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Crystal structure, thermal decomposition mechanism and catalytic performance of hexaaquaaluminum methanesulfonate

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Hexaaquaaluminum methanesulfonate crystals, $[Al(H_2O)_6][CH_3SO_3]_3$ were synthesized by a hydrothermal reaction of $Al(OH)_3$ with methanesulfonic acid. Single crystal diffraction determination revealed that Al^{3+} was coordinated by six water molecules in octahedral geometry, while the $CH_3SO_3^-$ anion connected with Al^{3+} through coordinated water molecules by hydrogen bonds. The six-coordinate environment of Al was also determined by ²⁷Al MAS NMR measurement. Thermogravimetric analysis and Fourier transform infrared spectroscopy showed that the decomposition intermediate at 265-365 °C was $Al_2(\mu-OH)(CH_3SO_3)_5$ and the final product was amorphous Al_2O_3 residue with about 0.8 wt% SO₃ at 520-800 °C. A pure phase of $[Al(H_2O)_6][CH_3SO_3]_3$ was confirmed by powder X-ray diffraction analysis. Esterification of *n*-butyric acid with *n*-butanol and ketalization of cyclohexanone with glycol catalyzed by $[Al(H_2O)_6][CH_3SO_3]_3$ and $Al_2(\mu-OH)(CH_3SO_3)_5$, respectively, proceeded in 100% yield by continuously removing the produced water. In the case of tetrahydropyranylation of *n*-butanol at room temperature in dichloromethane, the catalytic activity of $[Al(H_2O)_6][CH_3SO_3]_3$ was much lower than that of $Al_2(\mu-OH)(CH_3SO_3)_5$. Furthermore, both $[Al(H_2O)_6][CH_3SO_3]_3$ precursor and $Al_2(\mu-OH)(CH_3SO_3)_5$.

Keywords: Hexaaquaaluminum methanesulfonate; Crystal structure; Thermal decomposition; Catalytic activity; Lewis acid

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1. Introduction

Transition-metal trifluoromethanesulfonates as Lewis acid catalysts have received attention in organic synthesis since they are stable to water (water-tolerant) [1-6]. Metal methanesulfonates as less expensive, water-tolerant and reusable Lewis acid catalysts were also reported in catalytic reactions such as esterification [7-9], acylation [10], condensation [11-16], tetrahydropyranylation [17] and diacetylation of aldehydes [18, 19].

The hydrated aluminum methanesulfonate (Al(CH₃SO₃)₃, abbreviated as Al(MS)₃) is a good candidate for its acid catalytic performance due to strong Lewis acidity of Al³⁺; for example, Al(MS)₃·4H₂O could be designed to prepare a promising industrial organic-inorganic hybrid silica catalyst [20] and employed as a promoter for styrene hydroesterification catalyzed by a triphenylphosphine-palladium (PPh₃–Pd) complex [21]. Song *et al.* reported that Al(MS)₃·4H₂O could be a reusable catalyst for the Biginelli reaction [15] and three-component condensation of 2-naphthol, aldehydes and carbamates [16]. However, the synthesis and characterization of hydrated Al(MS)₃ was obscure and structure-utility relationships as well as catalysis mechanisms were seldom considered. This prompted us to determine the structure of hydrous and anhydrous aluminum methanesulfonates in order to understand their catalytic mechanism.

Herein hexaaquaaluminum methanesulfonate ($[Al(H_2O)_6][MS]_3$) with a well-defined structure is reported and general strategies for preparing water-tolerant catalyst from the hydrate precursor with high catalytic performance are also discussed. Crystalline $[Al(H_2O)_6][MS]_3$ was synthesized by the hydrothermal reaction of $Al(OH)_3$ with methanesulfonic acid and crystal structures were determined by single crystal diffraction. The thermal decomposition mechanism of $[Al(H_2O)_6][MS]_3$ was investigated by Thermogravimetric/Differential thermogravimetric (TG/DTG) analysis and Fourier transform infrared (FTIR) spectra. The catalytic activity and reusability of $[Al(H_2O)_6][MS]_3$ and its decomposition intermediate $Al_2(\mu-OH)(MS)_5$ for the esterification, ketalization and tetrahydropyranylation of alcohol reactions are reported. Their catalytic mechanisms are also proposed.

