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# Grafted Ta–calixarenes: Tunable, selective catalysts for direct olefin epoxidation with aqueous hydrogen peroxide

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## 1. Introduction

# Tantalum complexes are known to mediate a number of interesting catalytic transformations including olefin oxidation [1] and polymerization [2], arene hydrogenation [3], metathesis of alkanes [4], imines and olefins [5], or activation of C–N bonds as in hydrodenitrogenation [6] and hydroamination [7]. However, a limited range of ancillary ligands have been employed to modulate the reactivity of the tantalum center. Moreover, most Ta catalysts are employed as homogenous catalysts, while the development of heterogeneous catalysts lags behind, comprising approximately 0.05% of supported oxide catalysts [8]. In this respect, immobilization of homogeneous complexes may be a viable strategy route to increase the diversity and utility of Ta heterogeneous catalysts.

Epoxidation is one of the most studied reactions in organic synthesis, for both commodity and fine chemicals. In particular, "green oxidants" such as  $H_2O_2$  have become highly desirable, since the only by-product ( $H_2O$ ) is environmentally benign and the process economics are not dependant on selling alcohol co-product [9]. However, a number of supported transition metal oxide catalysts employed in this reaction are poisoned by coordination of water to the active site, so non-aqueous organic oxidants such as *tert*-

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# ABSTRACT

Supported Ta(V) oxide catalysts were prepared by grafting calixarene–Ta(V) and TaX<sub>5</sub> complexes on SiO<sub>2</sub> at coverages less than 0.25 Ta nm<sup>-2</sup>. Thermogravimetric and elemental analyses and UV–visible spectroscopy indicate that catalysts consist of isolated, 1:1 Ta:ligand surface sites. Catalysts obtained by this one-pot procedure were studied in cyclohexene and cyclooctene epoxidation with H<sub>2</sub>O<sub>2</sub>. In sharp contrast with bare oxides, calixarene-containing catalysts had initial cyclohexene direct epoxidation turnover rates of  $3.9 \pm 0.1 \times 10^{-2} \text{ s}^{-1}$  unaffected by surface density, demonstrating single-site character. Calixarene-containing catalysts were up to  $3 \times$  more active than the corresponding TaCl<sub>5</sub>-based catalysts at high surface densities and were also up to 95% selective to direct (non-radical) cyclohexene epoxidation versus <65% selectivity for TaCl<sub>5</sub>-based catalysts or only ~20% selectivity for grafted calixarene-Ti(IV) catalysts. Capping silanols with octanol reduced epoxide hydrolysis from >50% to <30%. These catalysts demonstrate that a surface ligand on an otherwise traditionally prepared supported oxide can selectively direct oxidation down mechanistically distinct pathways.

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butyl hydroperoxide and cumene hydroperoxide are often necessary to achieve high activity [10]. Titania–silica supported and mixed oxide materials are highly studied and active catalysts for olefin and allylic alcohol epoxidation, but comparable group five Nb and Ta catalysts have been shown in a limited number of studies to give high rate, selectivity and stability, especially when using aqueous H<sub>2</sub>O<sub>2</sub> as the oxidant [11,12]. In particular, group five cations have been observed to be more tolerant to the presence of water than the analogous Ti(IV) systems, as a result of the ability to coordinate an additional anionic ligand when equal numbers of surface Si–O–M linkages are assumed [11].

For supported oxides in general, active site structures can, in principle, be controlled by grafting well-defined transition metal complexes onto a solid support. If retained during catalysis, the organic ligand cooperates with the rigid inorganic oxide surface to define the active site, rather than it arising solely as a consequence of the surface density of the metal oxide and the relative strength of metal-metal and metal-support interactions [13]. Bulky, multi-dentate ligands are ideal for this purpose, since they create stable surface species, and their bulk ensures metal atom site isolation during catalytic turnover. Here, calixarene-metal complexes similar to those reported previously for Ti or V active species are extended to Ta to take advantage of the diverse chemistry of this cation [14–16]. It is shown here that the calixarene ligands lead to well-defined behavior, with epoxidation rates that are not a



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function of surface density, and are higher than those of the bare Ta–SiO<sub>2</sub>.

Since catalytic epoxidation with aqueous  $H_2O_2$  can result in a complicated reaction network that includes direct epoxidation with  $H_2O_2$ , radical oxidation of the olefin to yield allylic hydroperoxides that in turn act as stoichiometric oxidants, epoxide hydrolysis, and unproductive  $H_2O_2$  decomposition, reaction pathway control is critical. It is also shown here that grafted calixarene–Ta is substantially more selective to direct epoxidation than either the bare Ta–SiO<sub>2</sub> or an analogous grafted calixarene–Ti. Finally, it is shown that the diversity of commercially available calixarenes enables tuning of the reactivity and selectivity of the Ta center in cyclohexene epoxidation with  $H_2O_2$ , particularly to minimize the relative rate of unselective radical reactions.

## 2. Materials and methods

## 2.1. General remarks

All syntheses were carried out under N<sub>2</sub> using standard Schlenk lines techniques or under Ar in a controlled atmosphere glove box. Cyclohexene, cyclooctene, and solvents were obtained at the highest purity available, dried as recommended [17], degasified and stored inside the glove box. Aqueous H<sub>2</sub>O<sub>2</sub> solution 30 wt.% (Aldrich) was used as received. Fresh tantalum pentachloride (TaCl<sub>5</sub>) anhydrous 99.9%, pentamethylcyclopentadienyltantalum tetrachloride (Cp\*TaCl<sub>4</sub>) 98%, and pentakis(dimethylamino)tantalum (Ta(dma)<sub>5</sub>) 99% (all from Strem Chemicals) were used as received.

Benzylmagnesium chloride 1.0 M in diethyl ether (Aldrich) was used as received to synthesize pentabenzyltantalum  $(Ta(Bz)_5)$  according to published procedures, to yield a brown complex [18]. p-*tert*-Butylcalix[4]arene (Cal4) 98% (Aldrich), p-*tert*-butylcalix[6]arene (Cal6) 98% (Aldrich), and p-*tert*-butylthiacalix[4]arene (SCal4) 98% (TCI) were used as received. 1,3-Dimethoxy-*tert*-butylcalix[4]arene (dmCal4) was prepared according to a previously published procedure [19].

