

Structures of aluminum chloride grafted on silica surface

Satoshi Sato ^{a,*}, Gary E. Maciel ^b

^a Department of Applied Chemistry, Faculty of Engineering, Chiba University, Inage, Chiba 263, Japan

^b Department of Chemistry, Colorado State University, Ft. Collins, CO 80523, USA

Received 20 January 1995; accepted 28 March 1995

Abstract

The structures of silica-grafted aluminum chloride catalysts were investigated by solid-state NMR measurements, together with their catalytic properties in the alkylation of benzene with cyclohexene. Catalyst samples prepared by contacting aluminum trichloride vapor with a silica gel surface at temperatures between 140 and 250°C were found to be active for the alkylation, while other samples prepared at higher temperatures were inactive. The grafted aluminum chloride species were classified into two structural types, corresponding to monomeric and dimeric aluminum chloride. The combination of ²⁷Al and ²⁹Si NMR experiments elucidates important structural features of these aluminum chloride/silica systems. The active catalysts were found to have a dimeric aluminum chloride structure, with chemical shifts of 85 and 42 ppm in the ²⁷Al magic-angle spinning NMR spectra. Those peaks correspond to aluminum species coordinated to chloride and/or oxygen with coordination numbers of 4 and 5, respectively. It is speculated that the catalytically active species is the product of reaction of the aluminum trichloride dimer with one hydroxyl on the silica surface.

Keywords: ²⁷Al MAS NMR; AlCl₃; Solid acid

1. Introduction

Solid-state NMR spectroscopic techniques are among the most valuable methods for obtaining structural information on inorganic materials [1–7]. Crystalline solids such as silicate minerals and synthetic zeolites are well characterized by ²⁷Al and ²⁹Si NMR measurements [1,2]. These techniques are especially effective in studying the microstructures of amorphous solids such as aluminosilicates [3–5], silica gels [6], and alumina-supported silica [7]. In aluminosilicates, ²⁷Al chemical shifts are observed between 0 and 70 ppm, and provide information about the coordination numbers of aluminum atoms. 6-, 5-, and 4-

coordinate aluminum atoms have chemical shifts at around 0, 35, and 60 ppm, respectively [1,2,8–11]. ²⁷Al chemical shifts also vary with the types of ligands, as well as the coordination number of the aluminum species [12–18]. In chloroaluminates, the chemical shifts of 4-coordinate aluminum are observed in the frequency range higher than that observed in aluminosilicates. Although solid aluminum trichloride (Al₂Cl₆), which has an aluminum coordination number of 6, has a chemical shift of 0 ppm, Al₂Cl₆ has different coordination in the solution state. Al₂Cl₆ in toluene solution has 4-coordinate aluminum and shows a chemical shift of 91 ppm [12]. A complex of aluminum trichloride with tetrahydrofuran (AlCl₃–2THF) in CH₂Cl₂ solution shows 5 coor-

* Corresponding author.

dination and a chemical shift of 63 ppm [14]. Although solid-state ^{27}Al NMR spectra of samples which contain 6-, 5-, and 4-coordinate aluminum are complicated by spinning side bands at low spinning speed [9,10], high-speed magic-angle spinning (MAS) techniques that have been developed recently improve the quality of spectra for quadrupolar nuclides [11,19,20]. In addition, ^{29}Si cross-polarization (CP) MAS NMR techniques selectively enhance the signals of surface silanol groups of silicas because magnetization can be transferred from protons of hydroxyl groups to surface silicon atoms [6,21].

Aluminum trichloride is a well-known strong acid catalyst, and is widely used for various organic reactions. Several research groups have studied supported types of aluminum trichloride catalysts for alkane isomerization [22–25]. Since aluminum trichloride is readily sublimed and reacts with hydroxyl groups of a silica surface, Gates and coworkers prepared aluminum trichloride on support materials such as silica and a sulfonated polymer; the resulting materials were catalytically active for n-butane isomerization [22]. In the catalysis of benzene acylation by aluminum chloride molten salts, Boon et al. found that dimeric Al_2Cl_7^- ions were active species and that monomeric AlCl_4^- ions were not active [26]. Whereas some studies have been carried out on the structures of ionic chloroaluminate species in molten salts containing aluminum trichloride [15–18,26], little research has been done on structures of aluminum chloride grafted onto support materials. Melchor et al. proposed a Al-O-AlCl_2 structure, based on the reaction of AlCl_3 with surface hydroxyl groups on alumina for an alumina-grafted AlCl_3 sample [23]. Getty and Drago reported both ^{27}Al and ^{29}Si NMR spectra of silica-supported aluminum chloride prepared by reacting aluminum trichloride with a silica dispersed in refluxing carbon tetrachloride [25], and they concluded that the aluminum chloride species had 4-coordinate aluminum with composition Si-O-AlCl_2 .

