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^{27}Al MAS-NMR Study of Nanoporous Alumina

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Nanoporous alumina membranes differing in pore size (15, 18, and 25 nm diameter) and containing SO_2 by mass of 8.02%, 8.95%, and 11.14%, respectively, were mainly studied by solid state ^{27}MAS NMR. All of the samples showed three-peak spectra similar to alumina gels, showing the presence of 4- and 6-coordinated Al with an intermediate phase, presumably 5-coordinated Al. The relative proportions of ^{27}Al in the various sites were estimated by Lorentzian fitting of the spectra. The ratio of Al in octahedral site decreased at the expense of increasing occupancies for tetrahedral and intermediate (5-coordinated) sites. Nanoporous membrane containing SO_2 at highest content suggested the presence of tetrahedral Al and the intermediate (presumably 5-coordinate) Al to be present at a highest ratio, and this provided evidence that this membrane had the highly disordered structure.

Key words: alumina, nanoporous membrane,^{27}MAS NMR, tetrahedral Al, penta-coordinated Al

1. INTRODUCTION

With increasing concerns on health issues and environmental protection, air gas filters capable of removing particulates and sulfur from gases exhausted from furnaces and combustors are demanded [1]. From this point of view, filters made of ceramic materials are preferred in that gas with higher temperature can be reused. It is well-known that nanoporous alumina membranes having regularly arranged cylindrical hexagonal pores can be obtained by anodically oxidizing aluminum in oxalic acid, acetic acid, chromic acid, sulfuric acid, etc. [2]. Since the size of nanopores of this material is fully controllable by changing applied voltage and requires no vacuum chambers, nanoporous alumina membranes have attracted attention not only because of the applications to filters, but also to various fields such as catalyst supports, electronic devices, luminescent devices, biological applications, templates, and various other functional material systems [3].

The present authors have been characterizing anodic alumina membranes prepared by Inada et al. [4] by anodizing 5N purity aluminum foil in a sulfuric acid electrolyte. The present authors have made studies on the thermal change of the anodically prepared amorphous alumina, and found that this material undergoes distinguished features on forming crystalline phases and in the subsequent polymorphic phase transformations [7, 8]. By detailed study using TMA and dilatometry in combination with simultaneous TG-DTA/FTIR, it was confirmed that carbon retards the initiation of the kinetic reaction, i.e., dissociation of SO_2 at ca. 1210K. Furthermore, it was presumed that the transition temperature at ca. 1523K is influenced by the pore size, presumably due the critical crystallite (domain) size necessary to develop the stable α-Al_2O_3, since the transition temperature of the membranes shifted to higher side with increasing pore size [9].

However, the influence of sulfur was still questioned, since larger pore size meant higher sulfur concentration. Thus, the distribution of sulfur was investigated by mainly using XPS, and it was confirmed on the anodic alumina membrane having 25-nm diameter pores that sulfur was concentrated on the surface up to a depth of 10 nm from the surface [10].

Solid state ^{27}MAS NMR was used to determine the aluminum coordination in aluminum-oxygen compounds [11], and was found to be effective for studying amorphous and poorly crystalline aluminate phases [12-15]. It is known that Al-O in four-coordination yields chemical shift in a range of 60-80 ppm, and that chemical shift near 0 ppm (0-20 ppm) correspond to Al-O in octahedral coordination. However, the chemical shift in the intermediate range is still under discussion; it is generally believed that chemical shift about 30-50 ppm is assigned to a penta-coordinated intermediate phase [16], but it is also proposed that a so-called "tri-cluster" defect, i.e., three Al–O tetrahedral sharing one oxygen atom between them per molecular unit is also postulated [17].

Accordingly, the aim of the present invention is to evaluate the crystallinity of the nanoporous alumina membranes differing in pore size by mainly using solid-state ^{27}Al MAS NMR.

2. EXPERIMENTAL

2.1 Samples

Amorphous alumina membranes differing in pore size and wall thickness were obtained by anodizing aluminum in sulfuric acid electrolyte while changing the applied voltage to 15, 18, 25 V, as described previously [9]. Thus were prepared each of the alumina membranes with pore diameter of 15 nm (wall thickness=30 nm), 18 nm (36 nm), and 25 nm (50 nm). The SO_2 content by mass of the samples is 8.02%, 8.95%, and 11.14%, respectively. The samples were all decarbonated by bubbling gaseous nitrogen during anodization.

