

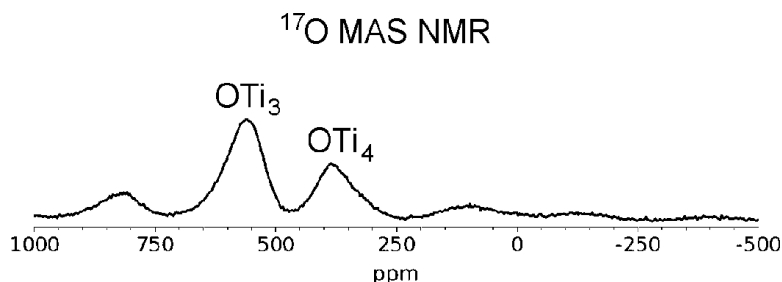
Article

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# $^{17}\text{O}$ and $^{15}\text{N}$ Solid State NMR Studies on Ligand-Assisted Templating and Oxygen Coordination in the Walls of Mesoporous Nb, Ta and Ti Oxides

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**Abstract:** A multinuclear solid state NMR approach is applied to four templated mesoporous oxides (silica, titania, niobia and tantalum) to include  $^{15}\text{N}$  and  $^{17}\text{O}$  magic angle spinning (MAS) NMR and double resonance  $^{15}\text{N}$ – $^{93}\text{Nb}$ ,  $^{17}\text{O}$  Rotational-Echo Adiabatic Passage Double Resonance (REAPDOR). The templated samples were ramped in steps of 20 °C for 2 days up to typically 110 °C where the samples were left for 2–4 days.  $^{15}\text{N}$  MAS NMR shows that amines are the only species present in the  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ , and  $\text{Ta}_2\text{O}_5$ . In  $\text{SiO}_2$ , amines are only present as a minor coordination ( $10 \pm 2\%$ ), but there are several strong ammonium  $^{15}\text{N}$  resonances. The REAPDOR experiments show that the nitrogen interacts with niobium, confirming a ligand interaction between the Nb and N, as previously believed. In the case of silica, the amine is quaternized and there is apparently no interaction with the Si, suggesting a  $\text{RNH}_3^+ \text{ } ^-\text{O}-\text{Si}$ -hydrogen-bonding interaction with the walls.  $^{17}\text{O}$  MAS NMR provides the clearest indication of the local wall structure. In the aged, templated samples in all cases only  $\text{OM}_2$  coordinations are present which is very different from the pure bulk oxides (apart from  $\text{SiO}_2$ ) and must be due to the effects of amine coordination at the metal centers. On removal of the template, these oxides behave differently, with  $\text{Ta}_2\text{O}_5$  showing a mixture of  $\text{OTa}_2$  ( $85 \pm 5\%$ ) and  $\text{OTa}_3$  ( $15 \pm 5\%$ ) which is similar to the types of coordination found in the bulk oxide. The previously reported  $^{17}\text{O}$  MAS NMR data from heat-treated mesoporous niobia shows only  $\text{ONb}_2$ , which is very highly ordered. In contrast for titania, the  $\text{OTi}_2$  coordination is immediately lost on removal of the template to be replaced by a mixture of  $\text{OTi}_3$  ( $60 \pm 5\%$ ) and  $\text{OTi}_4$  ( $40 \pm 5\%$ ), with the  $\text{OTi}_4$  becoming dominant above 250 °C, very different behavior from the corresponding bulk oxide. In summary, this NMR study shows that the local oxygen coordination in amine-templated mesoporous transition metal oxides is present as  $\text{OM}_2$  which is relatively rare in bulk oxides. The data indicates that the template interaction is largely controlled by the N–M dative bond to the wall, suppressing higher oxygen coordination numbers. Qualitatively it appears that the strength of this interaction varies greatly in the different mesoporous oxides.

