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Solid state NMR of SiO₂ nanotube coated ammonium tartrate crystal

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Abstract

Ammonium tartrate crystal and SiO₂ nanotube coated ammonium tartrate crystal were studied by ¹³C CP/MAS NMR, and the structure of two samples were verified using the ¹³C NMR spectrum. The spin–lattice relaxation times for the carbons in the rotating frame, $T_{1\rho}$, have been measured as a function of temperature. All relaxation times of the carbons in the two materials undergo slow motions, i.e. motions on the slow side of the $T_{1\rho}$ minimum. From these relaxation times, we determine the activation energy for the ammonium tartrate crystal and SiO₂ nanotube coated ammonium tartrate crystal, respectively. The activation energies for the SiO₂ nanotube coated ammonium tartrate crystal were found to be generally higher than those of ammonium tartrate crystal. We think that the higher activation energy for the hydrocarbon in the SiO₂ nanotube coated ammonium tartrate crystal is because of the bonding between the oxygen in the SiO₂ nanotube and the hydroxyl group of the ammonium tartrate crystal. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Inorganic hollow carbon [1-6], boron nitride [7-9], and silica tubes [10,11] were prepared under high temperature reaction conditions. Nakamura and Matsui reported on the synthesis of SiO₂ nanotubes, which were synthesized in a solution of DL-tartaric acid (TTA), water, absolute ethanol, and tetraethyl orthosilicate (TEOS) via the addition of ammonium hydroxide [12]. They had square shapes with an outer diameter of $0.8-1.0 \mu m$, inner diameters of $0.02-0.8 \mu m$, shell thicknesses of $0.015-0.3 \mu m$, and

200–300 μ m in length. The SiO₂ nanotube coated ammonium tartrate crystal was also obtained using the sol–gel method at room temperature by the Novak group [13]. The mechanism of fiber formation has been recently elucidated. It was discovered that upon addition of ammonium hydroxide TTA forms an ammonium tartrate (ATT) salt which crystallizes in the form of long prisms with rectangular crosssections. Simultaneous with crystal formation, SiO₂ rapidly condenses and coats the crystal surfaces. Washing the products with water dissolves the ammonium tartrate crystals out from within the SiO₂ coating leaving a hollow tube. Washing the products with ethanol leaves the ammonium tartrate crystals in place yielding a SiO₂ coated ATT crystal. Condensing

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Fig. 1. The hollow SiO₂ nanotubes by scanning electron microscopy.

SiO₂ that does not encounter a crystal forms spherical particles as is commonly obtained when using a strong base as sol-gel catalyst [14]. The ammonium tartrate crystals have a monoclinic structure with cell dimensions of a = 7.083 Å, b = 6.128 Å, c = 8.808 Å and $\beta = 92.42^{\circ}$ at room temperature [15]. The crystals are known to have piezoelectric properties. Fig. 1 shows the hollow SiO₂ nanotubes. The rectangular inner shapes of these tubes are remarkably uniform. Fig. 2 shows the SiO₂ nanotube coated ammonium tartrate crystal, and shows the end of one of these fibers and the X-ray spectra collected from the shaft and the tip of fiber. The end appears to have fractured off exposing the interior. X-ray spectra show that the tip is composed primarily of carbon and the shaft is silicon and oxygen.

In this article, we confirmed the structure of the ammonium tartrate crystal and the SiO₂ nanotube coated ammonium tartrate crystal (ATT) by ¹³C CP/MAS NMR. The quantitative distribution of the various groups in the SiO₂ nanotube were also obtained from the ²⁹Si CP/MAS NMR spectra. In addition, the ¹³C spin–lattice relaxation times in the rotating frame, $T_{1\rho}$, were measured as a function of temperature for two samples. From these results, the activation energy for each carbon in the ATT and SiO₂ nanotube coated ATT were obtained.

2. Experimental

2.1. Nanotube synthesis

Tetraethyl orthosilicate (TEOS) and DL-tartaric acid (TTA) were obtained from Aldrich Chemical.

Spectroscopic grade water and reagent grade ammonium hydroxide (30% NH₃) were obtained from Fisher Scientific. All reagents were used without further purification. Synthesis of the nanotubes was carried out in a 50 ml Erlenmeyer flask by dissolving 30 mg of DL-TTA in a solution of 7.5 absolute ethanol and 0.09 ml of water. When a clear room temperature solution was obtained, 1.18 ml of TEOS was added and the solution was allowed to stand for 30 min. During this time the solution remained clear and there was no noticeable change in viscosity. After 30 min, 3 ml of ammonium hydroxide were added to the solution. After this addition, a cloudy white layer formed on the top of the solution. The solution became clear upon mixing and then increasingly cloudy and viscous until it was completely opaque and non-flowing. This state was achieved 15-20 min after the addition of ammonium hydroxide. The reaction scheme is show in Fig. 3. The precipitate was washed with ethanol, collected via vacuum filtration on a 0.45 µm filter, and dried in an oven at 50°C for 24 h.