2. Experimental

2.1. General information

Methanesulfonic acid (99%, extra pure, MSH) was purchased from Acros. Analytical grade Al(OH)₃ was purchased from Shanghai Meixing Chemical Co., Ltd., China. All other reagents were purchased from Shanghai Chemical Reagent Co., Ltd., Shanghai, China and used without further purifications.

2.2. Synthesis of [Al(H₂O)₆][MS]₃

3.0 g of Al(OH)₃, 11.1 g CH₃SO₃H and 20 mL double distilled water were charged into a 45 mL PTFE bottle and sealed in a stainless steel autoclave. The reaction was carried out at 140 °C for 24 h in a dynamic hydrothermal process. After cooling slowly to ambient temperature, the mixture was filtered and the filtrate was evaporated with a rotary evaporator at 60 °C for 2 h at 8.0 KPa. The product slowly crystallized when cooled to room temperature; then it was recrystallized from 95 vol% isopropanol (5 vol% water) at -20 °C. Finally, the solid was dried under high vacuum at RT for 12 h. Aluminum analysis was carried out by complexometric titration with EDTA using xylenol orange as an indicator. Calculated for $[Al(H_2O)_6][MS]_3$: Al, 6.42%. Found: Al, 6.40%.

2.3. Preparation of Al₂(µ-OH)(MS)₅

2.5000 g of crystalline $[Al(H_2O)_6][MS]_3$ was put into an alumina crucible with a cover and then heated to 265 °C at a rate of 5.5 °C/min in a muffle furnace and maintained at this temperature for 5 h. After calcination, it was cooled to room temperature in a desiccator and 1.635 g product was obtained. Calculated for $Al_2(\mu$ -OH)(MS)₅: Al, 9.88%. Found: Al, 9.81%.

2.4. Hygroscopic property of Al₂(µ-OH)(MS)₅

Using 3.12 g of $Al_2(\mu$ -OH)(MS)₅ scattered on a watch glass and exposing in the air at a relative humidity 17-37%, the weight increase was monitored by analytical balance for every 5-12 h interval times. At ambient relatively humidity, the moisture sorption weight change *versus* time is shown in figure S4.

2.5. Characterization

TG/DTG analysis was carried out in air on a Perkin-Elmer Pyris 1 with a flow rate of 20 mL min⁻¹ at 20 K min⁻¹ from 30 to 800 °C. Ceramic crucibles for TG/DTG were used and the sample powder mass was 7-8 mg. FTIR spectra were obtained in Nujol mulls on a Perkin-Elmer Spectrum GX. Sixty-four scans were co-added with a resolution of 4 cm⁻¹ from 4000-400 cm⁻¹. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer. All samples were dissolved in D₂O. ¹H NMR chemical shifts (δ) were provided in ppm relative to TMS as the internal reference with a resonant frequency of 500 MHz. The resonant frequency of ¹³C NMR was 125.8 MHz and there was no internal standard. ²⁷Al MAS NMR spectra were recorded on a Bruker AVANCE III 500 solid state spectrometer (11.7 T) at a Larmor frequency of 130.3 MHz with pulse length of 0.22 ms, relaxation delay of 2 s and rotor spinning speed of 10 kHz. The spectra were referenced to a 1.0 M AlCl₃ solution. The chemical composition of the decomposition product of [Al(H₂O)₆][MS]₃ calcinated at 800 °C for 3 h was measured by an X-ray fluorescence (XRF) spectrometer (ZSX-100E, Rigaku). XRF generator was operated at 200 V and 65 A. Powder X-ray diffraction (PXRD) data were collected with a D/max-RB X-ray diffractometer (Rigaku) using Cu-Ka radiation ($\lambda = 1.5418$ Å) in the 20 range of 3-50° with a step size of 0.02° and a scanning rate of 6° min⁻¹. For analyzing products of esterification, ketalization and tetrahydropyranylation, gas chromatograph (GC) determinations were performed using a Perkin Elmer Autosystem XL equipped with FID detector. The separation column was an Elite-5 (30 m×0.53 mm ID×1.5µm df, 5% phenyl-95% dimethyl polysiloxane). The temperatures of the injector and detector were set to 280 °C and 260 °C, respectively. The oven temperature was held at 80 °C for 2 min and then increased to 240 °C at 20 °C min⁻¹. The carrier gas was highly pure nitrogen with a flow rate of 4 mL min⁻¹. The split ratio was 20:1.

