# Rate and Selectivity Control in Thioether and Alkene Oxidation with H<sub>2</sub>O<sub>2</sub> over Phosphonate-Modified Niobium(V)–Silica Catalysts

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Supported metal oxide catalysts are versatile materials for liquid-phase oxidations, including alkene epoxidation and thioether sulfoxidation with  $H_2O_2$ . Periodic trends in  $H_2O_2$  activation was recently demonstrated for alkene epoxidation, highlighting Nb-SiO<sub>2</sub> as a more active and selective catalyst than Ti-SiO<sub>2</sub>. Three representative catalysts are studied consisting of Nb<sup>V</sup>, Ti<sup>V</sup>, and Zr<sup>V</sup> on silica, each made through a molecular precursor approach that yields highly dispersed oxide sites, for thioanisole oxidation by  $H_2O_2$ . Initial rates trend Nb > Ti  $\ge$  Zr, as

Introduction

Metal oxide catalysts are important materials for many transformations in chemical synthesis and manufacturing.<sup>[1]</sup> Selective liquid-phase oxidations with environmentally benign oxidants such as  $H_2O_2$  have received significant attention from the catalysis community in recent years, with particular emphasis on alkene, alkane, aromatic, and thioether oxidations.<sup>[1b,2]</sup> Of the supported oxides, titania–silica (Ti-SiO<sub>2</sub>) is the most commonly studied catalyst for these and other transformations with alkyl hydroperoxide oxidants,<sup>[3]</sup> and formulations of these catalysts have been studied extensively for use with  $H_2O_2$  for alkene epoxidation<sup>[4]</sup> and for thioether oxidation.<sup>[4a,5]</sup>

Sulfoxides are important primary reagents in organic synthesis and serve as valuable synthons for many chemically and biologically active molecules,<sup>[6]</sup> such as omeprazole and other proton-pump inhibitor drugs.<sup>[7]</sup> While sulfoxides are important building blocks for pharmaceuticals, a key environmental application of thioether oxidation is the oxidative desulfurization (ODS) of liquid hydrocarbon transportation fuels, which contain 200–1100 ppm fused ring thiophenic sulfides following conventional hydrodesulfurization processes.<sup>[8]</sup> Increasing regulation of ultralow sulfur content (10–15 ppm) in many countries has motivated the research and process development of oxidation by  $H_2O_2$  and downstream separations to remove residual benzothiophene derivatives. Additionally, an important sulfoxidation application is the selective detoxification of

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for epoxidation, and Nb outperforms Ti for a number of other thioethers. In contrast, selectivity to sulfoxide vs. sulfone trends Ti > Nb >> Zr at all conversions. Modifying the Nb-SiO<sub>2</sub> catalyst with phenylphosphonic acid does not completely remove sulfoxidation reactivity, as it did for photooxidation and epoxidation, and results in an unusual material active for sulfoxidation but neither epoxidation nor overoxidation to the sulfone.

organosulfide-containing chemical nerve agents, wherein a high selectivity to the less toxic sulfoxide product is critical.<sup>[9]</sup>

Few studies have comparatively assessed supported transition-metal oxide catalyst systems, particularly those outside of titania–silica, for thioether versus alkene oxidation by  $H_2O_2$ .<sup>[5c, 10]</sup> Undercoordinated Group 4 and 5 oxide sites dispersed on silica are observed to give the highest rates of epoxidation with  $H_2O_2$ .<sup>[4a, 11]</sup> and separately for thioether oxidation.<sup>[5b,c, 10c, 12]</sup> However, active site and/or surface modifications, such as silylation, have significant implications for  $H_2O_2$  activation and for the resulting product selectivities in both reactions.<sup>[3b,4c, 11b, 13]</sup>

We have recently reported periodic trends in alkene epoxidation with  $H_2O_2$  over a series of highly-dispersed silica-supported Group 4 and 5 metal oxides.<sup>[14]</sup> From this study, we demonstrated that niobia–silica (Nb-SiO<sub>2</sub>) is a high performer for epoxidation, proceeding with two-fold faster rate and higher selectivity for direct, heterolytic (that is, non-radical)  $H_2O_2$  pathways in cyclohexene epoxidation relative to benchmark Ti-SiO<sub>2</sub> catalysts. We followed this investigation with a detailed study of synthesis–structure–function relationships for a broad series of Nb-SiO<sub>2</sub> catalysts,<sup>[15]</sup> and we applied an in situ poisoning experiment using phenylphosphonic acid (PPA) to count the number of Lewis acid sites active for *cis*-cyclooctene epoxidation.<sup>[16]</sup> This study also demonstrated mechanistic differences between the Nb<sup>V</sup> and benchmark Ti<sup>IV</sup> cyclooctene epoxidation catalysts.<sup>[15]</sup>

In the past, we have used cyclooctene epoxidation as a probe reaction during PPA titration and to investigate different supported oxides because this reaction is intrinsically selective to the epoxide.<sup>[13g, 16, 17]</sup> Herein, we expand our prior studies to examine thioanisole and other thioether oxidations with  $H_2O_2$  over three representative, highly dispersed supported oxides, Nb-SiO<sub>2</sub>, Ti-SiO<sub>2</sub>, and Zr-SiO<sub>2</sub>, each made through a molecular

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precursor method that yields highly dispersed sites. We then demonstrate the impact of PPA-modification on Nb-SiO<sub>2</sub> in thioanisole sulfoxidation and cyclohexene epoxidation to highlight how product selectivity is impacted by this site modification method.

#### **Results and Discussion**

We have recently demonstrated periodic trends in  $H_2O_2$  activation via a series of highly dispersed Group 4 and 5 metal oxide catalysts supported on silica, for which catalyst activity and pathway selectivity in cyclohexene epoxidation trends Nb > Ti > Ta  $\gg$  Zr > Hf.<sup>[14]</sup> We now examine thioether oxidation using catalysts from three representative regimes for epoxidation: the high-performing Nb-SiO<sub>2</sub>, the classically-studied Ti-SiO<sub>2</sub>, and the low-performing Zr-SiO<sub>2</sub>. These catalysts are synthesized as before by grafting calixarene coordination complexes of niobium(V), titanium(IV), and zirconium(IV) onto mesoporous silica gel under reflux conditions in toluene, followed by air calcination of the recovered solids at 550 °C.<sup>[14]</sup> An exemplary synthesis of Nb-SiO<sub>2</sub> is depicted in Scheme 1.



**Scheme 1.** Synthesis of Nb-SiO<sub>2</sub> (at right) catalyst from grafting of niobium(V)–calixarene complex to mesoporous SiO<sub>2</sub>. Protocol: (i) reflux under N<sub>2</sub>, anhydrous toluene, 14 h; (ii) SiO<sub>2</sub>, reflux under N<sub>2</sub>, 24 h; (iii) calcine, 550 °C, O<sub>2</sub>/N<sub>2</sub>, 6 h. See the Experimental Section for details. Catalyst is drawn hydroxylated to reflect likely state under reaction conditions.<sup>[18]</sup> Additional water molecules may also be coordinated.

Physicochemical data for these catalysts are summarized in Table 1. We and others have extensively reported the use of metallocalixarene precursors as a generalizable route to the synthesis of highly dispersed supported oxide catalysts for Nb<sup>V</sup><sup>[14,15]</sup> Ti<sup>IV</sup><sup>[19]</sup> Ta<sup>V</sup><sup>[119,17b]</sup> Zr<sup>V<sup>[14,20]</sup></sup> and Hf<sup>V<sup>[14]</sup></sup>. The steric bulk and chelation of the calixarene ligand ensure high dispersion of the metal centers during grafting and subsequent calcina-

Table 1. Physicochemical data for Nb-SiO $_{2^{\prime}}$ Ti-SiO $_{2^{\prime}}$ and Zr-SiO $_{2}$ catalysts.						
Catalyst	mmol g <sup>-1[a]</sup>	M atoms nm <sup>-2[b]</sup>	wt%	Optical edge <sup>[c]</sup> [eV]	Ref	
Nb-SiO <sub>2</sub>	0.27	0.28	2.2	3.3, <sup>[d]</sup> 3.9	this	
Zr-SiO <sub>2</sub>	0.20	0.21	0.96 2.1	3.8 3.7	[14, 15] [15, 20]	

[a] Determined from ICP-OES of digested catalysts. [b] Normalized to BET specific surface area of bare SiO<sub>2</sub> (570 m<sup>2</sup>g<sup>-1</sup>). There are negligible changes to surface area after grafting and calcination at these loadings. [c] Calculated from *x*-intercept of indirect Tauc plot of  $[F(R)-hv]^{1/2}$  vs. hv (eV), where F(R) is Kubelka–Munk pseudoabsorabnce.<sup>[21b,23]</sup> [d] Shoulder feature.

tion,<sup>[14,15]</sup> and the metal surface densities reported here (0.21– 0.28 atoms nm<sup>-2</sup>) are consistent with a previously reported geometric limit for grafting of these bulky precursors.<sup>[19a]</sup> Upon calcination, diffuse–reflectance UV/Vis (DRUV/Vis) spectroscopy of Nb-SiO<sub>2</sub>, Ti-SiO<sub>2</sub>, and Zr-SiO<sub>2</sub> show strong absorbance only in the UV range (Figure 1), evidence of highly dispersed metal



Figure 1. Diffuse reflectance UV/Vis spectra of Nb-SiO<sub>2</sub> (blue), Ti-SiO<sub>2</sub> (green), and Zr-SiO<sub>2</sub> (orange) normalized to the sole intense feature.

oxide centers.<sup>[21]</sup> The small shoulder at about 340 nm for Nb-SiO<sub>2</sub> suggests a small extent of aggregation.<sup>[11f,22]</sup> Further, all three materials have optical edge energies of 3.7–3.9 eV, as calculated from a separate Tauc plot,<sup>[21b,23]</sup> in agreement with previous edge values for highly dispersed oxides reported by us<sup>[14–16,20]</sup> and by others<sup>[11f,21b,22,24]</sup> for similar catalysts. We briefly note that if the calixarene ligand is unavailable, catalysts with moderately diminished performance can often be synthesized from metallocene chloride precursors,<sup>[15]</sup> although they are typically more expensive than if the metal alkoxide/chloride and calixarene ligand were obtained separately.<sup>[11a]</sup>

We first examine the catalytic activity of these three catalysts for the oxidation of thioanisole by  $H_2O_2$  (Scheme 2). Reaction conditions of 0.11  $\mu$  thioanisole, 0.32  $\mu$   $H_2O_2$  and 1.0 mol% metal at 45 °C are used to assess overall catalytic activity and selectivity to the intermediate product, methyl phenyl sulfoxide.