In this paper, we report the investigation of the structures of silica-grafted aluminum chloride sys-

tems by use of solid-state NMR measurements, together with their catalytic activities for the alkylation of benzene with cyclohexene. The grafted type solid acids were prepared by contacting aluminum trichloride vapor with a silica surface at various temperatures. It was found that the catalytic activities of the grafted aluminum chloride vary with the temperature of sample preparation: samples prepared at lower temperatures (below 250°C) exhibited high catalytic efficiencies for the alkylation of benzene with cyclohexene. Since both the aluminum chloride contents and their catalytic activities varied with the preparation temperature, we applied both ^{27}Al MAS NMR and ^{29}Si cross-polarization (CP) MAS NMR to the study of the silica-supported aluminum trichloride catalysts in order to clarify the surface structures of these catalyst systems.

2. Experimental

2.1. Catalyst preparation

A silica gel with a specific surface area of $460\text{ m}^2/\text{g}$ and a pore volume of 0.80 ml/g (B-type supplied by Fuji Davison Ltd.) was used as the catalyst support. A commercial silica-alumina with a specific surface area of $420\text{ m}^2/\text{g}$ and a pore volume of 0.47 ml/g (N631-L supplied by Nikki Chemical Co., Ltd.) was used.

A catalyst sample was prepared by contacting aluminum trichloride vapor with the support material in a Pyrex tube reactor under nitrogen flow conditions at a prescribed temperature, while the flow rate of nitrogen was 120 mmol/h . Prior to the aluminum trichloride charge, the support was preheated under the same conditions for 1 h. The aluminum trichloride vapor, together with the nitrogen carrier gas, was introduced for 1 h by sublimation of aluminum trichloride ($0.05\text{--}0.8\text{ g}$), which was charged into the upper part of the support material (0.5 g).

Hydrogen chloride produced during a reaction of aluminum trichloride vapor with hydroxyl groups of the silica support was collected by bub-

bling the flowing gas through a sodium hydroxide solution; the HCl generated was measured by titrating the NaOH solution with hydrochloric acid. The aluminum chloride loading ($\text{g} \cdot \text{g} \cdot \text{support}^{-1}$) was determined by measuring the increase in weight after the grafting procedure. After a prepared catalyst sample was immersed in an aqueous solution, the chlorine content of the catalyst was determined as HCl by titrating the resulting solution with a sodium hydroxide solution.

2.2. NMR measurements

^{27}Al magic-angle spinning (MAS) NMR spectra were recorded at 156.34 MHz on a Bruker AM-600 multinuclear spectrometer, with a MAS speed of 15 kHz. Samples were handled in a glove box, and loaded in hand-made spinners with a sample volume of 0.022 cm^3 . Since every catalyst sample readily adsorbs water, each sample filled spinner was sealed with a sealing tape made of polytetrafluoroethylene to prevent water vapor from invading the inside of the spinner. Recovery times of 0.1 s were allowed between the $0.5 \mu\text{s}$ pulses, which correspond to a 10° tip, and 150000 free induction decays (FID) were accumulated per spectrum. ^{27}Al NMR chemical shifts (in ppm) reported in this article are referenced to a 1.0 M aqueous $\text{Al}(\text{H}_2\text{O})_6^{3+}$ solution used as an external standard; higher values correspond to lower shieldings.

^{29}Si NMR spectra were obtained at 51.154 MHz on a Chemagnetics M-260S multinuclear spectrometer under the conditions of ^1H -to- ^{29}Si cross polarization (CP), MAS, and ^1H decoupling. Signals were accumulated with a CP contact time of 10 ms, and repetition delay times of 1.0 s. Samples were loaded in a 0.50-cm^3 'bullet' spinner in a glove box. The sample was rotated at a rate of 3 kHz during measurement. ^{29}Si chemical shifts are referenced to liquid tetramethylsilane (TMS).

2.3. Catalytic tests

The alkylation of benzene with cyclohexene was carried out at room temperature in a micro-

batch reactor with ultrasonic vibration. A freshly prepared catalyst sample (0.5 g) was added to a solution of benzene and cyclohexene with a composition of 110 and 10 mmol, respectively. The reaction products were analyzed by a gas chromatograph using a column of PEG-HT (1 m). For active catalysts, which attained a cyclohexene conversion of 100%, catalytic tests were repeated by adding another solution of benzene and cyclohexene to the recovered catalyst samples. Similarly, a third run was done when the second run was finished. The catalytic efficiency was evaluated by both the consumption of cyclohexene and amount of cyclohexylbenzene produced.

The skeletal isomerization of n-hexane was performed at 25°C in a microbatch reactor. A freshly prepared catalyst sample (0.5 g) was added to a solution of n-hexane (80 mmol). The reaction products were collected periodically and analyzed by a gas chromatograph using a column of benzyl ether 25% on Uniport C (2 m).

