Highly selective olefin epoxidation with aqueous H_2O_2 over surface-modified TaSBA15 prepared *via* the TMP method†

Daniel A. Ruddy[ab] and T. Don Tilley*[ab]

Trialkylsiloxy-modified Ta(v) centers on mesoporous silica exhibit excellent selectivity for epoxide formation (>98% after 2 h) in the oxidation of cyclohexene using aqueous H_2O_2 as the oxidant; the modified catalysts exhibit an increased lifetime, retaining high selectivity after 6 h of reaction (>95% epoxide).

The search for catalysts that allow highly selective transformations of readily available alkanes and alkenes to more synthetically useful oxygenated compounds such as alcohols, ketones, and epoxides remains an important research challenge. In particular, "green oxidants" such as hydrogen peroxide have become highly desirable, since the only by-product (H_2O) is environmentally benign. A number of supported transition metal oxide-based catalysts have been employed towards these ends.[1] However, many of the highly active oxide-based catalysts are poisoned by coordination of water to the active site, so non-aqueous organic oxidants such as *tert*-butyl hydroperoxide (TBHP) and cumene hydroperoxide (CHP) are necessary to achieve high activity.[2]

The chemical properties of the support surface have been shown to play an important role in determining catalyst activity and selectivity.[3] It was recently demonstrated that surface modification of TiSBA15 materials, prepared *via* the *thermolytic molecular precursor* (TMP) method, with (*N,N*-dimethylamino)trialkylsilanes creates more active epoxidation catalysts and increases the epoxide selectivity to a maximum of 58% (over about 12% for untreated catalysts) using aqueous H_2O_2.[4] Experimental and theoretical studies of titania-silica catalysts have suggested that a $Ti(OSi)_4$ center is more Lewis acidic than a $HO–Ti(OSi)_3$ center, resulting in a more electrophilic oxygen in the TiOOH intermediate and enhancing catalytic performance.[5] Considering the possible role of Lewis acidity in titania-silica catalyzed epoxidations, tantala-silica materials would seem to offer considerable promise as potent oxidation catalysts. Hydrated tantala and tantala-silica mixed oxides are known to possess moderate to strong Lewis acidic sites, but tantala-silica materials have been much less studied as oxidation catalysts.[6,7] A previous report from this laboratory demonstrated that $Ta(v)SiO_2$ materials prepared *via* the TMP method are active catalysts for the epoxidation of cyclohexene with aqueous H_2O_2 as the oxidant, and exhibit epoxide selectivities as high as 43% after 2 h.[8] This selectivity with aqueous H_2O_2 oxidant

is markedly greater than that of comparable $Ti(IV)SiO_2$ catalysts (10–20%) that have been the focus of much research. Here we communicate the synthesis, characterization, and catalytic oxidation performance of TaSBA15 and hydrophobic TaSBA15 materials obtained by chemical modification of the silica SBA15 surface, using aqueous H_2O_2 as the oxidant. In addition, insights into the reaction mechanism and the structure of the active Ta(v) site are described.

The details of the synthesis and grafting chemistry of the molecular precursor $Ta(O^iPr)_2[OSi(O^tBu)_3]_3$ (**1**) were recently reported.[8] The protonolysis reactions employed to create the TaSBA15 and surface-modified materials, R_{cap}TaSBA15, are outlined in Scheme 1a,b. The composition of TaSBA15 was determined to be 1.80 wt% tantalum by inductively coupled plasma atomic emission spectroscopy. The degree of surface functionalization for each catalyst was determined by combustion analysis and confirmed by thermogravimetric analysis (TGA) (Table 1). The surface coverage of the R_{cap}TaSBA15 materials was similar for all three capping groups, and ranged from 1.1 to 1.4 –$SiMe_2R$ groups per nm^2. Following the surface capping reaction, the intensity of the FT-IR stretch for isolated SiOH groups at 3745 cm^{-1} decreases dramatically and is extremely weak. Unfortunately, no separate stretching band for a Ta–OH was observed, presumably due to the low concentration of this species. The parent TaSBA15 material was found to have a BET surface area of 450 $m^2 g^{-1}$ with a pore volume of 0.51 cc g^{-1} (1.8 wt% Ta corresponds to
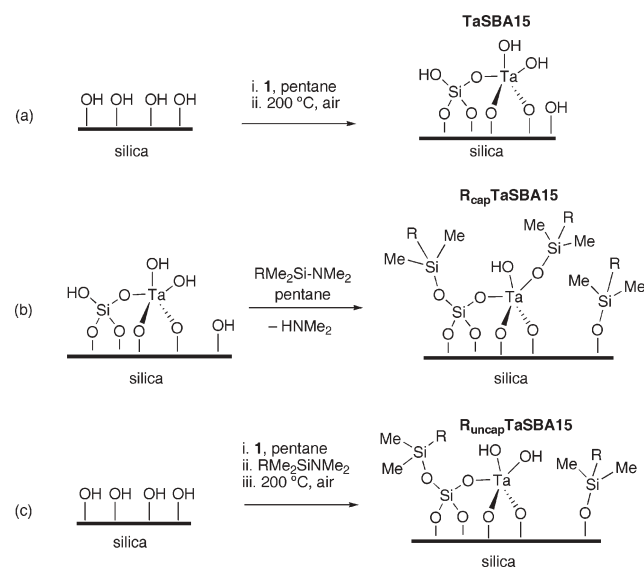
Scheme 1 Synthesis of TaSBA15, R_{cap}TaSBA15 and R_{uncap}TaSBA15, where R = Me, ^nBu, or ^nOc.