Scheme 2. Catalytic oxidation of thioanisole by H<sub>2</sub>O<sub>2</sub>.

The catalytic rates of thioanisole consumption under these conditions trend as Nb > Ti  $\gg$  Zr (Table 2), in the same order we previously observed for the epoxidations of cyclooctene,<sup>[15]</sup> cyclohexene,<sup>[14]</sup> and styrene.<sup>[14]</sup> All catalysts reach complete conversion within 6 h, with Nb-SiO<sub>2</sub> and Ti-SiO<sub>2</sub> converting all thioanisole within 30 min of reaction (Figure 2). Nb-SiO<sub>2</sub> and Ti-SiO<sub>2</sub> also have similarly high selectivities towards the sulfoxide intermediate, with maximum values of about 80% observed at short reaction times (Table 2), consistent with prior

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Table 2. Summary of thioanisole oxidation by $H_2O_2$ in $CH_3CN$ at 45 $^\circ C.^{[a]}$						
Catalyst	Initial rat [mol L <sup>-1</sup> min <sup>-1</sup> ]	e <sup>(b)</sup> [min <sup>-1</sup> ] <sup>[c]</sup>	Max. sulfoxide sel. <sup>[d]</sup> (Conv. at max. sel.) [%	$k_1/k_2^{[e]}$		
Nb-SiO <sub>2</sub>	9.5×10 <sup>-3</sup>	9.0	78 (51)	$2.4\pm0.1$		
Ti-SiO <sub>2</sub>	8.8×10 <sup>-3</sup>	7.9	84 (48)	$4.6\pm0.3$		
Zr-SiO <sub>2</sub>	$2.6 \times 10^{-3}$	2.3	54 (4)	$0.21\pm0.02$		

[a] See text for reaction conditions. [b] From linear fit through thioanisole disappearance vs. time over first 15 min. [c] Initial rate relative to moles total Nb, Ti, or Zr. [d] Selectivity =  $mol_{sulfoxide}$  ( $mol_{sulfoxide} + mol_{sulfoxide}^{-1} \times 100\%$ . [e] Ratio of rate constants corresponding to Scheme 2. See Figure 2 for fits and the Supporting Information for methods of fitting and estimating uncertainty.



**Figure 2.** Concentration time-course plots for thioanisole oxidation at 45 °C via a) Nb-SiO<sub>2</sub>, b) Ti-SiO<sub>2</sub>, and c) Zr-SiO<sub>2</sub>. Legend: thioanisole (green), methyl phenyl sulfoxide (blue), methyl phenyl sulfone (red), sum of sulfoxide and sulfone products (yellow). Solid lines are best fits to an overall second order rate law (see the Supporting Information). See reaction conditions in the text.

reports by others for similar catalysts.<sup>[5b-d]</sup> In contrast, Zr-SiO<sub>2</sub> notably facilitates almost exclusive formation of the methyl

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phenyl sulfone overoxidation product; few reports exist in the literature for silica-supported zirconium(IV) catalysts for sulfoxidation, but similarly poor (< 20%) sulfoxide selectivities have been noted by others under similar conditions in acetonitrile.<sup>[25]</sup> At high conversions of thioanisole, all three catalysts here give total oxidation to the sulfone (Figure 2), as would be expected for a series reaction.

To further evaluate sulfoxide selectivity across the entire extent of reaction, we estimate the apparent rate constants  $k_1$ and  $k_2$  for the overall reaction (Scheme 2). Others have previously observed this reaction to be first order with respect to each H<sub>2</sub>O<sub>2</sub> and the substrate (either thioanisole and sulfoxide) when catalyzed by Ti-containing silicates under similar reaction conditions,<sup>[26]</sup> and this assumed model fits our data well (Figure 2; see the Supporting Information for details). Nb-SiO<sub>2</sub> and Ti-SiO<sub>2</sub> exhibit intrinsically good selectivity to the sulfoxide intermediate, with  $k_1/k_2$  ratios of 2.4 and 4.6, respectively, whereas Zr-SiO<sub>2</sub> gives a nearly inverted ratio of 0.21 (Table 2). Sulfoxidation rate constant  $k_1$  values trend Nb > Ti  $\gg$  Zr (Supporting Information, Table S1) and decrease substantially with decreasing Lewis acidity, as we have previously observed for cyclohexene and styrene epoxidation systems.<sup>[14]</sup> Clearly, the identity and strength of the Lewis acid are each critical factors for promoting high activity and selectivity in the sulfoxidation of thioanisole.

The fast rates of Nb-SiO<sub>2</sub> and Ti-SiO<sub>2</sub> for thioanisole oxidation motivates examining the oxidation of fused ring thiophenic sulfides, which are important for the oxidative desulfurization (ODS) of liquid transportation fuels. The oxidation of benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (DMDBT) are evaluated at a representative concentration of 1030 ppm sulfide, in acetonitrile solvent with 3 equiv  $H_2O_2$  and 3 mol% metal at 45 °C. For a given substrate under our conditions, Nb-SiO<sub>2</sub> generally proceeds at about 2- $3 \times$  the initial rate of Ti-SiO<sub>2</sub> (Table 3). In all cases, selectivities to the corresponding sulfone products are > 85 %, consistent with prior reports by others for supported oxides.<sup>[13i,27]</sup> Relative to titania-silica systems, literature studies of silica-supported niobium oxide catalysts for ODS are scarce and do not report rates and conversions compared to Ti benchmarks.  $^{\left[ 27d,28\right] }$  The higher rates of Nb-SiO<sub>2</sub> compared here head-to-head with Ti-SiO<sub>2</sub> highlight how niobium is at least as good a catalyst as

Catalyst Substrate Initial			e <sup>[b]</sup>	Conv. at
		$[mol L^{-1} min^{-1}]$	$[min^{-1}]^{[c]}$	24 h [%]
Nb-SiO <sub>2</sub>	BT	8.1×10 <sup>-5</sup>	0.34	89
	DBT	8.8×10 <sup>-5</sup>	0.51	>99
	DMDBT	$2.4 \times 10^{-5}$	0.16	77
Ti-SiO₂	ВТ	3.7×10 <sup>-5</sup>	0.16	84
	DBT	3.6×10 <sup>-5</sup>	0.21	>99
	DMDBT	$7.7 \times 10^{-6}$	0.053	50
[a] 1030 ppm of the benzothiophene derivative. See the text for reaction conditions. [b] From sulfide disappearance over first 30 min. [c] Initial rate				



the more classically studied titanium. Niobium-based materials certainly warrant more attention in future ODS investigations.

Along with differences in rate, these catalysts exhibit significant differences in thioanisole oxidation selectivity. An outstanding question for many selective oxidation reactions is whether the observed differences in behavior are due to differences in the number or intrinsic activity of the active sites. For example, is a given Nb-SiO<sub>2</sub> active site more selective than the corresponding Zr-SiO<sub>2</sub> active site, or are there relatively more active sites of high selectivity in the Nb material than in the Zr material? For sulfoxidation, there also remain questions about the basic mechanism of catalysis. Some reports of sulfoxidation over Ti-substituted zeolites and polyoxometalates propose homolytic activation<sup>[5c, 26a, 29]</sup> of  $H_2O_2$  with peroxygen transfer to thioether radical cation intermediates,<sup>[30]</sup> while other reports suggest heterolytic activation pathways<sup>[26c, 31]</sup> akin to classical epoxidation systems.<sup>[32]</sup>

To address these questions for the high-performing niobium case, we revisit a site titration technique previously established by our group for epoxidation<sup>[15, 16]</sup> and photooxidation.<sup>[33]</sup> The titrant phenylphosphonic acid (PPA) selectively poisons undercoordinated, Lewis acidic Group 4 and 5 oxide sites in situ during cyclooctene epoxidation with  $H_2O_2$ ; this behavior is due to electron donation by the titrant that strongly inhibits rate-limiting peroxygen transfer to the alkene.<sup>[15,16]</sup> Using this method, it was shown that large families of Ti-SiO<sub>2</sub> and Nb-SiO<sub>2</sub> materials differ in the numbers of active sites, but not their intrinsic activity. However, the intrinsically selective formation of cyclooctene epoxide<sup>[13g, 17a]</sup> left unaddressed the question of intrinsic selectivity.