3. Results and discussion

3.1. Catalyst preparation

Fig. 1 shows the relation between the aluminum chloride (Al_2Cl_x) loading (determined gravimetrically) and the amount of aluminum trichloride charged at 200°C . The broken line in Fig. 1

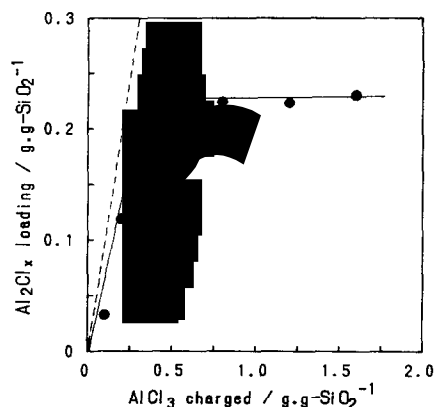


Fig. 1. Change in aluminum chloride loading with aluminum trichloride charged. The indicated amount of aluminum chloride was contacted with 0.5 g of silica gel at 200°C .

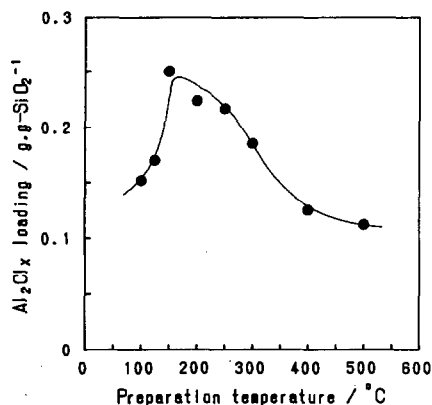


Fig. 2. Change in the saturation aluminum chloride loading with preparation temperature. Aluminum trichloride (0.4 g) was contacted with 0.5 g of silica.

expresses the maximum loading of aluminum trichloride that could in principle result for each amount of aluminum trichloride charged. The Al_2Cl_x loading increased linearly with increasing amount of aluminum trichloride charged for low loading levels, but was saturated at a loading of $0.25 \text{ g} \cdot \text{g-silica}^{-1}$.

Fig. 2 shows the change in saturation Al_2Cl_x loading with preparation temperature. The saturation Al_2Cl_x loading has a maximum at a preparation temperature of 150°C . The saturation loading was not so high at 130°C because the rate of sublimation was too slow below 140°C . The saturation loading obtained at 150°C was about twice as large as that at 500°C . Since hydrogen chloride was produced during the grafting proce-

Table 1
Contents of chlorine and aluminum in different catalysts

Preparation conditions		Cl^- remaining on support (A)	HCl produced (B)	x in Al_2Cl_x ^a	Aluminum content ^b mmol/g
Pre-treatment (°C)	Grafting (°C)	mmol/g	mmol/g		
400	400	2.75	1.49	3.9	1.35
300	300	4.01	2.19	3.9	1.90
150	150	5.50	1.99	4.4	2.38
300	150	5.34	1.45	4.7	2.20
400	150	5.17	0.98	5.0	1.91

^a Al_2Cl_x is grafted aluminum chloride, and a value x was calculated from the values of A and B after $A + B$ was normalized to 6.

^b This value was calculated from both a molecular weight estimated by use of the ratio A:B and the weight increase of the support after aluminum chloride deposition, as shown in Fig. 2.

ure, the value of x in the molecular formula of Al_2Cl_x grafted should be less than 6.

In order to determine the chemical composition of a silica-grafted Al_2Cl_x , both the chlorine content of the catalyst and the amount of hydrogen chloride produced were measured. The x value was determined by the ratio of the chlorine content of the catalyst to the amount of hydrogen chloride produced⁻¹ and the aluminum content ($\text{mmol} \cdot \text{g-support}^{-1}$) was calculated from the Al_2Cl_x loading ($\text{g} \cdot \text{g-support}^{-1}$) divided by the formula weight of Al_2Cl_x . The results are summarized in Table 1. The molecular formula of the grafted Al_2Cl_x was found to vary with the preparation temperature. Samples prepared at high temperatures of 300 and 400°C had a formula of $\text{Al}_2\text{Cl}_{3.9}$. This means that the grafted aluminum chloride is monomeric in the form of AlCl_2 . In contrast, when samples were prepared at 150°C , they had Al_2Cl_x formulas that varied with the pretreatment temperature of the silica prior to grafting in this case; the value of x was found to increase from 4.4 to 5 with increasing pretreatment temperature. This range corresponds to mixtures of AlCl_2 and Al_2Cl_5 , a situation that will be discussed later (in connection with Fig. 7). It has been reported that aluminum trichloride vapor consists mainly of dimeric Al_2Cl_6 molecules at 200°C , and that the portion of AlCl_3 monomers increases with increasing temperature or decreasing pressure, with the monomers predominating at temperatures above 750°C [27]. We can, thus, expect the surface Al_2Cl_x species to be of the two types, Al_2Cl_5 and AlCl_2 .

