

# Mesoporous Ta oxide reduced with bis(toluene)Ti: electronic properties and mechanistic considerations of nitrogen cleavage on the low valent surface †

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Mesoporous Ta oxide with a pore size of *ca.* 22 Å and a BET surface area of 486 m<sup>2</sup> g<sup>-1</sup> was reduced by bis(toluene)Ti in the presence of dinitrogen and the product characterized by XPS, XRD, elemental analysis, nitrogen absorption, and variable temperature conductivity measurements. The XPS spectrum shows three different Ti species on the surface, in addition to a strong emission for a reduced nitrogen species and ammonia. There is also evidence for slight reduction of the Ta oxide mesostructure, consistent with the framework acting as an oxidizing agent. The conductivity measurements show a gradual increase in resistance with decreasing temperature, consistent with a semiconductor. In general the nitrogen content ranged from 1.5 to 3%. In order to gain insight into the nature of the cleavage of nitrogen on the reduced surface, the materials were prepared in the absence of nitrogen and then treated with nitrogen at room temperature and pressure for varying lengths of time. Surprisingly, these materials absorbed a maximum of 0.8% N and were almost insulating. This indicates that the initial Ti phase formed on the surface of the mesoporous Ta oxide is highly reactive and that it rapidly quenches itself, most likely through oxidation by the hydrated Ta oxide beneath the surface, before it has a chance to react in a second step with nitrogen. Maximum absorption of nitrogen occurred within the first 2 h, indicating that this reaction is fast. Treatment with excess moisture led to complete conversion of the nitride to ammonia in minutes, indicating that access to moisture is the rate-limiting step of the surface protonation process.

## Introduction

The cleavage and selective functionalization of dinitrogen is one of the most challenging areas of modern catalysis.<sup>1-4</sup> Although dinitrogen is inert from a kinetic standpoint, the reduction into ammonia by hydrogen is thermodynamically feasible. While dinitrogen can be converted to ammonium by exposure to Li, or many other strongly electropositive metals, followed by treatment with a strong acid, this process is not practical because of the cost and difficulty of using these hazardous reagents on a large scale. Commercially, the reduction of dinitrogen is carried out with hydrogen at high pressures and temperatures in excess of 400 °C.<sup>5</sup> Efforts to mediate this process or related nitrogen functionalization reactions at lower temperatures using organometallic complexes have led to enormous insights into possible strategies of cleaving the N≡N triple bond using relatively mild reductants and electrophiles, but no applicable catalysts have yet been developed.<sup>6-8</sup> Recent work by our group showed that mesoporous titanium oxide reduced by bis(toluene)Ti<sup>9</sup> or mesoporous niobium oxide reduced by bis(toluene)Nb<sup>10</sup> stoichiometrically cleave dinitrogen and that the resulting surface nitride species reacts readily with moisture present beneath the surface of the walls of the mesostructure to give 1–3 wt% ammonia. This reaction relies on the ability of the mesoporous transition metal oxide to act as an oxidizing agent.<sup>11-16</sup> While this process is stoichiometric with respect to the active surface sites, the controlled porosity offered by mesoporous materials,<sup>17-20</sup> surface areas of up to 900 m<sup>2</sup> g<sup>-1</sup>, and high reactivity of the surface in its reduced form are properties which may be advantageous in the development of new mesoporous catalysts for nitrogen fixation. Furthermore, the high conductivities of the surfaces of these materials may facilitate electron transport in any catalytic system in which electron transfer

between active sites is important. Since any catalytic process arising from this system is likely to involve hydrogen to deliver the proton and reduce the surface, and this may occur at a higher temperature, it is important to make the mesoporous catalysts as stable as possible. Mesoporous titanium oxide begins to collapse at 300 °C, while mesoporous niobium oxide begins to collapse at 400 °C.<sup>21</sup> The stability of these materials under operating conditions for long periods of time is likely to be even lower. For this reason, it is important to use a more stable framework with similar properties. Mesoporous tantalum oxide is much better in this regard, with thermal stability in excess of 500 °C. However, reducing this material with bis(toluene)tantalum to make the metal rich phase is unfeasible due to the cost and lack of effective routes to this compound. For this reason, the surface would have to be reduced with the much cheaper and more widely available bis(toluene)titanium. This would potentially leave a low valent coat of Ti on the surface, which would serve as the active phase. The advantage of this over the Ti–Ti system would thus be much greater thermal stability, a property crucial in the development of a catalyst. In addition to this, the Ti–Ta system would also allow for more clear XPS observation of the surface because it is difficult to discern which emissions in the Ti region arise from the original framework Ti species, and which arise from the bis(toluene)titanium. In the Ti–Ta system, this would not be a problem, and so a much greater degree of insight into the chemical processes on the surface should be possible.