We now instead assess cyclohexene and thioanisole oxidation using this PPA titration technique to probe reaction selectivity relevant to H<sub>2</sub>O<sub>2</sub>-based oxidation. If the oxide catalyst possesses a distribution of sites with different selectivities, one would expect to observe selectivities that change with the extent of site titration. First, we and others<sup>[14, 34]</sup> have observed cyclohexene epoxidation to be highly selective to non-radical pathways via highly dispersed Nb-SiO<sub>2</sub> catalysts. The reaction network for cyclohexene epoxidation proceeds along parallel allylic radical vs. heterolytic non-radical ("direct") oxidation pathways (Supporting Information, Scheme S1);<sup>[13g, 14, 35]</sup> the former pathway proceeds via cyclohexenyl hydroperoxides generated in situ from unproductive catalytic decomposition of H<sub>2</sub>O<sub>2</sub>. We assess catalyst performance using the pathway branching selectivity,<sup>[14]</sup> S<sub>D/R</sub>, for this network, defined as the ratio of products from direct epoxidation vs. products from a radical route. Epoxide and diol produced via the direct pathway are represented by the sum of epoxide+diol-cyclohexenol-cyclohexenone), with the final term subtracting coproducts specifically generated during epoxidation by cyclohexenyl hydroperoxide; all other C<sub>6</sub> oxygenates are considered to be radical-derived. We note that this definition of pathway selectivity necessarily represents integrated product distributions from reaction start-up to a given reaction time in a batch reactor.

Figure 3 a shows a typical time-course plot of oxygenate product evolution during batch reaction at  $65 \,^{\circ}$ C for  $1.0 \,\text{m}$  cy-



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**Figure 3.** a) Time-course concentration plot for cyclohexene oxidation products with  $H_2O_2$  via Nb-SiO<sub>2</sub> at 65 °C. Legend: epoxide (blue triangles), diol (green diamonds), cyclohexenol (red squares), cyclohexenone (yellow circles). See reaction conditions in the text. b) Cyclohexene oxidation initial rates (total, blue; direct [epoxide + diol–(cyclohexenol–cyclohexenone)], dark green; radical (total–direct), red) versus PPA added to the reactor during in situ titration experiments. Initial rates from first 10 min of reaction. c) Initial total rate versus ratio of direct products to radical products ( $S_{D/R}$ ) formed after 15 min during in situ PPA titrations in (b). In (b) and (c), open circles represent rates of materials pre-treated with PPA, isolated and then used as catalysts, with P content from ICP-OES. Error bars in (c) represent alternative calculations of direct/ radical product yields at 10 min and 60 min of reaction. In (a) and (b), error bars are approximately the size of the data points. Solid and dashed lines are guides to the eye.

clohexene,  $0.12 \text{ M} \text{ H}_2\text{O}_2$  and 1.1 mol% Nb in acetonitrile. Nb-SiO<sub>2</sub> is then pre-treated with different amounts of PPA for 1 h prior to the start of reaction. Across otherwise identical parallel batch reactors, total initial rates of reaction diminish with increasingly added PPA, but the decrease is almost entirely from the direct pathway. As shown in Figure 3 b,c, the direct rate is titrated away, while the radical rate contribution remains small, but essentially unchanged. This observation suggests that PPA

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selectively targets sites that are both the most active *and* the most pathway-selective for direct epoxidation.

Further, two Nb-SiO<sub>2</sub> samples were treated with 0.26 and 1.0 equivalents of PPA (Scheme 3), recovered, washed with acetonitrile, and then used as catalysts (labeled 0.25-PPA-Nb-SiO<sub>2</sub>



**Scheme 3.** Synthesis of PPA-Nb-SiO<sub>2</sub> catalyst from treatment of Nb-SiO<sub>2</sub> with 1.0 equivalent of PPA. Analogous treatment with 0.26 equiv yields 0.25-PPA-Nb-SiO<sub>2</sub>. See the Experimental Section for details.

and PPA-Nb-SiO<sub>2</sub>, respectively). Consistent with prior observations over related materials,<sup>[15, 16]</sup> essentially all of the added PPA is captured by the surface, which gives an increase in the optical edge energy (Supporting Information, Figure S1) and apparent coordination number from X-ray absorption (Supporting Information, Figure S2). Finally, <sup>31</sup>P CP-MAS NMR shows only one type of surface phosphonate regardless of the Nb:P ratio (Supporting Information, Figure S3).<sup>[15, 16]</sup> No loss of Nb is observed.

The activity and pathway selectivity of these materials fits in the trend of the in situ titrations described above, as shown in the open circles in Figure 3 b,c. Thus, phenylphosphonic acid appears to be a permanent modifier of the catalyst, functioning as an electron-donating group that weakens site Lewis acidity and suppresses direct epoxidation activity, leaving a background of radical allylic oxidation unaffected.

Next, we examine the PPA-modified materials in thioanisole oxidation. PPA-Nb-SiO<sub>2</sub> and 0.25-PPA-Nb-SiO<sub>2</sub> are examined under the same conditions as the supported oxides at 45 °C, and the resulting batch reaction profiles are again fitted to a pseudo second-order model in Figure 4a,b. Total rate and corresponding values of rate constants decrease with increasing PPA loading, similar to what was observed with epoxidation. Consistent with our study of in situ titration of Nb-SiO<sub>2</sub> during cyclooctene epoxidation,<sup>[15]</sup> we observe a supralinear decrease in rate constants with added PPA, with about 50% of the rate lost after the catalyst is treated with only 0.25 equiv. PPA.

Adding a full equivalent of PPA decreased the initial sulfoxidation rate by about 70% (Table 4), whereas about 90% was lost for direct cyclohexene oxidation or for prior studies of cyclooctene oxidation. Even though sulfoxidation retains more of its activity than does cyclohexene oxidation, the significant loss of activity with PPA modification does suggest that both thioether and alkene oxidations operate predominantly through non-radical mechanisms over these catalysts.

Interestingly, Nb site modification with PPA significantly boosts the selectivity towards the intermediate product,



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**Figure 4.** a)–b) Concentration time-course plots for thioanisole oxidation at 45 °C using a) 0.25-PPA-Nb-SiO<sub>2</sub> and b) PPA-Nb-SiO<sub>2</sub>. Legend: thioanisole (green), methyl phenyl sulfoxide (blue), methyl phenyl sulfone (red), sum of sulfoxide and sulfone products (yellow). Solid lines best fits to an overall second order rate law (see the Supporting Information). See reaction conditions in the text. c) Relationships among apparent rate constants  $k_1$  (red circles, left vertical axis,  $M^{-2}min^{-1}$ ),  $k_2$  (blue circles, left vertical axis,  $M^{-2}min^{-1}$ ), and ratio  $k_1/k_2$  (yellow triangles, right vertical axis) with PPA/Nb ratio (horizontal axis). Uncertainties are approximately the size of data points unless otherwise shown as bars (see the Supporting Information).

methyl phenyl sulfoxide. The intrinsic selectivities of Nb-SiO<sub>2</sub>, 0.25-PPA-Nb-SiO<sub>2</sub>, and PPA-Nb-SiO<sub>2</sub> are captured in the relative values of the apparent rate constants  $k_1$  and  $k_2$  (Table 4, Figure 4c). Although the magnitude of each rate constant decreases with increasing PPA loaded, the ratio of  $k_1/k_2$  increases by more than twofold upon modification with a full equivalent of PPA. This increase in the relative rate constants gives a maximum of 87% integrated sulfoxide selectivity for that catalyst (Table 4).

The secondary reaction of methyl phenyl sulfoxide to methyl phenyl sulfone with 3 equiv  $H_2O_2$  is also assessed via separate

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Table 4. Kinetic summary of thioanisole oxidation by H <sub>2</sub> O <sub>2</sub> in CH <sub>3</sub> CN with Nb-SiO <sub>2</sub> and PPA-modified catalysts. <sup>[a]</sup>						
Catalyst	<i>T</i> [°C]	Initial Rate <sup>(b)</sup> [mol L <sup>-1</sup> min <sup>-1</sup> ]	[min <sup>-1</sup> ] <sup>[c]</sup>	Max. Sulfoxide Sel. <sup>[d]</sup> (Conv. at Max. Sel.) [%]	$k_1/k_2^{[e]}$	$E_{\rm a}  [\rm kcal  mol^{-1}]^{\rm [f]}$
	25	5.2×10 <sup>-3</sup>	4.9	82 (23)	$3.3\pm0.25$	5 91 06
Nb-SiO <sub>2</sub>	45	9.5×10 <sup>-3</sup>	9.0	78 (51)	$2.4 \pm 0.12$	$E_{a1} = 8.1 \pm 0.6$ $E_{a2} = 13.9 \pm 1.0$
	65	$> 1.6 \times 10^{-2[g]}$	$> 15^{[g]}$	52 (72)	$1.0\pm0.03$	
0.25-PPA-Nb-SiO <sub>2</sub>	45	5.4×10 <sup>3</sup>	4.9	78 (65)	$3.3 \pm 0.26$	
	25	1.4×10 <sup>-3</sup>	1.3	80 (23)	$2.1\pm0.06$	F 11 1 4 0 2
PPA-Nb-SiO <sub>2</sub>	45	$2.8 \times 10^{-3}$	2.6	87 (33)	$5.4 \pm 0.37$	$E_{a1} = 11.1 \pm 0.3$
	65	$5.0 \times 10^{-3}$	4.7	84 (66)	5.2±0.43	$E_{a2} = 6.4 \pm 0.8$

[a] See the text for reaction conditions. [b] From linear fit of thioanisole disappearance vs. time over first 15 min. [c] Initial rate relative to moles total Nb. [d] Selectivity =  $mol_{sulfoxide}$  ( $mol_{sulfoxide}$  +  $mol_{sulfoxide}$  + mol

batch reactions for comparison (Supporting Information, Table S2). While Nb-SiO<sub>2</sub> proceeds about  $3 \times$  faster than PPA-Nb-SiO<sub>2</sub> for the primary oxidation of the thioether, Nb-SiO<sub>2</sub> is observed to have  $> 6 \times$  larger rate than that of PPA-Nb-SiO<sub>2</sub> for the oxidation of sulfoxide to sulfone, consistent with the rate constant ratios calculated from the fit to Figure 4b.