# 2.2. Catalyst synthesis

Tantalum calixarene complexes were synthesized by adding 0.1 mmol TaCl<sub>5</sub> or Cp\*TaCl<sub>4</sub> to a stirred suspension of the calixarene (0.11 mmol) in anhydrous, degassed toluene (25 mL) at room temperature inside the glove box. Sealed flasks were removed from the glove box, and the mixtures were heated to reflux for 14–36 h under N<sub>2</sub> following previously described methods to yield Cal4TaCl [20], dmCal4TaCl<sub>2</sub> [21], SCal4TaCl [22], Cal6TaCl<sub>2</sub> [23], and Cal4TaCp\* [24]. In all cases, yellow or orange complexes were formed. Specific synthesis details are given in the Supplementary material. Other Ta compounds were dissolved in anhydrous, degassed toluene at the same concentration. SiO<sub>2</sub> (Selecto Scientific, 500 m<sup>2</sup> g<sup>-1</sup> surface area, average pore diameter 6.0 nm, particle sizes 32-63 µm, treated under dynamic vacuum at 300 °C for 24 h) was transferred to the flasks containing the previously synthesized precursors. Ratios of 0.02, 0.05, 0.1, 0.15, 0.2, and 1.0 mmol Ta per g SiO<sub>2</sub> were used in the grafting step by altering the amount of SiO<sub>2</sub> added. Nomenclature used for the catalysts is, e.g. for Cal4TaCl precursor, *n*-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>, where n is the synthesis ratio. Suspensions were refluxed under N<sub>2</sub> with the exception of Ta(Bz)<sub>5</sub> which was stirred at room temperature in the glove box. The color of the Ta complexes was gradually transferred from the solutions to the solid. After 24 h, the solid was filtered and washed with 300 mL of hot anhydrous toluene under N<sub>2</sub> and dried under dynamic vacuum at 25 °C overnight. When dry, all solids acquired the color of the soluble complex, with the exception of Cal6**Ta**(OSi $\equiv$ )<sub>2</sub>, which became green and Cp\***Ta**O(OSi $\equiv$ )<sub>2</sub>, which became pink, in contrast to a yellow, previously reported  $Cp^*Ta(CH_3)_3OSiPh_3$  [25]. The color changes were not accompanied by dramatic changes in diffuse reflectance spectra, as discussed below. Solid Ta-containing catalysts were stored inside the glove box. For comparison, an analogous grafted calixarene–Ti(IV) catalyst 0.2-dmCal4**Ti**(OSi=) was prepared as described previously [14].

#### 2.3. Heat treatment

Some catalysts were heated at 550 °C for 6 h in air to remove organic ligands. The resulting catalysts, denoted, e.g. 0.2-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>-**c** are assumed to have identical Ta content per g SiO<sub>2</sub> as the starting materials.

#### 2.4. Analytical characterization

The mass loss of all grafted materials was determined by thermogravimetry (TGA; TA Instruments Q500) in a flow of dry synthetic air at a heating rate of 8 °C min<sup>-1</sup> from room temperature to 800 °C. Mass losses were corrected for hydroxyl condensation, which was determined from TGA of unmodified SiO<sub>2</sub> previously treated identically to the catalyst supports. Ligand contents were estimated by assuming that mass losses reflect combustion of a molecular weight of 612 g mol<sup>-1</sup> site in material Cal4**Ta**(OSi $\equiv$ )<sub>2</sub> and were adjusted accordingly for other grafted species.

Ta content in the catalyst was measured using inductively coupled plasma techniques. Tantalum standards (from  $1000 \ \mu g \ mL^{-1}$  Specpure AAS standard solution) were prepared for the calibration of the instrument, and linear calibration curves were obtained in the range 1–50 Ta ppm. To achieve quantitative removal of Ta for the support, it was necessary to use 0.7 mL piranha reagent (H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> = 3:1) per 10 mg catalyst, which was stirred for 1 h in an ultrasound bath, and diluted to 14 mL. [CAUTION: make and handle piranha reagent with extreme care.] Residual H<sub>2</sub>O<sub>2</sub> was decomposed before the ICP measurement. Multiple trials were averaged to obtain accurate results.

UV-visible spectra were measured at ambient conditions using a UV-visible spectrophotometer (UV-3600 Shimadzu). Absorption spectra of Ta complexes were collected in toluene solution and diffuse reflectance spectra of Ta-containing catalysts were collected using a Harrick Praying Mantis diffuse reflectance accessory. Samples for diffuse reflectance were exposed to ambient air. Pressed poly-(tetrafluoroethylene) powders were used as perfect reflector standard in calculating Kubelka-Munk pseudoabsorbances. Optical edge energies of the catalysts were calculated by assuming that the lowest energy transitions (calixarene-Ta LMCT) were allowed indirect transitions [26]. Solid-state <sup>13</sup>C CP/MAS NMR was performed at the Northwestern IMSERC facility using a solids 400 Varian spectrometer at 400 MHz, a spinning rate of 7 kHz and 5680 scans. Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTS) was performed in the Keck-II facility of NUANCE Center at Northwestern using a Nexus 870 FTIR spectrometer with diffuse reflectance accessory. Spectra were normalized with respect to the SiO<sub>2</sub> support. Sixty-four scans were averaged with 8 cm<sup>-1</sup> resolution.

## 2.5. Catalysis

Reaction flasks were prepared inside the glove box, where the catalysts were stored to prevent contact with atmosphere. A 6-mL screw-cap flask was loaded with 30 mg of the catalyst, 4 mL acetonitrile, 200  $\mu$ L dichlorobenzene (internal standard), and 4 mmol of substrate (400  $\mu$ L cyclohexene or 250  $\mu$ L cyclooctene). The reaction flask was sealed and moved outside the glove box just immediately prior to the injection of aqueous H<sub>2</sub>O<sub>2</sub> (200  $\mu$ L) to start the reaction. Initial cyclohexene and H<sub>2</sub>O<sub>2</sub> concentrations

were 0.82 M and 0.41 M, respectively, giving a 50% maximum conversion of cyclohexene. Analogous cyclooctene experiments were performed with 20 mg catalyst, 2 mL acetonitrile, 100  $\mu$ L dichlorobenzene, 250  $\mu$ L cyclooctene, and 130  $\mu$ L aqueous H<sub>2</sub>O<sub>2</sub>. Reaction flasks were stirred and heated at 65 °C. Aliquots (10  $\mu$ L) were removed periodically using a syringe, filtered to remove the catalyst, and analyzed using a Shimadzu 2010 GC system equipped with a flame ionization detector using a TR-1 capillary column.

# 3. Results

# 3.1. Materials synthesis and characterization

The synthesis of grafted calixarene–Ta(V) and TaX<sub>5</sub> complexes is depicted in Schemes 1 and 2. All catalysts were prepared using

one-pot procedures in controlled atmosphere conditions to prevent premature hydrolysis of the Ta chloride precursors. The syntheses of all calixarene–Ta(V) complexes are known to the literature to be very high yielding, and thus no effort was made to purify the intermediates, making this catalyst synthesis method general and scalable.

