Aluminium-Containing Polymethylsiloxane as a New Solid Acid Catalyst

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An aluminium-containing polymethylsiloxane (AMS) was prepared in an aqueous system using methyltrichlorosilane, dimethyldichlorosilane, and aluminium hydroxide as the starting materials, and its applicability as a new solid acid catalyst was examined. AMS is an amorphous hydrophobic solid with a high surface area (ca. 250 $m^2\,g^{-1}$) and a relatively high thermal stability (max. 573 K in air). The adsorption of basic indicators indicated that acid sites with a medium strength ($pK_a=1.5$) exist on AMS, and protic acid sites were detected on AMS by the IR spectra of adsorbed pyridine. These acid sites differ from the aprotic sites found on alumina. Though those on AMS are able to catalyze the dehydration of pinacol in the vapor phase, they are inactive for the hydrolysis of methyl acetate in an aqueous system.

As is well-known, organopolysiloxanes containing various kinds of organic groups (CH_3, C_2H_5, C_6H_5, ClC_6H_4, etc.) have many excellent properties such as good thermal stability, electric insulation, and resistance to chemicals and water, and have been used widely as oil, grease, rubber, resin, and so on. For improvements in the thermal and oxidative stabilities of these materials, various kinds of polymetalloorganosiloxanes,[1,2] in which portions of silicon atoms of siloxanes are replaced by other metals (Al, Zn, Ti, B, etc.) have also been prepared. These organometallic polymers are interesting as materials for the preparation of solid catalysts, especially owing to their relatively high heat stability. In fact, Suzuki et al.[3] have recently reported that polyorganosiloxanes bearing sulfo groups are better catalysts for the nitration of benzene in the vapor phase than are their corresponding ion-exchange resins.

It is well-known that many binary oxide catalysts, such as silica–alumina[4] and silica–titania,[5] exhibit acid properties different from those of component single oxides, and that these phenomena may be explained[6] in terms of the localization of electric charge due to changes in the coordination numbers of oxygen atoms, accompanied by the formation of M–O–M′ bonding (M and M′ stand for different metal atoms whose coordination numbers differ from each other). A similar phenomenon was reported for the case of organosilane compounds: Saegusa et al.[7] reported that aluminium silanolates might act as acid catalysts for the polymerization of cyclic and vinyl ethers as a result of the development of acid properties from their Si–O–Al bondings.

From the information described above, it is strongly expected that polyorganosiloxanes containing various kinds of metals such as Al, Mg, and Ti would be acid, and that there is a possibility that these materials might act as solid acid catalysts with relatively high thermal stability. However, such a possibility has scarcely been examined so far.

In the present study, as a first step toward examining this possibility, an aluminium-containing polymethylsiloxane (AMS) was prepared and several fundamental properties were measured in order to examine its applicability as a solid acid catalyst.

Experimental

Materials. Methyltrichlorosilane (MTCS) and dimethyldichlorosilane (DMCS) were obtained from Shin-Etsu Chemical Industry Co. and were used without further purification. Aluminium hydroxide (Kanto Chemical Co., GR grade) was used as the source of aluminium. A series of commercially available basic indicators (Tokyo Kasei Kogyo Co., GR or EP grade), Methyl Red ($pK_a=4.8$), 4-phenylaminoazobenzene ($pK_a=4.0$), *p*-dimethylaminoazobenzene ($pK_a=3.3$), 4-(phenylazo)diphenylamine ($pK_a=1.5$), dicinnamylideneacetone ($pK_a=-3.0$), benzylideneacetophenone ($pK_a=-5.6$), and anthraquinone ($pK_a=-8.2$), was used in a 0.1 wt% dry benzene solution to measure the strength of acid sites. Commercially available silica–alumina catalyst (Nikki Chemical Co., N631-L, 13 wt% Al_2O_3) having a specific surface area of 500 $m^2\,g^{-1}$, was used as a reference. Methyl acetate (Wako Pure Chemical Industries) and pinacol (Aldlich, hydrated form) were used as reactants in order to examine catalytic activity; pinacol was dried before use by recrystallization from ether followed by desiccation with Molecular Sieve 3A.