3.2. Catalytic activities of aluminum chloride grafted on silica

Fig. 3 shows a typical progress in catalytic alkylation of benzene by cyclohexene, using a silica-grafted aluminum chloride catalyst prepared at 200°C . Since cyclohexene was rapidly consumed during the first catalytic run (top left), the second run was done by adding recovered catalyst to another reaction mixture of benzene and cyclohexene. Although the second run (middle

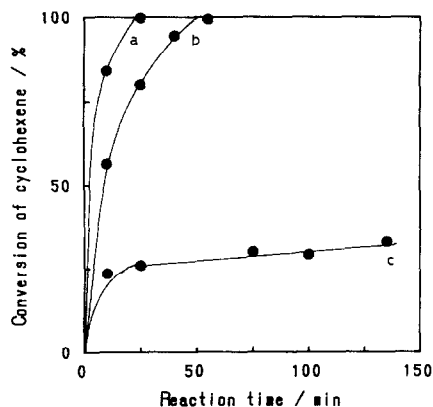


Fig. 3. Change in cyclohexene consumption in benzene alkylation on silica-grafted aluminum chloride with reaction time. A catalyst sample (0.5 g) was prepared at 150°C, and added to a solution of benzene (110 mmol) and cyclohexene (10 mmol). Top left, first run; Middle, second run; Bottom, third run.

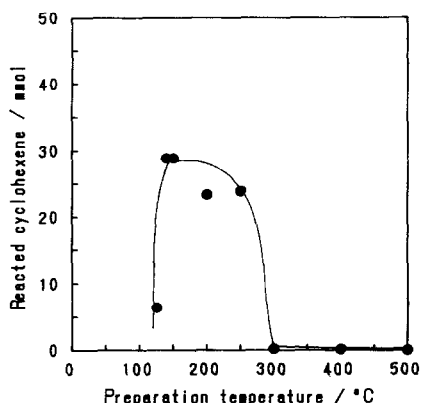


Fig. 4. Relation between catalytic activity for benzene alkylation by cyclohexene and catalyst preparation temperature. A sample containing 0.5 g of silica was used as the catalyst for the reaction at room temperature.

plot) was completed, the third run was not complete because of deactivation of the catalyst (bottom). The total amount of cyclohexylbenzene produced was used as the basis for the evaluation of catalytic activity for the alkylation reaction. This silica-grafted aluminum chloride sample catalyzed the alkylation reaction, and produced more than 30 cyclohexylbenzene molecules per aluminum atom.

Fig. 4 shows the relation between the catalyst preparation temperature and the total amount of cyclohexylbenzene produced. One sees that the silica-grafted aluminum chloride prepared at temperatures lower than 250°C worked catalytically, whereas the catalysts prepared at temperatures

higher than 250°C were much less active, producing less than one product molecule per aluminum atom. Similar results were obtained for the skeletal isomerization of *n*-hexane: the catalyst prepared at 200°C catalyzed the isomerization reaction at a rate of 0.36 mmol·g-catalyst⁻¹·h⁻¹ at 27°C, whereas the catalyst prepared at 500°C was inactive. Thus, the two types of grafted aluminum chloride species, Al₂Cl₅ and AlCl₂, have different catalytic activities.

3.3. ²⁷Al NMR spectra of catalysts

Fig. 5 shows ²⁷Al MAS NMR spectra of the silica-grafted AlCl₂ catalyst prepared at 300°C. This spectrum has three main peaks, at 2, 36, and 65 ppm (Fig. 5-a). When the sample was exposed to air for 4 h, intensities of the peaks at 36 and 65 ppm decreased, and the intensity of the peak at 2 ppm increased (Fig. 5-b). The peak at 2 ppm is due to 6-coordinate aluminum species. The peaks at 36 and 65 ppm changed into the peak at 2 ppm after 48 h of exposure to air (Fig. 5-c). This indicates that water molecules are readily chemisorbed to 4- or 5-coordinate aluminum species,

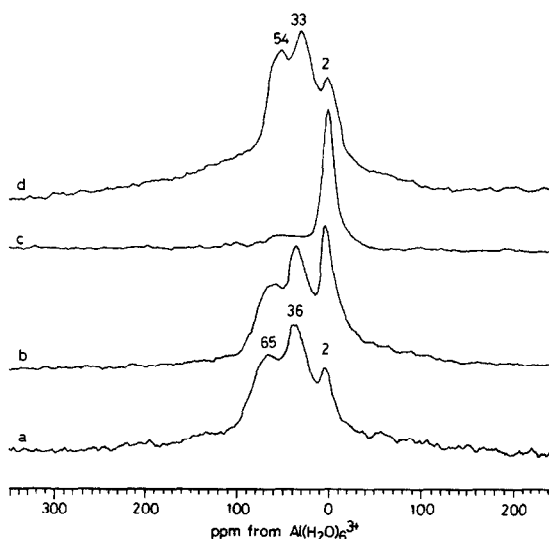


Fig. 5. ²⁷Al MAS NMR spectra of silica-grafted aluminum chloride prepared at 300°C. a: the sample was sealed with sealing tape; b: exposed to air without sealing tape for 4 h, c: for 48 h, d: sample 'a' hydrolyzed by contacting water vapor (180 mmol·g-sample⁻¹) at 500°C for 1 h.

and that all aluminum species are thereby changed into 6-coordinate aluminum.