## Experimental

### Materials

All chemicals were obtained from Aldrich unless otherwise stated. Silver paste was obtained from Alfa-Aesar. The solvent was removed *in vacuo* and replaced with dry, degassed THF. Samples of mesoporous tantalum oxide (Ta-TMS1) were

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obtained from Alfa-Aesar and used without further purification. Mesoporous tantalum oxide samples were dried at 150 °C overnight under vacuum and then treated with chlorotrimethylsilane in diethyl ether at room temperature for 4 h. Bis(toluene)titanium was prepared by metal vapor synthesis with the assistance of Professor F. G. N. Cloke at the University of Sussex.<sup>22</sup>

### Synthesis

Excess bis(toluene)titanium, as calculated on the basis of Ta content derived from the elemental analysis data (*ca.* 64%), was added to a suspension of mesoporous tantalum oxide in dry toluene under nitrogen. In a typical preparation, 1.0 g of the mesoporous solid is treated with 0.60 g of bis(toluene)titanium in 50 ml of toluene. The mesoporous solid immediately went from a light faun color to a deep blue–black. After one day of additional stirring to ensure complete absorption of the organometallic, the reduced material was collected by suction filtration under nitrogen and washed several times with toluene. The resulting black material was dried *in vacuo* at  $10^{-3}$  Torr on a Schlenk line until all condensable volatiles had been removed. Materials synthesized in the absence of nitrogen were prepared using similar quantities as in the procedure described above; however, all reactions were carried out at  $10^{-3}$  Torr on a Schlenk line in which the toluene was vacuum transferred at  $-78$  °C. The reaction was allowed to proceed for 8–48 h. After suction filtration under vacuum, the materials were transferred to an Ar glove box and stored at  $-40$  °C until further use. Unreacted bis(toluene)titanium could be recovered from the filtrate and used again. In each of the above procedures, roughly 0.40 g of bis(toluene)titanium are consumed per g of the mesoporous solid. Treatment of the nitrogen-free materials with nitrogen was performed as described in the text.

### Methods

Nitrogen adsorption and desorption data were collected on a Micromeritics ASAP 2010 instrument. X-Ray powder diffraction (XRD) patterns (Cu-K $\alpha$ ) were recorded in a sealed glass capillary on a Siemens D-500  $\theta$ – $2\theta$  diffractometer. All X-ray photoelectron spectroscopy (XPS) data were obtained with a Physical Electronics PHI-5500 spectrometer using charge neutralization. All emissions were referenced to the carbon C–(C,H) peak at 284.8 eV. The room temperature conductivity measurements were recorded on a Jandel 4-point universal probe head combined with a Jandel resistivity unit. The equation used for calculating the resistivity is:  $\rho = 2\pi S(V/I)$ , where  $\rho$  = resistivity,  $\pi/\log n^2$  = sheet resistivity,  $V$  = voltage,  $I$  = current, and  $S$  = spacing of the probes (0.1 cm). Variable temperature resistivity measurements were conducted on samples prepared by pressing pellets of the material and affixing four copper wires with conducting silver paste, the ensemble was then coated with epoxy resin. A programmable current source and voltameter were used in conjunction with a thermocouple and a liquid nitrogen bath. All elemental analysis data (conducted under an inert atmosphere) were obtained from Guelph Laboratories, Guelph, Ontario, Canada.

### Results and discussion

Mesoporous tantalum oxide samples treated with bis(toluene)titanium generally absorb about 400 mg per g of mesoporous solid. This corresponds to 8% Ti by weight or roughly a 2 : 1 Ta : Ti molar ratio, and is reflected in the elemental analysis values, which show a general decrease in Ta from *ca.* 64 to *ca.* 59% and a slight decrease in C from *ca.* 4 to *ca.* 3.5%. The small decrease in C indicates that the organometallic has acted as a Ti transfer reagent and that the toluene ligands are not consumed by the mesostructure. This reaction can be viewed as a direct analogue to the reduction of mesoporous titanium oxide by bis(toluene)-

titanium.<sup>9</sup> In previous work bis(toluene)titanium was used to deposit Ti clusters on the surface of mesoporous alumina.<sup>23</sup> This process is thermal and contrasts to the process in this study, which appears to be electrochemical in nature, as it stops once reduction of the mesostructure is complete. Heating the Ti–Ta reaction mixture at temperatures above 65 °C, however, leads to continuous decomposition of the organometallic in a second thermally driven process. Depending on exposure conditions and procedure, the materials treated with bis(toluene)titanium absorb between 0.30 and 3.0% N from the reaction environment. The cleavage of dinitrogen by metal oxides is a rare process and usually occurs under much more forcing conditions,<sup>24–26</sup> leading to materials with an inert nitride coat.