Preparations. MTCS (4.5 g) and 2.0 g of DMCS (MTCS/DMCS molar ratio 2.0) were dissolved in 20 cm^3 of ethanol with cooling. Aluminium hydroxide (0.7 g) was dissolved in 200 cm^3 of aqueous 3.8 wt% sodium hydroxide solution. The two solutions were mixed once at a time with vigorous stirring, the Si/Al ratio in the solution being 4.5. Then, the pH of the solution was lowered rapidly to 9 with concentrated hydrochloric acid. Stirring was continued for ca. 12 h at room temperature, then for an additional 5 h at 353 K to completion of the reaction. The precipitate formed was filtered and washed with distilled water. The solid obtained, which will hereinafter be designated AMS-1 (aluminium ion-containing methylpolysiloxane-1), was dried at 373 K. AMS-1 was mixed with a small amount of ethanol, dispersed in distilled water, washed three times with 0.5 mol dm^{-3} ammonium chloride solution to remove the remaining sodium cations, and finally washed with distilled water until no chloride ion was detected in the filtrates. The obtained solid (hereinafter designated AMS-2) was dried overnight at 373 K.

By a similar method, methylpolysiloxane (MS), one of the components of AMS-1 and -2, was prepared from only a mixture of MTCS and DMCS as a reference. Similarly, alumina (AL), the other component of AMS, was also prepared as a reference from aluminium hydroxide. Each of the samples was activated at 473—773 K in air before use.

Measurements. The acid strength was measured in dry benzene using the conventional indicator method.[8] In this study the strengths of the acid sites were expressed semiquantitatively in terms of the pK_a value of the weakest indicator that can be adsorbed in its acid form; thus, stronger acid sites have smaller pK_a values. IR spectra were measured with a spectrophotometer (Shimadzu Corp., IR-400) on pelletized mixtures of 1 mg of sample powder and 250—300 mg of KBr powder. The IR spectra of the adsorbed pyridine were measured qualitatively using the same spectrophotometer by a simplified method as follows. Fifteen milligrams of an activated sample were pressed into a disk without using KBr, heated at the activation temperature for 1 h, and transferred quickly into a 50 cm^3 Erlenmeyer's flask provided with a tight ground-glass cap. A four mmol/g-catalyst of pyridine was injected into the flask, and the flask was kept at 393 K for 1 h for adsorption. The sample disk was taken out, and its IR spectrum was recorded. X-Ray powder diffraction patterns were recorded on an X-ray diffractometer (Rigaku Denki Co., Geigerflex RAD-1A). Surface areas were measured with an instrument (Shimadzu Corp., ADS-1B) by the BET method using the adsorption of nitrogen at 77 K.

Test Reactions. For the hydrolysis of ester, 1.0 cm^3 of methyl acetate was dissolved in 20 cm^3 of distilled water. A sample powder (0.1 g) was suspended in the solution and stirred at 323 K for 1—12 h. A 5.0 cm^3 aliquot of the supernatant liquid was titrated with 0.1 mol dm^{-3} sodium hydroxide solution in order to determine the acetic acid produced as a poduct.

Dehydration of pinacol was carried out by a pulse method. Fifty milligrams of an activated sample powder were charged in a U-shaped glass reaction tube (i.d. 3.0 mm) and pretreated at 523 K for 1 h in a helium flow (30 cm^3 min^{-1}); then, pinacol was injected in 3.5 μl pulses. The products were analyzed with a gas chromatograph (Shimadzu Corp., GC-4BT). Major products, pinacolon and 2,3-dimethyl-1,3-butadiene, were identified and determined by comparing their retention times and peak areas with those of respective commercially available reagents.

Results and Discussion

Acid Strength and Affinity to Water. The effect of the activation temperature on the acid strength of AMS-1, AMS-2, and their components, MS and AL, is given in Table 1. The affinity to water of the samples, namely whether a sample is hydrophobic or not, is also shown in the table. This property can easily be determined because a hydrophobic sample, when added to distilled water, is allowed to float on the water, and never caused to enter the liquid phase. When a sample is hydrophilic, it sinks immediately into the water. Since the hydrophobic property can be regarded as being due to the existence of a methyl group, the highest activation temperature at which the hydrophobic property is maintained is useful for roughly determining the thermal stability of AMS and MS.