## 1. Introduction

Since the first report of M41S mesoporous molecular sieves by Mobil Oil Corporation researchers in 1992, interest in mesoporous materials has been growing.<sup>1,2</sup> These materials possess a hexagonal arrangement of uniformly sized meso-pores in the range from 20 to 100 Å and large surface areas of up to 1400 m<sup>2</sup>/g, which makes them attractive in a wide variety of applications such as small molecule adsorption<sup>3</sup> and catalysis.<sup>4</sup> The mechanism of formation of these materials has also been

an area of great interest and has been explored by a wide variety of techniques including  $^{29}\text{Si}$  and  $^{15}\text{N}$  NMR.<sup>5–7</sup> The first successful synthesis of thermally stable mesoporous transition metal oxide analogues of MCM-41 were reported by Ying et al. in 1995 and 1996.<sup>8,9</sup> These titanium oxide<sup>8</sup> and niobium oxide<sup>9</sup> materials (Ti-TMS1 and Nb-TMS1) were synthesized via a novel mechanism in which a long-chain amine surfactant is believed to be covalently bonded to the metal alkoxide precursor through an M–N dative bond on the basis of  $^{15}\text{N}$  NMR solution shifts of the precursor mixture prior to hydrolysis,

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as well as after condensation and aging. The interaction between the amine headgroup and the metal atom has not been completely elucidated by spectroscopy. Tanev et al.<sup>10</sup> reported a closely related neutral templating route for preparing mesoporous silica molecular sieves (HMS) in 1995 using the same amine template. The authors proposed a hydrogen-bonding interaction mechanism between the neutral primary amine surfactant (S<sup>0</sup>) and the neutral inorganic precursor (I<sup>0</sup>). <sup>14</sup>N NMR further verified that templating in this mesoporous material occurs primarily by the assembly of neutral amine surfactants, and not tetrahedral ammonium species. There are no other reports in the literature focusing on the interaction between the headgroup and the wall in these systems, although there are numerous NMR studies on the templating mechanism of mesoporous oxides synthesized with cationic trimethylammonium surfactants.<sup>11</sup> While there is some evidence of a Nb–N bond in the templating of Nb–TMS1, the results of this earlier study<sup>9</sup> are not strong enough to preclude the possibility that Nb–TMS1 and HMS are formed via a similar templating mechanism. M–TMS1 (M = Nb, Ti, Ta) materials are of increasing interest due to the wide range of physical properties accessible due to the variable-oxidation-state-capacity of the walls<sup>12</sup> and their high surface acidities. These unique properties have already led to applications in hydrogen storage,<sup>13</sup> nitrogen activation,<sup>14</sup> Friedel-Crafts alkylations,<sup>15,16</sup> and hydrocarbon skeletal rearrangements,<sup>17</sup> and therefore warrant a more detailed study of the synthesis mechanism and wall structure.

Solid state NMR spectroscopy is an extremely useful and informative tool in identifying and characterizing local environments in materials, even in those that lack long-range order.<sup>18</sup> Oxygen is a key chemical element and solid state <sup>17</sup>O NMR can provide unique insight into the local environment and its structural role in a wide range of materials and molecules.<sup>19–21</sup> The large chemical shift range of <sup>17</sup>O produces high sensitivity to even subtle differences in the structure.<sup>18–21</sup> The major problem with <sup>17</sup>O NMR is the low natural abundance of the NMR-active <sup>17</sup>O isotope (0.037%) and subsequent poor sensitivity, which can be overcome by even modest enrichment of the material (e.g., using 20 at% in the precursor material).<sup>19,20</sup> A recent <sup>17</sup>O NMR study on Nb–TMS1<sup>22</sup> showed its walls are exclusively constructed of ONb<sub>2</sub> linkages, which is very unusual as all other <sup>17</sup>O NMR data reported on niobia have shown a mixture of ONb<sub>2</sub> and ONb<sub>3</sub> environments.<sup>22,23</sup> This suggests that the amine template may play a role in suppressing the

formation of ONb<sub>3</sub> units, which would represent an unprecedented example of a structure directing agent not only templating the formation of a pore structure, but also the discrete local structure. There are numerous papers concerning <sup>29</sup>Si MAS NMR of mesoporous silicas; there are few if any studies using <sup>17</sup>O, apart from in the precursor solutions.<sup>24</sup> To further investigate the surfactant organization mechanism in these mesoporous materials, a detailed NMR study on the mechanism of formation and wall structure of doubly labeled (<sup>15</sup>N and <sup>17</sup>O) M–TMS1 (M = Nb, Ta, Ti) materials is presented. The thermal stability of the template-formed wall structure is examined by following changes of the local structure with heat treatment. These NMR results are compared to these same oxides prepared in bulk form, as well as dodecylamine-templated HMS silica. NMR results are also reported from <sup>15</sup>N, along with some double resonance experiments that include <sup>15</sup>N–<sup>93</sup>Nb and <sup>15</sup>N–<sup>17</sup>O REAPDOR.<sup>25,26</sup> This series of NMR experiments provides insight into how the nitrogen in the template is bound to the walls of the different mesoporous oxides and the effect of this templating interaction on the structure of these walls.