The X-ray diffraction patterns for the mesoporous tantalum oxide precursor and that of the material treated with bis(toluene)titanium in toluene for one day are shown in Fig. 1. Apart from a slight broadening and diminishing in intensity of the peak centered at  $d = 32$  Å, the pattern of the reduced material is little different to that of the starting material. The XRD pattern of the treated material after exposure to air for 15 min is virtually identical to that in Fig. 1(b), demonstrating that the wormhole mesostructure is retained, even after air oxidation of the reduced framework. Reduced samples of mesoporous Nb and Ti oxide show less stability after air exposure and show either significantly broadened central peaks or no peak at all in their XRD patterns, depending on the sample. These results are expected on the basis of the greater stability of mesoporous Ta oxide compared to its Nb or Ti counterparts. Air oxidation of reduced mesoporous oxides is strongly exothermic, and this sudden release of heat may account for the observed loss of long range order in the Nb–Nb and Ti–Ti systems. The nitrogen adsorption/desorption isotherms are shown in Fig. 2. In this case, treatment with bis(toluene)titanium resulted in a decrease in specific surface area from 486 to 372 m<sup>2</sup> g<sup>-1</sup> and a corresponding decrease in the Horvath–Kawazoe (HK) pore size from 22.2 to 19.6 Å. The cumulative HK pore volume decreased from 0.19 to 0.16 cm<sup>3</sup> g<sup>-1</sup>. These results are consistent with the increase in mass and slight shrinkage of pores expected from depositing a layer of a low valent Ti species on the inner and outer surfaces of the mesostructure. The lack of hysteresis suggests that the Ti phase is deposited evenly through the structure, rather than as clusters blocking the pores. This is what would be expected from a redox-driven process in which the exposed surface Ta species oxidize proximate bis(toluene)titanium molecules in a local process on the inner and outer surfaces of the mesostructure.

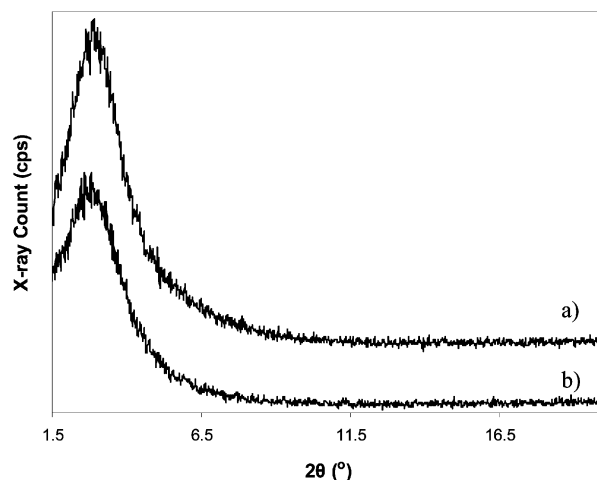


Fig. 1 X-Ray powder diffraction patterns for (a) mesoporous Ta oxide and (b) mesoporous Ta oxide treated with bis(toluene)Ti.

In order to gain more insight into the oxidation states of the surface Ti, Ta, and N species, XPS measurements were carried out. Fig. 3(a) shows the Ta 4f<sub>5/2, 7/2</sub> region, displaying a broad 7/2