aDepartment of Chemistry, University of California, Berkeley, Berkeley, California, 94720-1460, USA. E-mail: tdtilley@berkeley.edu
bChemical Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California, 94720, USA
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Table 1 Surface modification of TaSBA15, nitrogen physisorption, and thermal analysis data

Material	–SiMe$_2$R/ nm^{-2}	S_{BET}/ m^2 g^{-1}	Pore radius^a/ nm	Wt% H$_2$O adsorbed	Desorption T/°C
SBA15	—	585	3.0	—	—
TaSBA15	—	450	2.8	31.0	68
Me$_{cap}$TaSBA15	1.2	280	2.6	3.32	50
Bu$_{cap}$TaSBA15	1.4	270	2.5	3.23	51
Oc$_{cap}$TaSBA15	1.1	190	2.2	3.18	51

^{a} Determined from the adsorption branch of the isotherm.

0.13 Ta nm^{-2}). Upon surface modification, both the surface area and pore volume of the resulting material decreased according to the size of the silylating agent. The Me$_{cap}$TaSBA15 material had a BET surface area of 280 m^2 g^{-1}, whereas the Oc$_{cap}$TaSBA15 material had a surface area of 190 m^2 g^{-1} (Table 1). The hexagonal mesoporous structure of the TaSBA15 was maintained after surface modification, as evidenced by retention of the (100) reflection in low-angle powder X-ray diffraction (PXRD) patterns, and by transmission electron microscopy (TEM).

To analyze the hygroscopic nature of the surface-modified materials, they were placed in a sealed container with a saturated H$_2$O atmosphere for 24 h and then directly examined by TGA. The water desorption temperature was determined by concurrent differential scanning calorimetry (DSC). Table 1 lists the wt% of H$_2$O adsorbed on each material and the desorption temperature, measured as the minimum of the endothermic transition corresponding to water loss. The unmodified TaSBA15 exhibits a H$_2$O loss of 31.0 wt% below 150 °C. However, the modified materials exhibit very little H$_2$O loss (3.2–3.3 wt%) in this temperature range, confirming the hydrophobic nature of the materials after modification with trialkylsilyl groups.

Addition of a low concentration of **1** to the SBA15 substrate via the TMP method is expected to result in isolated Ta centers on the surface of the material.[9] The exact structure of the surface-bound Ta species is difficult to determine, due in part to the lack of previous spectroscopic assignments of similar low wt% Ta materials.[7,10] To investigate the structures of the supported Ta centers, a catalyst was prepared having only the Si–OH (and not the Ta–OH) sites capped with –SiMe$_2$R groups. This was accomplished by capping the catalyst surface Si–OH sites after introduction of **1**, but before the calcination procedure that generates the Ta–OH sites (Scheme 1c). After silylation, calcination at 200 °C under air decomposes the organic groups of the supported Ta precursor without affecting the silyl groups, which decompose at temperatures greater than 250 °C. The resultant materials, termed R$_{uncap}$TaSBA15, had –SiMe$_2$R surface coverages (1.0–1.2 nm^{-2}) and hydrophobicities (H$_2$O loss by