2.2 ^{27}Al MAS NMR spectroscopy

Magic Angle Spinning measurements were performed using JEOL ECP300W at a magnetic field of 7.06T, and the spectra acquired at 78.308MHz. Typically, 300000 transients were accumulated in each spectrum at a relaxation delay of 0.1s. Center peak of α-Al_2O_3 was used as the external standard. To identify the satellite bands, the sample was spun at 3.4 kHz and 5.1 kHz.

3. RESULTS AND DISCUSSION

Figure 1 shows the ^{27}Al MAS NMR spectra of 25-nm diameter nanoporous alumina membrane taken at 3.4 kHz and 5.1 kHz. Reference α-Al_2O_3 shows a single octahedral resonance set at 0 ppm, accompanied by the side bands. The 25-nm diameter sample shows a three-peak spectrum, typical of many aluminate gels [13,14]. The resonances at 65 ppm and 8 ppm correspond to tetrahedrally and octahderally coordinated aluminum respectively. The resonance at 36 ppm is generally assigned as penta-coordinated aluminum. However, because of the overlapping of the side bands, the spectrum obtained at 3.4-kHz spinning does not show the true intensity. The influence of the side bands can be excluded by spinning at 5.1 kHz, as shown by asterisks (*1 and *2) in the figure. After eliminating the influence of the side bands, the intensity of the peaks at the higher frequency side, i.e., those at