Fig. 5-d exhibits the ^{27}Al MAS-NMR spectrum of the silica-grafted aluminum chloride sample after hydrolysis. The hydrolyzed sample displayed 3 chemical shifts, around 2, 33, and 54 ppm. In aluminosilicates, 4-coordinate aluminum atoms have ^{27}Al chemical shifts at around 60 ppm, while 6-coordinate species appear around 0 ppm [1,2]. In addition, 5-coordinated aluminum has been found at about 35 ppm in several alkoxides [8] and minerals [9–11]. The 3 peaks at 2, 33, and 54 ppm of the hydrolyzed sample (Fig. 5-d) are assigned to aluminum species coordinated with 6, 5, and 4 oxygen atoms, respectively. The 4-coordinate and possibly the 5-coordinate aluminum peaks are different from those of the samples before hydrolysis: this treatment moves the chemical shifts to lower frequency (higher shielding) when chlorine ligands are exchanged with hydroxyl groups. This indicates that the coordination numbers of aluminum atoms grafted onto silica are retained after hydrolysis, and that the aluminum species are dispersed atomically on the surface. Thus, the peak at 2 ppm in Fig. 5-a and b is due to aluminum species coordinated with 6 chlorine and oxygen atoms, including water molecules, and the peaks at 65 and 36 ppm are 4- and 5-coordinate species, respectively. The peak at 65 ppm is considered to be due to aluminum species coordinated either with 2 chlorines and 2 oxygens or with 3 chlorines and one oxygen atom. Since one hydrogen chloride molecule is produced during the reaction of each silanol with aluminum trichloride, the results shown in Table 1 indicate that the peak at 65 ppm is due to aluminum species coordinated with 2 chlorines and 2 oxygen atoms, which is expressed here as $\text{Al}(\text{2Cl},\text{2O})$. The peak at 36 ppm is due to aluminum species coordinated with 2 chlorines and 3 oxygen atoms, expressed as $\text{Al}(\text{2Cl},\text{3O})$.

Fig. 6 shows ^{27}Al MAS-NMR spectra of silica-grafted aluminum chloride samples prepared at different temperatures. The spectrum of silica-grafted AlCl_2 catalyst prepared at 300°C has 3 peaks, at 2, 36, and 65 ppm, as shown in Fig. 6-b,

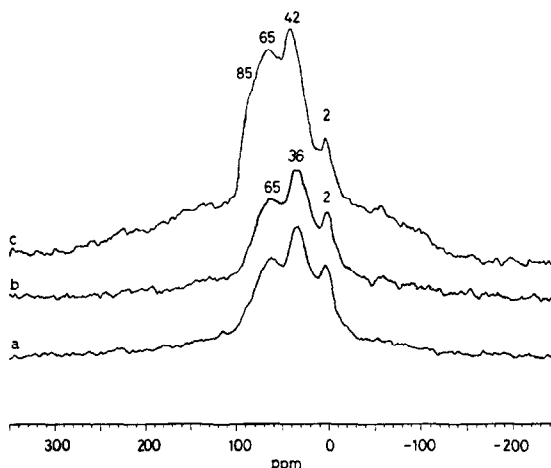


Fig. 6. ^{27}Al MAS-NMR spectra of silica-grafted aluminum chloride samples prepared at different temperatures; prepared at a: 500°C; b: 300°C; c: 150°C.

which is the same as Fig. 5-a. The spectrum of a catalyst prepared at 500°C also has 3 peaks at 2, 36, and 65 ppm (Fig. 6-a), and is essentially the same as that prepared at 300°C (Fig. 6-b).

Fig. 6-c shows the spectrum of the silica-grafted $\text{Al}_2\text{Cl}_{4.4}$ sample prepared at 150°C; this spectrum is different from those discussed above for Fig. 6-a and Fig. 6-b. It has an additional shoulder at 85 ppm, along with the 3 peaks at 2, 42, and 65 ppm. The chemical shifts at 2, 42, and 65 ppm correspond with 6-, 5-, and 4-coordinate aluminum species, respectively. The shoulder at 85 ppm is due to the presence of aluminum species coordinated with 4 chlorine atoms, expressed here as $\text{Al}(\text{4Cl})$; 4-coordinate aluminum in Al_2Cl_6 in solution shows chemical shifts between 83 and 98 ppm [12]. The peak at 65 ppm is due to the resonance of 4-coordinate aluminum species of the type $\text{Al}(\text{2Cl},\text{2O})$. The peak at 42 ppm, which is due to 5-coordinated aluminum is, however, different from the peak at 36 ppm in Fig. 6-a and b. The difference is due to different numbers of chlorine atoms coordinated to each aluminum: the peak at 42 ppm is due to aluminum species coordinated with 3 chlorines and 2 oxygens, expressed as $\text{Al}(\text{3Cl},\text{2O})$, whereas the peak at 36 ppm is due to aluminum species coordinated with 2 chlorines and 3 oxygens, $\text{Al}(\text{2Cl},\text{3O})$. Although Getty and Drago obtained ^{27}Al chemical shifts at 55 and 65