2.6. Single crystal X-ray crystallography

Single-crystal X-ray diffraction data measurements for $[Al(H_2O)_6][MS]_3$ were performed on a Bruker D8 QUEST COMS diffractometer operating at 292(2) K using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal structures were solved with direct methods and refined by full-matrix least squares on F^2 using the SHELXL-2014/7 program package [22]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogens were refined as riding with isotropic displacement parameters 1.2-1.5 times the Ueq of the attached

atoms. Structure refinement details, selected bond lengths and angles, and hydrogen bonds for $[Al(H_2O)_6][MS]_3$ are given in tables 1, S1 and S2, respectively. The crystallographic data has been deposited in the Cambridge Crystallographic Data Center with CCDC reference number 1486614.

2.7. Typical procedure catalytic reaction

Esterification: In a 100 mL RB flask equipped with a Dean-Stark trap attached to a water cooled reflux condenser, 1.0 mmol of $[Al(H_2O)_6][MS]_3$ or 0.5 mmol of $Al_2(\mu$ -OH)(MS)_5, 0.24 mol of *n*-butanol, 0.2 mol of butyric acid and 15 mL of cyclohexane were added. The mixture was refluxed for 60 min to continuously remove water in a magnetic stirrer equipped with an oil bath at 110-115 °C. The catalyst was insoluble in the mixture and can be separated by decantation for reuse.

Ketalization: In a 100 mL RB flask equipped with a Dean-Stark trap attached to a water cooled reflux condenser, 1.0 mmol of $[Al(H_2O)_6][MS]_3$ or 0.5 mmol of $Al_2(\mu$ -OH)(MS)₅, 0.2 mol of glycol, 0.2 mol of cyclohexanone and 15 mL of cyclohexane were added. The mixture was refluxed for 50 min to continuously remove water in a magnetic stirrer equipped with an oil bath at 110-115 °C. The catalyst was insoluble in the mixture and can be separated by decantation for reuse.

Tetrahydropyranylation: In a 25 mL RB flask, 15 mmol of *n*-butanol, 16.5 mmol of 3,4-dihydro-2H-pyran (DHP), 1.0 mmol of $[Al(H_2O)_6][MS]_3$ or 0.5 mmol of $Al_2(\mu$ -OH)(MS)_5 and 10 mL of dichloromethane were charged. The mixture was stirred at room temperature for 45 min. The catalyst was insoluble in the mixture and can be separated by decantation for reuse.

3. Results and discussion

3.1. Single-crystal X-ray determination

The structure of $[Al(H_2O)_6][MS]_3$ was determined by X-ray single crystal structure analysis. Crystallographic data and structure refinement (table 1) indicate that the compound crystallized in the monoclinic system, space group $P2_1/c$ and Z=4. The asymmetric unit includes one Al ion coordinated with six water molecules and three methanesulfonate groups (figure S1). Figure 1 presents the local coordination environment around the Al1 and hydrogen bonds between Al(H₂O)₆ group and ten methanesulfonates. The charges on the Al³⁺ cation are counter-balanced by the methanesulfonates [23]. Al has a slightly distorted octahedral geometry. The bond length of Al–O is 1.8521(14) to 1.8980(14) Å. The angle of O5–Al–O6 is 178.86(7)° and the angle O5–Al–O4 is 89.50(7)° (table S1). Hydrogen bonds are formed between hydrogens of coordinated water and O of methanesulfonate with average distance of 1.7936(2) Å and 2.5995(18) Å for H···O and O–H···O, respectively (table S2). The $[Al(H_2O)_6]^{3+}$ layers and CH₃SO₃⁻ layers stacking along the crystallographic *b* axis are shown in figure S2. The methanesulfonates have the same orientation, with the –SO₃ groups alternating up or down towards the nearest cation [24, 25].

