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Mesoporous Materials

A Solid-State ^{17}O NMR Study of Local Order and Crystallinity in Amine-Templated Mesoporous Nb Oxide**

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The study and modification of materials on the nanoscale has attracted a great deal of attention from a wide variety of scientific disciplines ranging from medicine to physics.[1,2] One of the most important classes of nanoscale materials is those with a repeat and regular pore structure on the nanometer scale.[3,4] The discovery of M41S mesoporous silica in 1992 led to new techniques of fabrication of highly ordered, high-surface-area mesoporous materials, especially those of metal oxides.[5] The first synthesis of mesoporous Ti oxide was reported in 1995,[6] followed by mesoporous niobia,[7] materials, which displayed pore sizes in the range 2–5 nm and surface areas up to 1200 $m^2 g^{-1}$. The advantage of these mesoporous transition-metal oxides over the traditional silica-based materials is that these oxides are capable of existing in various oxidation states. Recent advances showed that such mesoporous oxides can act as stoichiometric electron acceptors, thus allowing the fine tuning of electronic properties of the mesostructure and making them potential candidates for battery applications, fuel-cell fabrication,[8] and hydrogen-storage materials.[9] Mesoporous sulfated niobia has also been shown to have very high activity for acid-catalyzed benzylation of anisole.[10]

Despite the intriguing and promising properties of mesoporous transition-metal oxides, there is still very little detailed information concerning the atomic-scale structure. The degree of local ordering is extremely important for tailoring catalytic properties into porous materials. Although conventional analytical techniques such as X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) have provided information on the degree of medium-range order and surface electronic states, respectively, in these materials, the local structure of the walls remains largely unknown. The lack of discrete high-angle reflections in the XRD pattern suggests that the structure is amorphous. Tatsumi and co-workers used XRD along with UV/Vis and X-ray absorption near-edge structure (XANES) spectroscopy to probe the structure of mesoporous Ti oxide.[11] The effectively amorphous structure was made up of coexisting TiO_5 and TiO_6 units according to XANES. In $V_2O_5{\cdot}n\,H_2O$ xerogels, conventional XRD revealed little, but analysis of the atomic-pair distribution function suggested that the lamellar structure was made up of bilayers of perfect V_2O_5 units in which the vanadium center is coordinated as VO_5 and the bilayers are separated by water.[12] Despite this recent progress, deeper insight into the local structure of mesoporous transition-metal oxides is still required.

Solid-state NMR spectroscopy has proved to be an extremely useful and informative tool in identifying and characterizing local environments in materials.[13] The large chemical-shift range of ^{17}O produces high sensitivity to even subtle differences in the structure in both amorphous and crystalline solids.[13,14] The major problem with ^{17}O NMR spectroscopy is the low natural abundance of ^{17}O (0.037 %) and subsequent poor sensitivity, which can be overcome by even modest enrichment of the material (e.g. by using 20 at % in the precursor material).[13,14] Solid-state ^{17}O NMR data are reported herein for both conventional sol–gel bulk niobia and mesoporous niobia. These data indicate that the wall in the latter has an unprecedented, highly ordered local structure about the oxygen site, with the oxygen exclusively present as ONb_2, unlike conventional Nb_2O_5, which is a mixture of ONb_2 and ONb_3 environments. Static ^{93}Nb NMR data are also reported for the mesoporous sample.

^{17}O magic-angle-spinning (MAS) NMR spectra were collected from sol–gel-produced bulk Nb_2O_5 for comparison. The resonances observed in the Nb_2O_5 can be compared to data from a previous study of hydrolyzed niobium ethoxide in the as-prepared sample,[15,16] which were assigned on the basis of solution-state NMR spectroscopy of niobium-containing cluster compounds[17] as ONb_2 at $\delta = 540$ ppm and ONb_3 at $\delta = 358$ ppm (Figure 1, Table 1). The structural development of niobia gels is shown herein for the first time by means of ^{17}O MAS NMR spectroscopy. The peak at $\delta = 540$ ppm is more intense than the other peak. Upon heating the sample first to 250 °C for 4 h, the intensities of the two peaks become more comparable. After heating the sample to 500 °C for 4 h, the peak at $\delta = 375$ ppm is more intense than the peak at $\delta =$

