Supporting Information

for

Controlled Deposition of Silica on Titania-Silica to Alter the Active Site Surroundings on Epoxidation Catalysts

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Supporting Information Section 1. Catalyst Synthesis

SiO_2 overcoating was attempted on several different Ti precursors before settling on Cp*$TiCl_3$. $TiCl_4$, Cp_2TiCl_2, 4-tert-Butylcalix[4]arene-TiCl, Cp*$TiCl_3$, and Ti-TADDOLate were grafted onto wide pore SiO_2 at ~0.2 Ti/nm^2 surface loadings. Calixarene was grafted under toluene reflux for 18 h and the others were grafted at RT for 4 h. The sol-gel SiO_2 overcoat method was applied for two deposition cycles with the template left intact on the surface. Ti ICP-OES (Supplementary Table 1) and ambient DRUV-vis were used to determine whether the (i) template and (ii) TiOx remained after overcoating. These two measurements are semi-quantitative indicators of the strength of the ligand-Ti bond and the as-grafted Ti-surface bonds.

Cp_2TiCl_2 and Ti-TADDOLate were eliminated from contention because their DRUV-vis LMCT bands disappeared after overcoating (example in Supplementary Figure 1), which indicates loss of the ligand (Cp or TADDOL) but retention of Ti. In contrast, calix[4]arene-TiCl was not used because its TiOx content dropped by 30 % after overcoating, indicating loss of the entire surface complex during the overcoat process.
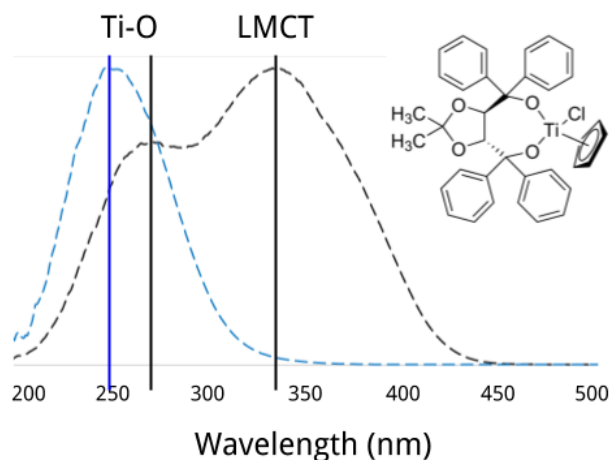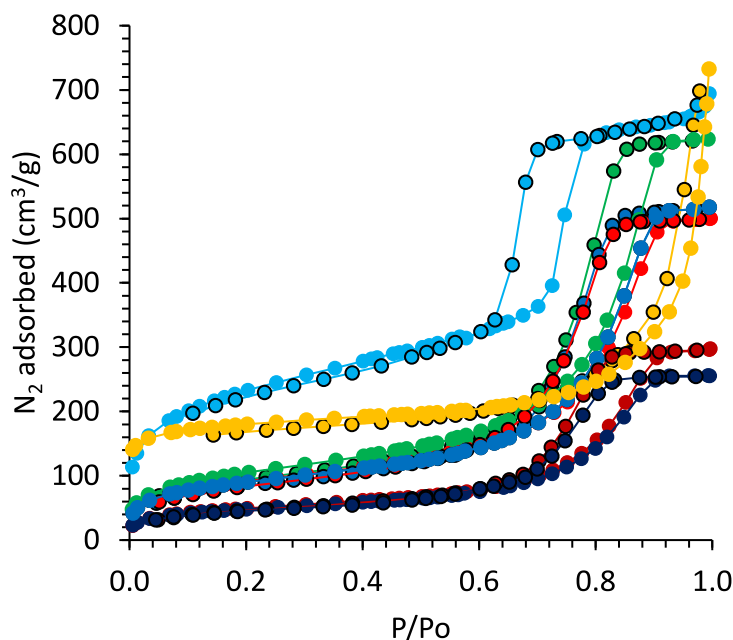

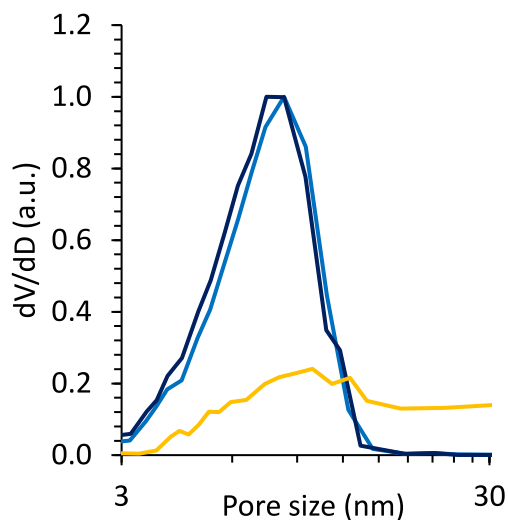**Supporting Information Figure S1.** DRUV-vis spectra for as-made (black) and 2cPO variant (blue) of Ti-TADDOLate.