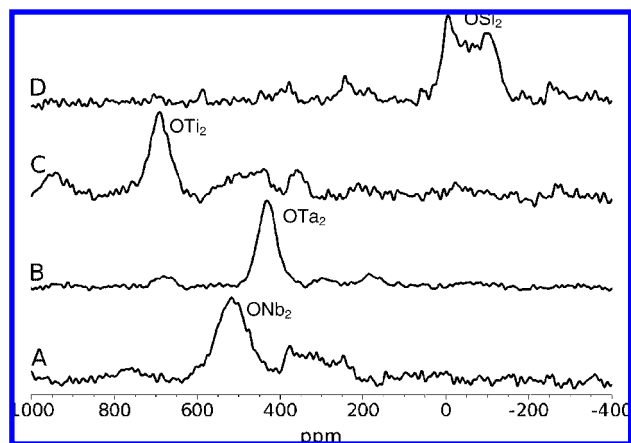
## 2. Experimental Section

**Sample Preparation.** Mesoporous Nb and Ta samples were prepared using the ligand-assisted templating approach with long-chain <sup>15</sup>N dodecylamine surfactant as described previously.<sup>9,27</sup> In a typical procedure, 10 g of niobium ethoxide or tantalum ethoxide was treated with 0.3 mol equiv of 100% enriched [<sup>15</sup>N]-dodecylamine. The resulting clear solutions were further treated with 100 mL of deionized water, and a white gelatinous precipitate formed immediately. These samples were then aged usually from 30–110 °C over 10 days with gradual temperature ramping in steps of 20 °C each of 2 days being left at the final temperature for 2–4 days. The samples were then collected by filtration and dried in air in an oven at 95 °C for 2 h. Mesoporous titania samples were prepared in an analogous fashion, except that the samples were aged in water from 30–80 °C for 7 days followed by filtration and further aging of the dried sample at 110 °C in the absence of water for 2 days.<sup>28</sup> Mesoporous silica samples were prepared by the method of Tanev et al.<sup>10</sup> The <sup>17</sup>O enrichment of these as-synthesized samples was carried out by heating the mesoporous metal oxides and [<sup>17</sup>O] water (20% enriched) together in a sealed vessel under an inert atmosphere at 80 °C overnight and then at 120 °C for 24 h. For all template-free samples, the template was removed by stirring the sample in methanol for 24 h with 1.1 equivalents of *p*-toluenesulfonic acid with respect to the amine. This was followed by filtration and four additional cycles of stirring the sample in methanol for 24 h followed by filtration. The samples were then dried in an oven at 95 °C for 24 h. <sup>17</sup>O-labeling of these template-free samples was done after template removal using the same method as noted above for the as-synthesized materials. X-ray diffraction (XRD) patterns (see Supporting Information, Figure S1) were recorded with CuK<sub>α</sub> radiation on a Siemens D500 θ/2θ diffractometer to confirm the mesostructure of all the samples.

<sup>15</sup>N magic angle spinning (MAS) NMR was conducted on a Chemagnetics Infinity Plus spectrometer equipped with a 7.05 T magnet at 30.41 MHz, using a 4 mm Doty probe spinning at 12 kHz. A 2.5 μs 90° excitation pulse was used, followed by a 1 ms ramped cross-polarization (CP) pulse and 65 kHz of TPPM decoupling. Using a 3 s recycle delay, between 2000 and 28 000 acquisitions were obtained depending on the sample. Referencing