Upon lowering the reaction temperature to 25 °C, initial rates of thioanisole disappearance remain fast for both catalysts (Tables 4; Supporting Information, Table S3); while reaction at 65 °C gives >94% thioether conversion in less than 10 minutes for Nb-SiO<sub>2</sub>. As above, batch reaction data at these temperatures are fit to a second order kinetic rate law to calculate rate constants  $k_1$  and  $k_2$  (Tables 4; Supporting Information, Table S3, Figure S4), and apparent activation barriers for the formations of methyl phenyl sulfoxide ( $E_{a1}$ ) and of methyl phenyl sulfore ( $E_{a2}$ ) over both catalysts are calculated from Arrhenius plots (Figure 5, Table 4).

The sulfoxidation barrier  $E_{a_1}$  increases slightly upon addition of PPA, but the sulfonation barrier  $E_{a_2}$  decreases significantly with the PPA modification. As a result, the sulfonation barrier  $E_{a_2}$  for PPA-Nb-SiO<sub>2</sub> is ca. 5 kcal mol<sup>-1</sup> lower than its sulfoxidation barrier  $E_{a_1}$ . Practically, this results in the useful sit-



**Figure 5.** Relationship of  $ln(k_1)$  (circles) and  $ln(k_2)$  (diamonds) vs. 1000/T (K<sup>-1</sup>) for Nb-SiO<sub>2</sub> (blue) and PPA-Nb-SiO<sub>2</sub> (pink). Dashed lines are best linear regression fits. Data points enlarged to illustrate approximate uncertainty in  $k_1$  and  $k_2$  from second-order rate law fitting (see the Supporting Information).

uation where sulfoxidation selectivity increases with increasing temperature, and thus rate. Mechanistically, these relative differences in apparent activation energies suggest a trade-off between changes in oxidation rate constants and Lewis base binding constants as the PPA is added (Scheme 4).



**Scheme 4.** Proposed catalytic cycle for thioanisole oxidation by  $H_2O_2$  over Nb-SiO<sub>2</sub> and PPA-Nb-SiO<sub>2</sub> catalyst sites. An analogous cycle can be drawn for the conversion of methyl phenyl sulfoxide to methyl phenyl sulfone.

Scheme 4 illustrates possible simplified catalytic cycles for niobium-based catalyst sites with or without added PPA. The cycles are drawn for sulfoxidation; analogous cycles can be drawn for sulfone formation. In these cycles, equilibrated hydrogen peroxide binding ( $K_{H2O2}$  or  $K'_{H2O2}$ ) is followed by ratelimiting electrophilic attack ( $k_1$  or  $k'_1$ ). The prime notation is used for rate constants and equilibrium constants over the PPA-modified catalyst. Over Nb-SiO<sub>2</sub>, there are also additional binding events that are strongly disfavored after PPA modification because of the coordinating P=O. Critically, this creates two different potential reaction pathways. Nb-SiO<sub>2</sub> can oxidize a bound thioether, while PPA-Nb-SiO<sub>2</sub> can only oxidize the substrate through direct attack at the coordinated hydroperoxide, analogous to epoxidation mechanisms. Because of the different Lewis basic groups (substrate or P=O) occupying sites on the Nb, rate constants take the following forms [Eqs (1), (2), (3), and (4)]:

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$$k_{1,\rm Nb} = k_1 K_{\rm thioanisole} K_{\rm H2O2} \tag{1}$$

 $k_{2,\rm Nb} = k_2 K_{\rm sulfoxide} K_{\rm H2O2} \tag{2}$ 

$$k_{1,\text{PPA-Nb}} = k_1 K_{\text{H2O2}} \tag{3}$$

$$k_{2,PPA-Nb} = k'_{2} K'_{H2O2}$$
(4)

In all of these expressions, relatively weak binding is assumed for the other species, as required to keep the kinetics overall first order in the substrate and in H<sub>2</sub>O<sub>2</sub>. Evaluating selectivities, ratios of  $k_1/k_2$  for each catalyst yield different expressions [Eq. (5) and (6)]:

$$\frac{k_1}{k_2}\Big|_{\rm Nb} = \frac{k_1 K_{\rm thioanisole}}{k_2 K_{\rm sulfoxide}} \tag{5}$$

$$\left. \frac{k_1}{k_2} \right|_{\text{PPA-Nb}} = \frac{k_1'}{k_2'} \tag{6}$$

Thus, differences in intrinsic selectivities across temperatures and the resulting observed activation barriers of Nb-SiO<sub>2</sub> may be attributable in part to competitive binding of thioanisole vs. methyl phenyl sulfoxide and their associated adsorption enthalpies. In contrast, PPA-Nb-SiO<sub>2</sub> selectivity is influenced only by intrinsic rate constants, since the ligand's internal P=O group preferentially occupies the open Nb coordination site in a likely resting state.

As a consequence, PPA-Nb-SiO<sub>2</sub> maintains high selectivity even at 65 °C, whereas both sulfoxidation and sulfonation occur over Nb-SiO<sub>2</sub> with nearly equivalent rate constants at this higher temperature (Table 4). Hence, PPA-Nb-SiO<sub>2</sub> advantageously still affords high  $k_1/k_2$  selectivities while operating at faster rates, suggesting formulations of this catalyst are more amenable to flow reactor optimization in practical applications.

This mechanism relies on the phosphonate capping groups hindering the secondary oxidation to methyl phenyl sulfone by out-competing the sulfoxide intermediate for Nb site binding. In contrast, addition of up to 4 catalytic equiv of triphenylphosphine oxide (TPPO) did not affect the reactivity or selectivity of the Nb-SiO<sub>2</sub> catalyst (Supporting Information, Figure S5), demonstrating the importance of direct connectivity to the Nb site. Along this vein, we hypothesize that alternative phosphonate ligands with greater electron-donating character and/or bulkiness may impart further improved sulfoxide selectivities.

To our knowledge, this is the first report of activation energy effects of sulfoxidation catalysts due to a modifying ligand, though values here are consistent with similar (7–13 kcal mol<sup>-1</sup>) apparent barriers reported by others for the disappearance of thioanisole<sup>[36]</sup> and of benzothiophene derivatives<sup>[27b, 37]</sup> by oxidations with H<sub>2</sub>O<sub>2</sub> over related catalysts. Neither internal nor external diffusion appears to influence the observed reaction kinetics from control reactions at 25 °C for Nb-SiO<sub>2</sub> (Supporting Information, Figure S6), as is expected for these mesoporous materials. Lastly, the uncatalyzed reaction is also observed to have a relatively low barrier of 14 kcal mol<sup>-1</sup> (Supporting Information, Figure S7), albeit proceeding almost three orders of magnitude slower than either catalyzed reaction; bare silica

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gel is similarly inactive (Supporting Information, Table S2), achieving < 9% thioanisole conversion after 6 h at 45 °C.

Re-examining activity trends among the bare oxide catalysts, PPA-Nb-SiO<sub>2</sub> operates with nearly identical rate to Zr-SiO<sub>2</sub>, because of the suppressed Lewis acidity and/or steric hindrance at the capped Nb site, but performs with substantially higher selectivity than Zr-SiO<sub>2</sub>. Figure 6 shows the relationships between sulfoxide selectivity and extents of reaction for each catalyst in this study. All oxide catalysts and 0.25-PPA-Nb-SiO<sub>2</sub> exhibit sulfoxide selectivities that tend towards 0% (that is, full oxidation to the sulfone) as thioanisole conversion approaches 100%. The difference is that, unlike other catalysts, PPA-Nb-SiO<sub>2</sub> affords a large reaction window in time where there are high yields of sulfoxide, most markedly illustrated in Figure 6a. Clearly, the identity and strength of the Lewis acid are each critical factors for promoting high activity and selectivity in the sulfoxidation of thioanisole, and in the case of Nb, the addition of phenylphosphonate capping groups significantly enhances the selectivity towards the sulfoxide intermediate.

An interesting consequence of the behavior of Nb-SiO<sub>2</sub> and PPA-Nb-SiO<sub>2</sub> is that thioanisole oxidation proceeds significantly faster than *cis*-cyclooctene epoxidation at 45 °C, by a factor of thirty for Nb-SiO<sub>2</sub> and by nearly three orders of magnitude for



 $\begin{array}{l} \label{eq:sufforce} \textbf{Figure 6.} a) \ \text{Sulfoxide selectivity } (\text{mol}_{\text{sulfoxide}} [\text{mol}_{\text{sulfone}}]^{-1} \times 100 \, \%) \\ \text{vs. batch reaction time (min). b) \ \text{Sulfoxide selectivity} \\ (\text{mol}_{\text{sulfoxide}} [\text{mol}_{\text{sulfoxide}} + \text{mol}_{\text{sulfone}}]^{-1} \times 100 \, \%) \ \text{vs. conversion of thioanisole.} \\ \text{Legend: Nb-SiO}_2 \ (\text{blue circles}), \ 0.25\text{-PPA-Nb-SiO}_2 \ (\text{purple circles}), \ \text{PA-Nb-SiO}_2 \\ (\text{pink circles}), \ \text{Ti-SiO}_2 \ (\text{green triangles}), \ \text{Zr-SiO}_2 \ (\text{orange diamonds}). \\ \end{array}$ 



PPA-Nb-SiO<sub>2</sub> (Table 5). When these two substrates are co-reacted in batch, initially each at 0.11  $\mu$ , both catalysts preferentially oxidize thioanisole to complete conversion and virtually do not react at all with cyclooctene. Thioanisole rates of disappearance decrease only slightly relative to rates observed in isolation, while epoxidation production is further suppressed by at least an order of magnitude.