Supporting Information Table S1. Ti ICP-OES results for as-made and 2cPO variants using various Ti templates.

|	As-made Ti content (M/nm^2)	2cPO Ti content (M/nm^2)
$TiCl_4$	0.17	0.14
Cp_2TiCl_2	0.21	0.20
Calix[4]arene-TiCl	0.19	0.13
Cp*$TiCl_3$	0.21	0.21
Ti-TADDOLate	0.22	0.15

Supporting Information Section 2. Catalyst Characterization

Supporting Information Figure S2. N_2 physisorption isotherms obtained at -196 °C for Ti-SiO$_2$ (green), 2cFO (red), 2cPO (blue), 10cFO (dark red), 10cPO (dark blue), Ti-SBA-15 (cyan), and Ti-Beta (orange). Desorption points are labeled with a black border.
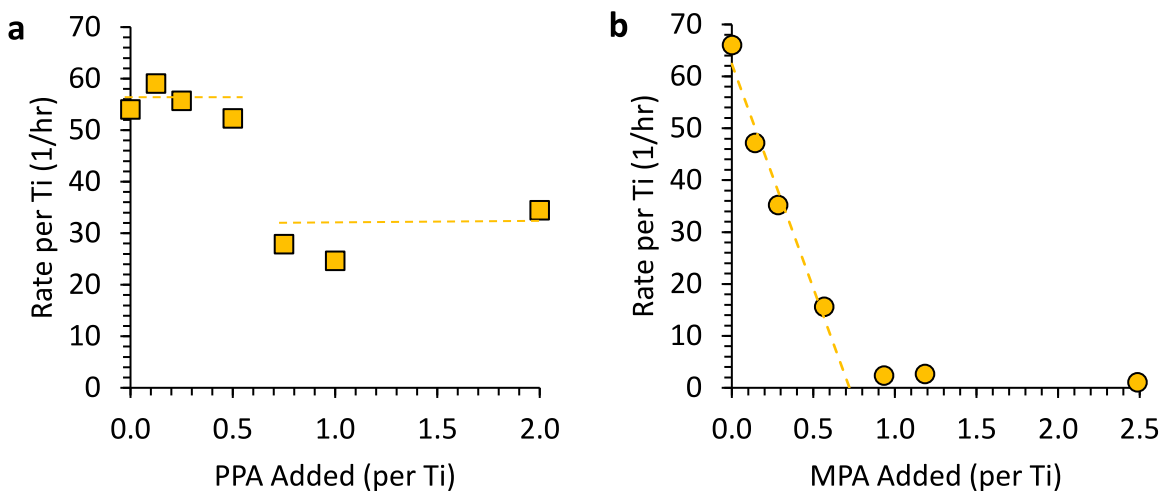