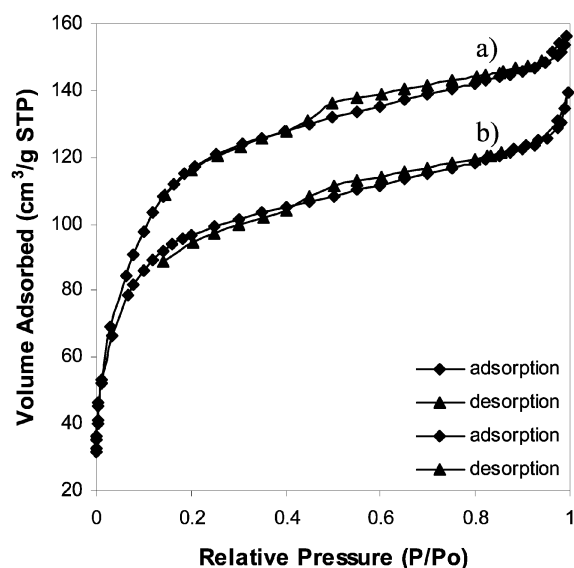


Fig. 2 Nitrogen adsorption/desorption isotherms for (a) mesoporous Ta oxide and (b) mesoporous Ta oxide treated with bis(toluene)Ti.

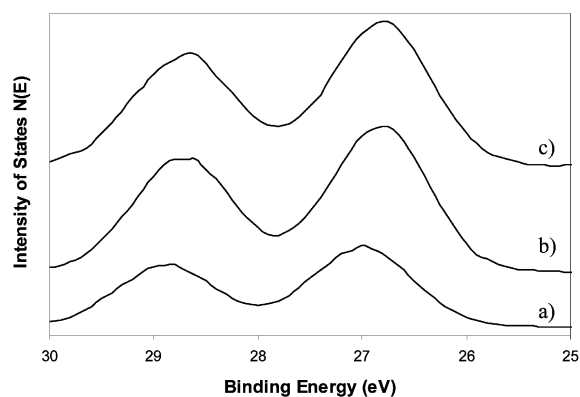


Fig. 3 XPS spectra of the Ta 4f region for mesoporous Ta oxide treated with bis(toluene)Ti under N<sub>2</sub> (a) and mesoporous Ta oxide treated with bis(toluene)Ti at 10<sup>-3</sup> Torr, followed by treatment with N<sub>2</sub> for 4 (b) and 264 h (c).

emission at 26.9 eV. Unreduced mesoporous Ta oxide has a 7/2 emission at 26.9 eV, while mesoporous Ta oxide reduced with 1.0 equivalent of Li has a 7/2 emission at 26.1 eV.<sup>13b</sup> The unsymmetrical nature of the emission at 26.9 eV, which stretches further towards lower binding energies than towards higher binding energies, supports a small degree of reduction of the surface Ta species. This is expected on the basis of the reaction with bis(toluene)titanium, which is driven by electron transfer from the organometallic to the walls of the mesostructure. On the basis of a 2 : 1 Ta : Ti ratio from the reaction stoichiometry and one electron transferred per molecule of organometallic, a minimum Ta oxidation state of +4.5 would be expected, corresponding to a Ta 7/2 emission at 26.5 eV, if the XPS of Li-reduced mesoporous Ta oxide can be used as an accurate scale of Ta 4f binding energies. This scale may not be completely accurate, as reduction of the framework by the same molar quantities of different alkali metals shows a trend towards decreasing binding energies with increasing size of the alkali metal (*ca.* 0.5 eV per row in Group IA) in the case of the Nb 3d emissions for samples of mesoporous Nb oxide.<sup>13b</sup> The Ti 2p region of the XPS spectrum of the reduced Ta oxide mesostructure is shown in Fig. 4(a). While the spectrum of mesoporous titanium oxide reduced with bis(toluene)titanium in the presence of dinitrogen shows one broad peak each for the 1/2 and 3/2 emissions, there are clearly several species present in the Ti–Ta material, as evidenced by 3/2 emissions at

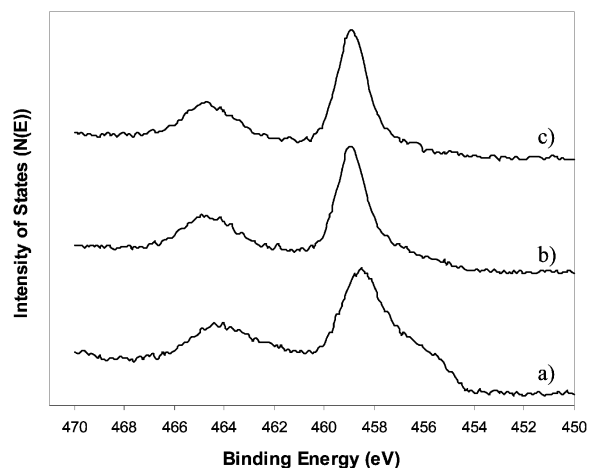


Fig. 4 XPS spectra of the Ti 2p region for mesoporous Ta oxide treated with bis(toluene)Ti under N<sub>2</sub> (a) and mesoporous Ta oxide treated with bis(toluene)Ti at 10<sup>-3</sup> Torr, followed by treatment with N<sub>2</sub> for 4 (b) and 264 h (c).