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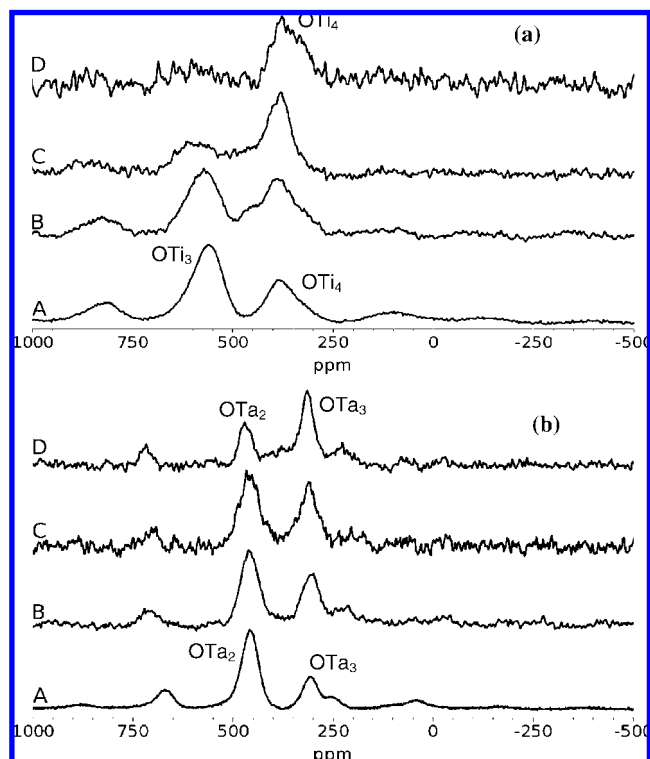
**Figure 1.**  $^{17}\text{O}$  MAS NMR spectra of mesoporous oxides with amine template in place. (A) Niobia, (B) tantala, (C) titania, and (D) silica, with the centerbands identified.

was conducted using  $^{15}\text{N}$ -enriched glycine at  $-347.4$  ppm, relative to  $\text{CH}_3\text{NO}_2$ .  $^{17}\text{O}$  NMR was conducted on a Chemagnetics Infinity spectrometer equipped with a 7.05 T magnet at 40.67 MHz using a 4 mm Bruker probe spinning at 10 kHz. To increase the signal, Rotor Assisted Population Transfer (RAPT)<sup>29–31</sup> was used, which consisted of 17 cycles of the RAPT sequence using  $1.5 \mu\text{s}$  pulses. A recycle delay of 3 s was also used and approximately 25 000 acquisitions were obtained. Referencing was against  $\text{H}_2\text{O}$  at 0 ppm.

$^{15}\text{N}$ – $^{17}\text{O}$  Rotational-Echo Adiabatic Passage Double Resonance (REAPDOR)<sup>24,25</sup> was conducted on a Bruker Avance II<sup>+</sup> spectrometer equipped with a 14.1 T magnet using a 3.2 mm Bruker HXY probe spinning at 5 kHz. The detection nucleus was  $^{15}\text{N}$  (at 60.81 MHz) with CP from  $^1\text{H}$  (at 600.09 MHz) with a contact time of 1 ms; 40 000 acquisitions were required with a 3 s recycle delay. The recoupling pulse was applied to  $^{17}\text{O}$  (at 81.39 MHz). A Spinal64 decoupling pulse sequence<sup>32</sup> was used on  $^1\text{H}$  during the REAPDOR and acquisition period; the  $B_1$  field used for this was 100 kHz. The  $B_1$  field used for the REAPDOR pulse sequence was 50 kHz.  $^{15}\text{N}$ – $^{93}\text{Nb}$  REAPDOR was conducted on the same spectrometer system using a 4 mm Varian T3 probe spinning at 5 kHz; 288 repetitions were acquired per increment with a recycle delay of 2 s. The recoupling pulse was applied to  $^{93}\text{Nb}$  (at 146.72 MHz). The same pulse sequence as for  $^{15}\text{N}$ – $^{17}\text{O}$  REAPDOR was employed except that during the REAPDOR and acquisition period; the  $B_1$  field used was 50 kHz.

### 3. Results

The  $^{17}\text{O}$  MAS NMR spectra from the as-formed templated mesoporous oxides are shown in Figure 1. In all these cases, a relatively broad  $^{17}\text{O}$  resonance is observed, much broader than expected for crystalline samples of the more ionically bonded materials, titania, tantala, and niobia.<sup>18,19</sup> In all cases, only a single major resonance is observed, with any other resonances present only having minor intensity in comparison. There are also some low intensity spinning sidebands. Mesoporous niobia, titania and tantala, all show a major Gaussian-like resonance, peaking at 518, 690, and 432 ppm respectively, which correspond to  $\text{ONb}_2$ ,  $\text{OTi}_2$ , and  $\text{OTa}_2$ . The spectrum from meso-



**Figure 2.**  $^{17}\text{O}$  MAS NMR spectra of mesoporous (a) titania and (b) tantala with the template removed after (A) no extra heat treatment, (B) heating to 250 °C, (C) heating to 500 °C, and (D) heating to 750 °C with the centerbands identified at the highest and lowest temperatures.