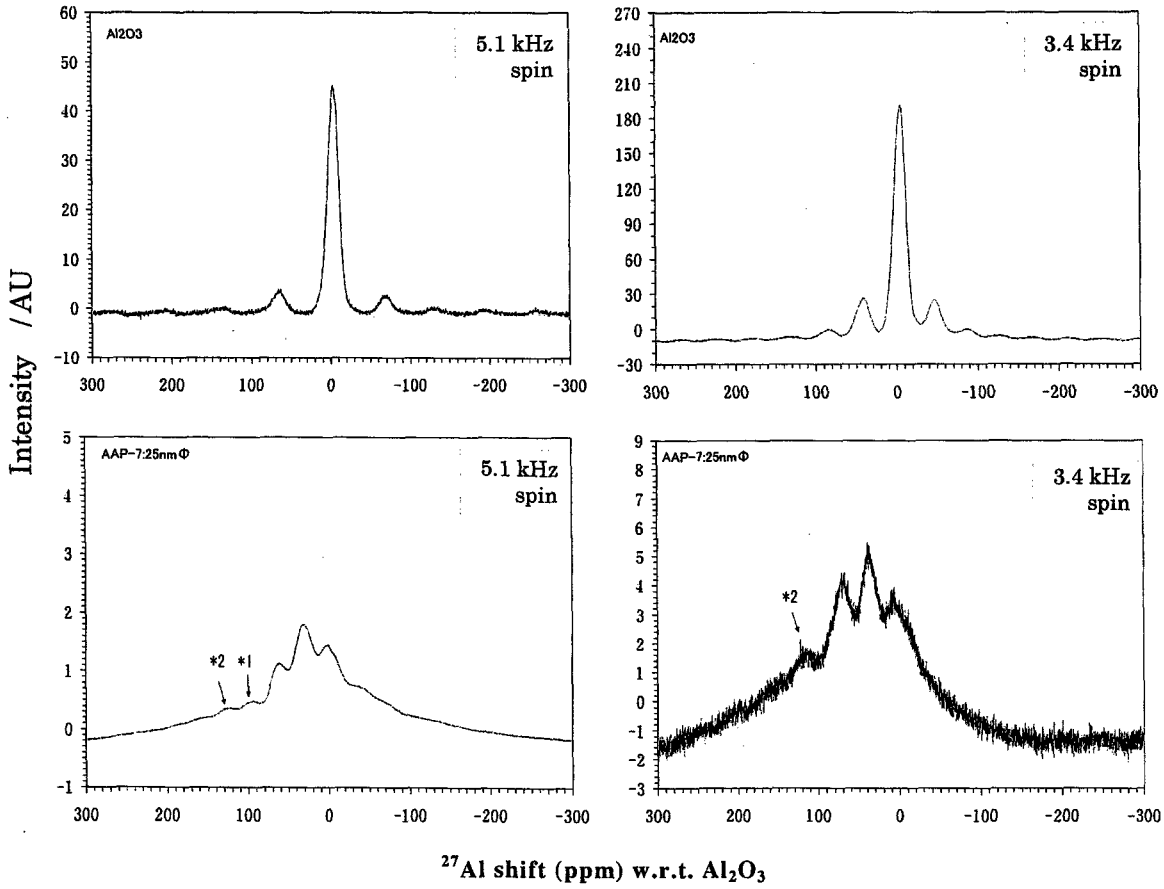

Fig. 1 ^{27}Al MAS NMR spectra of 25-nm diameter nonporous alumina membrane taken at 3.4 kHz and 5.1 kHz. An asterisk indicates the side band.

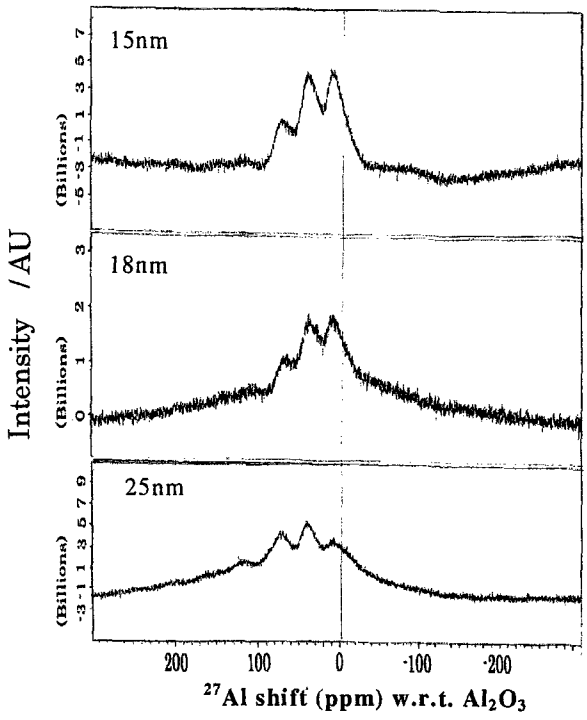

Fig. 2 ^{27}Al MAS NMR spectra of 25-nm diameter nonporous alumina membranes with pores sizes of 15, 18, and 25 nm diameter, spun at 3.1 kHz.

ca. 65 ppm and at ca. 8 ppm, is reduced to about 70% and to 92%, respectively.

Figure 2 shows the ^{27}Al MAS NMR spectra of nanoporous alumina membranes differing in pore size spun at 3.4 kHz. All of the samples show the three-peak spectra, however, the samples show different intensity ratios for the three peaks, and the resonance for the tetrahedral Al is shifted to a higher frequency side. Thus, semi-quantitative estimation of the relative proportions of ^{27}Al in the various sites was made by Lorentzian fitting of the curves after removing the side bands. Since pure α-Al_2O_3 is octahedrally coordinated, the presence of 4-coordinated and presumably 5-coordinated Al at higher proportions may provide evidence that anodic alumina membrane having 25-nm pores has the highest structural disordering. Furthermore, since the wall thickness changes directly with the pore size as shown in Table 1, the results can be related to wall thickness. The results are given in Table 1 and in Figure 3.

Table 1 Relative Ratio of ^{27}Al occupancies (Total ratio normalized to unity)

Pore diameter (nm)	Wall thick-ness (nm)	Coordination number		
		6	5 (Inter-mediate)	4
15	30	0.45	0.40	0.15
18	36	0.45	0.41	0.14
25	50	0.31	0.43	0.26

The plots are shown by regression curves at excellent fitting as follows:

(1) Octahedral Al occupancy ratio:
y=-0.0004x^2+0.0262x+0.0441 (R^2=1)
where y represents the relative occupancy ratio and x represents the wall thickness, and the same hereinafter;

(2) Tetrahedral Al occupancy ratio:
$y = 0.0004x^2 - 0.0297x + 0.637$ (R^2=1);