Although understanding the atomic connectivity of supported metal oxides remains an area of intense research, a structure for  $SiO_2$ -grafted calixarene–Ta(V) is proposed based on known molecular species. In particular, the reaction between Cal4**Ta**Cl and excess sodium phenoxide coordinates two monomeric phenolates [27]. By analogy, it is proposed that the surface Ta coordinates two  $SiO^-$  species on the surface, and three of the calixarene phenolates. Depending on the environment and ligand, a calixarene phenolor ether oxygen, or  $H_2O$  or oxidized products, will complete the



**Scheme 1.** Calixarene–Ta(V) syntheses and grafting on SiO<sub>2</sub>. (a) Cal4, (b) Cal4TaCl, (c) dmCal4, (d) dmCal4TaCl<sub>2</sub>, (e) Cal6, (f) Cal6TaCl<sub>2</sub>, (g) SCal4, (h) SCal4TaCl, (i) Cp\*TaCl<sub>4</sub>, (j) Cal4TaCp\*, (k) generic calixarene–Ta species on surface, Cal4**Ta**(OSi=)<sub>2</sub> from b, dmCal4**Ta**(OSi=)<sub>2</sub> from d, Cal6**Ta**(OSi=)<sub>2</sub> from f, SCal4**Ta**(OSi=)<sub>2</sub> from h and Cal4**Ta**<sup>Cp\*</sup>(OSi=)<sub>2</sub> from j. Pentamethylcyclopentadienyl Ta grafting directly produces (m) Cp\***Ta**Cl<sub>4-x</sub>(OSi=)<sub>x</sub>, which forms (n) Cp\***Ta**O(OSi=)<sub>2</sub> upon air exposure. Regardless of precursor, (l) **Ta**O(OSi=)<sub>3</sub> are oxo-Ta species formed after heat treatment. The structure of generic supported calixarene–Ta(V) (k) is by analogy to known molecular species [27]. The structure of heat-treated catalyst (l) is as proposed for traditionally synthesized, supported Ta oxides [28,29].



**Scheme 2.** Grafting  $TaX_5$  on SiO<sub>2</sub> directly forms (p)  $TaX_4(OSi\equiv)_2$ , which forms the surface oxo-Ta complex (l) upon standing in moist air. The structure of heat-treated catalyst (l) is as proposed for other supported Ta oxides at low coverage [28,29].

coordination sphere. Before exposure to any moisture, grafting  $TaX_5$  complexes likely results in a mixture of Ta species connected to the surface by one or two bonds [1,4].

Calixarene and Cp<sup>\*</sup> contents were determined from the sharp mass loss near 350 °C in thermogravimetric analysis in O<sub>2</sub> (Fig. 1 and Supplementary material, Fig. S1). The organic content was estimated from mass losses assuming complete loss of the calixarene or Cp\* fragment shown in Scheme 1, and gain of two oxygen atoms to form  $TaO(OSi\equiv)_3$ . This corresponds to  $612 \text{ g mol}^{-1}$ for  $Cal4Ta(OSi\equiv)_2$ , 641 g mol<sup>-1</sup> for dmCal4Ta(OSi=)<sub>2</sub>, 936 g mol<sup>-1</sup> for  $Cal6Ta(OSi\equiv)_2$ , 684 g mol<sup>-1</sup> for  $SCal4Ta(OSi\equiv)_2$ , 135 g mol<sup>-1</sup> for  $Cp^*TaO(OSi\equiv)_2$ , and 779 g mol<sup>-1</sup> for  $Cal4Ta^{Cp*}(OSi\equiv)_2$ . In this experiment,  $TaCl_{5-x}(OSi\equiv)_x$ ,  $(dma)_{5-x}Ta(OSi\equiv)_x$  and  $(Bz)_{5-x}$ - $Ta(OSi \equiv)_{r}$  show negligible mass loss compared to SiO<sub>2</sub> due to the instability of these ligands under air atmosphere. Hydrolysis is expected to occur after only brief exposure of these supported compounds to air. Table 1 compares ligand content determined by TGA and Ta content determined by ICP (Supplementary material, Tables S1 and S2) for the calixarene-containing catalysts. The table shows Ta:ligand ratios of approximately 1:1 for all samples except in the low-loaded catalysts, where small mass losses do not allow sufficiently precise measurement of the ligand content. This equimolecular ratio is consistent with intact grafting of species that deposit as monomers.

Near quantitative grafting of Ta and calixarene is observed up to 0.2 mmol per g SiO<sub>2</sub> (0.25 groups nm<sup>-2</sup>) which indicates strong interactions between Ta, surface, and calixarene. At larger amounts of Ta complex in the synthesis solution (1 mmol Ta per g SiO<sub>2</sub>), Ta contents in the final catalyst do not pass the maximum geometrical surface density of calixarenes (at ~0.25 groups nm<sup>-2</sup>), consistent with previous observations of Ti-containing calixarenes [14] and consistent with a Ta-calixarene interaction that is stronger than the Ta-surface interaction in refluxing toluene. Cal4**Ta**<sup>Cp+</sup>(OSi=)<sub>2</sub> grafts at a lower surface density than other species, consistent with hindered loss of the large Cp<sup>+</sup> ligand. In the absence of Ta, no

#### Table 1

Tantalum (ICP) and ligand (TGA) contents for catalysts synthesized with 0.02-1.0 mmol Ta per g SiO<sub>2</sub> and various precursors. Ligand loadings are accurate to 0.02 mmol/g. Ta loadings are reproducible to 0.2 wt%.

Catalyst	Ta in synthesis (%)	mmol ligand/ g <sub>catalyst</sub>	Ta ICP analysis (%)	Ta:ligand
$0.2$ - <b>Ta</b> Cl <sub>5-x</sub> (OSi $\equiv$ ) <sub>x</sub>	3.5	-	3.4	-
$0.2-(dma)_{5-x}$ <b>Ta</b> $(OSi\equiv)_x$	3.1	-	2.5	-
$0.2-(Bz)_{5-x}$ <b>Ta</b> $(OSi\equiv)_x$	3.3	-	0.5	-
$0.02$ -Cal4 <b>Ta</b> $(OSi \equiv)_2$	0.4	0.05	0.5	n/a
$0.05$ -Cal4 <b>Ta</b> $(OSi \equiv)_2$	0.9	0.06	0.8	n/a
$0.10$ -Cal4 <b>Ta</b> $(OSi \equiv)_2$	1.7	0.09	1.8	1.1
$0.15$ -Cal4 <b>Ta</b> $(OSi \equiv)_2$	2.4	0.16	2.6	0.9
$0.2$ -Cal4 <b>Ta</b> $(OSi \equiv)_2$	3.1	0.19	2.9	0.9
$1.0$ -Cal4 <b>Ta</b> (OSi $\equiv$ ) <sub>2</sub>	15.4	0.19	3.3	0.9
$0.2$ -dmCal4 <b>Ta</b> (OSi $\equiv$ ) <sub>2</sub>	3.1	0.19	3.3	1.0
$0.2$ -Cal6 <b>Ta</b> $(OSi \equiv)_2$	2.9	0.16	3.3	1.1
$0.2$ -SCal4 <b>Ta</b> $(OSi \equiv)_2$	3.1	0.18	3.3	1.0
$0.2$ -Cp*TaO(OSi $\equiv$ ) <sub>2</sub>	3.3	0.19	3.5	1.0
$0.2$ -Cal $4$ Ta <sup>Cp*</sup> $(OSi \equiv)_2$	3.0	0.13	2.4	1.0

detectable calixarenes are attached to the surface under these conditions.