porous silica also shows a single resonance, although there is some structure due to second-order quadrupolar broadening<sup>18</sup> from the larger quadrupolar interaction that is experienced in this more covalently bonded system. Simulation of this line shape using an in-house computer program<sup>33</sup> gives interaction parameters of  $\chi_Q = 5$  MHz and  $\eta = 0$  (the quadrupole coupling constant and asymmetry parameter, respectively<sup>34</sup>) and the isotropic chemical shift,  $\delta_{\text{iso}} = 33$  ppm. This is as expected from an Si–O–Si environment.<sup>18,19</sup> The data also show that there is no indication of Si–OH species being present as have been reported from silica gel samples.<sup>35</sup>

The evolution of the  $^{17}\text{O}$  MAS NMR spectra with removal of the template and subsequent heat treatment are shown for  $\text{TiO}_2$  (Figure 2a) and  $\text{Ta}_2\text{O}_5$  (Figure 2b). There is a clear change in the spectra which start off from the single coordination observed in the initial templated oxide. For  $\text{TiO}_2$  there are two observed peaks at 562 and 380 ppm, with linewidths of  $\sim 2$  kHz (Table 1). This corresponds to there being a mixture of  $\text{OTi}_3$  ( $60 \pm 5\%$ ) and  $\text{OTi}_4$  ( $40 \pm 5\%$ ) coordinations.<sup>36</sup> There is a very large change from the surfactant-containing sample, suggesting a very strong effect of the templating interaction on the wall, the structure of which is not stable with respect to template removal. With increasing heat treatment there is increasing  $\text{OTi}_4$  content and it becomes the dominant coordination above 500 °C, corresponding to  $65 \pm 5\%$  of the oxygen

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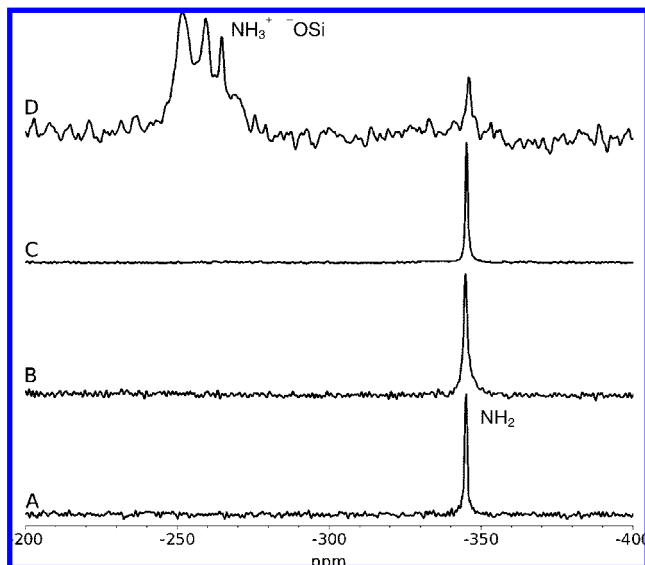
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**Figure 3.** <sup>15</sup>N MAS NMR spectra of mesoporous oxides with the amine in place in (A) niobia, (B) tantalum, (C) titania, and (D) silica.

sites at 500 °C. For all cases, these <sup>17</sup>O resonances remain broad with the width probably indicating a spread of environments from a range of chemical shifts. For the case of tantalum (Ta<sub>2</sub>O<sub>5</sub>) the initial spectrum after the template has been removed shows a dominant resonance (85 ± 5%) at 459 ppm (Table 1) corresponding to OTa<sub>2</sub> and a smaller peak (15 ± 5%) at 306 ppm arising from OTa<sub>3</sub>.<sup>37</sup> These peaks exhibit linewidths of ~1.2 kHz and the OTa<sub>2</sub> resonance does have significant spinning sidebands. Then with heat treatment the relative intensity of the OTa<sub>3</sub> peak increases and becomes dominant (60 ± 5%) in the 750 °C heat-treated sample, although there is still significant intensity in both sites. These two sets of spectra make an interesting comparison with our recently reported <sup>17</sup>O MAS NMR data from mesoporous niobia.<sup>22</sup> In the case of niobia the one dominant ONb<sub>2</sub> resonance observed in the as-formed material persists in the heat treated samples, but with a remarkable difference to the transition metal oxides reported here in the observed line width of only ~200 Hz once the template is removed. The line width remains small at all heat treatment temperatures, with an increase to 340 Hz at 500 °C and then two distinct ONb<sub>2</sub> resonances at 750 °C at 590 and 557 ppm.<sup>22</sup>