TGA) that were similar to those of the R$_{cap}$TaSBA15 materials. Solid-state ^{29}Si magic-angle-spinning (MAS) NMR spectroscopy of TaSBA15, Bu$_{cap}$TaSBA15, and Bu$_{uncap}$TaSBA15 was employed to investigate the silicon environments of each material. The spectrum of TaSBA15 reveals Q^3 and Q^4 Si environments in the −95 to −110 ppm range. A resonance at ca. 23 ppm is observed in both the Bu$_{cap}$- and Bu$_{uncap}$TaSBA15 spectra. This is assigned to butyldimethylsiloxy-groups bonded directly to the silica. The observation of a low intensity, broad resonance at ca. −8 ppm in the Bu$_{cap}$TaSBA15 spectrum is assigned to the silicon of a ^{n}BuMe$_2$SiOTa center. A similar, but less significant upfield shift was recently assigned to a trimethyl-siloxy-capped Ti center in TiSiO$_2$.[11]

To compare the activities of the heterogeneous catalysts described above, results were standardized with respect to mass of catalyst (0.035 g). As previously reported for TaSBA15, no leaching was detected under the oxidation conditions.[8] Table 2 reports the results of cyclohexene oxidation using the TaSBA15 and R$_{cap}$TaSBA15 catalysts with aqueous H$_2$O$_2$ as the oxidant. Similar to the results observed with R$_{cap}$TiSBA15, the surface-modified TaSBA15 catalysts exhibit a higher activity than the unmodified catalyst. Use of an R$_{cap}$TaSBA15 material as the catalyst with H$_2$O$_2$ yielded 4.3–7.4% of oxidation products after 2 h (based on hydrogen peroxide), whereas the unmodified TaSBA15 catalyst yielded 3.9%. The effect of surface modification on the epoxide selectivity is much more significant. The modified catalysts demonstrate epoxide selectivities greater than 98%, while the unmodified catalyst is only ca. 32% selective for the epoxide after 2 h, with cyclohexenone being the major product (53%).

As stated above, aqueous conditions generally promote catalyst deactivation, and result in poor conversions and selectivities to epoxide. The high epoxide selectivities associated with R$_{cap}$TaSBA15 suggest that these are robust epoxidation catalysts and should produce greater epoxide yields at longer reaction times. The results of cyclohexene oxidation with H$_2$O$_2$ oxidant at 65 °C after 6 h of reaction are presented in Table 2. The epoxide selectivity of the unmodified TaSBA15 catalyst decreases from 31.6% to 10.9%, with a total oxidation product yield of 22.9%. This results in an epoxide yield of just 2.5%. In stark contrast, the epoxide selectivities of all R$_{cap}$TaSBA15 catalysts are above 95%. In addition, these Ta catalysts are rendered more active after surface modification. The epoxide yields of 10.0 to 12.8% exhibited by the R$_{cap}$TaSBA15 catalysts represent a 4.0- to 5.1-fold increase in productivity after 6 h versus the unmodified TaSBA15 material, and this is a direct consequence of the excellent epoxide selectivity displayed by these materials. This is the highest cyclohexene oxide selectivity reported by a surface modified catalyst using aqueous H$_2$O$_2$, and it is markedly greater than that of analogous

Table 2 TaSBA15-catalyzed oxidation of cyclohexene with H$_2$O$_2$ oxidant at 65 °C^a

Catalyst	Reaction time 2 h			Reaction time 6 h			
	Epoxide selectivity (%)	Total yield based on H$_2$O$_2$ (%)	TON^b	Epoxide selectivity (%)	Total yield based on H$_2$O$_2$ (%)	Epoxide yield based on H$_2$O$_2$ (%)	TON^b
TaSBA15	31.6	3.9	40	10.9	22.9	2.50	237
Me$_{cap}$TaSBA15	98.2	4.3	47	97.0	10.3	10.0	112
Bu$_{cap}$TaSBA15	98.4	7.4	84	95.1	13.5	12.8	152
Oc$_{cap}$TaSBA15	>99	6.9	82	>99	10.5	10.4	124

^{a} Reaction conditions: 5 mL CH$_3$CN solvent, 24.7 mmol cyclohexene, 35 mg catalyst. ^{b} TON = mol products/mol Ta at a reaction time of 2 or 6 h.
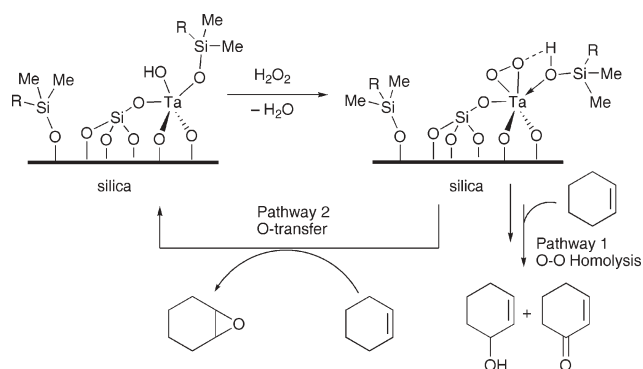
Scheme 2 Proposed pathways of cyclohexene oxidation over TaSBA15 and R$_{cap}$TaSBA15 catalysts with hydrogen peroxide.