## 3.2. Materials spectroscopic characterization

Solution and diffuse reflectance UV-visible (DRUV-vis) spectroscopies were used to characterize the precursors and solid catalysts, respectively. For d<sup>0</sup> metals, the energy of the ligand to metal charge transfer (LMCT) band is dependent on the local metal coordination environment. In general, a red-shift in the LMCT band occurs upon increasing the coordination number of the metal center or agglomeration via bridging oxygen ligands [11,28,29]. One advantage of the grafted calixarene–Ta(V) complexes is that the molecular precursor contains most of the Ta-O connectivity of the final catalyst and is thus a spectroscopic model for the active site prepared after grafting. In 10<sup>-4</sup> M toluene solution, the starting calixarene ligands have an absorption maximum at 270-290 nm (295–305 nm for SCal4) arising from  $\pi$ – $\pi$ \* transitions and have no absorption features above 350 nm. calixarene-Ta(V) complexes have the same  $\pi - \pi^*$  transitions as well as a broad phenol-to-Ta LMCT centered near 350 nm (Fig. 2A). This band is very weak for SCal4TaCl. Related transitions are also weak for Cp\*TaCl<sub>4</sub> and Cal4TaCp<sup>\*</sup> (Fig. 2B).  $TaCl_{5-x}(OSi\equiv)_x$ ,  $(dma)_{5-x}Ta(OSi\equiv)_x$ , and  $(Bz)_{5-x}$ **Ta** $(OSi \equiv)_x$  show negligible absorbance above 300 nm.

DRUV-vis spectra of the calixarene-containing catalysts (Fig. 3) show three features: charge transfer of the bare oxide at  $\sim$ 230 nm,



**Fig. 1.** TGA for calixarene–Ta(V) grafted catalysts with 0.2 mmol Ta per g SiO<sub>2</sub>. Mass loss has been scaled to 150 °C to account for solvent or weakly adsorbed fragments of monomeric precursors. From top to bottom: SiO<sub>2</sub>, (h) 0.2-SCal4**Ta**(OSi $\equiv$ )<sub>2</sub>, (b) 0.2-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>, (d) 0.2-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>, (f) 0.2-Cal6**Ta**(OSi $\equiv$ )<sub>2</sub>, (n) 0.2-Cp<sup>\*</sup>**Ta**O(OSi $\equiv$ )<sub>2</sub>, and (j) 0.2-Cal4**Ta**<sup>Cp\*</sup>(OSi $\equiv$ )<sub>2</sub>. Letters corresponds to the catalyst precursors in Scheme 1.



Fig. 2. UV-visible absorption spectra for synthesized tantalum compounds in toluene  $10^{-4}$  M. (d) 0.2-dmCal4TaCl<sub>2</sub>, (f) 0.2-Cal6TaCl<sub>2</sub>, (b) 0.2-Cal4TaCl, (h) SCal4TaCl, (i) Cp<sup>+</sup>TaCl<sub>4</sub>, and (j) 0.2-Cal4TaCp<sup>+</sup>. Letters corresponds to the catalysts precursors in Scheme 1.



**Fig. 3.** DRUV-vis spectra for calixarene–Ta(V) complexes grafted on silica surface. (f) 0.2-Cal6**Ta**(OSi $\equiv$ )<sub>2</sub>, (d) 0.2-dmCal4**Ta**(OSi $\equiv$ )<sub>2</sub>, (h) SCal4**Ta**(OSi $\equiv$ )<sub>2</sub>, (b) 0.2-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>, (l) 0.2-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>, (j) 0.2-Cal4**Ta**(O

the  $\pi$ - $\pi$ <sup>\*</sup> of the ligand at ~290 nm, and LMCT that extend to 400-500 nm, which are more intense than for the precursor structures. These latter features are used diagnostically for calixarene-to-Ta connectivity. The as-synthesized forms of  $TaCl_{5-x}(OSi\equiv)_x$ ,  $(dma)_{5-x}$ **Ta** $(OSi\equiv)_x$  and  $(Bz)_{5-x}$ **Ta** $(OSi\equiv)_x$  are insufficiently air-stable to provide meaningful diffuse reflectance UV-visible spectra in this experiment. The position of the calixarene-Ta LMCT edge is extrapolated from the linear region to the intercept (Table 2). The LMCT edge energies of the chloride-containing precursors are lower than those of the resulting catalysts, consistent with loss of halide upon grafting and confirming that the Ta precursor has been covalently grafted to the surface. No significant or systematic changes in LMCT edge energies were observed when comparing two different Ta loadings, providing first evidence that these catalysts consist of a single type of active site unaffected by surface density. Neither were large nor systematic differences observed in the edge energy for different calixarene precursors used, indicating electronically similar sites in all catalysts. Heating the catalysts in dry air at 550 °C for 6 h removed all absorption features above 290 nm, confirming that those electronic transitions arise from the calixarene or Cp<sup>\*</sup> ligands or from the ligand-Ta connectivity. Previous assignments of supported Ta catalysts treated above 500 °C have identified numerous surface species: crystalline Ta<sub>2</sub>O<sub>5</sub> with peak maxima at 265–270 nm, non-crystalline tantala at 260 nm, and isolated terminal tantalum-oxo structures at 220–235 nm [28,29]. The edge energies of Ta<sub>2</sub>O<sub>5</sub> films were reported to be 4.18 eV (297 nm) [30]. Thus, the peak maxima at ~230 nm for heat-treated catalysts here indicates that these species are isolated terminal tantalum-oxo structures with minimal crystalline or non-crystalline Ta<sub>2</sub>O<sub>5</sub>. This is consistent with an assynthesized structure of an isolated Ta atom protected by a calixarene ligand. Table 2 also shows the position of the absorption maximum and the edge energy for all catalysts after heat treatment. Additional DRUV-vis spectra are included in the Supplementary material (Figs. S2–S4).

DRIFTS of 0.2-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>, 0.2-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>-**c** and calixarene covalently grafted to SiO<sub>2</sub> in the absence of Ta [31] (Supplementary material, Fig. S5) show evidence of the intact calixarene ligand as synthesized and its complete removal by heat treatment. The solid state <sup>13</sup>C CP/MAS NMR of 0.2-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub> (Supplementary material, Fig. S6) also confirms that the calixarene ligand was grafted intact. As observed previously for Ti-based catalysts [14], a resonance at ~158 ppm for the ispo carbon indicates calixarene-Ta coordination on the surface.

Table 2

Absorption edge energies for the lowest energy LMCT band for Ta–calixarenes in toluene solution, after grafting on SiO<sub>2</sub> with different Ta:SiO<sub>2</sub> ratios and calixarene–Ta(V) and TaX<sub>5</sub> complexes, and after heat treatment for 0.2 mmol Ta g<sup>-1</sup> catalysts.