3.2. Thermal decomposition mechanism

The dehydration of $[Al(H_2O)_6][MS]_3$ is investigated in air by TG/DTG. Figure 2 shows that the thermal decomposition of $[Al(H_2O)_6][MS]_3$ takes place in two stages. $[Al(H_2O)_6][MS]_3$ is stable up to 100 °C. The intermediate product at the first stage between 265 °C and 350 °C is assumed as $Al_2(\mu$ -OH)(MS)_5. The calculated weight loss for $Al_2(\mu$ -OH)(MS)_5 is 35.0% according to scheme 1, which agrees with the observed value 34.5% as shown in figure 2. The experimental result of the calcinating $[Al(H_2O)_6][MS]_3$ at 265 °C for 3 h shows that the weight loss is 34.6%. The calculated aluminum content for $Al_2(\mu$ -OH)(MS)_5 intermediate is in agreement with the experimental value of the complexometric titration analysis. These results of instrumental, titration analysis and gravimetric analysis strongly support the assumption of $Al_2(\mu$ -OH)(MS)_5 as the first stage decomposition intermediate. The thermal decomposition mechanism of the first stage may be loss of five coordinated water molecules and one MSH by dehydration and hydrolysis dimerization of $[Al(H_2O)_6][MS]_3$.

After the first stage decomposition (from the TG curve in figure 2) the assumed $Al_2(\mu$ -OH)(MS)₅ decomposes rapidly at 365 °C to 520 °C and the weight percent of final decomposition product is 13.9%, which is slightly higher than the theoretical value of 12.1% for the formation of pure Al_2O_3 . The XRF determination of the decomposition product of $[Al(H_2O)_6][MS]_3$ calcinated at 800 °C for 3 h shows that the mass percent of Al_2O_3 and SO_3 is 99.2% and 0.8%, respectively. Compared with pure Al_2O_3 , the FTIR spectrum of the decomposition product of $[Al(H_2O)_6][MS]_3$ calcinated at 800 °C for 3 h clearly shows a weak broad peak at 1150 cm⁻¹ (figure S6), which is the characteristic vibrational frequency of SO_4^{2-} [26]. These results confirm the second stage decomposition path as described in scheme 1. The

PXRD result shows that the powder is an amorphous solid (figure S7). The residual SO_4^{2-} delays the conversion of amorphous Al₂O₃ to its crystalline form [27].

The assumed $Al_2(\mu$ -OH)(MS)₅ is verified by FTIR (figure 3). From figure 3(a) the bending vibrational mode of H-O-H is 1689 cm⁻¹ and the vibrational frequencies of free $CH_3SO_3^-$ is at 1208 cm⁻¹, 1155 cm⁻¹ and 1045 cm⁻¹. However, when $[Al(H_2O)_6][MS]_3$ was calcinated at 265 °C for 5 h, the FTIR spectrum of $Al_2(\mu$ -OH)(MS)₅ in figure 3(b) clearly shows a sharp peak at 3393 cm⁻¹, indicating that the –OH forms a bridge between two Al^{3+} ions [28]. In hydroxyl containing polynuclear metal complexes, the hydroxyl group is usually bridged between two metals [29-33]. For example, $[Cu(HL)(OH^{-})]_n$ shows a strong band close to 3500 cm⁻¹ [32], (R₃R'N)[Ru(OH)₂Cl₂]·0.5H₂O exists in a polymeric form with bridging hydroxyl groups evidenced by v-OH at 3460 cm⁻¹ [31]. The X-ray structure determination results of some of these hydroxyl containing polynuclear metal complexes directly supported the FTIR analysis [29, 30]. The peak at 789 cm⁻¹ can be attributed to the bridging –OH bending mode [34]. The vibration frequencies of CH₃SO₃⁻ at 1288 cm⁻¹ and 1090 cm⁻¹ in figure 3(b) are completely different from those of $[Al(H_2O)_6][MS]_3$ in figure 3(a), indicating that $CH_3SO_3^-$ coordinates bidentate with Al³⁺ in a bridged binuclear complex. Indeed, as indicated by packing diagram of [Al(H₂O)₆][MS]₃ in figure S3, the nearest distance between two adjacent Al centers is 6.394 Å, which is favorable to an $Al_2(\mu$ -OH)(MS)₅ unit in the dehydration process.

 $Al_2(\mu$ -OH)(MS)₅ is strongly hygroscopic. The moisture sorption curve in figure S4 shows that the weight increases rapidly in 48 h. It is calculated that $[Al_2(\mu$ -OH)(H₂O)₁₀][MS]₅ is formed according to the average saturated adsorption weight as shown in figure S4. The FTIR spectra of moisture sorption products for 12 h and 36 h in figure S5 clearly show that the peaks at 1288 cm⁻¹ and 1090 cm⁻¹ gradually disappear and the characteristic peaks of free CH₃SO₃⁻ are observed at 1208 cm⁻¹, 1155 cm⁻¹ and 1045 cm⁻¹.