2.2. Solid state NMR spectroscopy

The solid state NMR experiments were performed using Brucker 200 NMR and Varian 300 NMR spectrometer. Cross-polarization, magic-angle spinning (CP/MAS) ²⁹Si and ¹³C NMR experiments were performed at the Larmor frequencies of 39.73 and 75.46 MHz, respectively. The samples were measured in powder form using solid state NMR spectroscopy. The samples were placed in a CP/MAS probe of 7 mm and the magic-angle spinning rate was 5 kHz to minimize spinning sideband overlap. In order to measure A.R. Lim et al. / Solid State Communications 110 (1999) 333-338



Fig. 2. Scanning electron microscopy picture of SiO₂ nanotube coated ATT crystal and X-ray spectra from shaft (left) and (tip).

the ¹³C spin–lattice relaxation time, the $\pi/2$ pulse time was 5 µs, corresponding to a spin-locking field strength of 50 kHz. ¹³C $T_{1\rho}$ was determined by varying a ¹³C spin-locking pulse after a 0.8 ms CP preparation period. The decay of the ¹³C magnetization in the spin-locking field was recorded for spin-locking times of up to 30 ms.

3. Results and discussion

The solid state structures and dynamics of the ATT and SiO₂ nanotube coated ATT were examined using solid state NMR. Fig. 4 shows the solid state ¹³C CP/ MAS NMR spectrum for the ATT. The spectrum consisted of four signals at chemical shifts of δ = 180.20, 178.58, 76.71 and 74.45 ppm at room temperature. The splitting of the 180.20 and 178.58 ppm (76.71 and 74.45 ppm) can be explained by the effect of isomerization of the samples. Peaks of 1 and 2 are assigned with the carbon and hydrocarbon, respectively, as shown in Fig. 4. Spinning sidebands are marked with asterisks. The ¹³C CP/MAS NMR spectrum in the case of the SiO₂ nanotube coated ATT is very similar to the ATT.

The structure of silicate anions commonly uses a Q^n notation. In this notation, Q represents a silicon atom bonded to four oxygen atoms forming a tetrahedron. The superscript *n* indicates the connectivity, i. e. the number of oxygen atoms attached to the Si. Thus, Q^0 denotes the monomeric orthosilicate anion Si, Q^1 the end-group chains, Q^2 the middle groups in chains or

cycles, Q^3 the chain branching sites and Q^4 the threedimensionally cross-linked groups [16,17]. The solid state ²⁹Si NMR spectrum is shown in Fig. 5. The total range of ²⁹Si chemical shifts is usually observed in the ²⁹Si NMR spectra in the range of about -60 to about -160 ppm, i.e. about 100 ppm [18]. Within this range, two dominant resonances are observed at the chemical shifts -111 and -102 ppm. Based on a model compound, the resonances are assigned to the Q^3 and Q^4 units, respectively. The Q^2 unit at chemical shift -92 ppm has a relatively small intensity. The relative concentrations of the Qⁿ structural units can be obtained directly from the integrated peak areas. The resultant percentages of Q^2 , Q^3 , and Q^4 branching points (i.e. cross-links) are 4.0, 40.3, and 55.7%, respectively.

The ¹³C spin–lattice relaxation time in the rotating frame, $T_{1\rho}$, for the ATT and SiO₂ nanotube coated ATT was taken in several temperature ranges with variable spin-lock on the carbon channel following cross-polarization. Normal cross-polarization uses a time delay during which the proton rf field is turned



Fig. 3. Reaction scheme for nanotube synthesis.



Fig. 4. Solid state ¹³C CP/MAS NMR spectrum of ATT at room temperature.

off. This delay is introduced after the carbons are pulsed into the rotating frame. The time interval allows the carbon magnetization to decay by dipolar coupling [19]. The $T_{1\rho}$ relaxation process follows this exponential function [20]:

$$M(t) = M_0 \exp(-t/T_{1\rho}),$$
(1)

where M_0 is the initial height of the free induction decay when the radiofrequency field is switched off. Thus, monitoring of the decay of magnetization intensities, M(t), permits an analysis of the $T_{1\rho}$ spin-lattice relaxation behaviour and determination of the $T_{1\rho}$ relaxation times.