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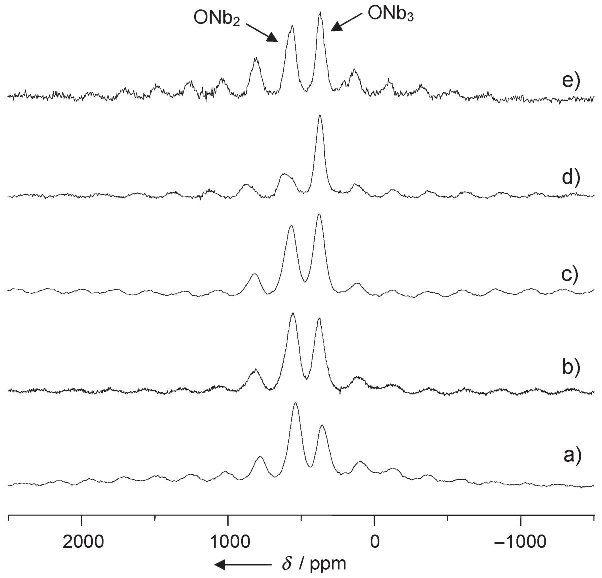

Figure 1. ^{17}O MAS NMR spectra of ^{17}O-enriched sol–gel Nb_2O_5 a) as-formed, and after heating to b) 250 °C, c) 500 °C, d) 750 °C, and e) 1000 °C. (Main peaks identified, all others are spinning sidebands).

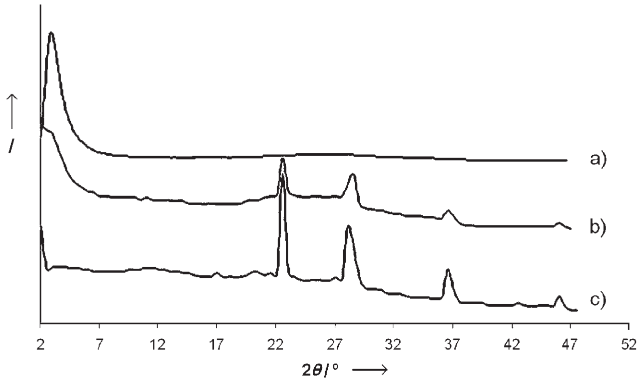

Figure 2. X-ray diffraction pattern of mesoporous Nb oxides a) at room temperature, and after heating for 2 h at b) 500 °C and c) 750 °C.

Table 1: Summary of NMR spectral characteristics of mesoporous niobia samples.[a]

Heat treatment	Mesoporous niobia ^{93}Nb static NMR		 ^{17}O MAS NMR		Bulk sol–gel-prepared niobia ^{17}O MAS NMR	
	δ_{peak} [(±5) ppm]	Δ [(±3) kHz]	δ_{peak} [(±0.2) ppm]	Δ [(±10) Hz]	δ_{peak} [(±1) ppm]	Δ [(±80) Hz]
none	−1145	122	565.5	395	358	5540
					540	5320
250 °C	−1145	171	559.3	320	374	4580
					556	5320
500 °C	−1195	237	556.0	530	375	4630
					565	5060
750 °C	−1660	341	589.0	250	372	3370
			556.3	275	617	6990
1000 °C	n.m.	n.m.	n.m.	n.m.	371	3900
					565	4340

[a] δ_{peak} is the peak position without correction for any second-order quadrupole contribution to the peak position away from the chemical shift; Δ = full width at half maximum; n.m. = not measured.

565 ppm, and there is also a slight narrowing of the line at $\delta = 375$ ppm (Table 1). After heating the sample to 750 °C, the peak at $\delta = 565$ ppm disappears almost completely and is replaced by a much broader, less intense peak centered at $\delta = 617$ ppm, which indicates that the material has undergone a significant structural change. After heating to 1000 °C, the material crystallized and had two peaks present at $\delta = 371$ and 565 ppm, which were approximately 30 % narrower than they were in the amorphous state. These ^{17}O NMR peaks can be assigned to ONb_3 and ONb_2 respectively, as expected for a niobium phase consisting of NbO_6 units sharing a mixture of edges and corners.

