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High Resolution Solid State NMR of $^{27}AlF_3$ Particles Observed by a Conventional Fourier-Transform Spectrometer[1)]

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In a AlF_3 colloidal dispersion, high resolution ^{27}Al NMR in solid is reported using a conventional Fourier-Transform NMR spectrometer. Five well resolved peaks are observed and the relative intensity of which strongly depends on the diameter of particles. Comparing the chemical shifts of these lines with the XPS data, the bonding between Al and F atoms in a small particle is less ionic than the bulk one.

Although high resolution NMR in solids is now very popular and instruments are available from commercial source, a special set up is needed for samples and sample tubes. It is not applicable to a system composed of solids and liquids even though often encountered in many supported catalytic systems nor to small amount of samples. We report here high resolution solid state NMR of $^{27}AlF_3$ particles dispersed in an organic liquid observed by a conventional Fourier-Transform(FT) spectrometer for liquid NMR and compare the result with that by a magic angle spinning(MAS) NMR spectrometer. The basic idea is that the Brownian motion of an ultrafine particle(UFP) in a liquid makes narrow the line width of NMR likewise in a molecular NMR. Hence this method may be called as "UFP NMR".

Let us estimate first the upper diameter of a particle in which the Brownian motion causes a narrowing of line width at the level of high resolution NMR. In AlF_3, a main contribution of dipole interaction comes from fluorine nuclei and the strength of the dipole field is about 15 kHz. Therefore the correlation time must be shorter than 70 μs at least in order to get a high resolution spectrum. With the use of Debye's theory of dielectric dispersion[2)] which correlates the rotational correlation time with a diameter(D) of a particle, we can calculate the critical diameter of a particle at which the rotational motion of particles averages the local field fluctuation and an anisotropy of chemical shift. Figure 1 shows relaxation time vs. D diagram in which I is the usual molecular NMR region, II the UFP NMR region and III the solid NMR region. Motional narrowing starts from a particle with D < 30 nm for

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AlF_3 solid and the diameter is within the target of the current technology of the production of UFP's.

Recently, we proposed general procedures to prepare ultrafine metal particles in liquids in which the sizes of particles can be controlled in the range from 1 to 100 nm.[3)] Though these procedures, the gas-flow cold trap method, the gas-flow solution trap method and the matrix isolation method were mainly applied to metal particles so far, they are also able to use for the formation of ionic UFP's. Briefly, AlF_3 from commercial source were heated on a Mo boat under the flow of 20 Torr Ar gas. Fine particles produced were collected by a liquid nitrogen cold trap with co-deposition of methanol. After warming at room temperature, transparent colloidal dispersion in methanol was obtained. The diameter of a deposited sample on a carbon film is distributed from 2 to 20 nm determined by transmission electron micrograph(TEM).

Solid state NMR of $^{27}AlF_3$ powdered sample was obtained by JEOL GX270 spectrometer equiped with a high resolution multinuclear probe for solid in MAS mode without the heterodecoupling. The spinning rate was 3 kHz. Figure 2a