Precursor	Edge (eV) in $10^{-4}$ M	Grafted on silic	Treated at 550 °C		
	toluene solution	0.05 mmol Ta per g SiO <sub>2</sub>	0.2 mmol Ta per g SiO <sub>2</sub>	Edge (eV)	Max (nm)
<b>Ta</b> Cl₅	-	-	-	4.7	240
Ta(dma)5	-	-	-	4.9	228
$Ta(Bz)_5$	-	-	-	4.8	230
Cal4 <b>Ta</b> Cl	3.1	3.4	3.4	4.8	225
dmCal4 <b>Ta</b> Cl <sub>2</sub>	3.0	3.3	3.4	4.9	229
Cal6 <b>Ta</b> Cl <sub>2</sub>	3.1	3.3	3.2	5.0	222
SCal4 <b>Ta</b> Cl	3.6	3.3	3.6	4.7	231
Cp*TaCl <sub>4</sub>	2.9	3.1	3.0	4.8	228
Cal4 <b>Ta</b> Cp*	3.0	3.1	3.0	4.8	232

#### 3.3. Catalytic behavior

The catalytic activity of these materials was probed with cyclohexene and cyclooctene oxidation with aqueous  $H_2O_2$  in acetonitrile. For all supported calixarene–Ta catalysts tested here, the selectivity to cyclooctene epoxide is higher than 98%. Allylic oxidation and epoxide hydrolysis to the *trans*-diol are both negligible, as is typical for cyclooctene in similar supported  $d^0$  metal oxide catalysts [32]. Oxidation rates are similar for all calixarene–Ta(V) catalysts but higher than for TaX<sub>5</sub>-type precursors. Yields are given in the supporting data (Table S3) and a full kinetic analysis will be published elsewhere.

Table 3 shows initial rates and the 3-h conversions, turnover numbers, and product distributions at 3 h for cyclohexene oxidation with aqueous  $H_2O_2$  in acetonitrile for 0.2 mmol g<sup>-1</sup> Ta and Ti catalysts. Full data for other metal loadings are included in the Supplementary material (Tables S4 and S5). In contrast to cyclooctene, cyclohexene oxidation typically yields a number of products under similar conditions with other supported d<sup>0</sup> metal oxide catalysts [33], making this substrate more useful for detecting patterns of reactivity among different catalysts.

Following reaction networks postulated for Ti–SiO<sub>2</sub> oxidation [33], allylic oxidation produces cyclohexenyl hydroperoxides, and this unstable molecule can oxidize cyclohexene to generate cyclohexane epoxide and cyclohexanol, or it can decompose to cyclohexanone. Alternately, cyclohexane epoxide can be formed directly via a direct pathway catalyzed by Lewis acids. Epoxide generated from either pathway can hydrolyze to the *trans*-diol,

which is catalyzed by both Brønsted and Lewis acids. These pathways are illustrated in Scheme 3. A key metric therefore is the pathway selectivity to epoxide via radical or direct routes, which is the ratio of apparent rate constants  $S = k_1/(k_1 + k_2)$ . Selectivity to direct epoxidation or non-radical processes is defined in Eq. (1) from the ratios of concentrations of various products.

Direct Epoxide Selectivity = 
$$\frac{\text{epoxide} + \text{diol} - \text{cyclohexenol}}{\text{all C6 products}}$$
 (1)

In parallel, these catalysts can also decompose  $H_2O_2$  without generating product, accounting for lower than maximum conversion of cyclohexene (maximum conversion is  $\sim$ 50% under these conditions).

First, dmCal4**Ta**(OSi $\equiv$ )<sub>2</sub> and dmCal4**Ti**(OSi $\equiv$ ) catalysts were compared under identical conditions in cyclohexene epoxidation with H<sub>2</sub>O<sub>2</sub> (Table 3, entries 8 vs. 9). Ti–SiO<sub>2</sub> is a ubiquitous catalyst, and dmCal4**Ti**(OSi $\equiv$ ) has been shown previously to be an extremely active and selective catalyst in cyclohexene epoxidation with organic hydroperoxides [14]. Here, the Ti-containing catalyst is slightly more productive than the Ta-based catalyst with respect to total cyclohexene conversion. However, the initial direct epoxidation turnover rates are higher for Ta due to a much higher direct epoxide selectivity (90% for Ta vs. 21% for Ti). The Ta catalyst also shows much lower hydrolysis activity. This substantial improvement in epoxide yield when compared to a workhorse catalyst motivates a more extensive investigation into these materials.

 $Cal4Ta(OSi \equiv)_2$  and  $TaCl_{5-x}(OSi \equiv)_x$  catalysts were compared for Ta loadings of 0.02, 0.05, 0.15, and 0.2 mmol per g SiO<sub>2</sub>. All  $Cal4Ta(OSi \equiv)_2$  catalysts have similar initial direct epoxidation rates  $(r_i = (mol_{epoxide} + mol_{diol} - mol_{cyclohexenol}) mol_{Ta}^{-1} s^{-1})$  up to the maximum surface density of Ta possible. Low Ta loadings also give nearly identical turnovers to products as a function of time over 3 h. (Fig. 4 and Table 4; complete product distributions and kinetic data in the Supplementary material Table S4 and Fig. S6). The maximally loaded catalyst 0.2-Cal4**Ta**( $OSi \equiv$ )<sub>2</sub> maintains the same initial turnover rate but uniquely shows a drop off in reactivity, the mechanistic origin of which is under investigation. Table 4 shows that selectivity to direct epoxidation through the non-radical route increases with calixarene–Ta(V) surface density. Given that direct epoxidation rates are constant with surface density, this is equivalent to decreasing radical oxidation with increasing surface density. To check the role of lower-selectivity background reactions that may be competitive at the lower total conversions of the low surface density catalysts, an experiment was run with 250 mg of 0.02-Cal4Ta( $OSi \equiv$ )<sub>2</sub> to give a Ta content

Та	ble	3
14	DIC	_

C	clohexene e	poxidation	with Ta	and	Ti-grafted	catalysts	with	0.2 mmol	Та	per	g SiC	)-
-	veromenene e	pomulation	vvitil it	i unu	ii giuiteu	cuturysts	**ICII	0.2 1111101	1 u	per	5 510	11