To better understand the interaction between the wall and the template, <sup>15</sup>N CP MAS NMR spectra were collected from all of the initial samples. Spectra with good signal-to-noise ratios were obtained from all samples. The mesoporous titania, niobia, and tantalum show a single peak in the range -343.6 to -345 ppm, with the corresponding line width increasing 28, 36, to 45 Hz. A peak at similar resonance frequency was observed in previous solid state <sup>15</sup>N NMR studies on Nb-TMS1.<sup>9</sup> These peaks are in the range expected for amines. In the mesoporous silica, although there is a small peak (~10% of the intensity) in this region at -346 ppm with a width of 80 Hz, there are several much stronger peaks around -250 ppm. A simulation of the <sup>15</sup>N spectrum in this region indicates 4 inequivalent nitrogen sites (see Supporting Information, Figure S2). This spectrum can be interpreted as the amine<sup>38,39</sup> becoming protonated by the acidic Si-OH groups and forming a series of

tertiary amines bonded in different, but chemically similar places in the structure. Solution <sup>15</sup>N NMR has shown that protonation causes the <sup>15</sup>N isotropic chemical shift to become more positive.<sup>38</sup>

In solid state NMR a whole series of experiments have been devised that reintroduce dipolar couplings so as to assist in identification of different sites. The methods work on the principle of a comparison between two sequences, with the only difference being produced by dipolar coupling if there is spatial proximity between different nuclei. Many of these sequences were originally designed for spin-1/2 nuclei. However the REAPDOR experiment is specifically designed to involve at least one quadrupolar nucleus and in fact does not work on systems containing only spin-1/2 nuclei. These MAS-based experiments rely on the modulation of the heteronuclear dipolar coupling to prevent an echo from refocusing, with the modulation in the REAPDOR experiment provided by a train of rotor-synchronized 180° pulses applied to the spin-1/2 nucleus, spaced half a rotor period apart. With faster MAS the limitations placed on the sequence by the T<sub>2</sub> decay of the quadrupolar nucleus is alleviated. The decay of the <sup>15</sup>N-<sup>93</sup>Nb REAPDOR signal was observed (see Supporting Information, Table T1). Although the effect is relatively weak given the strong T<sub>2</sub> dephasing of <sup>93</sup>Nb detecting any effect is significant and clearly shows that there are definite dipolar couplings between the nitrogen and the niobium. <sup>15</sup>N-<sup>17</sup>O REAPDOR on the mesoporous templated silica shows no difference indicating effectively no interaction between the oxygen and the nitrogen.

#### 4. Discussion

The <sup>15</sup>N NMR results demonstrate that nitrogen from the template exists probably in the form of a protonated ammonium species for the silica and as neutral amines for the titania, tantalum, and niobia. In the case of silica, the majority of the template is held in the structure by a RNH<sub>3</sub><sup>+</sup> O-Si- hydrogen-bonding interaction with the walls, which is clearly strong enough that that bonding configuration can no longer be described as an NH<sub>2</sub>-HOSi hydrogen-bonding interaction. The presence of a small amount of free amine in this material is expected on the basis of the weak acid-base equilibrium between these two structures. The different fully protonated ammonium species most likely arise from interactions with 0, 1, 2, or 3 SiO<sup>-</sup> groups in the walls. The shift observed here between the amine and the shifted species is ~100 ppm in silica is larger than the 10–20 ppm often seen for simple protonation of an amine or ammonia in solution.<sup>39</sup> However being constrained in the mesopores and interacting with the wall, as well as being in the solid state, could lead to this effect. The lack of a signal in previous solution state <sup>14</sup>N NMR study of a mixture has been taken to indicate neutral templating occurred.<sup>10,40</sup> The quadrupole spin-1 nature of <sup>14</sup>N complicates interpretation of NMR spectra,<sup>18</sup> both in the solution mixture and for solids. The state of the sample here is different from previous studies, i.e., in the solid state and not the solution mixture. Here the template interacting with the wall in the solid state after any liquid phase has been removed. For Nb-TMS1, the <sup>15</sup>N-<sup>93</sup>Nb REAPDOR shows that there is a measurable interaction between the template