Fig. 6(a) and (b) shows $T_{1\rho}$ for each carbon in both the ATT and SiO₂ nanotube coated ATT as a function of temperature. The ¹³C spin–lattice relaxation time in the rotating frame decreases with increasing temperature. The $T_{1\rho}$ corresponding to two carbons in the SiO₂ nanotube coated ATT shows long relaxation times relative to the ATT. The relaxation times of carbon similarly decrease at increasing temperatures for both the ATT and SiO₂ nanotube coated ATT. However, the greatest difference between the ATT and SiO₂ nanotube coated ATT samples appears in the alcohol side chains: the relaxation times for the hydrocarbons here differ substantially, with the SiO₂ nanotube coated ATT showing the larger value.

The relaxations of all carbons undergo motions on the slow side of the $T_{1\rho}$ minimum (i.e., under slow



Fig. 5. Solid state $^{29}\mbox{Si}$ CP/MAS NMR spectrum of ATT at room temperature.

motion conditions $\omega \tau_c \gg \omega_1 \tau_c \gg 1$ [21,22]. On the slow side of the $T_{1\rho}$ minimum a decrease in $T_{1\rho}$ implies a smaller value of τ_c , and therefore, an increased mobility at higher temperatures.

For the spin–lattice relaxation time in the rotating frame, the experimental value of $T_{1\rho}$ can be expressed in terms of a correlation time $\tau_{\rm C}$ for the molecular motions by the BPP (Bloembergen–Purcell–Pound) function [23].

Further insight into the relative molecular motions can be gained by examining the activation energies associated with the various carbons. The theoretical temperature dependence of the rate of rotational motions is a simple Arrhenius expression [24]

$$\tau_{\rm C} = \tau_0 \exp(E_{\rm a}/{\rm R}T) \tag{2}$$

where E_a is activation energy for the molecular motions and R is the molar gas constant. Thus, a plot of the natural logarithm of the relaxation time as a function of the inverse temperature is linear with a slope that is proportional to the activation energy for motion. Fig. 7(a) and (b) shows representative plots of the correlation time as a function of the inverse temperature for carbon and hydrocarbon in the ATT and SiO_2 nanotube coated ATT. The activation energies for all the carbons are derived from the slope of the straight line passed through the $\tau_{\rm C}$ data. The activation energies for all carbons of the SiO₂ nanotube coated ATT are longer than those measured for the ATT. In carbons, the activation energy for ATT and SiO₂ nanotube coated ATT is 2.87 and 5.91 kJ mol⁻¹, respectively, while hydrocarbons show activation energy in ATT and SiO2 nanotube coated ATT of



Fig. 6. (a) Temperature dependence of the ¹³C spin–lattice relaxation time, $T_{1\rho}$, for carbon in the ATT and SiO₂ nanotube coated ATT. (b) Temperature dependence of the ¹³C spin–lattice relaxation time, $T_{1\rho}$, for hydrocarbon in the ATT and SiO₂ nanotube coated ATT.

2.42 and 11.68 kJ mol⁻¹, respectively. Hence, the molecular motions of the ATT are restricted by interpenetration of the SiO₂ nanotube. It is clear that strong interactions, be they covalent C–O–Si linkages or hydrogen bonding, do exist. This is best evidenced by comparing the activation energies of the hydrocarbon immediately adjacent to the hydroxyl group in the ATT and SiO₂ nanotube coated ATT. The activation energy for hydrocarbon in the SiO₂ nanotube coated ATT is nearly five times larger than in ATT alone, which indicates that substantially restricted motion occurs.



Fig. 7. Arrhenius plot of the natural logarithm of the correlation times as a function of the inverse temperature. (a) carbon, and (b) hydrocarbon in the ATT and SiO_2 nanotube coated ATT.

4. Conclusions

Activation energy is a quantitative measure of rigidity, and the activation energies for each carbon were obtained from the correlation times as a function of the temperature. Molecular motions in the SiO_2 nanotube coated ATT have higher activation energies than in ATT alone. Higher activation energies indicate a higher rigidity for the polymer chains in the SiO_2 nanotube coated ATT sample. It is worth noting that the activation energy of the hydrocarbon in SiO_2 nanotube coated ATT is distinctly greater than that in ATT. This higher activation energy is associated with

strong bonding between hydroxyl group in ATT and the oxygen atoms attached to the Si for Q^3 or Q^4 type in SiO₂ nanotube.

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