<b>Table 5.</b> Kinetic summary of Nb-SiO <sub>2</sub> and PPA-Nb-SiO <sub>2</sub> catalysts for thio anisole versus <i>cis</i> -cyclooctene oxidation by $H_2O_2$ in CH <sub>3</sub> CN at 45 °C <sup>(a)</sup>						
Catalyst	Substrate	Initial Rate <sup>(b)</sup> [mol L <sup>-1</sup> min <sup>-1</sup> ] [min <sup>-1</sup> ] <sup>[c]</sup>		6-h Sel. <sup>[d]</sup> [%]		
Nb-SiO <sub>2</sub>	thioanisole cyclooctene thioanisole vs. cyclooctene	$9.5 \times 10^{-3}$ $2.8 \times 10^{-4}$ $8.0 \times 10^{-3}$ vs. $2.3 \times 10^{-6}$ (e)	9.0 0.27 8.0 vs. 0.002 <sup>[e]</sup>	0 n/a 4		
PPA-Nb-SiO <sub>2</sub>	thioanisole cyclooctene thioanisole vs. cyclooctene	$2.8 \times 10^{-3}$ $9.6 \times 10^{-6}$ $2.0 \times 10^{-3}$ vs. $3.5 \times 10^{-7}$ [f]	2.6 0.0092 2.0 vs. 0.0003 <sup>[f]</sup>	53 n/a 55		
[a] See the text for reaction conditions. Competitive oxidations carried out with 0.11 $ mu$ of each substrate at the start of reaction. [b] Substrate disappearance basis over first 15 min of reaction. [c] Initial rate relative to moles total Nb. [d] Selectivity = mol <sub>sulfoxide</sub> (mol <sub>sulfoxide</sub> + mol <sub>sulfone</sub> ) <sup>-1</sup> × 100%, reported after 6 h of reaction. [e] Evaluated over 2 h of reaction. [f] Evaluated over 6 h of reaction.						

Hence, while both catalysts are fast for sulfoxidation, PPA-Nb-SiO<sub>2</sub> suppresses epoxidation rates more so than unmodified Nb-SiO<sub>2</sub>, while still maintaining the advantage of high sulfoxide selectivity at complete sulfide conversion. This unusual functional group tolerance between alkene and thioether could find application in the synthesis of medicinally relevant unsaturated sulfoxides,<sup>[6]</sup> such as proton pump inhibitor drugs,<sup>[7]</sup> in oxidative desulfurization processes for olefin-rich fuel fractions,<sup>[38]</sup> and in the selective detoxification of chemical warfare agents.<sup>[9]</sup>

#### Conclusions

Highly dispersed supported oxide catalysts of Nb<sup>V</sup>, Ti<sup>IV</sup> and Zr<sup>IV</sup> are synthesized by grafting calixarene coordination complexes to mesoporous SiO<sub>2</sub> and subsequently calcining in air. These materials are comparatively examined for the oxidation of thioanisole by H<sub>2</sub>O<sub>2</sub> oxidant at 45 °C in acetonitrile solvent, for which initial rates trend Nb > Ti  $\gg$  Zr, and selectivities toward the sulfoxide intermediate trend Ti > Nb  $\gg$  Zr; the Zr-SiO<sub>2</sub> catalyst notably gives almost exclusive formation of the secondary sulfone product, even at low levels of thioanisole conversion. The highly active Nb-SiO<sub>2</sub> also gives 2–3× faster rates than benchmark Ti-SiO<sub>2</sub> catalyst for the oxidation of three ppm-level benzothiophene derivatives, as is relevant to the oxidative desulfurization of liquid hydrocarbon fuels.

To further investigate reaction selectivity behavior in the case of Nb-SiO<sub>2</sub>, we apply a site-specific titration technique with phenylphosphonic acid, previously demonstrated by our

group for benzyl alcohol photooxidation and cis-cyclooctene epoxidation. When cyclohexene epoxidation is examined during in situ and ex situ titration with PPA, the titrant effectively suppresses direct, non-radical oxidation pathways, the major contribution to overall rates via Nb-SiO<sub>2</sub>. For thioanisole oxidation, the materials 0.25-PPA-Nb-SiO<sub>2</sub> and PPA-Nb-SiO<sub>2</sub> exhibit diminished activity with a higher-order dependence on PPA, as we previously observed in the case of cyclooctene, suggesting thioether oxidation follows a similar mechanism to alkene epoxidation. However, here selectivities towards the methyl phenyl sulfoxide intermediate are enhanced. Ratios of the apparent rate constants  $k_1/k_2$  for sulfoxide vs. sulfone formation, respectively, improve from 2.4 for the bare Nb-SiO<sub>2</sub> to 5.4 for the fully capped PPA-Nb-SiO<sub>2</sub>. Thus, while PPA greatly inhibits direct cyclohexene epoxidation pathways, the presence of this site capping group greatly improves sulfoxide selectivities even at complete thioanisole conversions. This selectivity boost and the resulting control over sulfonation activation barriers may be attributable to the Lewis basic P=O moiety outcompeting the binding of thioanisole and methyl phenyl sulfoxide, reactants which may strongly coordinate to (and hence appear in the rate constant expressions for) bare Nb-SiO<sub>2</sub>.

Furthermore, both Nb-SiO<sub>2</sub> and its PPA-modified analogue exhibit exceptional reactant selectivity to thioanisole when coreacted with a stoichiometric amount of cyclooctene. This unusual functional group tolerance in the presence of stoichiometric unsaturated compounds could be utilized in organic synthesis, such as to generate pharmaceutically relevant sulfoxides (for example, via PPA-Nb-SiO<sub>2</sub>), or alternately for the oxidative desulfurization of benzothiophene derivatives (via Nb-SiO<sub>2</sub>) that contaminate olefin-rich transportation fuels. With appropriate design of a continuous reactor, formulations of the intrinsically selective PPA-modified catalyst may be further amenable to these and other commercially relevant applications.

Few studies in the supported metal oxides literature have comparatively assessed thioether versus alkene oxidation, and even more scarcely for more than one transition metal at a time. This report highlights how the lesser-studied yet highperforming Nb-SiO<sub>2</sub> is at least as good a catalyst as Ti-SiO<sub>2</sub> for thioether oxidations by  $H_2O_2$ . Its unique activity, functional group tolerance and tunable selectivity via capping agents like PPA warrant further investigation from the catalysis research community.

#### **Experimental Section**

The Nb-SiO<sub>2</sub> catalyst was prepared by grafting a niobium–calix[4]arene coordination complex to partially dehydroxylated silica gel (Selecto Scientific, 32–63  $\mu$ m, 570 m<sup>2</sup>g<sup>-1</sup> BET, ca. 60 Å pore diameter) following a similar procedure to one recently reported by us. Nb(OC<sub>2</sub>H<sub>5</sub>)<sub>5</sub> (2.62 mmol, Strem Chemicals) and *p*-tert-butylcalix[4]arene (2.62 mmol, Sigma) were dissolved in anhydrous, degasified toluene (120 mL) in an Ar glovebox. The contents were sealed and transferred to Schlenk line under N<sub>2</sub> purge. After affixing a reflux condenser, the solution was refluxed for 24 h, followed by the airfree addition of SiO<sub>2</sub> (10.0 g) that was previously partially dehydroxylated at 300 °C for 10 h under dynamic vacuum (< 25 mTorr). The suspension was refluxed for an additional 24 h. Solids were re-





covered via vacuum filtration in air, then washed with toluene and dried overnight under dynamic vacuum. As a final step, the material was calcined in air immediately before catalysis at 550 °C for 6 h using a ramp rate of  $10^{\circ}$ C min<sup>-1</sup>.

Syntheses of catalysts Ti-SiO<sub>2</sub> and Zr-SiO<sub>2</sub> were previously reported by us.<sup>[14]</sup> In brief, stoichiometric amounts of 1,3-dimethoxy-*tert*-butylcalix[4]arene<sup>[39]</sup> and a metal precursor (TiCl<sub>4</sub>(THF)<sub>2</sub> or ZrCl<sub>4</sub>(THF)<sub>2</sub>, Strem) were refluxed in anhydrous, degasified toluene under N<sub>2</sub> for 14 h, followed by the addition of silica gel which had previously undergone partial dehydroxylation as above. The suspensions were refluxed for 24 h, vacuum-filtered in air, washed with toluene, and dried under dynamic vacuum overnight. The resulting solids were air-calcined following the conditions listed above immediately before use as catalysts.

