^{47,49}Ti NMR: Evolution of Crystalline TiO_2 from the Gel State

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^{47,49}Ti NMR has been used to monitor the transition to the crystalline state of titania gels, formed by the hydrolysis of titanium isopropoxide, which were progressively annealed to 700 °C. The gel spectrum consists of a single unresolved line, considerably narrower than that for anatase. The spectra from the intermediate anneals indicate the additional presence of only crystalline TiO_2 anatase and rutile (the final product) and that these polymorphs coexist over a range of temperatures of at least 100 °C in the specimen, indicating the spatially inhomogeneous development of crystallinity in these gel specimens.

Introduction

The use of NMR as an analytical technique for the study of gels and the processes involved in crystallization began with work on silicate gels using the isotope ^{29}Si, in conjunction with magic-angle spinning (MAS), to give resolved solid-state spectra.[1] The fortunate circumstance of ^{29}Si possessing nuclear spin $I = {}^1/_2$ allowed the observation of NMR spectra free of the polycrystalline line-broadening nuclear quadrupole interactions attendant on $I > {}^1/_2$. Subsequently it was realized that the isotope ^{17}O, despite having $I = {}^5/_2$, had a useful chemical shift range together with a quadrupole interaction that in many cases could be substantially eliminated in the solid state by MAS,[2] making ^{17}O a revealing structural probe for oxygen-containing gels undergoing a transition to the crystalline state. Successful investigations of the crystallization of zirconia[3] and titania[4] (^{17}O-enriched) gels were subsequently made using ^{17}O MAS NMR. The various zirconia and titania polytypes are identifiable from both the ^{17}O chemical shift and the multiplicity of the lines observed.

In many of the oxide gels studied, the counterion is a transition metal, e.g., Ti and Zr, and these elements are not user friendly to NMR spectroscopists, due to the low abundance, high spin, and low magnetic moment of their NMR-active isotopes. The large quadrupole interaction that generally characterize ^{47,49}Ti and ^{91}Zr solid state NMR spectra lead to very wide lines which can be difficult to encompass in FTNMR. For this reason transition metal oxides have largely gone unstudied by this technique. However frequency-stepped broad line ^{91}Zr NMR has been used[5] to characterize the *crystalline* zirconium oxide (ZrO_2) polytypes (monoclinic, tetragonal, orthorhombic, cubic) in terms of the quadrupole interaction specific to each polytype, rather than the isotropic shift. Two accounts of ^{47,49}Ti NMR work on polycrystalline titanium compounds have reported the quadrupole interaction in TiO_2 anatase determined from MAS[6] and static[7] spectra. More recently it has recently been shown[8] that ^{47,49}Ti NMR can give a sharp characterization of a number of Ti-based oxides and metals based on a combination of chemical (Knight) shift and the observed nuclear quadrupole interaction. In particular well-differentiated spectra of the anatase (tetragonal) and the rutile (orthorhombic) polytypes of TiO_2 have been observed.[8]

In the present work the characteristic ^{47,49}Ti NMR spectrum of titania gel formed by the hydrolysis of titanium isopropoxide is reported. The subsequent evolution of the anatase and rutile phases is monitored from the ^{47,49}Ti NMR spectra of the gel by annealing in stages up to 700 °C, at which point the transformation to rutile is complete. Despite the rather complex line shape, all peaks and edges have been identified by comparison with spectra taken from single phase anatase and rutile specimens.

Experimental Section

The spectra were obtained using a Bruker MSL 400 spectrometer operating at around 22.55 MHz in a nominal field of 9.395 T, using a probe with a 10-mm transverse coil. The spectra were obtained using a two-pulse echo sequence where the whole echo was collected and Fourier transformed to give the absorption line shape.[9] Each pulse was 4-μs duration, which excited and detected a frequency region of 250 kHz. The

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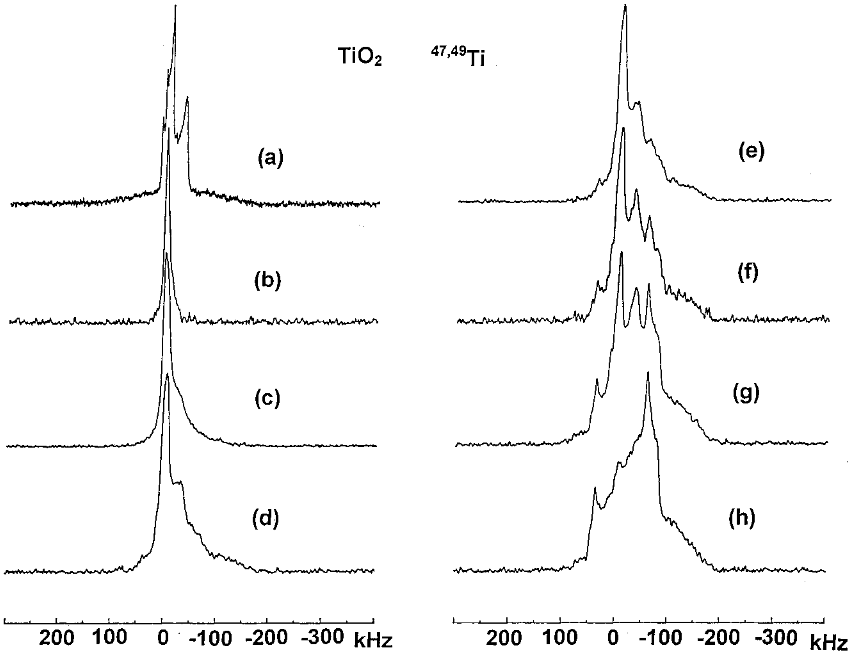