approximately 458.3, 456.2, and 455.2 eV. For further comparison, mesoporous Ti oxide exhibits a 3/2 emission at 458.9 eV, while mesoporous Ti oxide reduced by 1.0 equivalent of Li displays a 3/2 emission at 458.0 eV, corresponding to Ti(IV) and Ti(III), respectively. The higher intensity emission at 458.3 eV for the Ti–Ta material thus corresponds to a species intermediate between Ti(IV) and Ti(III), while the emissions at lower binding energies can be related to Ti species in lower oxidation states than Ti(III). The same trend is reflected in Fig. 5(a), which shows the Ti 3p region and displays a large unsymmetrical emission spanning from 37.5 to below 34 eV. In this region, the spectra of mesoporous Ti oxide and mesoporous Ti oxide reduced by 1.0 equivalent of Li display emissions centered at 37.9 and 36.8 eV, respectively. The presence of three discernable species due to the Ti originating from bis(toluene)titanium, and a Ta oxide wall existing in an oxidation state between Ta(IV) and Ta(V), is surprising given that only one large and broad emission with a small shoulder at lower binding energy was observed for mesoporous Ti oxide reduced by bis(toluene)Ti. This is fortuitous, since one of the reasons for studying this Ti–Ta system was to differentiate between the metal species in the wall and those due to the organometallic so that a more complete understanding of nitrogen activation at the surface could be achieved. In the case of the Ti–Ti system, independent Ti emissions are not discernable. This is because the different species have coincident emissions or the material has a homogeneous distribution of Ti oxidation states through the wall.

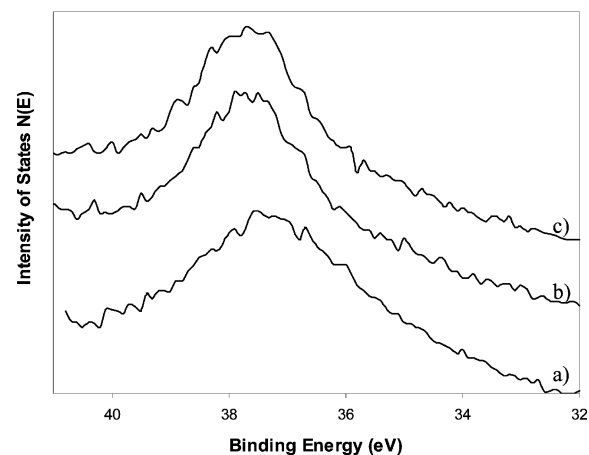
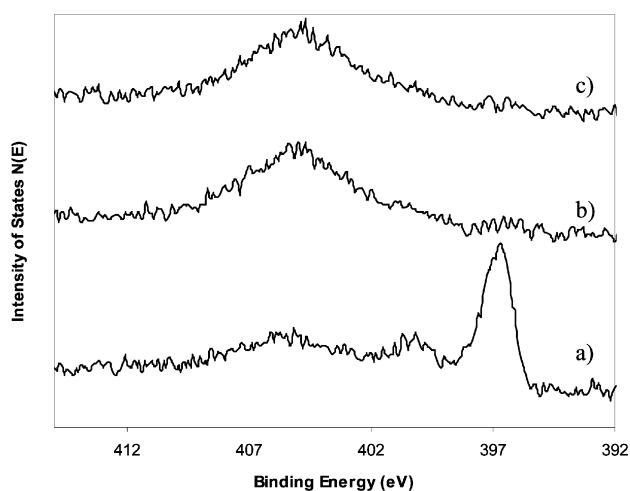