R$_{cap}$TiSBA15 catalysts, which exhibit the highest Ti-based selectivity with H$_2$O$_2$.

A general cyclohexene oxidation mechanism for the TaSBA15 catalysts is proposed in Scheme 2. Activation of H$_2$O$_2$ results in the formation of a (SiO$_{surf}$)$_3$Ta(η^2-O$_2$) intermediate. Direct observation of a Ta–(O$_2$) moiety *via* vibrational spectroscopy could not been achieved due to intense Si–O–Si absorption in the low wavenumber region of the TaSBA15 materials. However, a recent report attributes thioether oxidation over tantala-silica mixed oxides to the presence of a tantalum-η^2-peroxo intermediate, and numerous Ta(η^2-O$_2$) complexes have been characterized.[12] In addition, the tetraperoxotantalate complex K$_3$Ta(O$_2$)$_4$, synthesized according to the literature procedure, was found to be an active catalyst for the epoxidation of cyclohexene (5.6% yield of oxidation products, 73% epoxide selectivity after 2 h with aqueous H$_2$O$_2$ as the oxidant). These values are comparable to the catalytic performance of the analogous Nb compound,[13] and this result is consistent with electrophilic oxygen transfer from a Ta(η^2-O$_2$) species. This intermediate is likely stabilized through hydrogen bonding to at least one trialkylsilanol. On the basis of computational studies, hydrogen bonding interactions involving peroxo species appear to be critical in Ti-based oxidations, and in oxidations with hydrogen peroxide in fluorinated alcohol solvents.[14]

It has been suggested that, for metal oxide based catalysts, allylic oxidation occurs through a radical pathway, whereas epoxidation occurs through an electrophilic oxygen-transfer pathway as outlined in Scheme 2.[5] To investigate the role of radicals in the TaSBA15 catalyzed epoxidation of cyclohexene, a low concentration of a radical trap (1.93 × 10^{-3} M 2,6-di-*tert*-butyl-4-methylphenol) was added to the reaction mixture with the unmodified TaSBA15 catalyst. After 2 h of reaction time, the yield of cyclohexene oxide remained fairly constant (1.3%), but the selectivity for epoxide increased to 99%. This strongly suggests that the tantalum-catalyzed allylic oxidation pathway is similar to the titanium one, in that radicals play a key role (Scheme 2, pathway 1). Also similar to the TiSBA15 system, radical chemistry does not seem to affect the unmodified tantalum-catalyzed epoxidation pathway (Scheme 2, pathway 2).[4] With the siloxy-capped TaSBA15 catalysts, electrophilic oxygen transfer to the olefin is greatly favored, and the hydrogen-bonded silanol should rapidly react to re-form a Ta center with the –OSiMe$_2$R cap. It is worth noting that free trialkylsilanol is not detected in the oxidation product analysis, which is consistent with a mechanism involving

efficient retention of the siloxy group within the coordination sphere of tantalum.

To further probe the influence of surface modification at the Ta center, the R$_{uncap}$TaSBA15 materials were tested as catalysts. The cyclohexene oxide selectivities for Me-, ^{n}Bu-, and ^{n}Oc$_{uncap}$TaSBA15 catalysts were similar to the capped catalysts (>95%) after 2 h, but decreased dramatically to 55–65% after 6 h. This differs from the analogously prepared R$_{uncap}$TiSBA15 catalysts, where no increase in epoxide selectivity was observed after 2 h without siloxy-capped Ti sites.[4] This interesting result suggests that Ta may be less susceptible to poisoning by water, and supports the idea that the hydrophobicity of the R$_{uncap}$TaSBA15 catalyst slows water coordination to the Ta center and/or preferentially increases the affinity of cyclohexene for the surface. These conditions appear to suppress the formation of radicals, but capping of the Ta site is essential to maintain high epoxide selectivity over several hours.

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