Figure 1. $^{47,49}Ti$ line shapes for (a) crystalline TiO_2 (anatase) and TiO_2 gel annealed at (b) 200 °C, (c) 500 °C, (d) 520 °C, (e) 550 °C, (f) 580 °C, (g) 600 °C, and (h) 670 °C (rutile).

pulses were less than $\pi/2$ for each isotope and represented a compromise between signal gathering efficiency and bandwidth. The delay between scans was 0.1 s and between 200 000 and 500 000 scans were collected for each spectrum.

The gel was prepared by the hydrolysis of $Ti(i\text{-}OPr)_4$ (ex. Aldrich; 99.999%). It was then filtered, taken to damp dryness in a Buchner funnel, and subsequently annealed in ambient atmosphere, for ~1 h, in successive steps to 700 °C. After each annealing stage, the specimen was cooled to room temperature and $^{47,49}Ti$ NMR spectra were recorded.

Results and Discussion

The $^{47,49}Ti$ NMR spectra from selected stages of the annealing process are displayed in Figure 1. Because it is a component of the intermediate stages of annealing, a clear spectrum from a separate specimen of crystalline anatase (ex. BDH laboratory grade) is included as a reference as Figure 1a. The subsequent spectra Figure 1b–h are identified in the caption by their annealing temperature. Simulations of each of the anatase and rutile spectra, yielding the nuclear quadrupole coupling constant and asymmetry parameter, are given in ref 8.

The spectrum for each distinguishable Ti site is a superposition of the line shapes from the isotopes ^{47}Ti ($I = {}^5/_2$, 7.3%) and ^{49}Ti ($I = {}^7/_2$, 5.5%). The appreciable quadrupole moment of each of these isotopes leads to a strongly second-order quadrupole-perturbed ($^1/_2$,$-^1/_2$) line shape for any Ti atom not at a strictly cubic site. In this case, since the magnetic moments are such that at a field of 9.395 T the difference in Larmor frequencies $^{49}\nu - {}^{47}\nu = 6$ kHz, and the quadrupole moment ratio $^{49}Q/^{47}Q = 0.819$, the spectrum from the central ($^1/_2$, $-^1/_2$) transition of ^{49}Ti will be nested within that of the ^{47}Ti. For the final rutile phase the quadrupole interaction is large enough that, in the present study, only the ^{49}Ti line shape is fully detected in a scan centered near the mid region of the anatase line shape. The unstructured wings on either side of the rutile ^{49}Ti line shape edges (Figure 1h) are from the incompletely detected edges of the ^{47}Ti spectrum.[8] Note that the width of the powder spectrum for a second-order quadrupole-perturbed ($^1/_2$,$-^1/_2$) transition is inversely proportional to the magnetic field.

A surprising feature is the observation of a narrow, rather asymmetric resonance for the damp dry state, which remains, essentially unchanged, on annealing at temperatures up to ~200 °C. The line is comparable in width and general appearance to that from polycrystalline $^{47,49}Ti$ in $CaTiO_3$ and $BaTiO_3$[8] where X-ray determined structures[10] show small distortions (orthorhombic and tetragonal, respectively) from the TiO_6 regular octahedral oxygen coordination that obtains in the cubic perovskite phase (e.g., $SrTiO_3$). The nuclear quadrupole coupling at the Ti site (determined precisely for single-crystal $BaTiO_3$[11]) in both these perovskites is less than that for anatase, but the intrinsic line width for both isotopes must be greater than their Larmor frequency separation of 6 kHz (at 9.4 T), leading to a line shape which is isotopically unresolved, but skewed to low frequencies. It is apparent from the 200 °C gel line width that the distortion from cubic is similarly less than that for crystalline anatase. However the gel peak has a shift value very close to the centroid of the sharp ^{49}Ti component of the anatase spectrum.

On the other hand it was noted that the 100 and 200 °C anneals of the gel yielded powder XRD spectra characterized by broad lines centered at the crystalline anatase 2θ values (Figure 2). The obvious interpretation is that the damp-dry gels, and those annealed at low temperatures are nanocrystalline anatase. They are clearly distinguishable from XRD traces from unannealed rutile[12] and brookite[13] specimens prepared via sol–gel routes. The above observations are compatible if, in the 100 and 200 °C gels (at least), the Ti atoms