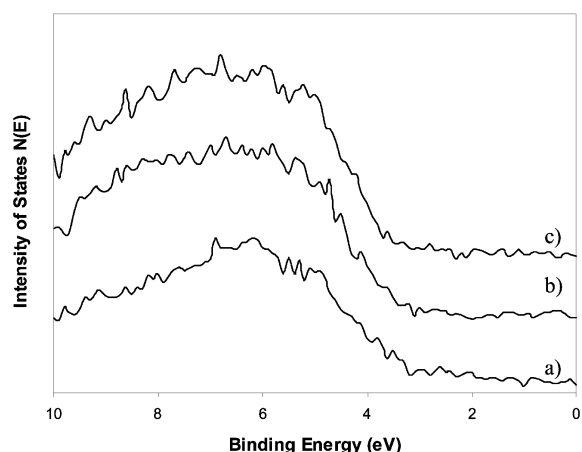
Fig. 5 XPS spectra of the Ti 3p region for mesoporous Ta oxide treated with bis(toluene)Ti under N<sub>2</sub> (a) and mesoporous Ta oxide treated with bis(toluene)Ti at 10<sup>-3</sup> Torr, followed by treatment with N<sub>2</sub> for 4 (b) and 264 h (c).

The N 1s region of the XPS spectrum is shown in Fig. 6(a) and exhibits two emissions which can be assigned to a surface nitride or amide species (396.8 eV) and surface ammonia (400.0 eV), according to previous work.<sup>26–28</sup> The broad peak at 405 eV is due to the Ta 4p<sub>3/2</sub> emission and obscures any emissions that could be due to surface-bound N<sub>2</sub> or ammonium, although such emissions were not present in the Ti–Ti or Nb–Nb systems. The specific nature of the surface nitride could not be discerned by <sup>15</sup>N-NMR analysis of labeled samples of the Ti–Ti material, as this resonance was invisible, possibly due to paramagnetic effects. The ammonia is believed to be formed as a result of the interaction of moisture beneath the surface of the mesostructure with the nitrides. Although treatment with chlorotrimethylsilane eliminates surface hydroxyl groups, the lack of complete condensation of the inorganic phase results in the presence of trapped OH groups beneath the surface which can act as proton donors through slow diffusion processes. As in the case of the Ti–Ti and Nb–Nb systems, the complete conversion of the nitride to ammonia proceeds smoothly at room temperature with excess moisture, as determined by the appearance of a dominant N–H stretch in the IR spectrum. This supports a mechanism in which highly reactive Ti species deposited by oxidative decomposition of bis(toluene)titanium cleave dinitrogen to give a surface nitride, which reacts with moisture locked beneath the surface of the walls, although a second pathway involving formation of a surface hydride by reaction of a reduced Ti species with moisture beneath the surface, followed by insertion of coordinated dinitrogen, in a process similar to that observed by Fryzuk *et al.* in organometallic Zr systems,<sup>8</sup> cannot be completely ruled out on the basis of these data. However, it is clear that the initial nitride species at low binding energy can be converted to ammonia by treatment with water. Mesoporous Ta oxide not treated with chlorotrimethylsilane leads to a material with only 0.13% N by weight when treated with bis(toluene)titanium, suggesting that the presence of higher levels of surface moisture is detrimental to the activation of nitrogen, possibly due to secondary processes where the active Ti species are quenched by reaction with surface O–H bonds to give Ti(IV) oxide species. Low valent Ti species often react with water to form Ti(IV) oxy hydroxides.



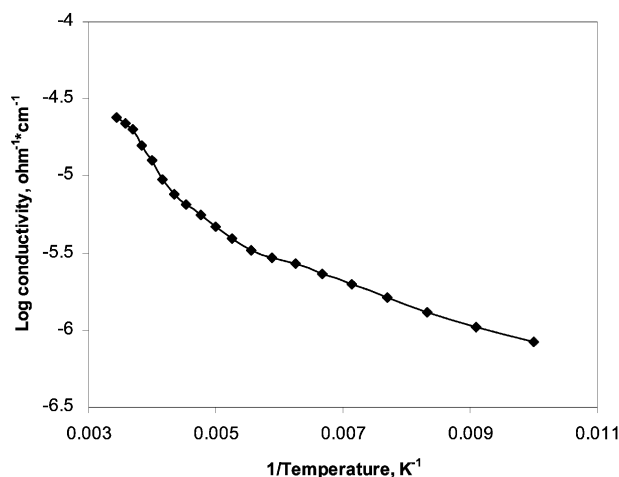
**Fig. 6** XPS spectra of the N 1s region for mesoporous Ta oxide treated with bis(toluene)Ti under N<sub>2</sub> (a) and mesoporous Ta oxide treated with bis(toluene)Ti at 10<sup>-3</sup> Torr, followed by treatment with N<sub>2</sub> for 4 (b) and 264 h (c). Emission at 406 eV due to Ta 4p<sub>3/2</sub>.