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**Table 1.** Summary of the  $^{17}\text{O}$  NMR Spectral Characteristics of Mesoporous Oxides with and without the Template and Then Heated after Template Removal<sup>a</sup>

	$\text{TiO}_2$		$\text{Ta}_2\text{O}_5$		$\text{Nb}_2\text{O}_5$	
	$\delta_p(\text{ppm})$	$\Delta(\text{Hz})$	$\delta_p(\text{ppm})$	$\Delta(\text{Hz})$	$\delta_p(\text{ppm})$	$\Delta(\text{Hz})$
template in place	690 ± 10	2400 ± 50	432 ± 5	2220 ± 30	518 ± 10	3900 ± 50
template removed	380 ± 2	2080 ± 10	306 ± 3	1200 ± 10	566 ± 2	290 ± 10
unheated	562 ± 2	2130 ± 10	459 ± 3	1270 ± 10		
250 °C	387 ± 3	2500 ± 20	306 ± 3	1480 ± 10	558 ± 2	210 ± 10
	574 ± 2	2705 ± 20	460 ± 3	1380 ± 10		
500 °C	387 ± 2	1640 ± 20	310 ± 3	1330 ± 10	554 ± 2	340 ± 10
	594 ± 5	2650 ± 50	460 ± 3	1520 ± 10		
750 °C	363 ± 5	2610 ± 50	314 ± 3	970 ± 10	557 ± 2	200 ± 10
	599 ± 10	4270 ± 100	469 ± 3	1110 ± 10	591 ± 2	220 ± 10

<sup>a</sup>  $\Delta$  = full width at half maximum,  $\delta_p$  = peak position.  $\text{Nb}_2\text{O}_5$  data taken from ref 22.

and the Nb centers in the wall indicative of bonding. There is also a range of line width in the  $^{15}\text{N}$  MAS NMR of the three transition metal samples with the narrower line from the titania probably indicating a weaker interaction with the wall (hence leading to weaker constraint by the wall). The interaction of the template with the wall can also be judged by how easily the template can be washed out. In the case of silica the template is removed by simple washing in ethanol. Titania shows a stronger interaction, as the template cannot be washed out by ethanol, but leaches out at 90 °C during aging in water. The interaction is stronger still and in tantalum/niobia where the template remains within the structure even after heating at 180 °C in an aqueous environment. For all the transition metal oxides the template must be protonated with *p*-toluenesulfonic acid followed by repeated methanol washings to ensure complete template removal.

The  $^{17}\text{O}$  MAS NMR data immediately indicates a very significant difference between these mesoporous templated oxides and their bulk analogues. For mesoporous silica the oxygen is in the expected Si–O–Si linkages (i.e.,  $\text{OSi}_2$ ) with the NMR interaction parameters typical of such linkages within bulk tetrahedrally coordinated silica phases. However, for the transition metal oxides examined here, their bulk crystalline forms have well-defined local oxygen coordinations that are, respectively,  $\text{OTi}_3$  for  $\text{TiO}_2$ ,  $\text{ONb}_2$  and  $\text{ONb}_3$  for  $\text{Nb}_2\text{O}_5$ , and  $\text{OTa}_2$  and  $\text{OTa}_3$  for  $\text{Ta}_2\text{O}_5$ . The  $^{17}\text{O}$  MAS NMR data shows that in *all* cases in the mesoporous templated samples the oxygen is only coordinated by two metal centers (i.e., M–O–M). Hence the templating must have a strong effect and force the wall to assume an unusual local coordination with only 2-fold oxygen environments. Stated differently, the ligand-assisted templating effect uses a dative N–M interaction which suppresses higher coordinate oxygen by blocking the Lewis acidic metal sites, which would otherwise be coordinated to the O ligands. Essentially the template not only directs the structure of the mesophase, but also influences the local coordination environment in the walls. There are also very different stabilities and degrees of order within the mesoporous walls as the sample is heated after template removal. Our previously reported  $^{17}\text{O}$  MAS NMR data on mesoporous niobia<sup>22</sup> indicates that the wall retains its unusual single  $\text{ONb}_2$  coordination and it takes on a remarkably ordered structure once the template is removed, with both these factors remaining after all heat treatments even up to 750 °C. This behavior is very different from bulk niobia where crystallization of a gel leads to various mixtures of  $\text{ONb}_2$  and  $\text{ONb}_3$  as the temperature is varied.<sup>22</sup> For mesoporous tantalum, the  $\text{OTa}_2$  environment is immediately converted to a mixture of  $\text{OTa}_2$  and  $\text{OTa}_3$ . The line width remains similar to that observed in the initial oxide indicating resonances where the