Catalyst	Conv (%) <sup>a</sup>	TON <sup>b</sup>	Direct epoxide initial rate	Selectivity					Direct epoxide selectivity <sup>c</sup>
			$mol\ mol_{Ta}{}^{-1}\ s{}^{-1}\times 10^2$	Epoxide	Diol	Anone	Enol	Enone	
$0.2$ - <b>Ta</b> Cl <sub>5-x</sub> (OSi $\equiv$ ) <sub>x</sub>	6.7	39	1.7	39	33	9	9	11	63
$0.2-(dma)_{5-x}Ta(OSi\equiv)_x$	8.9	51	1.2	45	38	5	8	5	75
$0.2-(Bz)_{5-x}$ <b>Ta</b> $(OSi\equiv)_x$	2.2	15	1.2	8	67	1	11	12	63
0.2-Cal4 <b>Ta</b> (OSi≡) <sub>2</sub> -cap	8.7	53	3.6	59	30	1	6	4	83
$0.2$ -Cal4 <b>Ta</b> $(OSi \equiv)_2$	9.9	55	3.9	41	52	2	3	3	89
$0.2$ -Cal6Ta(OSi $\equiv$ ) <sub>2</sub>	9.9	56	3.1	12	85	1	2	1	95
$0.2$ -SCal4Ta(OSi $\equiv$ ) <sub>2</sub>	10.2	54	2.5	15	78	0	3	4	89
$0.2$ -dmCal4Ta(OSi $\equiv$ ) <sub>2</sub>	10.1	58	3.8	28	66	1	3	3	90
0.2-dmCal4Ti(OSi≡)	12.3	64	2.0	6	40	29	24	1	21
$0.2-Cp^*TaO(OSi\equiv)_2$	16.8	83	3.1	28	59	1	5	7	91
$0.2$ -Cal4Ta <sup>Cp*</sup> (OSi $\equiv$ ) <sub>2</sub>	13.4	95	5.4	9	82	1	3	6	87
$0.2$ -Cal4 <b>Ta</b> $(OSi \equiv)_2$ -c	6.1	34	1.1	34	17	2	45	2	53

<sup>a</sup> Reaction conditions: catalyst = 30 mg,  $V_{\text{total}}$  = 4.6 ml, [cyclohexene] = 0.82 M, [H<sub>2</sub>O<sub>2</sub>] = 0.41 M, T = 65 °C,  $t_{\text{R}}$  = 180 min.

<sup>b</sup> TON: mmol oxidation products/mmol Ta.

<sup>c</sup> Direct epoxide selectivity = 100 × (epoxide + diol – cyclohexenol)/(epoxide + diol + cyclohexenol + cyclohexenone + cyclohexanone).



Scheme 3. Proposed mechanism for cyclohexene oxidation with H<sub>2</sub>O<sub>2</sub> over Ta grafted catalysts.



**Fig. 4.** Turnover numbers vs. reaction time for Cal4**Ta**(OSi $\equiv$ )<sub>2</sub> and **Ta**Cl<sub>5-x</sub>(OSi $\equiv$ )<sub>x</sub> catalysts with different Ta content. (A)  $\blacklozenge$  0.02-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\Box$  0.05-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\blacktriangle$  0.15-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\bigcirc$  0.02-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\Box$  0.05-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\blacktriangle$  0.15-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\bigcirc$  0.02-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\Box$  0.05-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\blacktriangle$  0.15-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\bigcirc$  0.20-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\Box$  0.05-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\bigstar$  0.15-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\bigcirc$  0.20-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\Box$  0.05-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\bigstar$  0.15-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\bigcirc$  0.20-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\Box$  0.05-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\bigstar$  0.15-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\bigcirc$  0.20-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\Box$  0.05-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\bigstar$  0.15-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\bigcirc$  0.20-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\Box$  0.05-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\blacksquare$  0.05-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>,  $\Box$  0.05-Cal4**Ta**(

in the reactor equivalent to that for the 0.15-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub> trial. This increased cyclohexene conversion to 10%, but maintained direct selectivity constant at 76%. For all reactions, direct epoxide selectivities held constant from 10 min to 3 h, regardless of conversion, indicating that the reaction conditions themselves were not responsible for the observed behavior. Thus, the presence of calixarene at increasing surface coverage is shown to suppress radical reaction pathways.

In contrast, materials prepared with different TaCl<sub>5</sub> contents on SiO<sub>2</sub> showed initial direct epoxidation rates and 3-h turnovers that decreased markedly with increasing Ta loading (Fig. 4 and Table 4). The rates and selectivities to direct epoxidation are also substantially lower than those of Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>, and direct epoxidation selectivities are similar to the blank experiment.

Different calixarenes and Ta precursors were next compared at Ta contents of 0.2 and 0.05 mmol per g SiO<sub>2</sub>. At the higher Ta content (Table 3), calixarene- and Cp<sup>\*</sup>-containing catalysts exhibit 2-3 times higher initial epoxidation rates than catalysts derived from TaX<sub>5</sub> precursors. Ta(Bz)<sub>5</sub>-derived catalyst gives particularly low

rates and conversions under these conditions. There is some variation of initial direct epoxidation rates within the series, but all calixarene- and Cp\*-containing catalysts give ~90% selectivity to direct epoxidation, whereas materials derived from TaX<sub>5</sub>-type precursors give <75% direct epoxidation selectivity. Furthermore, heat treatment of the calixarene-containing catalysts, e.g. to produce 0.2-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>-**c**, dramatically reduces initial rates, total conversions, and selectivity to direct epoxidation. This result demonstrates that, rather than potentially limited by steric congestion at the metal, rates are enhanced in the presence of the organic ligand. Perhaps more importantly, the presence of the ligand during turnover decreases radical reactivity *and* enhances non-radical reactivity, with a total increase in the direct selectivity.

The decomposition of  $H_2O_2$  over Ta catalysts was studied by iodometric titration [34] to further understand the reactivity of this system. In the control experiment with neither catalyst nor SiO<sub>2</sub>, the concentration of  $H_2O_2$  remained within 98% of the initial concentration after 6 h at 65 °C. With only SiO<sub>2</sub>,  $H_2O_2$  remained within 93%. With 0.2-Cal4**Ta**(OSi=)<sub>2</sub>,  $H_2O_2$  remained within 89%.

#### Table 4

Cyclohexene epoxidation results as a function of Ta content.

Loading (mmol $g^{-1}$ )	TaCl <sub>5-x</sub> (OSi≡	) <sub>x</sub>			$Cal4Ta(OSi \equiv)_2$				
	Conv. (%) <sup>a</sup>	TON <sup>b</sup>	Direct epoxide initial rate <sup>c</sup>	Direct epoxide selectivity <sup>d</sup>	Conv. (%) <sup>a</sup>	TON <sup>b</sup>	Direct epoxide initial rate <sup>c</sup>	Direct epoxide selectivity <sup>d</sup>	
Blank	0.8	-	-	54	0.8			54	
0.00	0.8	-	-	50	0.8			50	
0.02					3.8	163	3.6	73	
0.02 <sup>e</sup>					10.0	73	2.9	76	
0.05	4.1	129	3.0	55					
0.10	7.5	95	2.7	63	7.3	165	4.0	80	
0.15	8.4	55	2.5	57	12.3	143	4.0	90	
0.20	6.7	39	1.7	63	9.9	55	3.9	89	

<sup>a</sup> Reaction conditions: catalyst = 30 mg,  $V_{\text{total}}$  = 4.6 ml, [cyclohexene] = 0.82 M, [H<sub>2</sub>O<sub>2</sub>] = 0.41 M, T = 65 °C,  $t_{\text{R}}$  = 180 min.