The XRD (Figure 2) shows a relatively simple pattern from mesoporous niobia. With no heat treatment (and after treatment at 250 °C, not shown), only a very low angle reflection is observed at approximately 2.5°. After further heat treatment, additional reflections are observed at approximately 22°, 28°, and 37° (2θ), and the main low-angle peak for the mesostructure gradually diminishes in intensity, which suggests a loss in pore structure as evidenced by a decrease in surface area from 700 $m^2 g^{-1}$ in the untreated material down to less than 5 $m^2 g^{-1}$ in the material heated to 750 °C. These reflections can best be indexed, although not exactly, on the orthorhombic phase (JSCPDS 27-1313) of niobia and not the usual room-temperature form.[18] The trend of gradual crystallization can also be clearly followed in the TEM images (Figure S1 in the Supporting Information).

^{93}Nb despite having a high nuclear spin of $I = 9/2$ can experience significant quadrupole broadening so that MAS is often ineffective in providing any line narrowing. Static ^{93}Nb NMR data collected on the as-synthesized sample showed a quite broad asymmetric spectrum (Figure S2 in the Supporting Information and Table 1). Up to 500 °C, the peak position (note that the peak position is not the isotropic chemical shift,[13] but the large shift range usually allows identification) does not change much, clearly indicating that niobium is present as NbO_6 throughout.[19] The increase in the line width suggests that there is some increase in the average interaction, probably as a result of the NbO_6 units becoming more distorted. After the sample was heated to 750 °C, there was a much larger change in the spectrum: the peak shifted by approximately −450 ppm. This shift is at the very extreme of the shift range of NbO_6 units,[19] probably suggesting an unusual NbO_6 unit. The significant increase in line width also suggests that the site has become further distorted.

The ^{17}O MAS NMR spectra (Figure 3, Table 1) show some intriguing results. The spectrum of the as-synthesized oxide is dominated by a single sharp resonance at $\delta = 565.5$ ppm, and some low-intensity spinning sidebands are also present, along

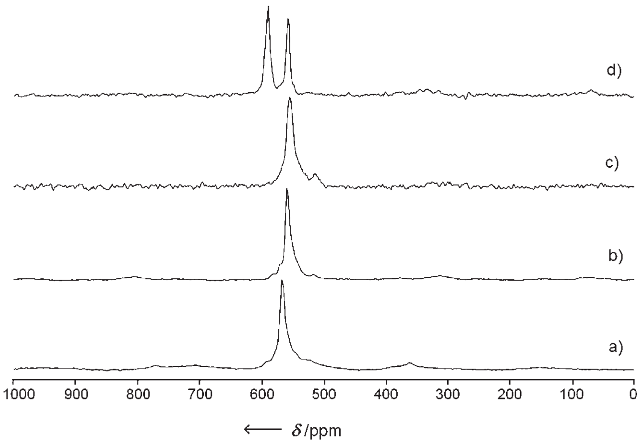

Figure 3. ^{17}O MAS NMR spectra of ^{17}O-enriched mesoporous niobia a) as-synthesized, and after heating to b) 250 °C, c) 500 °C, and d) 750 °C.

with a hint of some much weaker features—broader underlying intensity and some very much smaller peaks (e.g. at $\delta \approx 500$ ppm), all in the chemical shift range for ONb_2. There is relatively little change in the line shape upon heat treatment other than a small decrease in the shift successively to $\delta =$ 559.3 and 556.0 ppm in the samples heated to 250 and 500 °C, respectively. On heating the sample to 750 °C, the peak at $\delta =$ 556 ppm remains, but a second narrow peak of almost equal intensity appears at $\delta = 589$ ppm.

Hence it is very clear that the niobia walls in the sample are exclusively constructed of ONb_2 linkages, which is very unusual as all other ^{17}O NMR data reported on niobia have shown a mixture of ONb_2 and ONb_3 environments. Perhaps even more surprising is the line width. In sol–gel-prepared Nb_2O_5, the line widths are about 5 kHz at a similar magnetic field, and even on crystallization there is only a modest decrease of width to around 4 kHz. Crystalline niobates tend to exhibit significantly broader resonances than, for example, chemically similar titanates,[13,20] which is attributed to the generally observed relation that the quadrupole broadening depends on the electronegativity difference across the metal–oxygen bond.[14] This would suggest a typical quadrupole interaction (χ_Q) of 4 MHz for Nb–O, whereas on the basis of the small line width an upper estimate of χ_Q is only 2.5 MHz. Although XRD indicates that this mesoporous niobia has long-range order that resembles the orthorhombic phase, the local structure is different and consists of a single, highly symmetric oxygen site (only ONb_2 and no ONb_3). At 750 °C, the structure changes as two similar, but nonequivalent, ONb_2 sites appear, and the niobium probably remains as NbO_6, but with a large chemical shift, in a structure that is still very highly ordered locally.