Supporting Information Figure S3. BJH pore size distributions (not included in the main text) for 2cPO (blue), 10cPO (dark blue), and Ti-Beta (orange) based on the desorption branch of N_2 physisorption isotherms obtained at -196 °C. Distributions are normalized to their highest feature for ease of comparison. Note that Ti-Beta has a regular, crystalline structure with 0.67 nm pores.
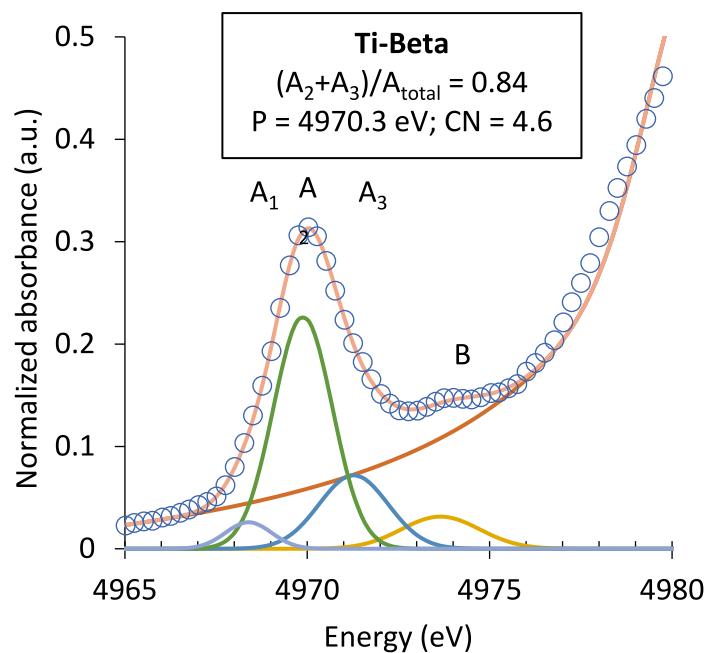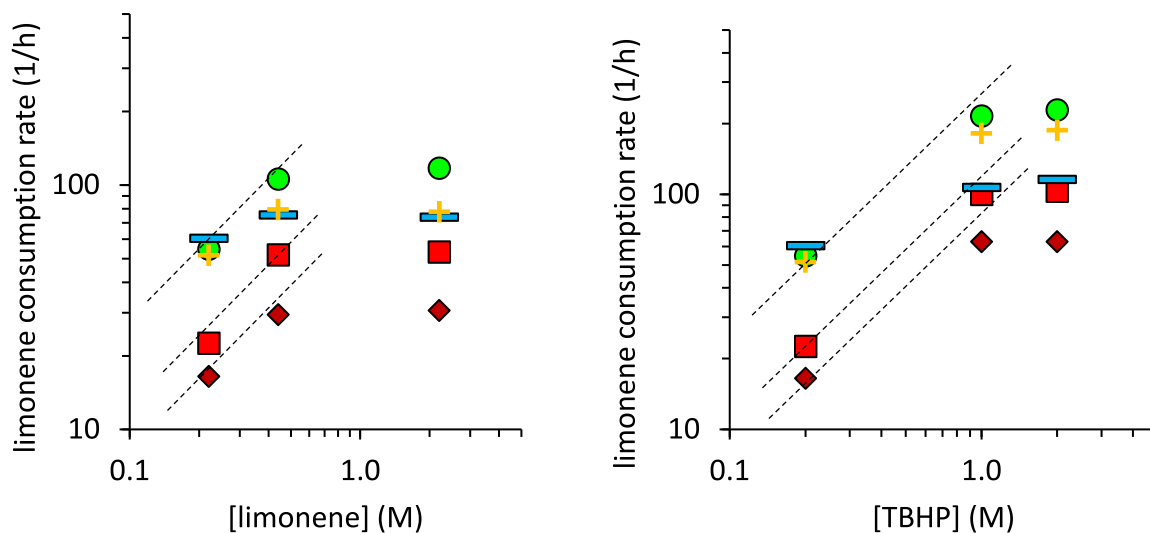
Supporting Information Figure S4. Example Ti K-edge XANES pre-edge peak fitting routine. An arctan baseline and four peaks were fitted based on literature methods [23-24].
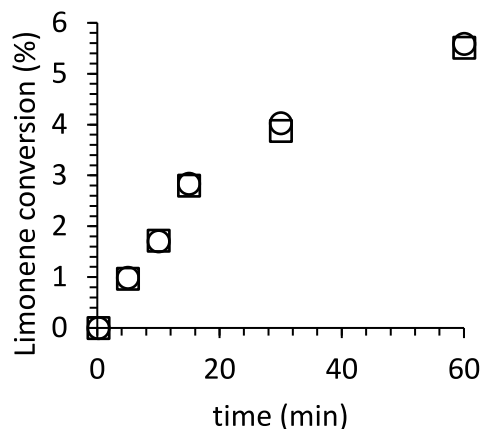
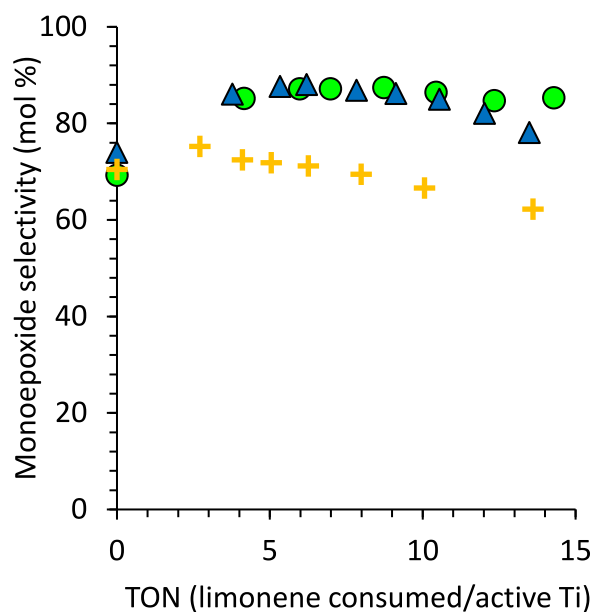**Supporting Information Section 3. Limonene Epoxidation**

Supporting Information Figure S5. Initial limonene epoxidation rates for Ti-Beta vs. a) PPA (□) or b) MPA (○) added to the reactor during *in situ* titration experiments at 65 ^{o}C. Initial rates from the first 15 min of reaction. PPA titration data indicates that PPA cannot titrate away ~50 % of limonene epoxidation active sites within the beta pore structure.