linewidths are determined by chemical shift dispersion, i.e., a range of environments exist. Hence a significant change of structure occurs on removal of the template. This is possibly brought about by the creation of open coordination sites at the metal upon removal of the N-donating template (pyridine adsorption studies on the walls of mesoporous niobia<sup>15</sup> have revealed a higher concentration of Lewis Acid Sites as compared to bulk niobia), and/or the paratoluenesulfonic acid acting as a network enhancer to promote crystallization and a higher degree of local ordering. The  $\text{OTa}_2$  environment also clearly changes with a chemical shift difference of  $\sim 30$  ppm (strictly the peak position, but with the small  $\chi_Q$ s that are typical for such an ionic system this can be closely identified with a chemical shift difference<sup>18</sup>). This can be compared with gel formation of bulk tantalum,<sup>37</sup> which has two peaks at 430 ( $\text{OTa}_2$ ) and 270 ppm ( $\text{OTa}_3$ ). On heat treatment, the mixture of two coordinations remains approximately constant until the highest temperature of 750 °C where the  $\text{OTa}_3$  becomes dominant. The variations observed in this heat-treated mesoporous tantalum show that  $\text{OTa}_3$  starts off as the less populated coordination but gradually becomes the more intense signal, although  $\text{OTa}_2$  and  $\text{OTa}_3$  remain throughout.

$\text{TiO}_2$  shows the largest change of all the oxides studied here in going from the templated oxide to the sample when the template has been removed. The  $\text{OTi}_2$  coordination at 690 ppm is immediately replaced by two peaks at 562 and 380 ppm, which can be attributed to  $\text{OTi}_3$  and  $\text{OTi}_4$ , respectively. In bulk sol–gel produced  $\text{TiO}_2$ , the initial oxide has an approximately equal concentration of  $\text{OTi}_3$  and  $\text{OTi}_4$ , with the  $\text{OTi}_3$  concentration increasing with heat treatment until just before crystallization at 300 °C there is a large excess of the  $\text{OTi}_3$ , with virtually all the  $\text{OTi}_4$  removed on crystallization.<sup>36</sup> There is also a large decrease in the line width of the  $\text{OTi}_3$  resonance at this point as well, an indication of the much higher order on crystallization. This again is very different in the mesoporous titania since initially  $\text{OTi}_3$  starts off as the dominant coordination which on heat treatment decreases in intensity with respect to the  $\text{OTi}_4$ , which becomes the dominant coordination after heat treatment at 750 °C. At all temperatures the line width remains typically at  $\sim 2$  kHz (see Table 1), which is comparable to that seen in amorphous, bulk gels at 3.5 kHz.

## 5. Conclusion

Amine-templated mesoporous silica, niobia, tantalum, and titania materials were synthesized and studied by solid state NMR.  $^{15}\text{N}$  NMR studies revealed that the amine template was bound in the structures as hydrogen-bonded ammonium species in the case of Si, and in amine form for Nb, Ta, and Ti. However

REAPDOR experiments revealed a substantial direct Nb–N interaction in the niobia material, confirming a N–M dative bonded ligand interaction, as previously hypothesized. <sup>17</sup>O NMR studies on the Nb, Ta, and Ti materials showed that the amine template suppresses the formation of higher coordinate oxygen, ubiquitous in oxide gels for these metals. This is most likely due to the influence of the template headgroup on the local structure of the wall via ligand interaction where the amine occupies a coordination site that would otherwise be taken by a triply coordinated oxygen. Thus, the amine surfactant plays an unprecedented dual role of templating the mesostructure while also directing the oxygen coordination in the walls. In the template-free samples there are more open metal Lewis Acid sites at the metal and more basic oxygen lone pairs present as compared to the corresponding oxide gels where the lone pairs of the oxygen block most open metal sites. This configuration

should have several advantages in catalysis and other applications such as gas separation.

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**Supporting Information Available:** The XRD data from mesoporous silica, niobia and tantalum are shown (Figure S1) and a fit of the <sup>15</sup>N MAS NMR spectrum of the templated mesoporous silica (Figure S2). The <sup>15</sup>N–<sup>93</sup>Nb REAPDOR loss of signal for the niobia sample is given (Table T1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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