As shown in Table 1, MS and AMS-1 treated below 573 K and AMS-2 treated below 673 K are hydrophobic. These results indicate that the methyl groups contained in these solids are stable up to ca. 573—673 K. Since

Table 1. Hydrophobic and Acid Property of MS, AL, AMS-1, and AMS-2

Sample	Heating condition		Hydrophobic property[a]	pK_a and color of indicator[b]						
	T/K	Time/h		4.8	4.0	3.3	1.5	−3.0	−5.6	−8.2
MS	373	>12	+	−	−	−	−	−	−	
	473	3	+	−	−	−	−	−	−	
	573	3	+	−	−	−	−	−	−	
	673	3	−	−	−	−	−	−	−	
	773	3	−	−	−	−	−	−	−	
AL	373	>12	−	+	+	−	−	−	−	
	473	3	−	+	+	−	−	−	−	
	573	3	−	+	+	+	+	±	−	
	673	3	−	+	+	+	+	±	±	−
	773	3	−	+	+	+	+	±	±	±
AMS-1	373	>12	+	−	−	−	−	−		
	473	3	+	−	−	−	−	−		
	573	3	+	−	−	−	−	−		
	673	3	−	+	+	±	−	−	−	
	773	3	−	+	+	−	−	−	−	
AMS-2	373	>12	+	−	−	−	−	−	−	
	473	3	+	+	−	−	−	−	−	
	573	3	+	+	+	+	+	±	−	
	673	3	+	+	+	+	+	+	±	−
	773	3	−	+	+	+	+	+	−	

a) +, hydrophobic; −, hydrophilic. b) +, acidic color; −, basic color; ±, physically adsorbed.

many types of silicone rubber are stable up to ca. 573 K, the thermal stability of MS and AMS can be regarded as being nearly equal to that of silicone rubber.

MS is not acid, as shown in Table 1, irrespective of the treating temperatures. On the other hand, AL is acid with a medium strength (pK_a=4.0—1.5). AMS-1 becomes slightly acid (pK_a=4.0) when treated above 673 K. Of the samples, only AMS-2 treated at 573—673 K is hydrophobic, with a strength (pK_a=1.5—−3.0) equal to or stronger than that of AL. Since the acid strength of a silica-alumina catalyst is pK_a=−8.2, the acid sites on MSA-2 are weaker than those on this catalyst. The remarkable difference in the acid strength between AMS-1 and AMS-2 can be explained as follows. Since sodium cations are capable of neutralizing both protic (Brønsted type) and aprotic (Lewis type) acid sites,[9] the acid sites on AMS-1 were neutralized with sodium cations which coexisted in quantity in the preparation stage of AMS-1. On the other hand, in the case of AMS-2, sodium cations were exchanged in advance with ammonium ions by treatments with an ammonium chloride solution, so that the acid sites could be formed on AMS-2 as a result of the decomposition of ammonium ions above 573 K in a similar manner as in the case of zeolites. With this case, it is known that the ammonium ion of Y-zeolite[10] is decomposed to ammonia and a proton by heat treatment at 413—633 K, the latter being retained on the surface as a Brønsted acid site.

IR Spectra. The IR spectra of AMS-2 treated at 473, 573, and 673 K (spectra 1, 2, and 3, respectively) are shown in Fig. 1. For a comparison, the spectrum of commercial silica-alumina treated at 723 K is also shown (spectrum 4) in this figure. The spectra of AMS-2 treated at 373 and 773 K are nearly identical with spectra 1 and 3, respectively; thus, they are not shown in this figure. AMS-2 treated at 473 K shows a strong absorption band at 1265 cm^{-1} and a weak one at 1400 cm^{-1}. These two bands may be ascribed to the symmetric and asymmetric deformation vibrations of the methyl group[11] bound to the silicon atom, respectively. The intensities of these bands are not changed substantially upon treatment at 373—473 K, but are reduced distinctly when AMS-2 is treated at 573 K. These bands disappear in the spectrum of AMS-2 treated above 673 K, and the spectrum is in qualitative agreement with that of silica-alumina. On the other hand, as shown in Table 1, AMS-2 treated at 673 K is hydrophobic. The explanation for this contrast may be that a small number of methyl groups (difficult to detect from IR spectra, but sufficient to impart a hydrophobic property) still remain on AMS-1. From these results it is concluded that AMS-2 is stable below 473 K, and that a portion of the methyl groups are decomposed by the treatment at 573 K.