Supporting Information Figure S6. Turnover rates (per site titrated by MPA) for limonene consumption as a function of a) [limonene] with [TBHP] = 0.22 M and 30 mg catalyst or b) [TBHP] with [limonene] = 0.2 M and 30 mg catalyst at 65 ^{o}C over Ti-SiO$_2$ (green, ●), 2cFO (red, ■), 10cFO (dark red, ♦), Ti-SBA-15 (cyan, --), and Ti-Beta (orange, +). Dashed lines show a first order dependence as a guide to the eye. Enthalpies and entropies of activation were all calculated at 0.22M TBHP and 0.2 M limonene, where the rates approach first order in both reactants.

Supporting Information Figure S7. Limonene conversion vs. time for two different Ti-SiO$_2$ particle sizes. Original 75-150 micron Ti-SiO$_2$ particles (squares) and a finely ground fraction (circles), sieved to < 325 mesh then filtered using a 0.7-micron Whatman syringe filter. Apparent activation enthalpies could, in principle, be influenced by internal diffusion limitations for the materials in this study. The Weisz-Prater criterion was calculated for all catalysts, and the highest value (most likely to be influenced by internal diffusion) of 0.60 was for Ti-SiO$_2$, due to its large particle size. Since this value approaches 1, diffusion limitations could be present. Therefore, two different particle sizes of the same catalyst were tested. The similarity in rates indicates the absence of significant internal diffusion limitations. Reaction conditions: 30 mg Ti-SiO$_2$, 4.6 mL acetonitrile, 1 mmol limonene, 1.1 mmol TBHP, 65 $^{\circ}$C, 0-6 h.

Supporting Information Figure S8. Selectivity to limonene monoepoxides (limonene 1,2-epoxide and limonene 8,9-epoxide) at 65 $^{\circ}$C for Ti-SiO$_2$ (green, circles), 2cPO (blue, triangles), and Ti-Beta (orange, plus signs). Epoxidation regioselectivity is similar between catalysts with ring epoxide accounting for 85 ± 3 mol % of epoxide yield.

Supporting Information Section 4. Limonene Adsorption

Limonene heats of adsorption on the freshly-calcined oxides were obtained using adsorption data at four different temperatures, 25-55 °C. ~30 mg of each material was separately loaded into four 20 mL vials containing 5 mL of 7×10^{-6} M limonene solution in acetonitrile. The vials were then shaken at 800 rpm for 2 h to allow for equilibrated adsorption. Using the experimental and theoretical relationships between K_L, the limonene concentration in solution at equilibrium ([limonene]$_{eq}$), the amount of limonene adsorbed on the surface at equilibrium ([limonene*]$_{eq}$), and ΔH_{ads}; we can obtain ΔH_{ads} and other thermodynamic parameters.

$$K_L = \frac{[limonene *]_{eq}}{[limonene]_{eq}[x]}$$

$$K_L = e^{\frac{-\Delta Gads}{RT}} = e^{\frac{-\Delta Hads}{RT} + \frac{\Delta Sads}{R}}$$

Here, X represents a vacant adsorption site on the material. Note that limonene is not assumed to adsorb at the Ti sites, but rather at some number of sites on the SiO_2 surface in general. Experimentally, we obtain the value [limonene*]$_{eq}$ by subtracting the measured [limonene]$_{eq}$ from the initial 7×10^{-6} M value. In some cases, limonene adsorption does not leave the Henry regime over the experimental conditions, and the equilibrium adsorption constant K_L cannot be separated from the total number of vacant sites on the SiO_2 surface, N_L. For other materials, the adsorption uptake curves fit adequately to a simplified Langmuir model, and K_L and N_L were independently determined. N_L was assumed to be independent of temperature. We then combine the above equations to obtain:

$$\ln(K_L \ x \ N_L) = \ln\left(\frac{[limonene *]_{eq}}{[limonene]_{eq}}\right) = \frac{-\Delta Hads}{RT} + \frac{\Delta Sads}{R} + \ln(N_L)$$

Plotting the natural log of the uptake data vs 1000/T results in a linear relationship with $-\Delta H_{ads}/R$ as the slope.