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

Natalia Morlanés, Justin M. Notestein *

Chemical and Biological Engineering Department. Northwestern University, 2145 Sheridan Road, Technological Institute E136, Evanston, IL 60208, USA

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ABSTRACT

Supported Ta(V) oxide catalysts were prepared by grafting calixarene–Ta(V) and TaX_5 complexes on SiO_2 at coverages less than 0.25 Ta nm^{-2}. 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_2O_2. In sharp contrast with bare oxides, calixarene-containing catalysts had initial cyclohexene direct epoxidation turnover rates of $3.9 \pm 0.1 \times 10^{-2}\ s^{-1}$ unaffected by surface density, demonstrating single-site character. Calixarene-containing catalysts were up to 3× more active than the corresponding $TaCl_5$-based catalysts at high surface densities and were also up to 95% selective to direct (non-radical) cyclohexene epoxidation versus <65% selectivity for $TaCl_5$-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 the utility of ligand-protected, supported Ta catalysts for epoxidation with H_2O_2 and demonstrate that a surface ligand on an otherwise traditionally prepared supported oxide can selectively direct oxidation down mechanistically distinct pathways.

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*-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_2O_2 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, multidentate 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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* Corresponding author. Fax: +1 847 491 3728.
E-mail address: j-notestein@northwestern.edu (J.M. Notestein).

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function of surface density, and are higher than those of the bare Ta–SiO_2.

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_2 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_2 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_2O_2 solution 30 wt.% (Aldrich) was used as received. Fresh tantalum pentachloride ($TaCl_5$) anhydrous 99.9%, pentamethylcyclopentadienyltantalum tetrachloride (Cp^*TaCl_4) 98%, and pentakis(dimethylamino)tantalum ($Ta(dma)_5$) 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 $TaCl_5$ or Cp^*TaCl_4 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_2 following previously described methods to yield Cal4TaCl [20], dmCal4$TaCl_2$ [21], SCal4TaCl [22], Cal6$TaCl_2$ [23], and Cal4$TaCp^*$ [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_2 (Selecto Scientific, 500 $m^2\,g^{-1}$ 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_2 were used in the grafting step by altering the amount of SiO_2 added. Nomenclature used for the catalysts is, e.g. for Cal4TaCl precursor, *n*-Cal4**Ta**$(OSi{\equiv})_2$, where n is the synthesis ratio. Suspensions were refluxed under N_2 with the exception of $Ta(Bz)_5$ 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_2 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**$(OSi{\equiv})_2$, which became green and Cp^***Ta**$O(OSi{\equiv})_2$, 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**$(OSi{\equiv})$ 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**$(OSi{\equiv})_2$-**c** are assumed to have identical Ta content per g SiO_2 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^{-1} from room temperature to 800 °C. Mass losses were corrected for hydroxyl condensation, which was determined from TGA of unmodified SiO_2 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^{-1} site in material Cal4**Ta**$(OSi{\equiv})_2$ and were adjusted accordingly for other grafted species.

Ta content in the catalyst was measured using inductively coupled plasma techniques. Tantalum standards (from 1000 μg 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_2SO_4:H_2O_2 = 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_2O_2 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 ^{13}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_2 support. Sixty-four scans were averaged with 8 cm^{-1} 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 μL dichlorobenzene (internal standard), and 4 mmol of substrate (400 μL cyclohexene or 250 μL cyclooctene). The reaction flask was sealed and moved outside the glove box just immediately prior to the injection of aqueous H_2O_2 (200 μL) to start the reaction. Initial cyclohexene and H_2O_2 concentrations