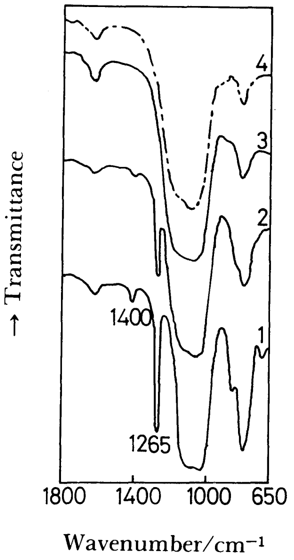

Fig. 1. IR spectra of AMS-2 heat treated for 3 h and of silica-alumina (N631-L) treated at 723 K for 3 h. Treating temperatures of AMS-2: 1, 473 K; 2, 573 K; 3, 673 K; 4, silica-alumina.

X-Ray Diffraction and Specific Surface Area. X-Ray diffraction measurements were carried out on AMS-2 treated at 373, 573, and 773 K; none of them produced diffraction lines. These resuls indicate that AMS-2 is amorphous at least up to 773 K. It is known[1] that polytitanomethylsiloxanes are also amorphous at room temperature. As is well-known, silica-alumina catalysts are amorphous, so that AMS-2 can be regarded as being a structure like silica-alumina in which a portion of the oxygen atoms have been replaced with methyl groups directly bound to the silicon atoms.

The relation between the treating temperature and the specific surface area of AMS-2 is shown in Fig. 2. AMS-2 heat treated at 473 K gave a value of about

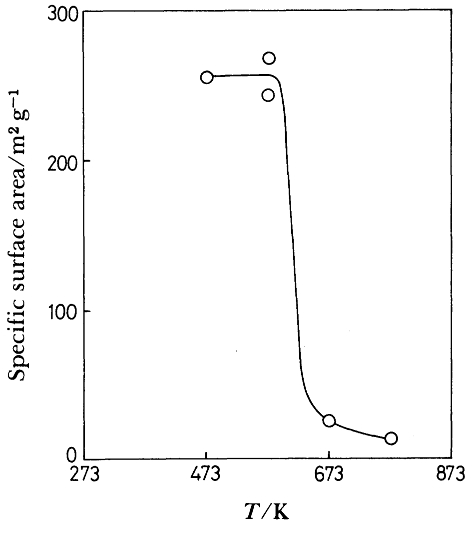

Fig. 2. Relation between specific surface area and heating temperature of AMS-2.

250 m^2 g^{-1}; this value was maintained after a treatment at 573 K. When AMS-2 was treated at temperatures higher than 573 K, a remarkable decrease in the surface area was observed. The surface areas of AMS-2 treated at 673—773 K are equal to about 1/10 of those treated at 473—573 K. Since the temperature range where the abrupt decrease in surface area occurs (573—673 K) is the same as the temperature range where the absorption bands of methyl groups disappear in the IR spectra, the decrease in the surface area may be taken to be caused by a destruction of the porous structure due to a pyrolysis of methyl groups. From these results it is concluded that 573 K is the highest temperature which can provide AMS-2 with high surface areas.

IR Spectra of Adsorbed Pyridine. The IR spectra of pyridine adsorbed on AMS-2 were measured using AMS-2 treated at 573 K for 3 h. The obtained spectra are shown in Fig. 3, together with the background spectrum (curve 1). Curve 2 shows the spectrum measured immediately after pyridine adsorption, so as to avoid the effect of moisture. By comparing the spectrum with the results reported by Parry,[9] the absorption peaks which appear around 1492 and 1548 cm^{-1} may be assigned to the pyridinium ion, and the peak around 1444 cm^{-1} may be taken as corresponding to hydrogen-bonded pyridine. A band of coordinately bound pyridine (1450 cm^{-1}) in association with Lewis acid sites was not observed. However, an absence of Lewis type sites cannot be concluded from this result. Since the sample was constantly exposed to moisture during the measurement of its spectrum, there is a possibility that all Lewis acid sites, if present, would have been converted into Brønsted-type sites due to the adsorption of water, in the same manner as in the case[9] of a silica–alumina catalyst. Curve 3 shows the spectrum of AMS-2 which was exposed to pyridine vapor and then heated at 573 K for 1 h. Though the bands corresponding to weak adsorption due to hydrogen bonding disappeared, the band for the strong adsorption due to pyridinium ion remained. From these results, it may be concluded that AMS-2 possesses at least Brønsted acid sites, a conclusion which is in harmory with the results obtained using the adsorption of basic indicators.