The PPA-Nb-SiO\_2 catalyst was prepared using a protocol adapted from previous work by our group.  $^{[15,16]}$  Nb-SiO\_2 (480 mg, 0.125 mmol Nb) were suspended in acetonitrile (12 mL, spectrophotometric grade, Alfa Aesar), followed by the addition of phenylphosphonic acid ("PPA", 0.140 mmol, Sigma) from a 100 mm solution in ultrapure  $H_2O$  (18 M $\Omega$ ·cm). The suspension was shaken for 2 h at 65 °C at 700 r.p.m. on a Glas-Col Heated Vortexer, then vacuum-filtered and washed with acetonitrile (150 mL). The 0.25-PPA-Nb-SiO<sub>2</sub> catalyst was prepared in the same manner, except with the addition of 0.0340 mmol PPA (P/Nb=0.26 during synthesis conditions). The resulting solids were dried under dynamic vacuum (<25 mTorr) and stored in a desiccator prior to catalysis. Diffuse-reflectance UV/Vis (DRUV/Vis) spectroscopy was performed using a Shimadzu UV-3600 spectrometer equipped with a Harrick Praving Mantis diffuse reflectance accessory. Spectra were collected at ambient conditions from 800 to 200 nm using a 1.0 nm sampling step and a slit width of 3.0 nm, calibrated to polytetrafluoroethylene (PTFE) powder as a perfect reflector for baseline measurements. Solid catalyst samples were diluted in a 20:1 ratio with PTFE using a mortar and pestle. Kubelka-Munk pseudoabsorbances (F(R)) were computed to calculate optical edge energies via the x-intercepts of corresponding indirect Tauc plots ( $[F(R)\cdot h\nu]^{1/2}$  vs.  $h\nu$ (eV)) following literature protocol.[21b,23]

X-ray absorption near-edge structure (XANES) spectroscopy was performed at the Sector 5, Bending Magnet Station D (5BM-D) of the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) of the Advanced Photon Source at Argonne National Laboratory. Spectra were collected at the niobium K-edge (18,985.6 eV) following tuning of the beam energy via a Si(111) monochromator  $(10^{-4}\,\text{eV}$  resolution) and calibrating using a pure niobium foil in transmission mode. Nb-SiO<sub>2</sub> and PPA-Nb-SiO<sub>2</sub> powder samples were ground using a mortar and pestle and packed into 10 mm  $\times$ 2 mm×1 mm voids bored-through self-supporting 13 mm dia., 1 mm-thick aluminum discs. The sample discs were then loaded into a controlled atmosphere cell, evacuated at room temperature (-30 inHg gauge), and purged with purified argon for three cycles, then evacuated continuously for 2 h at 120 °C. The sample cell was cooled to 50°C under dynamic vacuum, then backfilled with argon and sealed immediately before spectroscopy. The cell was oriented at  $45^{\circ} \pm 5^{\circ}$  relative to the incident beam, and spectra were collected at ambient temperature using a four-channel Canberra SII Vortex ME4 fluorescence detector.

Metal and phosphorus content was determined via inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Thermo ICAP 7600 spectrometer. Catalysts were digested using 1.0 mL concentrated hydrofluoric acid (HF, 48% w/w in H<sub>2</sub>O, Macron) diluted to 11.0 mL in 0.9% w/w HNO<sub>3</sub> in H<sub>2</sub>O. [CAUTION: HF is a severe contact poison. Handle and store concentrated HF solutions with extreme care.] Metal and phosphorus calibrants were prepared via serial dilution of commercially available stand-

ards (Fluka); phosphorus calibration solutions were prepared and analyzed separately from those of metals. All final metal and phosphorus surface densities are reported relative to the N<sub>2</sub> physisorption specific surface area of the bare, partially dehydroxylated  $SiO_2$  support (Micromeritics ASAP 2010 CE system).

The 0.25-PPA-Nb-SiO<sub>2</sub> and PPA-Nb-SiO<sub>2</sub> materials were analyzed using <sup>31</sup>P cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy. Spectra were collected at a spin rate of 5 kHz at ambient conditions using a Varian 400 MHz VNMRS instrument equipped with a 5 mm HPC probe previously calibrated to an ammonium phosphate standard.

Thioanisole oxidation experiments were performed as follows: 0.59 mmol thioanisole (Sigma) and 0.44 mmol DCB were added to 5.0 mL acetonitrile and 22 mg catalyst in a 20 mL septum-cap vial. After the vial was sealed, a vent needle was inserted, and the reactors were shaken at 700 r.p.m. on a Glas-Col Heated Vortexer at 25°C, 45°C or 65°C for 10 min. The reaction began after the instantaneous addition of 1.8 mmol H<sub>2</sub>O<sub>2</sub> delivered from a 4.0 M solution in acetonitrile, prepared by diluting 10 mL 30% H<sub>2</sub>O<sub>2</sub> (w/w in H<sub>2</sub>O, Sigma) in 20 mL acetonitrile, drying over 7 g anhydrous MgSO<sub>4</sub> (Macron), centrifuging, and decanting.<sup>[14,40]</sup> At the start of reaction, initial concentrations were [thioanisole]<sub>0</sub>=0.106 M,  $[H_2O_2]_0 = 0.323 \text{ M}$ , giving molar ratios thioanisole/ $H_2O_2/DCB/M =$ 106:323:79:1.0 and a total reaction volume of 5.6 mL. Aliquots were withdrawn with a syringe at specified time intervals, filtered using a 0.7 µm glass microfiber filter (Whatman), and contacted with silver powder (Sigma, < 250  $\mu$ m) to decompose unreacted H<sub>2</sub>O<sub>2</sub> prior to GC analysis.<sup>[14, 15, 40]</sup> Product identities were initially determined using GC-MS (Shimadzu QP2010, Zebron ZB-624 capillary column) and guantified using GC-FID (Shimadzu 2010, TR-1 capillary column) via calibrated standards. For two experiments, reactions over Nb-SiO<sub>2</sub> were performed as above at 45 °C, except with the addition of 0.0067 or 0.025 mmol (1.2 or 4.3 equiv. w.r.t. Nb) of triphenylphosphine oxide ("TPPO," Sigma) during preparation; reaction mixtures with TPPO were equilibrated at 45 °C for 1 h prior to addition of H<sub>2</sub>O<sub>2</sub>. For a separate subset of experiments, the oxidation of methyl phenyl sulfoxide was examined at 45°C following the same protocol as above except with batch reaction solutions prepared as follows: 0.60 mmol methyl phenyl sulfoxide (Sigma) was delivered from a 0.150 M solution in acetonitrile to a 20 mL vial containing catalyst (22 mg), followed by the addition of acetonitrile (1.0 mL) and DCB (0.44 mmol).

The oxidation of benzothiophene derivatives was performed as follows: separate 3000 ppm (e.g. mgL<sup>-1</sup>) solutions of benzo[b]thiophene ("BT," Alfa Aesar), dibenzothiophene ("DBT," Alfa Aesar), and 4,6-dimethyldibenzothiophene ("DMDBT," Alfa Aesar) were prepared in acetonitrile. For a typical reaction, Nb-SiO<sub>2</sub> or Ti-SiO<sub>2</sub> (6.0– 12.0 mg) were weighed into 20 mL septum-cap vials, to which fresh acetonitrile (6.6 mL), acetonitrile solution (3.5 mL) of BT, DBT, or DMDBT, and DCB (0.44 mmol) were added. The reactors were sealed and shaken at 700 r.p.m. for 5 min at 25 °C, 45 °C, or 65 °C, after which  $H_2O_2$  (0.16–0.24 mmol) was added from a 4.0  $\mu$  solution in acetonitrile as prepared above. At the start of reaction, reaction volumes were approximately 10.2 mL, and concentrations of reactive species were as follows:  $[BT]_0 = 7.7 \text{ mM}$ ,  $[H_2O_2]_0 = 23 \text{ mM}$ , with initial molar ratios BT/H<sub>2</sub>O<sub>2</sub>/M = 32:99:3.1; [DBT]<sub>0</sub> = 5.6 mм,  $[H_2O_2]_0 = 18 \text{ mm}$ , with initial molar ratios DBT/ $H_2O_2/M = 32:102:3.1;$ and  $[DMDBT]_0 = 4.9 \text{ mm}$ ,  $[H_2O_2]_0 = 15 \text{ mm}$ , with initial molar ratios DMDBT/H<sub>2</sub>O<sub>2</sub>/M = 31:100:3.1. GC sample collection and analysis was performed as before.

Epoxidation of cyclohexene with in situ PPA poisoning was executed following analogous protocols for previously reported by our group.<sup>[14–16]</sup> Cyclohexene (Sigma) was purified over a column of activated  $Al_2O_3$  (Selecto Scientific, 63–150 µm) immediately before

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use. In a typical experiment, acetonitrile (5.5 mL), cyclohexene (6.35 mmol), and 1,2-dichlorobenzene ("DCB", 0.44 mmol, Alfa Aesar) internal standard were each added to a series of 20 mL septum-cap vials, each containing Nb-SiO<sub>2</sub> (30 mg, 0.0080 mmol Nb). Subsequently, a variable amount of PPA spanning 0.0 to 0.0160 mmol was added to each reactor, delivered from a 100 mm aqueous solution. For a subset of experiments, PPA-Nb-SiO<sub>2</sub> and 0.25-PPA-Nb-SiO<sub>2</sub> were used in place of Nb-SiO<sub>2</sub>, without addition of soluble PPA. The reactors were sealed, fitted with a needle vent, and shaken for 1 h at 65 °C and 700 r.p.m. After 1 h, the reaction was initiated with the instantaneous addition of 1.42 mmol  $H_2O_2$ (50% w/w in  $H_2O$ , Sigma). At the start of reaction, the molar ratios of all species were as follows: cyclohexene/H2O2/H2O/DCB/Nb/ PPA = 1020:120:[230-1430]:70:1.3:[0.0-2.6]. Initial concentrations of reactant species were  $[cyclohexene]_0 = 1.02 \text{ M}$  and  $[H_2O_2]_0 = 0.120 \text{ M}$ , and total reaction volumes were 6.2-6.4 mL. GC sample collection and analysis was carried out as above.