The region of the XPS spectrum near the Fermi level is shown in Fig. 7(a) and exhibits a large O 2p emission. Unlike the spectra of the Nb–Nb and Ti–Ti materials in this region, there is no discernible emission crossing the Fermi level which might suggest metallic behavior.<sup>29</sup> Although the conductivity values for this material are very high for a nanostructured porous



**Fig. 7** XPS spectra of the region near the Fermi level for mesoporous Ta oxide treated with bis(toluene)Ti under N<sub>2</sub> (a) and mesoporous Ta oxide treated with bis(toluene)Ti at 10<sup>-3</sup> Torr, followed by treatment with N<sub>2</sub> for 4 (b) and 264 h (c).

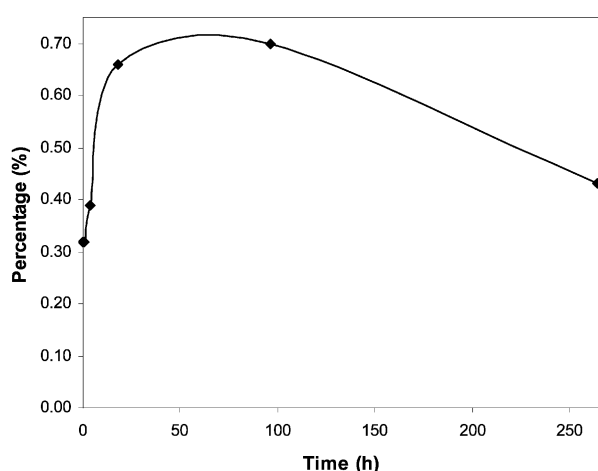
material with domain sizes defined by the 15–20 Å walls, the variable temperature conductivity measurements (Fig. 8) show that this material is a semiconductor with a room temperature conductivity between 10<sup>-4</sup> and 10<sup>-5</sup> Ω<sup>-1</sup> cm<sup>-1</sup>, about 100 times lower than those of the Nb–Nb and Ti–Ti systems synthesized in the presence of dinitrogen, which possess metallic conductivity in certain regions of the phase diagram. The reason for the difference in electronic behavior is likely due to the different composition, since metal–insulator transitions, especially in amorphous solids, are highly dependant on composition.<sup>30</sup> Unpublished results from our group, however, show that the Nb–Nb and Ti–Ti systems undergo transitions to semiconducting behavior on standing at room temperature for 5–10 days. This is likely due to internal reordering and redox processes between the species present in the walls and moisture or hydroxyl groups also contained therein.



**Fig. 8** Plot of log of conductivity versus inverse temperature for mesoporous Ta oxide treated with bis(toluene)Ti under nitrogen.

In order to gain insight on the rate of dinitrogen cleavage by the reduced mesoporous Ta oxide, a series of experiments were undertaken with varying times of dinitrogen exposure on materials initially synthesized in the absence of dinitrogen. Thus, mesoporous tantalum oxide was treated with bis(toluene)titanium under vacuum for 24 h, then collected by suction filtration and transferred to an Ar glove box. The sample was separated into six portions and exposed to dinitrogen for 0.25–264 h and then each material was characterized by XPS and elemental analysis. The electrical conductivity of the material after 0.25 h dinitrogen exposure was of the order of 10<sup>-5</sup> Ω<sup>-1</sup>