(3) 5-coordinated Al site ratio:
$y = 0.0035x + 0.3189$ (R^2=1);

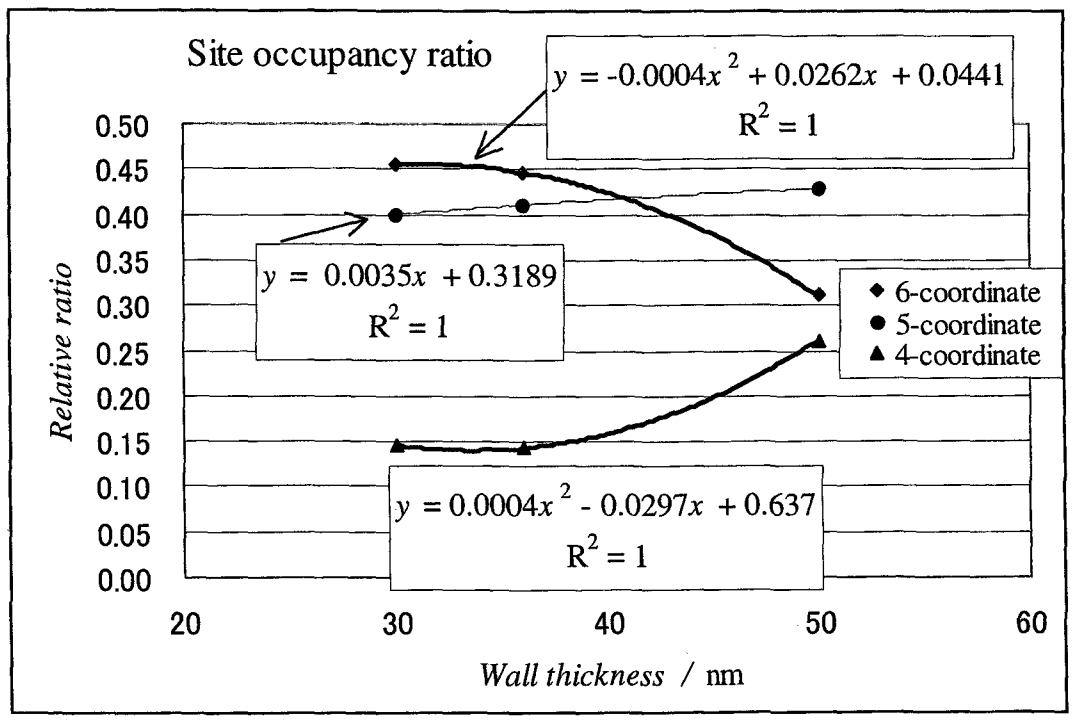

Fig. 3 Change in site occupancy ratios with changing wall thickness. The total ratio is normalized to unity.

From Figure 3, it can be understood that tetrahedral site and the intermediate site (or the penta-coordinated site) increases at the expense of octahedral site.

This can be explained by the critical size for forming α-Al_2O_3. There has been made extensive studies on the critical crystallite size for the development of α-Al_2O_3 [18,19], but it seems reasonable to accept a critical size of 17 nm [20]. Thus, in case of nanoporous alumina membranes having a pore size of 25 nm, the wall thickness is at least 50 nm. Taking the critical size as 17 nm, this thickness allows three crystallites to be accommodated in the wall. That is, even if one α-Al_2O_3 crystallite is developed along the pore, there is still place for other crystallites with high sulfur content to form as shown schematically in Figure 4. However, for alumina membranes having pore size of 15 nm or 18 nm, only one α-Al_2O_3 crystallite is accommodated around the cylindrical pore. Thus, for the alumina membrane with pores 15 nm or 18 nm in diameter, sulfur would be rather uniformly distributed to result in Al with same coordination. This is in conformity with our previous results obtained by TG-DTA, in which the 25-nm pored sample showed highest transition temperature.