Epoxidation of cis-cyclooctene (Alfa Aesar) was carried out in 20 mL sealed glass vial reactors equipped with a septum cap and needle vent, as above. Cyclooctene was purified over activated Al<sub>2</sub>O<sub>3</sub> immediately before use. Reaction mixtures were prepared by measuring Nb-SiO<sub>2</sub> or PPA-Nb-SiO<sub>2</sub> (22 mg), acetonitrile (5.0 mL), cyclooctene (0.58 mmol), and DCB (0.44 mmol). This suspension was heated to 45 °C and shaken at 700 r.p.m. for 5 min before the instantaneous addition of H<sub>2</sub>O<sub>2</sub> (1.80 mmol) delivered from a 4.0 м solution in acetonitrile previously dried over MgSO<sub>4</sub>. At the start of reaction, initial concentrations were [cyclooctene]<sub>0</sub>=0.105 m,  $[H_2O_2]_0\!=\!0.323\,\textrm{m},$  giving molar ratios cyclooctene/H\_2O\_2/DCB/Nb =105:323:78:1.0 and a total reaction volume of 5.6 mL. Aliguots were removed periodically, filtered and analyzed as above via GC-FID (Shimadzu 2010, TR-1 capillary column) using calibrated standards. Competitive oxidations of thioanisole vs. cyclooctene were carried out in the same manner, except with use of acetonitrile (5.5 mL), and thioanisole (0.59 mmol) during reactor preparation. This preparation gave initial concentrations of [thioanisole]<sub>0</sub>= 0.097 м,  $[cyclooctene]_0 = 0.096 \text{ м}, [H_2O_2]_0 = 0.297 \text{ M}, \text{ with molar}$ ratios thioanisole/cyclooctene/H<sub>2</sub>O<sub>2</sub>/DCB/Nb=97:96:297:72:1.0 and a total reaction volume of 6.1 mL.

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 a) J. M. Thomas, W. J. Thomas, Principles and Practice of Heterogeneous Catalysis, 2nd ed., Wiley-VCH, Weinheim, 2015; b) M. G. Clerici, O. A. Kholdeeva, Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications, Wiley, Hoboken, NJ, **2013**; c) C. H. Bartholomew, R. J. Farrauto, Fundamentals of Industrial Catalytic Processes, 2nd ed., Wiley, Hoboken, NJ, **2006**.

- [2] a) C. W. Jones, J. H. Clark in *Applications of Hydrogen Peroxide and Deriv-atives*, The Royal Society of Chemistry, **1999**, pp. 79–178; b) O. A. Kholdeeva, *Catal. Sci. Technol.* **2014**, *4*, 1869–1889.
- [3] a) R. A. Sheldon, J. A. Van Doorn, J. Catal. 1973, 31, 427–437; b) R. A. Sheldon, J. Mol. Catal. 1980, 7, 107–126; c) R. J. Davis, Z. Liu, Chem. Mater. 1997, 9, 2311–2324; d) L. Marchese, E. Gianotti, V. Dellarocca, T. Maschmeyer, F. Rey, S. Coluccia, J. M. Thomas, Phys. Chem. Chem. Phys. 1999, 1, 585–592.
- [4] a) P. Ratnasamy, D. Srinivas, H. Knözinger in Advanced Catalysis, Vol. 48, Academic Press, 2004, pp. 1–169; b) L. Y. Chen, G. K. Chuah, S. Jaenicke, J. Mol. Catal. A 1998, 132, 281–292; c) J. M. Fraile, J. I. García, J. A. Mayoral, E. Vispe, Appl. Catal. A 2004, 276, 113–122; d) N. S. Antonova, J. J. Carbó, U. Kortz, O. A. Kholdeeva, J. M. Poblet, J. Am. Chem. Soc. 2010, 132, 7488–7497; e) M. C. Capel-Sanchez, G. Blanco-Brieva, J. M. Campos-Martin, M. P. de Frutos, W. Wen, J. A. Rodriguez, J. L. G. Fierro, Langmuir 2009, 25, 7148–7155.
- [5] a) A. V. Ramaswamy, S. Sivasanker, *Catal. Lett.* **1993**, *22*, 239–249; b) A. Corma, M. Iglesias, F. Sánchez, *Catal. Lett.* **1996**, *39*, 153–156; c) O. A. Kholdeeva, A. Y. Derevyankin, A. N. Shmakov, N. N. Trukhan, E. A. Paukshtis, A. Tuel, V. N. Romannikov, *J. Mol. Catal. A* **2000**, *158*, 417–421; d) Y. Kon, T. Yokoi, M. Yoshioka, S. Tanaka, Y. Uesaka, T. Mochizuki, K. Sato, T. Tatsumi, *Tetrahedron* **2014**, *70*, 7584–7592.
- [6] a) J. Legros, J. R. Dehli, C. Bolm, Adv. Synth. Catal. 2005, 347, 19–31; b) I.
   Fernández, N. Khiar, Chem. Rev. 2003, 103, 3651–3706; c) K. Kaczorowska, Z. Kolarska, K. Mitka, P. Kowalski, Tetrahedron 2005, 61, 8315–8327.
- [7] P. Richardson, C. J. Hawkey, W. A. Stack, Drugs 1998, 56, 307-335.
- [8] A. Stanislaus, A. Marafi, M. S. Rana, Catal. Today 2010, 153, 1-68.
- [9] a) F. Carniato, C. Bisio, R. Psaro, L. Marchese, M. Guidotti, Angew. Chem. Int. Ed. 2014, 53, 10095–10098; Angew. Chem. 2014, 126, 10259– 10262; b) J. Dong, J. Hu, Y. Chi, Z. Lin, B. Zou, S. Yang, C. L. Hill, C. Hu, Angew. Chem. Int. Ed. 2017, 56, 4473–4477; Angew. Chem. 2017, 129, 4544–4548.
- [10] a) A. Feliczak-Guzik, A. Wawrzyńczak, I. Nowak, Microporous Mesoporous Mater. 2015, 202, 80–89; b) M. Ziolek, A. Lewandowska, M. Renn, I. Nowak, Stud. Surf. Sci. Catal. 2004, 154, 2610–2617; c) N. N. Trukhan, A. Y. Derevyankin, A. N. Shmakov, E. A. Paukshtis, O. A. Kholdeeva, V. N. Romannikov, Microporous Mesoporous Mater. 2001, 44–45, 603–608.
- [11] a) B. Notari, R. J. Willey, M. Panizza, G. Busca, *Catal. Today* 2006, *116*, 99–110; b) R. L. Brutchey, B. V. Mork, D. J. Sirbuly, P. Yang, T. D. Tilley, *J. Mol. Catal. A* 2005, *238*, 1–12; c) J. J. Bravo-Suárez, K. K. Bando, J. Lu, M. Haruta, T. Fujitani, T. Oyama, *J. Phys. Chem. C* 2008, *112*, 1115–1123; d) F. Bérubé, B. Nohair, F. Kleitz, S. Kaliaguine, *Chem. Mater.* 2010, *22*, 1988–2000; e) A. Gallo, C. Tiozzo, R. Psaro, F. Carniato, M. Guidotti, *J. Catal.* 2013, *298*, 77–83; f) C. Tiozzo, C. Bisio, F. Carniato, A. Gallo, S. L. Scott, R. Psaro, M. Guidotti, *Phys. Chem. Chem. Phys.* 2013, *15*, 13354–13362; g) N. Morlanés, J. M. Notestein, *J. Catal.* 2010, *275*, 191–201.
- [12] a) O. A. Kholdeeva, B. G. Donoeva, T. A. Trubitsina, G. Al-Kadamany, U. Kortz, *Eur. J. Inorg. Chem.* 2009, 5134–5141; b) M. Ziolek, I. Sobczak, A. Lewandowska, I. Nowak, P. Decyk, M. Renn, B. Jankowska, *Catal. Today* 2001, *70*, 169–181; c) M. Ziolek, I. Sobczak, I. Nowak, P. Decyk, A. Lewandowska, J. Kujawa, *Microporous Mesoporous Mater.* 2000, *35–36*, 195–207; d) M. Fadhli, I. Khedher, J. M. Fraile, *J. Mol. Catal. A* 2015, *410*, 140–148.
- [13] a) H. P. Wulff, (Shell Oil Company), United States, 3,943,823, 1975; b) J. Jarupatrakorn, T. D. Tilley, J. Am. Chem. Soc. 2002, 124, 8380–8388; c) D. A. Ruddy, R. L. Brutchey, T. D. Tilley, Top. Catal. 2008, 48, 99–106; d) D. A. Ruddy, T. D. Tilley, J. Am. Chem. Soc. 2008, 130, 11088–11096; e) P. J. Cordeiro, T. D. Tilley, J. Am. Chem. Soc. 2008, 130, 11088–11096; e) P. J. Cordeiro, T. D. Tilley, Langmuir 2011, 27, 6295–6304; f) P. J. Cordeiro, T. D. Tilley, ACS Catal. 2011, 1, 455–467; g) J. M. Fraile, J. I. García, J. A. Mayoral, E. Vispe, J. Catal. 2001, 204, 146–156; h) J. Gallo, H. Pastore, U. Schuchardt, J. Catal. 2006, 243, 57–63; i) J. M. Fraile, C. Gil, J. A. Mayoral, B. Muel, L. Roldán, E. Vispe, S. Calderón, F. Puente, Appl. Catal. B 2016, 180, 680–686; j) B. Karimi, M. Khorasani, ACS Catal. 2013, 3, 1657–1664; k) A. Chica, A. Corma, M. E. Dómine, J. Catal. 2006, 242, 299–308; l) J. M. Fraile, B. Lazaro, J. A. Mayoral, Chem. Commun. 1998, 1807–1808.