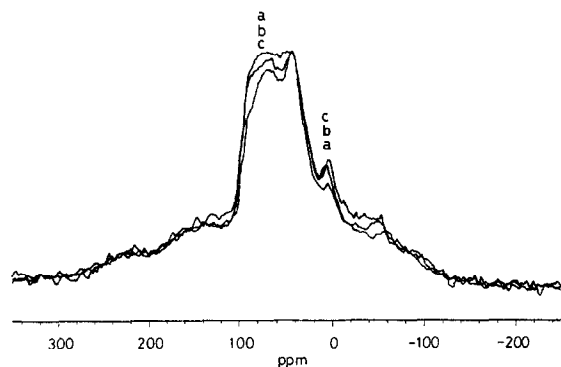


Fig. 7. ^{27}Al MAS NMR spectra of silica-grafted aluminum chloride preheated at different temperatures prior to grafting at 150°C : a: preheated at 500°C ; b: 400°C ; c: 150°C .

ppm in a spectrum of a sample of aluminum chloride reacted with silica in carbon tetrachloride solvent, they concluded that those peaks were due to 4-coordinate aluminum. However, we show here that the 5-coordinated aluminum chemical shifts are at 42 and 36 ppm. Furthermore, after the sample prepared at 150°C (Fig. 6-c) had been evacuated at 500°C , the spectrum of the resulting sample was the same as that of a sample prepared at 500°C (Fig. 6-a). This indicates that at 500°C the Al_2Cl_5 species changes into AlCl_2 species by evolving AlCl_3 . These results are in good harmony with the results shown in Fig. 4, because the 500°C -evacuated sample lost its catalytic activities.

Fig. 7 shows ^{27}Al MAS NMR spectra of samples of aluminum chloride grafted onto silica that had been preheated at one of three different temperatures prior to grafting at 150°C . Since aluminum chloride was grafted at 150°C , each sample has the chemical shifts at 2, 42, 65 and 85 ppm. The three spectra, however, are slightly different from each other in terms of the intensities of the peaks: the intensity of the peak at 85 ppm increased with the pretreatment temperature, and the intensity of the 2 ppm peak decreased. Because the ^{27}Al NMR spectrum of the sample pretreated at 500°C (Fig. 7-a) is dominated by peaks at 42 and 85 ppm, it consists mainly of aluminum chloride species of the Al_2Cl_5 type, as shown in Table 1. It was reported that the surface OH density of silica dried at 150°C is 4.5 nm^{-1} , and is 2

nm^{-1} for silica dried at 500°C [28]. On the other hand, for the sample pretreated at 150°C , having a formula of $\text{Al}_2\text{Cl}_{4.4}$ (Table 1), the dimeric Al_2Cl_5 species will react with another hydroxyl group because of the high surface OH density, and produce a moiety of the Al_2Cl_4 type, which is bonded with two oxygen atoms of the silica surface. The Al_2Cl_4 species has two 5-coordinate aluminum atoms of the type $\text{Al}(\text{3Cl},2\text{O})$, with a chemical shift of 42 ppm. Because the sample pretreated at 150°C has no signal with a chemical shift at 36 ppm, corresponding to $\text{Al}(\text{2Cl},3\text{O})$, the Al_2Cl_4 species does not dissociate to monomeric species. Thus, we speculate that the formula $\text{Al}_2\text{Cl}_{4.4}$ corresponds to a mixture of Al_2Cl_5 and Al_2Cl_4 .

Fig. 8 exhibits ^{27}Al MAS NMR spectra of aluminum chloride grafted onto a commercial silica–alumina. The commercial silica–alumina originally had both 6- and 4-coordinate aluminum, at 2 and 55 ppm, respectively (Fig. 8-a). The ^{27}Al NMR spectrum of a sample of aluminum chloride grafted onto the silica–alumina at 150°C has broad peaks that appear to be centered around 0, 36, 74, and 85 ppm (Fig. 8-b). This ^{27}Al NMR spectrum was changed by exposure to moisture: the broad signals attributed to aluminum chloride (36, 74, and 85 ppm) decreased with the exposure time and the 6-coordinate aluminum peak increased at

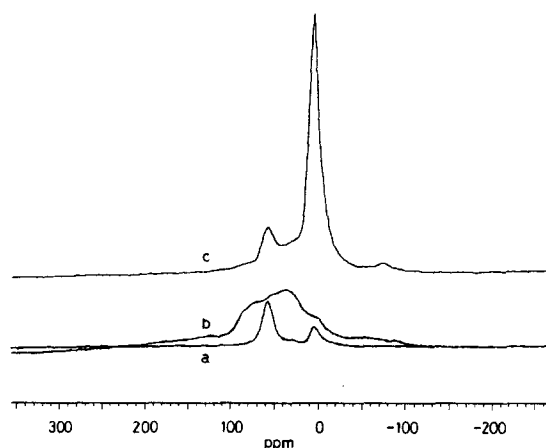


Fig. 8. ^{27}Al MAS NMR spectra of aluminum chloride grafted on commercial silica–alumina at 150°C : a: commercial silica–alumina; b: aluminum chloride grafted at 150°C ; c: sample 'b' exposed to moisture for 21 h.