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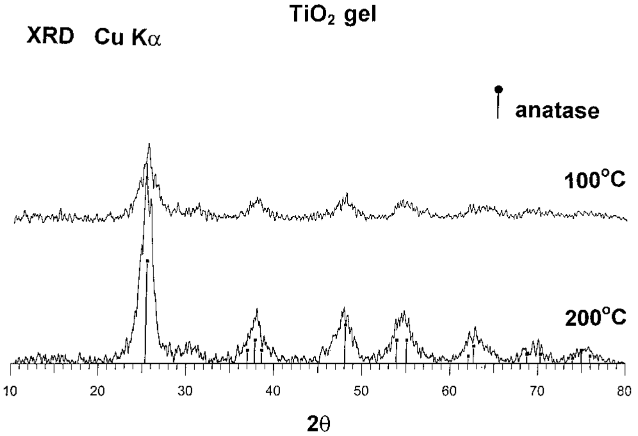

Figure 2. XRD scans of TiO_2 gels annealed at 100 °C (upper trace) and 200 °C (lower trace).

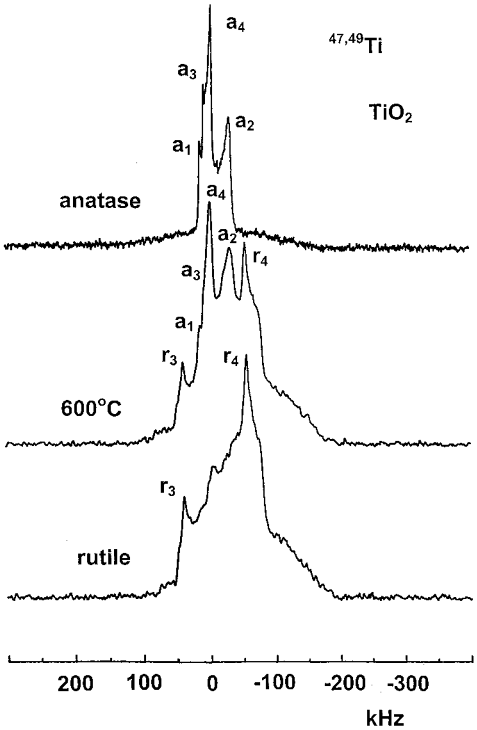

Figure 3. Assignment of the peaks observed in the ^{47,49}Ti line shape for the gel specimen annealed at 600 °C, showing the correspondence with those in anatase and rutile. Labeling: ^{49}Ti high- and low-frequency peaks (a_3, a_4) in anatase, and (r_3, r_4) in rutile; ^{47}Ti high- and low-frequency peaks (a_1, a_2) in anatase.

have *large amplitude* oscillations with vibrational frequencies fast on the time scale of the nuclear quadrupole interaction frequencies $^{47,49}\nu_q \approx 5$ MHz, where $\nu_q = 3e^2qQ/2I(2I - 1)h$, but with a period slow compared to the time ($\sim 10^{-12}$ s) for the X-ray photon to traverse the specimen. This condition would allow a partial motional averaging of the nuclear quadrupole interaction for crystalline anatase.

It should be noted that a previous study[4] has shown, using ^{17}O MAS NMR and ^{13}C CPMAS, that in a TiO_2 gel preparation (also via alkoxide hydrolysis) there were initially observed in the as-dried gel two broad ^{17}O lines at 514 and 368 ppm, corresponding to the presence of OTi_3 and OTi_4 groups, respectively. On annealing the gel in stages up to 300 °C, the OTi_3 ^{17}O line sharpened considerably and the shift progressively moved to that for anatase. (It may be noted in passing that the oxygen coordination in rutile and brookite is also OTi_3.) The line at 368 ppm, due to the OTi_4 component from a polyoxyalkoxide species,[14] present because of incomplete hydrolysis in the preparation, which used a severely limited amount of ^{17}O-enriched water to preserve enrichment in the gel, correspondingly diminished, and disappeared at 300 °C, along with the characteristic ^{13}C spectrum for the alkoxide. In the case of the gels prepared for the present ^{47,49}Ti investigation the hydrolysis was complete.

For the 500 °C gel the ^{47,49}Ti spectrum has broadened, such that the base has a width approaching that of anatase. The line shape, now with a more prominent low-frequency shoulder, is beginning to resemble a heavily smeared version of the anatase spectrum. However as the gel is further annealed up to 600 °C, peaks begin to appear that can be identified by their shift values as belonging to both anatase *and* rutile ^{47,49}Ti spectra. Figure 3 indicates the correspondence of the peaks observed in the specimen annealed at 600 °C with those of anatase and rutile. At 670 °C only well-crystallized rutile was present, judging by the sharpness of the spectral features. Further annealing to 700 °C and above did not appreciably further sharpen the rutile line shape.

It can also be seen from the line shape smearing that the anatase crystallites present in gels annealed at 600 °C and below were not well-ordered. Note that almost as soon as the spectrum had developed recognizable anatase features it was also developing rutile features, indicating that these two phases were developing in spatially separate regions.

Conclusions

The results presented here are illuminating as to the environment of the Ti in the gel state and the inhomogeneity of the thermally treated gel specimens. At higher magnetic field, where the whole of the rutile ^{47,49}Ti spectrum could be obtained at a single observation frequency, these observations indicate the basis for an NMR method of quantifying the phase content of such specimens.

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