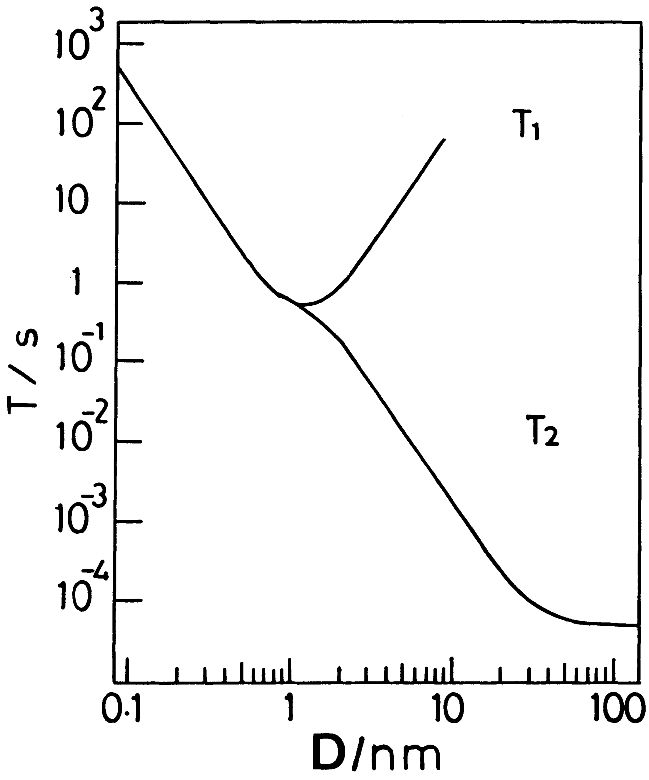

Fig. 1. Relaxation time as a function of particle diameter. The diagram is devided in three; the molecular, the UFP and the solid NMR reagions, respectively.

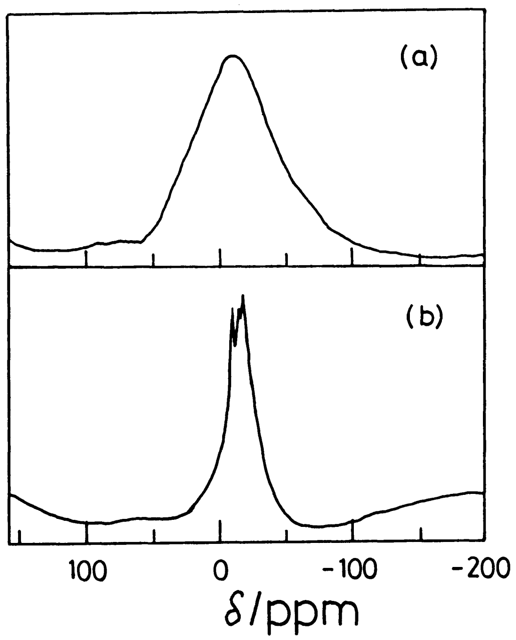

Fig. 2. a)MAS NMR of deposited $^{27}AlF_3$ UFP. Measurement conditions : 90° pulse, delay time 24.5 µs, interval time 500 ms, accumulation times, 10000, spinning rate 3 kHz. b) ^{27}Al NMR of colloidal solution of AlF_3 UFP. Measurement conditions: 10° pulse , delay time 25 µs, interval time 100 ms, accumulation times 25000.

shows the MAS NMR spectrum of a powdered sample. Dipole broadening by F nuclei is obvious in the figure. High resolution ^{27}Al NMR was obtained by a JEOL GX400 conventional FT spectrometer with the use of a 10 mm-diameter usual NMR tube with a 17 Hz spinning rate. The spectrum shows higher resolution than that by bulk solid samples as seen in Fig. 2b . We notice that there is splitting in a spectrum. Well separate spectrum is shown in Fig. 3a with a longer delay time condition which depressed the intensity of line 5 from the component of short relaxation time. Five peaks are seen in the figure. Upon application of ultra-filtration technique$^{4)}$ using a stirred cell, the sample particles were divided into three fractions corresponding to their sizes. Figure 3b to 3d show high resolution NMR spectra of these fractions. The spectrum from larger particles is shown in Fig. 3b where peaks 3(-8 ppm) and 5(-16 ppm) are present. From the X-ray diffraction of concentrated AlF$_3$ colloidal solution, the average diameter was about 9 nm coincided with that by the TEM observation. For smaller particles with diameter of ca. 2 nm, peak 5 disappears and new peaks 2(-5 ppm) and 4(-12 ppm) appear. It should be noted that the peak position does not shift but appears at a definite position when the size of particles changes. The component which passed through the membrane pore size 1 nm revealed exactly the same spectrum as those of Al ions in methanol and shown in Fig. 3d as peak 1(10 ppm). This fraction showed no light scattering upon irradiation of He-Ne laser indicating the entity of this component being complex ions. A very broad spectrum of Al ion may be due to quadrupole broadening of asymmetric complexes in methanol.