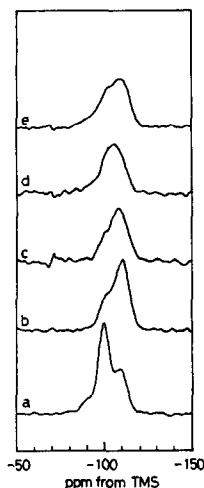


Fig. 9. ^{29}Si CP-MAS NMR spectra of silica-grafted aluminum chloride. a: silica gel heated at 150°C , 4000 scans; b: grafted aluminum chloride, preheated at 150°C , grafted at 150°C , 8000 scans; c: preheated at 500°C , grafted at 150°C , 20000 scans; d: preheated at 600°C , grafted at 150°C , 60000 scans; e: preheated at 500°C , grafted at 500°C , 20000 scans.

2 ppm, while the original silica–alumina peak due to 4-coordinate aluminum returned at 55 ppm. Thus, chloroaluminate species grafted onto silica–alumina were observed at 36, 74, and 85 ppm, as was observed on the silica support, as shown in Fig. 5, Fig. 6 and Fig. 7.

3.4. ^{29}Si NMR spectra of catalysts

Fig. 9 shows ^{29}Si CP-MAS NMR spectra of aluminum chloride grafted onto silica, together with that of the silica support. The silica gel used as a support has three chemical shifts at -90 , -100 , and -110 ppm (Fig. 9-a). The largest peak at -100 ppm is attributed to the silicons of single silanols, while those of geminal silanols and silicate species are observed at -90 and -110 ppm, respectively [6,21]. The relative intensity

of the single silanol peak at -100 ppm was decreased by grafting aluminum chloride onto the silica surface (Fig. 9-b, c, and d); and another chemical shift was observed in Fig. 9-c, d, and e, at -105 ppm. The chemical shift at -105 ppm is due to silicon which is coordinated with an aluminate and three SiO_4 units. This indicates that Si–O–Al bonds are formed through the reaction of surface silanol groups with aluminum trichloride vapor.

3.5. Structures of grafted aluminum chloride

The structures of catalytically active species are reported to be monomeric for grafted aluminum chloride [23–25]. Melchor et al. proposed an Al–O–AlCl₂ structure for an alumina-grafted AlCl₃ sample [23]. A monomeric aluminum structure of this general type seems possible because the sample was treated at 300°C . We agree with the predominance of monomeric species in samples prepared at high temperatures, i.e., above 250°C ; however, we disagree with the coordination number indicated for this type of structure. Getty and Drago speculated that the active species of silica-grafted aluminum chloride has 4-coordinate Al, with the composition Si–O–AlCl₂ [24,25]. They dried the silica sample at 80°C before refluxing the sample in an AlCl₃–CCl₄ solution. They may have overestimated the amount of hydrogen chloride produced by reaction with surface silanols because of residual water. We derived the AlCl_{2.2} structure even when the silica sample was dried at 150°C , as shown in Table 1.

In Fig. 10 we summarize the structures of aluminum chloride grafted onto the silica surface, as indicated by the data of this study. Numbers in the

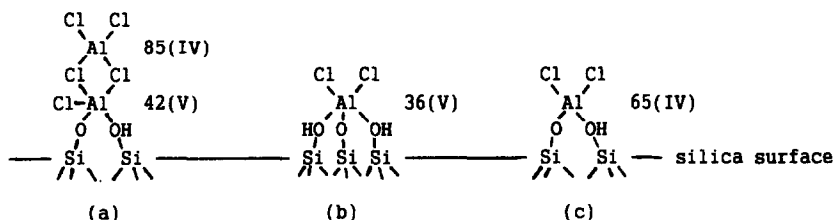


Fig. 10. Microstructures of silica-grafted aluminum chloride indicated by the results of this study. Numbers denote expected ^{27}Al chemical shifts (ppm), and Greek numbers are coordination numbers. a: dimeric species; b and c, monomeric species.

figure denote the value predicted for the ^{27}Al chemical shifts (in ppm), and the Greek numbers in parentheses show the corresponding coordination numbers. Fig. 10-a shows a dimeric Al_2Cl_5 moiety that is bonded to the silica surface through a Si–O–Al bond and coordinated to another oxygen of a hydroxyl group. This kind of structure has the following possible values of ^{27}Al chemical shifts: a chemical shift of 85 ppm for an aluminum atom which has four coordinated chlorines, $\text{Al}(4\text{Cl})$; a chemical shift of 42 ppm for an aluminum atom which has three coordinated chlorines and two oxygens, $\text{Al}(3\text{Cl},2\text{O})$. Fig. 10-b and c show monomeric AlCl_2 species with aluminum bonded to the silica surface through Si–O–Al bonds and coordinated to one or two other oxygens of hydroxyl groups. A five-coordinate aluminum atom of the type, $\text{Al}(2\text{Cl},3\text{O})$, shows a chemical shift of 36 ppm (Fig. 10-b); and a four-coordinate aluminum atom of the $\text{Al}(2\text{Cl},2\text{O})$ type has a chemical shift of 65 ppm (Fig. 10-c).