It is known that alumina, one of the components of AMS-2, contains only Lewis acid sites;[9,12,13] MS, the other component, is nonacidic, as shown in Table 1. From these facts, it can be concluded that the acid sites on AMS-2 do not originate from those on the components, but are newly produced by the formation of Si–O–Al bonding.

Hydrolysis of Methyl Acetate and Dehydration of Pinacol. Catalytic activity was examined using an AMS-2 which was heat-treated at 573 K for 3 h, because, among the samples, only this one possessed an acid property with moderate strength and high surface area, and contained a considerable number of methyl groups.

Namba et al.[14] reported that high-silica zeolites are active as acid catalysts for the hydrolysis of ester in aqueous solution because of their hydrophobic property, whereas silica–alumina catalyst, though hydrophilic in nature, is inactive. Since AMS-2 is hydrophobic, there is a possibility that this sample is active as a solid acid catalyst in aqueous solution. To examine this possibility, the hydrolysis of methyl acetate by AMS-2 was examined in an aqueous system. However, the expected reaction did not proceed substantially, which indicates that AMS-2 is not active in aqueous solution. This result implies that the hydrophobic property of AMS-2 is not effective to protect the acid sites from water.

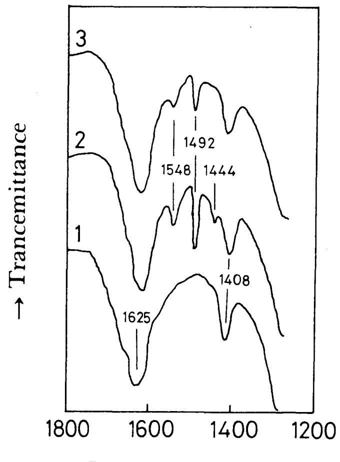

Fig. 3. IR spectra of pyridine adsorbed on AMS-2. 1, background; 2, immediately after pyridine adsorption at 393 K for 1 h; 3, heated at 573 K for 3 h after pyridine adsorption.

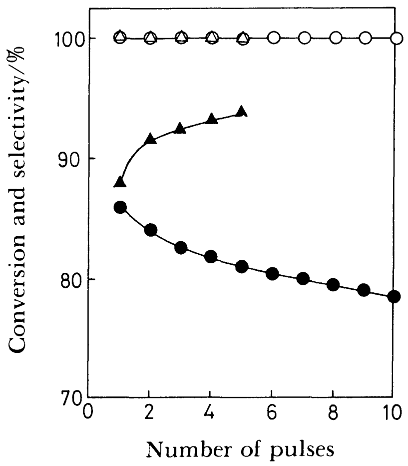

Fig. 4. Conversion of pinacol and the selectivity for pinacolone on AMS-2 and silica–alumina (N631-L) at 523 K. ○, △: conversion on AMS-2 and silica–alumina, respectively. ●, ▲: selectivity on AMS-2 and silica–alumina, respectively.

It is well-known that the dehydration of pinacol is allowed to proceed by acid catalyst; this reaction was therefore selected as the test reaction to examine the catalytic activity of AMS-2 in the gas phase. The obtained results are shown in Fig. 4. For a comparison, the results obtained with a commercial silica–alumina catalyst are included in the figure. The conversion of pinacol on AMS-2 is practically 100% within the 10 pulses tested, and the products obtained are pinacolon (PCN), 2,3-dimethyl-1,3-butadiene (DMB), and water. The selectivity for PCN gradually decreased from 86% for the first pulse to 78% for the final. These results are important because they demonstrate that AMS-2 acts as a solid acid catalyst in the gas phase. Silica–alumina also showed similar activity, though the selectivity is somewhat different from that of AMS-2 in that the selectivity for PCN gradually increased with the pulse number.

In conclusion, it has been demonstrated that aluminium-containing polymethylsiloxane is an amorphous, relatively heat-stable solid acid with a high surface area, and that the acid sites are active in the vapor phase, but are inactive in aqueous systems. The appearance of these acid sites can be ascribed to the formation of Si–O–Al bonding. This substance is interesting as a new type acid catalyst or support.

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