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10



- [14] N. E. Thornburg, A. B. Thompson, J. M. Notestein, ACS Catal. 2015, 5, 5077-5088.
- [15] N. E. Thornburg, S. L. Nauert, A. B. Thompson, J. M. Notestein, ACS Catal. 2016, 6, 6124–6134.
- [16] T. R. Eaton, A. M. Boston, A. B. Thompson, K. A. Gray, J. M. Notestein, *ChemCatChem* 2014, 6, 3215–3222.
- [17] a) R. Neumann, M. Levin-Elad, J. Catal. 1997, 166, 206–217; b) N. Morlanés, J. M. Notestein, Appl. Catal. A 2010, 387, 45–54.
- [18] a) J.-M. Jehng, I. E. Wachs, *Catal. Today* **1990**, *8*, 37–55; b) J.-M. Jehng,
   I. E. Wachs, *J. Mol. Catal.* **1991**, *67*, 369–387; c) Y. Chen, J. L. G. Fierro, T. Tanaka, I. E. Wachs, *J. Phys. Chem. B* **2003**, *107*, 5243–5250.
- [19] a) J. M. Notestein, E. Iglesia, A. Katz, J. Am. Chem. Soc. 2004, 126, 16478–16486; b) J. M. Notestein, L. R. Andrini, V. I. Kalchenko, F. G. Requejo, A. Katz, E. Iglesia, J. Am. Chem. Soc. 2007, 129, 1122–1131; c) J. M. Notestein, L. R. Andrini, F. G. Requejo, A. Katz, E. Iglesia, J. Am. Chem. Soc. 2007, 129, 15585–15595.
- [20] N. E. Thornburg, Y. Liu, P. Li, J. T. Hupp, O. K. Farha, J. M. Notestein, *Catal. Sci. Technol.* **2016**, *6*, 6480–6484.
- [21] a) X. Gao, I. E. Wachs, *Catal. Today* **1999**, *51*, 233–254; b) X. Gao, S. R. Bare, J. L. G. Fierro, M. A. Banares, I. E. Wachs, *J. Phys. Chem. B* **1998**, *102*, 5653–5666; c) B. Modén, L. Oliviero, J. Dakka, J. G. Santiesteban, E. Iglesia, *J. Phys. Chem. B* **2004**, *108*, 5552–5563.
- [22] a) P. Carniti, A. Gervasini, M. Marzo, J. Phys. Chem. C 2008, 112, 14064– 14074; b) C. Tiozzo, C. Palumbo, R. Psaro, C. Bisio, F. Carniato, A. Gervasini, P. Carniti, M. Guidotti, Inorg. Chim. Acta 2015, 431, 190–196.
- [23] a) D. G. Barton, M. Shtein, R. D. Wilson, S. L. Soled, E. Iglesia, J. Phys. Chem. B 1999, 103, 630–640; b) M. D. Argyle, K. Chen, C. Resini, C. Krebs, A. T. Bell, E. Iglesia, J. Phys. Chem. B 2004, 108, 2345–2353; c) J. Tauc, A. Menth, J. Non-Cryst. Solids 1972, 8–10, 569–585.
- [24] J. D. Lewis, S. Van de Vyver, A. J. Crisci, W. R. Gunther, V. K. Michaelis, R. G. Griffin, Y. Román-Leshkov, *ChemSusChem* 2014, 7, 2255–2265.
- [25] M. Hajjami, L. Shiri, A. Jahanbakhshi, Appl. Organomet. Chem. 2015, 29, 668-673.
- [26] a) O. A. Kholdeeva, L. A. Kovaleva, R. I. Maksimovskaya, G. M. Maksimov, J. Mol. Catal. A 2000, 158, 223–229; b) M. Iwamoto, Y. Tanaka, J. Hirosumi, N. Kita, Chem. Lett. 2001, 30, 226–227; c) P. Moreau, V. Hulea, S. Gomez, D. Brunel, F. Di Renzo, Appl. Catal. A 1997, 155, 253–263.
- [27] a) V. Hulea, F. Fajula, J. Bousquet, J. Catal. 2001, 198, 179–186; b) L. P. Rivoira, V. A. Vallés, B. C. Ledesma, M. V. Ponte, M. L. Martínez, O. A. Anunziata, A. R. Beltramone, Catal. Today 2016, 271, 102–113; c) M. C. Capel-Sanchez, J. M. Campos-Martin, J. L. G. Fierro, Energy Environ. Sci. 2010, 3, 328–333; d) G. Fabis, M. Lewandowski, Z. Sarbak, S. Czajkowska, Pol. J. Appl. Chem. 2010, 54, 41–48.
- [28] a) Y. Sun, J. Shen, J. Zhu, Y. Zhang, *Jingxi Shiyou Huagong* **2012**, *29*, 68–72; b) G.-J. Ji, J. Shen, *Tianranqi Huagong* **2014**, *39*, 25–28; c) G.-j. Ji, J. Shen, *Jingxi Huagong* **2014**, *31*, 852–856; d) B. Ruan, J. Shen, S. Li, N. Nie, *Liaoning Shiyou Huagong Daxue Xuebao* **2012**, *33*, 24–27.

- [29] a) O. A. Kholdeeva, *Top. Catal.* 2006, *40*, 229–243; b) O. A. Kholdeeva,
   R. I. Maksimovskaya, G. M. Maksimov, L. A. Kovaleva, *Kinet. Catal.* 2001, *42*, 217–222.
- [30] a) E. Baciocchi, O. Lanzalunga, S. Malandrucco, M. Ioele, S. Steenken, J. Am. Chem. Soc. 1996, 118, 8973–8974; b) C. Schoeneich, A. Aced, K. D. Asmus, J. Am. Chem. Soc. 1993, 115, 11376–11383.
- [31] a) V. Hulea, P. Moreau, F. Di Renzo, J. Mol. Catal. A 1996, 111, 325–332;
  b) I. Y. Skobelev, O. V. Zalomaeva, O. A. Kholdeeva, J. M. Poblet, J. J. Carbó, Chem. Eur. J. 2015, 21, 14496–14506; c) W. Adam, C. M. Mitchell, C. R. Saha-Möller, T. Selvam, O. Weichold, J. Mol. Catal. A 2000, 154, 251–255.
- [32] a) M. G. Clerici, P. Ingallina, J. Catal. 1993, 140, 71–83; b) P. E. Sinclair, C. R. A. Catlow, J. Phys. Chem. B 1999, 103, 1084–1095.
- [33] T. R. Eaton, M. P. Campos, K. A. Gray, J. M. Notestein, J. Catal. 2014, 309, 156–165.
- [34] a) S. Ahn, N. E. Thornburg, Z. Li, T. C. Wang, L. C. Gallington, K. W. Chapman, J. M. Notestein, J. T. Hupp, O. K. Farha, *Inorg. Chem.* 2016, *55*, 11954–11961; b) B. Kilos, I. Nowak, M. Ziolek, A. Tuel, J. C. Volta, *Stud. Surf. Sci. Catal.* 2005, *158*, 1461–1468; c) I. Nowak, B. Kilos, M. Ziolek, A. Lewandowska, *Catal. Today* 2003, *78*, 487–498.
- [35] a) J. M. Fraile, J. I. García, J. A. Mayoral, E. Vispe, *Appl. Catal. A* **2003**, *245*, 363–376; b) J. Fraile, J. Garcia, J. Mayoral, E. Vispe, *J. Catal.* **2005**, *233*, 90–99.
- [36] V. Hulea, A.-L. Maciuca, A.-M. Cojocariu, C.-E. Ciocan, E. Dumitriu, C. R. Chim. 2009, 12, 723-730.
- [37] F. M. Collins, A. R. Lucy, C. Sharp, J. Mol. Catal. A 1997, 117, 397-403.
- [38] a) A. V. Akopyan, E. V. Ivanov, P. D. Polikarpova, A. V. Tarakanova, E. V. Rakhmanov, O. V. Polyakova, A. V. Anisimov, V. A. Vinokurov, E. A. Karakhanov, *Pet. Chem.* 2015, *55*, 571–574; b) J. Burri, R. Crockett, R. Hany, D. Rentsch, *Fuel* 2004, *83*, 187–193; c) J. Xiao, L. Wu, Y. Wu, B. Liu, L. Dai, Z. Li, Q. Xia, H. Xi, *Appl. Energy* 2014, *113*, 78–85; d) E. V. Rakhmanov, A. V. Anisimov, A. V. Tarakanova, N. S. Baleeva, D. Guluzade, *Pet. Chem.* 2013, *53*, 201–204; e) L. Chen, S. Guo, D. Zhao, *Chin. J. Chem. Eng.* 2007, *15*, 520–523; f) L. J. Chen, F. T. Li, *Pet. Sci. Technol.* 2015, *33*, 196–202.
- [39] W.-G. Wang, Q.-Y. Zheng, Z.-T. Huang, Synth. Commun. 1999, 29, 3711– 3718.
- [40] P. A. A. Ignacio-de Leon, C. A. Contreras, N. E. Thornburg, A. B. Thompson, J. M. Notestein, *Appl. Catal. A* 2016, *511*, 78–86.

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## **FULL PAPERS**

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Rate and Selectivity Control in Thioether and Alkene Oxidation with H<sub>2</sub>O<sub>2</sub> over Phosphonate-Modified Niobium(V)–Silica Catalysts



#### Tunable catalyst selectivity: Nio-

bium(V)–silica catalysts are shown to be highly active and selective thioether oxidation catalysts for  $H_2O_2$  compared to benchmark titanium(IV)–silica. Simple modification of the highly active Nb-SiO<sub>2</sub> active sites with phenylphosphonic acid results in an unusually active and selective catalyst for sulfoxidation, but not for alkene epoxidation nor overoxidation to the sulfone.