We speculate that the nature of strong acidic behavior is due to sites in which a proton of a silanol group is coordinated to aluminum atom, as depicted in the dimeric structure in Fig. 10-a. A significant difference between the dimeric Al_2Cl_5 and monomeric AlCl_2 species is the presence of a four-coordinate AlCl_4 group in the dimeric species. The AlCl_4 group has a strong electron withdrawing character, and hence a proton eliminated from a silanol group adjacent to the Al_2Cl_5 is stabilized by the delocalization of a residual electron which results from electron transfer from the silanol oxygen to the adjacent Al_2Cl_5 .

Acknowledgements

We thank Professor F. Nozaki and Associate Professor T. Sodesawa, Chiba University, for valuable discussions and thank Mr. Y. Nakazato and Miss Y. Kitahara, Chiba University, for preparing catalyst samples and measuring catalytic activities. We also thank Dr. S. F. Dec and Mrs. C. Liu, Colorado State University, for assisting in the NMR measurements.

References

- [1] J.M. Thomas and J. Klinowski, *Adv. Catal.*, 33 (1985) 199.
- [2] G. Engelhardt and D. Michel, *High-Resolution Solid-State NMR of Silicates and Zeolites*, John Wiley & Sons, New York, 1987.
- [3] D. Müller, P. Starke, M. Jank, K.P. Wendlandt, H. Bremer and G. Scheler, *Z. Anorg. Allg. Chem.*, 517 (1984) 167.
- [4] L.B. Welsh, J.P. Gilson and M.J. Gattuso, *Appl. Catal.*, 15 (1985) 327.
- [5] S. Komarneni, R. Roy, C.A. Fyfe, G.J. Kennedy and H. Strobl, *J. Am. Ceram. Soc.*, 69 (1986) C42.
- [6] G.E. Maciel and D.W. Sindorf, *J. Am. Chem. Soc.*, 102 (1980) 7606.
- [7] S. Sato, T. Sodesawa, F. Nozaki and H. Shoji, *J. Mol. Catal.*, 66 (1991) 343.
- [8] O. Kriz, B. Casensky, A. Lycka, J. Fusek and S. Hermanek, *J. Magn. Reson.*, 60 (1984) 375.
- [9] M.C. Cruickshank, L.S.D. Glasser, S.A.I. Barri and I.J.F. Poplett, *J. Chem. Soc., Chem. Commun.*, (1986) 23.
- [10] L.B. Alemany and G.W. Kirker, *J. Am. Chem. Soc.*, 108 (1986) 6158.
- [11] L.F. Nazar, G. Fu and A.D. Bain, *J. Chem. Soc., Chem. Commun.*, (1992) 251.
- [12] P. Laszlo, *NMR of Newly Accessible Nuclei*, Vol. 2, Academic Press, New York, 1983.
- [13] H. Haraguchi and S. Fujiwara, *J. Phys. Chem.*, 73 (1969) 3467.
- [14] J. Derouault, P. Granger and M.T. Forel, *Inorg. Chem.*, 16 (1977) 3214.
- [15] J.L. Gray and G.E. Maciel, *J. Am. Chem. Soc.*, 103 (1981) 7147.
- [16] K. Ichikawa and T. Matsumoto, *J. Magn. Reson.*, 63 (1985) 445.
- [17] K. Ichikawa, T. Jin and T. Matsumoto, *J. Chem. Soc., Faraday Trans. 1*, 85 (1989) 175.
- [18] Y. Chauvin, F.D.M. Tiggelen and H. Olivier, *J. Chem. Soc., Dalton Trans.*, (1993) 1009.
- [19] S.F. Dec and G.E. Maciel, *J. Magn. Reson.*, 87 (1990) 153.
- [20] S. Hayashi, T. Ueda, K. Hayamizu and E. Akiba, *J. Phys. Chem.*, 96 (1992) 10922.
- [21] I.S. Chuang, D.R. Kinney, C.E. Bronnimann, R.C. Zeigler and G.E. Maciel, *J. Phys. Chem.*, 96 (1992) 4027.
- [22] G.A. Fuentes, J.V. Boegel and B.C. Gates, *J. Catal.*, 78 (1982) 436.
- [23] A. Melchor, E. Garbowski, M.-V. Mathieu and M. Primet, *J. Chem. Soc., Faraday Trans. 1*, 82 (1986) 1893.
- [24] R.S. Drago and E.E. Getty, *J. Am. Chem. Soc.*, 110 (1988) 3311.
- [25] E.E. Getty and R.S. Drago, *Inorg. Chem.*, 29 (1990) 1186.
- [26] J.A. Boon, J.A. Levisky, J.L. Pflug and J.S. Wiles, *J. Org. Chem.*, 51 (1986) 480.
- [27] *Comprehensive Inorganic Chemistry*, Vol. 1, Pergamon Press, Oxford, 1973, p. 1020.
- [28] R.K. Iler, *The Chemistry of Silica*, John Wiley & Sons, New York, 1979, p. 635; F. Figueras and L.C. Menorval, *Tetrahedron*, 49 (1993) 4073.