<sup>b</sup> TON: mmol oxidation products/mmol Ta.

<sup>c</sup> Rate as mol  $\text{mol}_{\text{Ta}}^{-1} \text{ s}^{-1} \times 10^2$ .

<sup>d</sup> Direct epoxide selectivity =  $100 \times (\text{epoxide} + \text{diol} - \text{cyclohexenol})/(\text{epoxide} + \text{diol} + \text{cyclohexenol} + \text{cyclohexenone} + \text{cyclohexanone}).$ 

<sup>e</sup> Reaction conditions: Catalyst = 250 mg,  $V_{\text{total}}$  = 4.6 ml, [cyclohexene] = 0.82 M, [H<sub>2</sub>O<sub>2</sub>] = 0.41 M, T = 65 °C,  $t_{\text{R}}$  = 180 min.

Finally, over 0.2-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>-**c**, the H<sub>2</sub>O<sub>2</sub> concentration fell to 70% of the initial value, clearly showing that coordination of the calixarene ligand inhibits radical peroxide decomposition relative to the bare oxide catalyst.

Results obtained in cyclohexene epoxidation with low surface coverage catalysts are given in the Supplementary material (Table S5). The lower surface coverages decrease the selectivity to direct epoxidation, but also decrease the extent of subsequent epoxide hydrolysis. While overall conversions at completion are lower at these lower surface densities, 3-h turnover numbers to product are higher. By comparing these data with those in Table 3, Cal4**Ta**(OSi $\equiv$ )<sub>2</sub> and Cal4**Ta**<sup>Cp+</sup>(OSi $\equiv$ )<sub>2</sub> are both seen to have initial direct epoxidation rates that are largely insensitive to surface density.

Catalysts 0.20-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub> and 0.05-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub> were treated with excess octanol (5 mmol per g catalyst) in refluxing toluene for 24 h, then washed and dried to study the effect of SiO<sub>2</sub> surface end-capping on reaction rates and selectivities [35,36]. After the surface modification, the catalyst weight increase in TGA corresponded to 0.32 and 0.53 mmol octanol per g catalyst (~9% and ~14% of the hydroxyl groups on surface) for 0.2-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub> and 0.05-Cal4**Ta**(OSi $\equiv$ )<sub>2</sub>, respectively (Supplementary material, Fig. S7). Accounting for the overall weight increase, the capped catalysts show only minimal decreases in conversion, turnovers, initial rates, and selectivity to direct epoxidation after capping, while the extent of hydrolysis, defined as mol<sub>diol</sub>/(mol<sub>diol</sub> + mol<sub>epoxide</sub>), decreases substantially from ~55% to ~30% (Table 3, entry 4 vs. 5 and Supplementary material, Table S5, entry

4 vs. 5). These results demonstrate that while bulk hydrophobicity effects can control the rates of hydrolysis by minimizing the role of exposed SiOH, these effects are independent of those of the calixarene-containing precursors that directly alter the active site chemistry.

## 3.4. Catalytically relevant species and stability

The catalytic behavior of  $dmCal4Ta(OSi\equiv)_2$  was compared to that of the dmCal4TaCl homogeneous complex in solution. Fig. 5A shows that turnover numbers for the solid catalyst are significantly higher than for the same compound in solution. Indeed, the homogeneous precursor gives comparable initial rates, but deactivates completely within 10 min. Further control experiments confirmed that the active catalyst site resides on the solid surface and that it is stable against leaching during the reaction. Fig. 5B shows that catalyst removal by hot filtration from the reactor after 60 min immediately halts cyclohexene conversion. In another experiment, 0.2-Cal4Ta( $OSi \equiv$ )<sub>2</sub> recovered after 12 h under standard reaction conditions showed only a nominal 0.2 wt% absolute change in Ta content, a small increase in mass loss by TGA, and no change to the DRUV-vis edge energy (Supplementary material, Table S1 and Fig. S8), indicating the absence of leaching or ligand loss.

To demonstrate that the decreasing rates with time in the batch reactors are due to reactant depletion, and not catalyst deactivation or poisoning by a product at typical reactor concentrations, an additional charge of  $H_2O_2$  (200 µL) was added after 3 h to standard



**Fig. 5.** Cyclohexene epoxidation turnovers or conversion with 0.2-Cal4**Ta**( $OSi \equiv$ )<sub>2</sub> solid catalyst ( $\blacklozenge$ ) and (A) dmCal4TaCl<sub>2</sub> in solution ( $\bigcirc$ ), (B) with filtration of the catalysts after one hour reaction ( $\bigcirc$ ), or (C) with H<sub>2</sub>O<sub>2</sub> addition (200 µL) after 3 h reaction ( $\bigcirc$ ). Reaction conditions: 30 mg 0.2-Cal4**Ta**( $OSi \equiv$ )<sub>2</sub> or 0.007 mmol 0.2-dmCal4TaCl<sub>2</sub>, [cyclohexene] = 0.82 M, [H<sub>2</sub>O<sub>2</sub>] = 0.41 M and *T* = 65 °C.

reaction conditions. Fig. 5C shows that after the second injection of  $H_2O_2$ , product formation rates are similar to those at the start of the reaction.

Together, these results indicate that calixarene–Ta(V) catalysts are stable with respect to ligand loss and inhibition/poisoning and do not leach into solution either as active or inactive homogeneous species. Active species are permanently immobilized under reaction conditions reported here, and immobilization of both the calixarene ligand and the Ta atom are required to observe optimal catalyst behavior.

# 4. Discussion

The proposed reaction pathway for cyclohexene epoxidation with  $H_2O_2$  on these catalysts was introduced in Scheme 3 [33]. All epoxidation steps, direct by Lewis acids or an indirect radical route via allylic hydroperoxides, are metal catalyzed. Under the conditions studied here, allylic radicals are expected to be exclusively generated at the metal center and to have very short lifetimes in solution.  $H_2O_2$  decomposition occurs both in solution and at the metal center. Epoxide hydrolysis is catalyzed by Lewis and Brønsted acids, and this may occur at the Lewis acidic Ta site or the Brønsted acidic SiO<sub>2</sub> surface. Thus, control of the metal environment is the key to designing better catalysts for this reaction.

Similar to that which was proposed for calixarene–Ti(IV) catalysts, the combination of the bulky multidentate calixarene ligand and the oxide surface improves catalyst reactivity, in large part by preventing the formation of larger, less active oxide clusters, especially as Ta-surface density increases and under conditions of turnover when monodentate ligands would be displaced by ligand exchange [14]. However, the differences between calixarene-containing and bare Ta–SiO<sub>2</sub> catalysts in epoxidation with H<sub>2</sub>O<sub>2</sub> are much more pronounced than observed for Ti-containing catalysts and epoxidation with organic hydroperoxides.