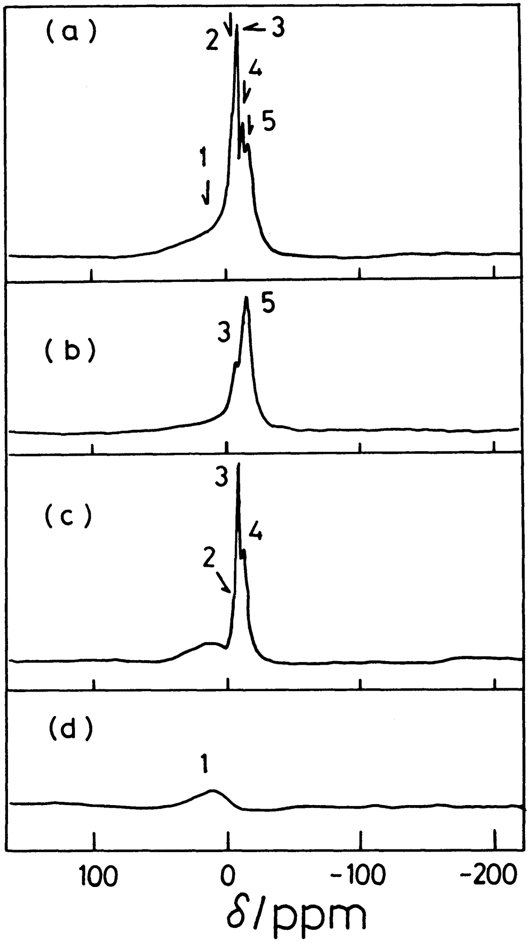

Fig. 3. High resolution ^{27}Al NMR of small AlF$_3$ particles dispersed in methanol. a) The same sample as in Fig. 2b but different pulse conditions : 45° pulse, delay time 200 μs, interval time 100 ms, accumulation times 5000. b) larger particle fraction. c)smaller fraction. d)smallest fraction (Al ion in methanol). Chemical shifts are quoted from Al(NO$_3$)$_3$ aqueous solution.

For smaller particles, the observed linewidth of peak 3 is plotted in Fig. 1. The deviation of the plot from the calculated line suggests that the quadrupole effect can not be neglected in this diameter. If we assume the difference of T$_2$ between the calculated value and the observed one being due to the quadrupole relaxation, quadrupole width can be given as 416 Hz for peak 3.

In order to determine the electronic state of particles, XPS measurements were done using deposited sample on a Ni sample holder. The Auger parameters of fluorine $KL_{23}L_{23}$ line of each fraction were 1339.55 eV, 1340.00 eV, and 1339.20 eV for Fig. 3b, 3c, and bulk sample respectively. The Auger parameter can be correlated to the ionicity of bond.$^{5)}$ The larger the ionicity, the smaller the parameter becomes. Hence XPS results indicate that AlF_3 small particles are less ionic than large particles. This is compatible with the calculation made on MgO ionic cluster in which the ionic charge is reduced in the order of volume, plane, edge and corner.$^{6)}$ It is apparent that the line position of ^{27}Al of small particles shifts to low field region indicating the nature of chemical bond being somewhat covalent in small particles completely consistent to XPS data. The assignment of peaks has not yet completed. Peak 1 comes from Al ion in solution. Tentatively, peak 5 (largest ionic shift) is ascribed to volume ion and other peaks may be correlated to the surface species.

The method proposed in this letter will open the wide application of high resolution NMR in solids for in situ measurement of catalytic reaction of suspended catalyst in solution and for the crystal growth/dissolution process from solution which are now in progress.

References

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