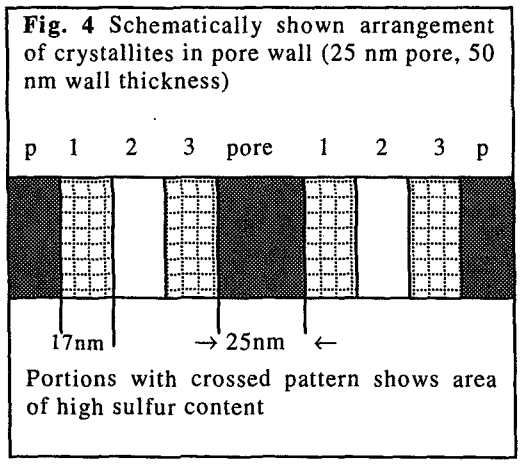

Fig. 4 Schematically shown arrangement of crystallites in pore wall (25 nm pore, 50 nm wall thickness)

Portions with crossed pattern shows area of high sulfur content

4. CONCLUSIONS

Nanoporous alumina membranes differing in pore size (15, 18, and 25 nm diameter) and containing SO_2 by mass of 8.02%, 8.95%, and 11.14%, respectively, were mainly studied by solid state ^{27}MAS NMR. All of the samples showed three-peak spectra similar to alumina gels, showing the presence of 4- and 6-coordinated Al with an intermediate phase, presumably 5-coordinated Al. The relative proportions of ^{27}Al in the various sites were estimated by Lorentzian fitting of the spectra. The ratio of Al in octahedral site decreased at the expense of increasing occupancies for tetrahedral and intermediate (5-coordinated) sites. Thus, nanoporous membrane with highest S content and with pore wall length of about 50 nm suggested tetrahedral Al and the intermediate (presumably 5-coordinate) Al to be present at a highest ratio, and this provided evidence that this membrane had the highly disordered structure.

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REFERENCES

[1] See, for example, Liu, K. Gao, Y. Riley, J T. Pan, W-P. Mehta, A K. Ho, K K. Smith, S R.,*Energy Fuels*, **15** (2001) 1173.
[2] R.C. Furneaux, W.G. Rigby and A.P. Davidson, *Nature*, **337** (1989) 147.
[3] See, for example, K. Kuroda, *Bull. Cer. Soc. Jpn.*, **36** (2001) 902 (In Japanese).
[4] T. Inada and T. Fukui, *Proc. 13th Korea-Japan Seminar on New Ceramics* (1996) 340
[7] R. Ozao, H. Yoshida, Y. Ichimura, T. Inada and M. Ochiai, *J. Therm. Anal. Cal.*, **64** (2001) 915.
[8] R. Ozao, M. Ochiai, H. Yoshida, Y. Ichimura and T. Inada, *J. Therm. Anal. Cal.*, **64**(2001) 923 .
[9] R. Ozao, H. Yoshida, T. Inada, M. Ochiai, *Trans. Materials Research Soc. Japan*, (2002).
[10] R. Ozao, H. Yoshida, T. Inada, *J. Therm. Anal. Cal.*, (2003).
[11] D. Muller, W.Gessner, H.-J.Behrens, G. Scheler, Chemical Physics Letters, **79** (1981) 59.
[12]K.J.D.MacKenzie, T. Kemmit, *Thermochim. Acta*, **325**(1999) 5.
[13] K.J.D.MacKenzie, T. Kemmit, *Thermochim. Acta*, **325**(1999) 13.
[14] K.J.D.MacKenzie, M. Schmucker, L. Mayer, *Thermochim. Acta*, **335**(1999) 73.
[15] K.J.D.MacKenzie, M. Schmucker, M.E. Smith, I.J.F. Poplett, T. Kemmit, *Thermochim. Acta*, **363**(2000) 181.
[16] A. Utsunomiya, K. Tanaka, H.Morikawa, F. Marumo, H. Kojima, *J. Solid State Chem.*, **75** (1988) 197.
[17] M. Schmucker, H. Schneider, *Ber. Bunsenges. Phys. Chem.***100** (1996)1550.
[18] B. Djuricic, S. Pickering, P. Glaude, D. Mcgarry, P. Tambuyser, *J. Mater. Sci.*, **32** (1997) 589.
[19] J. Ding, T. Tsuzuki, P.G. McCormick, *J. Amer. Ceram. Soc.*, **79** (1996) 2956.
[20] H-L. Wen, F-S. Yen, *J. Crystal Growth*, **208** (2000) 696.

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