Here, the higher rates of direct epoxidation for the grafted calixarene–Ta when compared to the bare oxide may reflect the role of the ligand in increasing the local hydrophobicity, thus decreasing the binding of  $H_2O$ , which is a likely inhibitor. Likewise, the ligand bulk may help prevent coordination of co-product alcohols or especially the *trans*-cyclohexanediol, which would rigidly coordinate and block reaction sites and is more electron-donating than the calixarene phenoxide ligands that can partially delocalize oxygen lone pairs into the ring [37]. The multidentate calixarene ligand may also distort the coordination environment away from the lowest energy configuration that would be adopted by the bare oxide, thus increasing reactivity. Spectroscopic support for an improved understanding of the role of the ligand in tuning the active site is under way.

The greater selectivity toward direct epoxidation and decreased  $H_2O_2$  decomposition relative to the ligand-free case are consistent with the ligand-bearing Ta being more Lewis acidic than the pure oxide under reaction conditions. In other studies, increasing Lewis acidity of metal centers enhances the rate of heterolytic relative to homolytic cleavage of the O–O bond of coordinated  $H_2O_2$ , as well enhancing the rate of olefin epoxidation relative to  $H_2O_2$  decomposition [38]. In sealed reactors such as in these experiments, homolytic decomposition of  $H_2O_2$  generates  $O_2$  that has been proposed to be responsible for allylic oxidation of cyclohexene [33].

Others have modified supported Ti and Ta oxides with ligands to control Lewis acidity; however, this has primarily resulted in changes in total rates and extents of hydrolysis. Fraile et al. [39] noted lower rates of hydrolysis for ligands that decreased the LUMO energy, creating less Lewis acidic sites, and Ruddy et. al. [11] created more Lewis acidic and more hydrophobic sites by silanizing supported Ta oxides, which were then less prone to epoxide hydrolysis. The catalysts studied in the current work also exhibit a range of extents of epoxide hydrolysis. A parametric plot for all catalysts (Fig. 6) shows that catalysts that promote direct oxidation generally have higher extents of hydrolysis, defined as  $mol_{diol}/(mol_{diol} + mol_{epoxide})$  at 3 h. For example,  $Cal6Ta(OSi \equiv)_2$ has the highest selectivity to direct epoxidation and highest diol selectivity at 3 h. This trend is consistent with the same Lewis acid site leading to direct epoxidation and to hydrolysis, but also to the simple presence of increased concentrations of epoxide over more Lewis acidic catalysts, which will increase hydrolysis regardless of mechanism. The latter is supported by increasing extents of hydrolysis with time (conversion). As shown here, modifying the surface by end-capping of hydroxyl groups reduces the extent of hydrolysis, but has a weaker and slightly detrimental effect on selectivity to direct epoxidation, indicating that the radical and non-radical routes to epoxide are both controlled by the same Ta site, which is influenced primarily by directly attached ligands.

The changes in reactivity for the different calixarene ligands are likely due to a combination of different steric bulk, different numbers of potentially coordinating groups (phenols, phenyl ethers, and thioethers), and different local H-bonding in the vicinity of the Ta cation. The ability to control the coordination environment at the grafted metal without perturbing the isolated nature of the active site is a unique feature of calixarene ligands for creating grafted oxide catalysts [40]. The different direct epoxidation rates and selectivities for different calixarenes, and the increasing direct epoxidation selectivities with surface density are not accompanied by correlated changes in the energy of relevant LMCT bands in the DRUV-vis spectra. Thus, the different calixarenes, which are all contain tert-butylphenol subunits, do not differently alter the Lewis acidity for these d<sup>0</sup> cations. This is in agreement with previously reported deperoxidation rates on SiO<sub>2</sub>-supported alkoxo-Ta complexes, which showed no effect of the number of bonds to SiO<sub>2</sub> or the identity of the alkoxo ligands [41]. Elsewhere, calixarene para-substitution had little effect on edge energies of modified photoluminescent materials [42].

The reactivity differences observed here are proposed to be strongly influenced by the different H-bonding environments in these different materials. Although no role of para-substitution of grafted calix[4]arene–Ti complexes was seen for the epoxidation rate of cyclohexene with organic hydroperoxides [43], changing the macrocycle structure as done here may be a more dramatic change to the local environment at the coordinated metal. Control over H<sup>+</sup> transfer is known to be critical in H<sub>2</sub>O<sub>2</sub> activation down homolytic or heterolytic pathways [38]. Each of the calixarenes will have a different intrinsic pKa, and different active site surface densities will alter the average pKa of the remaining surface



Fig. 6. Relationship between hydrolysis and non-radical epoxidation processes.



Scheme 4. Proposed cyclohexene epoxidation cycle on Ta-calixarene catalysts. An equivalent mechanism can be proposed for breaking Ta-O-surface bonds for  $\rm H_2O_2$  coordination.

silanols. At this time, it cannot be deduced which groups directly coordinating to Ta (phenol or silanol) are formally protonated in catalytically relevant steps when coordinating and activating  $H_2O_2$ , or whether outer-sphere effects of the general H-bonding environment override these local effects. Scheme 4 assumes that one of the bonds to the calixarene is broken, reflecting this proposal, but a surface bond could also be cleaved in catalytically relevant steps by analogy to a previous result with grafted calixarene–Ti in non-aqueous systems [43]. The mechanism remains under investigation.

# 5. Conclusions

Epoxidation catalysts were obtained by grafting Ta compounds on SiO<sub>2</sub>. Using calixarene–Ta(V) complexes as the Ta source synthesizes catalysts that are more active and selective for direct (non-radical) epoxidation than are monodentate TaX<sub>5</sub> precursors. Combined TGA, ICP, and diffuse reflectance UV–visible spectroscopy show that isolated, 1:1 Ta:calixarene complexes are formed on the surface and are stable under reaction conditions. The electronic structure and the reactivity per site were shown not to be a function of surface density, consistent with a single type of isolated catalyst site being present on the surface. Finally, the sites combining calixarene ligand, Ta, and surface are more active in epoxidation than either the ligand-free or the homogeneous cases.

It must be noted that while some of the same characteristics (high non-radical selectivity, moderately high epoxidation rates) are exhibited by Cp\*TaCl<sub>4</sub> as a precursor, this precursor is approximately  $4\times$  the cost to synthesize Cal4TaCl. Moreover, the synthetic diversity of the calixarene ligands opens up many more possibilities for modification of catalytic species. Finally, and as noted by others, Ta may be an ideal metal for Lewis acid catalysts because it can coordinate five anionic ligands, allowing for multidentate connection each to ligand and to surface for stability in coordinating solvents, while still leaving an exchange site for hydroperoxide [1]. This is experimentally bore out, as the grafted calixarene–Ta complex was substantially more selective than the equivalent grafted calixarene–Ti complex. Other calixarene li

gands, support modifications, and reactions are currently being explored for an improved understanding and expanded scope of grafted Ta catalysts, which will be reported in due course.

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# Appendix A. Supplementary material

Supplementary materials associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2010.07.010.

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