$\text{cm}^{-1}$ , lower than that of the material synthesized in the presence of dinitrogen, and rapidly dropped off over 48 h to an insulating state. All other materials in this series were insulating. The loss of electrical conductivity over time was also observed for the Nb–Nb system (in this case *ca.* 24 h) synthesized in the absence of dinitrogen and was attributed to internal phase changes and/or redox processes with trapped O–H groups, leading to a loss of electron density from the highly conducting outer layer. Many Ti(IV) oxides are semiconductors, while Ti(II) oxides and TiN are metallic. The conducting properties of the surface may be a potential advantage in any catalytic process involving dinitrogen reduction. Fig. 6(b) and (c) show the N 1s region of the XPS spectra of the materials after 0.25 and 264 h exposure to dinitrogen. Both materials have far less nitride and ammonia in them than the sample prepared under nitrogen, judging by the intensity of the peaks at 396.8 and 399.9 eV, and, even more surprisingly, the material exposed for the longest time contains less than that exposed for 0.5 h. Fig. 9 shows a plot of nitrogen content, as determined by elemental analysis, *versus* time for samples treated with bis(toluene)titanium prior to exposure to dinitrogen. The nitrogen content increases rapidly in the first 10 h and then slowly drops off over time. This can be interpreted as a rapid initial dinitrogen cleavage step, followed by hydrolysis and a slow desorption of ammonia from the surface in the stream of dinitrogen. The much lower nitrogen contents, from 0.3–0.7% by weight, compared to the sample treated with bis(toluene)titanium in the presence of dinitrogen can be attributed to a rapid self-quenching reaction on the surface of the material before dinitrogen exposure. This would certainly explain the drop off in conductivity of the material over time before dinitrogen exposure. Fig. 6(b) and (c) support this claim, as the Ta 4f emissions occur at a lower binding energy than in the material prepared under dinitrogen. This suggests that electron density has drifted from the reactive surface to the inner Ta oxide walls, thus making the surface less reactive towards dinitrogen. Fig. 4(b) and (c) as well as Fig. 5(b) and (c), showing the Ti 2p and 3p regions respectively, are in accord with this picture, as there is a distinct lack of the lower valent species observed in the material synthesized in the presence of dinitrogen. The region near the Fermi level is shown in Fig. 7, displaying only the O 2p region, with no evidence for any species at lower binding energy near the Fermi level.



**Fig. 9** Plot of %N in sample *versus* dinitrogen exposure time for samples of mesoporous Ta oxide treated with bis(toluene)Ti at  $10^{-3}$  Torr, followed by treatment with  $\text{N}_2$ .

The results indicate that the initial surface formed in the reaction of bis(toluene)titanium with mesoporous tantalum oxide is extremely reactive towards dinitrogen for only as long as the surface is stable towards an internal redox reaction or phase change in which some of the electron density drifts into the

inner region of the walls. The reaction with dinitrogen is faster than this internal process and, once formed, the surface nitride helps stabilize the lower valent Ti species on the surface from further reactions with the internal Ta oxide phase. This is reflected in the retention of higher conductivity values for longer periods of time in the Ti–Ti, Nb–Nb, and Ti–Ta materials with higher N content than those synthesized in the absence of dinitrogen. The metallic phase observed in the Nb–Nb and Ti–Ti systems prepared in the absence of dinitrogen appears to be unstable and a rapid phase change to a semiconducting state occurs over the first 48 h. The metallic states observed when the Nb–Nb and Ti–Ti materials are synthesized in the presence of dinitrogen are more stable, but, as mentioned earlier, do undergo a phase change to semiconducting materials with lower conductivities ( $10^{-4}$ – $10^{-5}$  from  $10^{-2}$   $\Omega^{-1}$   $\text{cm}^{-1}$ ) over 5–10 days. This suggests that the nitride is important in stabilizing the more highly conducting states of these materials. The mechanism for dinitrogen cleavage supported by this study precludes the possibility of Ti–H species, formed by reaction of the surface Ti units with moisture beneath the surface, being active in the formation of ammonia. The activation of dinitrogen by Ta–H has been observed by Fryzuk *et al.* in a Ta-based system.<sup>31</sup> The nitride species is also reactive towards water in what appears to be an instantaneous process. This is promising from the standpoint of developing a catalyst for nitrogen fixation, because it means that cleavage of dinitrogen and subsequent protonation steps will not be rate-limiting steps. This suggests that once a method of re-reducing the surface into the active form is found, a feasible catalyst should be possible.

## Conclusion

In conclusion, mesoporous tantalum oxide samples treated with bis(toluene)titanium under dinitrogen lead to new materials with a low valent titanium nitride coating on the surface. This reaction is similar to that observed in related mesoporous niobium and titanium oxide systems, in which bis(toluene)niobium and bis(toluene)titanium are used, respectively, as reducing agents. The use of more stable mesoporous Ta oxide makes it easier to observe the surface species by XPS, revealing at least three reduced Ti species on the surface of the Ta oxide mesostructure. The reaction with dinitrogen and subsequent conversion to ammonia are both fast; however, when this reaction is conducted in the absence of dinitrogen, a material is formed which has a lower propensity to activate dinitrogen. This is attributed to quenching of the reactive surface species by electron transfer to the inner Ta oxide phase. This self-reaction also leads to a drop in conductivity, a rare property in porous materials which may be useful in any catalytic processes in which electron mobility across a surface is important.

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