These results show that the walls of the mesoporous Nb oxide are made up of NbO_6 units that are linked through corner-sharing ONb_2 arrangements in three dimensions with very few edge-sharing units and probably hydroxy groups on the inner and outer surfaces. Such hydroxy groups are often not observed in ^{17}O MAS NMR spectra,[21] but they must be present, as previous work has shown that treatment of mesoporous niobium oxide with trimethylsilyl chloride leads to silicon incorporation in the materials.[9] ^{17}O NMR spectroscopy is shown herein to provide very clear information on the local order within this material. Although the vast majority of the octahedra are linked at the corners, the flexibility about the ONb_2 unit must allow enough dislocations and twisting that the orientation of the NbO_6 units changes, thus decreasing medium-/long-range order and preventing discrete Bragg reflections in the XRD pattern. This structure is surprisingly well ordered relative to other samples of niobia gels, as well as samples of mesoporous titania and tantala prepared through the same route. On heat treatment of the samples, the local order (as indicated by the narrow ^{17}O NMR resonances) remains much higher than indicated by the broad Bragg reflections. A consequence of this situation is that there must be regular microporous channels in the walls running between the three-dimensional array of octahedra. The appearance of this structure is unprecedented in surfactant-templated mesoporous materials, although organically modified mesoporous silicas with aryl groups in the channels display regular stacking of these organic functionalities.[22] Appearance of any order in the walls of surfactant-templated mesoporous structures typically occurs by crystallization at elevated temperatures and leads to collapse of the mesopores and formation of nanocrystalline grains, although in some cases individual nanocrystals can be formed in the walls prior to complete collapse of the pore structure.[23] Crystalline walls are more common in lower-surface-area polymer-templated structures with much thicker walls; however, surfactant-templated mesoporous germania and some Zintl salts possess a regular wall structure, but the template remains within the structure.[24] None of these oxide structures possess exclusively corner-shared octahedra and the order observed in the samples in this case is not related to crystallization. The reason that the walls of the mesoporous niobia adopt this highly ordered structure is presently unknown. The combination of a unique, template-free highly ordered structure with a surface area of $700\,m^2\,g^{-1}$ and thermal stability up to around 400 °C suggests a number of exciting applications. Furthermore, the suggested presence of regular microporous channels in the walls makes this material very interesting from the standpoint of gas separation and catalysis with small molecules (e.g. CH_4, CO, H_2O, and nitrogen oxides).

Experimental Section

Mesoporous niobia was prepared as described previously.[7] The ^{17}O enrichment was carried out by heating stoichiometric amounts of mesoporous metal oxide and [^{17}O]water (20 % enriched) together in a sealed vessel under an inert atmosphere at 140 °C for 24 h. The samples were subsequently heat treated under air at 250, 500, and 750 °C for 2 h at a time.

XRD patterns were recorded with $Cu_{K\alpha}$ radiation on a Siemens D500 $\theta/2\theta$ diffractometer. TEM images were obtained on a Hitachi H9000 high-resolution transmission electron microscope operating at 200 kV.

NMR experiments were carried out on a CMX Infinity 600 spectrometer equipped with a 14.1-T magnet for ^{93}Nb at an observation frequency of 146.7 MHz and a CMX Infinity 360 spectrometer equipped with a 8.45-T magnet for ^{17}O at an observation frequency of 48.2 MHz. The ^{93}Nb NMR experiments used a solid echo pulse sequence on a Bruker 5-mm static probe with an echo time of 25 μs and a recycle delay of 3 s, and typically 1500 scans were coadded. A frequency of 12 kHz was employed for the ^{17}O MAS on a Varian-Chemagnetics Apex 4-mm probe with the echo time set to the reciprocal of the spinning period. A recycle time of 1 s was used and typically 10^4 acquisitions were coadded. The ^{93}Nb NMR spectra were referenced by using the highest shift singularity of well-crystallized $LiNbO_3$ at $\delta = -1016.3$ ppm so that the shift is reported indirectly against the primary shift reference, whereas the ^{17}O NMR spectra were referenced against tap water at a shift of $\delta = 0$ ppm.

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