.1). These similarities seem to be a reasonable result of the nearly equivalent values for LMCT \( h_v \) for specific M-(O2) complexes on *BEA and SiO2 supports (i.e., LMCT \( h_v \) for Ti-BEA is not statistically different from that for Ti-SiO2), suggested by the corresponding UV–vis spectra (section 3.1, Figure 2). Consequently, these data (Figure 10) suggest that the electronic structure and the intrinsic reactivity of these M-OOH and M-(η2-O2) complexes do not depend on the choice of siliceous support.

The combination of nearly equal values for \( \Delta H^\text{Int} \) on a given transition metal to crystalline *BEA or SiO2, the similar LMCT \( h_v \) for these complex molecules, and the relationships depicted in
scheme, in conjunction with time-resolved UV–vis spectroscopy of the reaction of H₂O₂-activated materials with cyclohexene, reveal that Ti-materials primarily react through the Ti-OOH intermediate, while Nb- and Ta- catalysts react through the M-(η²-O₂) species. This suggests that changing the type of silica support from the *BEA framework to mesoporous SiO₂ does not significantly influence the identity or electronic properties of the reactive intermediates for epoxidation by these group IV and V catalysts. Moreover, the dependence of styrene oxide formation rates on reactant (i.e., C₆H₆ and H₂O₂) concentrations show that all M-BEA and M-SiO₂ react through a nearly identical mechanism. All catalysts first adsorb H₂O₂, followed by irreversible activation to form a pool of M-OOH and M-(η²-O₂) intermediates, which then react with styrene or H₂O₂ to form the corresponding epoxide or decomposition products, respectively. Correlation of activation enthalpies for C₆H₆ epoxidation and H₂O₂ decomposition, on all M-BEA and M-SiO₂ catalysts, to the ligand-to-metal charge transfer band energies of the reactive intermediates show more electrophilic M-OOH or M-(η²-O₂) species are both more reactive and selective for alkene epoxidation. Hammett analysis for the epoxidation of para-substituted styrene shows that all M-BEA and M-SiO₂ possess similar chemoselectivities for the epoxidation of alkenes with varying electronic properties. The rates and selectivities of C₆H₆ epoxidation are systematically higher on M-BEA than M-SiO₂ materials, which arise from increased dispersive interactions of the transition state for epoxidation with the walls of *BEA relative to that of SiO₂. This work reveals two discrete design criteria for epoxidation catalysts—the electron affinity of the catalytic site that affects the electrophilicity of the active complex, where more electrophilic intermediates are more active and selective for epoxidation, and the size of the surrounding pore, which can selectively stabilize transition states for epoxidation relative to H₂O₂ decomposition.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b03986. Characterization data, M-BEA active-site titrations, X-ray photoelectron data, in situ UV–vis data analysis, rate expression derivation, activation enthalpy and entropy calculations, and Hammett reaction constants, including Schemes S1 and S2, Tables S1–S5, and Figures S1–S13 (PDF).

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4. CONCLUSIONS

The intrinsic activation enthalpies (∆H^ff) for the epoxidation of C₆H₆ over M-BEA (closed symbols) and M-SiO₂ (open symbols) measured on a M-(O₂) saturated surface (Figure 8b) as a function of ligand-to-metal charge transfer energies (LMCT Eₜ). Color symbols represent: Ti (blue ▼), Nb (black ■), and Ta (orange ◆). Dashed line represents a linear regression to all data.

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Figure 10. Intrinsic activation enthalpies (∆H^ff) for the epoxidation of C₆H₆ over M-BEA (closed symbols) and M-SiO₂ (open symbols) measured on a M-(O₂) saturated surface (Figure 8b) as a function of ligand-to-metal charge transfer energies (LMCT Eₜ). Color symbols represent: Ti (blue ▼), Nb (black ■), and Ta (orange ◆). Dashed line represents a linear regression to all data.

Scheme 3 indicate that the differences in turnover rates, selectivities, and ∆H^ff are consequences of differences in the values of ∆H_ads for styrene within the pores of *BEA (∼35 ± 6 kJ mol⁻¹ in 0.7 nm siliceous pores)⁷⁴ and SiO₂ (∼18 ± 3 kJ mol⁻¹ in 5.4 nm siliceous pores). Thus, stronger, dispersive interactions within the smaller pores of *BEA preferentially stabilize the transition state for styrene epoxidation relative to that in SiO₂ (and also H₂O₂ decomposition transition states in both materials) and leads to ∆H^ff values that are systematically ∼20 kJ mol⁻¹ lower in M-BEA than on M-SiO₂ catalysts (Figure 8b). Notably, values of ∆H^ff (Figure 8a) do not depend on the pore size of the catalyst, which suggests that the same dispersive interactions that preferentially stabilize the transition state for C₆H₆ epoxidation do not affect H₂O₂ decomposition. H₂O₂ has a Stokes diameter (∼0.24 nm)⁷⁵ that is significantly smaller than the diameter of the pores within *BEA (∼0.7 nm) or SiO₂ (5.4 nm), which suggests that H₂O₂ cannot be stabilized as significantly as styrene by interactions with the pore walls at the transition state for decomposition. Previous studies investigating the oxidation of alkanes and alkenes on TS-1 and Ti-silicate (TiO₂–SiO₂) have shown that TS-1 possesses significantly higher rates and selectivities for 1-hexene epoxidation and cyclohexanone ammoxidation using aqueous H₂O₂.⁵⁴,⁷⁶,⁷⁷ These reports attributed the large differences in reactivity (i.e., a 30-fold increase in rates and 10-fold increase in selectivities for 1-hexene epoxidation) to a smaller number of Ti active sites that are available for reaction in TiO₂–SiO₂ than TS-1.⁵⁴ However, it seems likely that the differences may have arisen from greater heats of adsorption of 1-hexene (and likely cyclohexanone) in the MFI framework relative to mesoporous TiO₂–SiO₂ which results in a concomitant decrease in the apparent activation enthalpies for epoxidation⁵⁴ (and ammoxidation).⁷⁶,⁷⁷ Consequently, these data and interpretations reveal two orthogonal design criteria for alkene epoxidation catalysts. First, the design of materials with greater electron affinities (i.e., stronger Lewis acids) will result in more electrophilic M-(O₂) intermediates that possess both increased rates and selectivities for alkene epoxidation. Second, the pore environment (i.e., pore diameter, and likely the hydrophobic/hydrophilic character)⁷⁸–⁸¹ surrounding the active sites can be selected to maximize dispersive interactions with the desired alkene and increase the transition state stabilization for epoxidation to confer both greater rates and selectivities. Ongoing studies in our group seek to understand the effects of silanol density (and how this relates to hydrophilicity) on the rates and selectivities of alkene epoxidation within similar materials.
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The authors declare no competing financial interest.

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