3.3. NMR analysis

The ¹H and ¹³C NMR chemical shifts of $[Al(H_2O)_6][MS]_3$ in D₂O are 2.659 and 38.36 ppm, respectively (figure S8 and figure S9), consistent with that of In(MS)₃ and Bi(MS)₃ in D₂O [10]. The ²⁷Al MAS NMR study was carried out to investigate the coordination state of Al. The resonance signal at -3.911 ppm of $[Al(H_2O)_6][MS]_3$ (figure S10(a)) indicates six-coordinate octahedral Al [35]. However, the chemical shift of Al₂(µ-OH)(MS)₅ changes to higher field

at -25.680 ppm (figure S10(b)), which may arise from the electronegativity effect by coordinated $CH_3SO_3^-$ toward Al^{3+} [36]. Kotsarenko *et al.* reported the ²⁷Al NMR of anhydrous $Al_2(SO_4)_3$ [37] at -25 ppm, which was close to that of $Al_2(\mu$ -OH)(MS)₅ at -25.68 ppm. The crystal structure of anhydrous $Al_2(SO_4)_3$ (ICSD #38034) clearly showed that six oxygens from SO_4^{2-} were coordinated with Al^{3+} [38]. Therefore, it is reasonable to infer that oxygens from $CH_3SO_3^-$ are coordinated with Al^{3+} and the coordination number is six. The satellite resonance peaks in figure S10 are spinning sidebands [39], which are denoted as asterisks. The spinning sidebands are different between $[Al(H_2O)_6][MS]_3$ and $Al_2(\mu$ -OH)(MS)_5, however, the spinning sidebands of partially moisture sorption product of $Al_2(\mu$ -OH)(MS)₅ in figure S10(c) agree well with those of $[Al(H_2O)_6][MS]_3$ and $Al_2(\mu$ -OH)(MS)_5, respectively. The ²⁷Al NMR spectrum of $Al_2(\mu$ -OH)(MS)₅ moisture sorption product for 24 h clearly shows that a new peak at -4.016 ppm appears (figure S10(c)), which is closer to that of $[Al(H_2O)_6][MS]_3$, indicating part of $Al_2(\mu$ -OH)(MS)_5 is transformed to $[Al_2(\mu$ -OH)(H_2O)_10][MS]_5, as described in scheme S1.

3.4. PXRD analysis

The results of the PXRD pattern and a simulated pattern calculated from the single crystal data for $[Al(H_2O)_6][MS]_3$ are shown in figure S11. The experimental PXRD patterns are coincident with those simulated from X-ray single-crystal data, which indicates the presence of a pure phase of as synthesized $[Al(H_2O)_6][MS]_3$. The differences in diffraction intensities are probably due to the variation of the preferred orientation of crystallites in the powdered sample.

3.5. Catalytic esterification by [Al(H₂O)₆][MS]₃ and Al₂(µ-OH)(MS)₅

The catalytic activity of various aluminum salt catalysts is summarized in table S3. It can be seen from table S3 that the yields are 100% for the $[Al(H_2O)_6][MS]_3$ precursor and $Al_2(\mu$ -OH)(MS)_5 catalyzed esterification of *n*-butyric acid with *n*-butanol, while the yields of other aluminum salt catalysts such as $Al_2(SO_4)_3$ ·18H₂O, $AlCl_3·6H_2O$, $Al(NO_3)_3·9H_2O$ and $KAl(SO_4)_2·12H_2O$ are fairly low. It is presumed that the anions of the aluminum salt play an important role in the catalytic activity. In case of $[Al(H_2O)_6][MS]_3$ precursor, the FTIR characteristic peaks of $-SO_3$ of the separated catalyst after reaction appear at 1284 cm⁻¹ and 1087 cm⁻¹ (figure S12(b)), which are analogous to those of $Al_2(\mu$ -OH)(MS)_5 as illustrated in figure 3(b), indicating that the active species may be $Al_2(\mu$ -OH)(MS)_5.

Although the precise mechanism of the esterification is unclear, the following steps may occur in the present reaction: (1) Aluminum salt catalysts act as Lewis acids in systems, which coordinate the carbonyl of *n*-butyric acid to boost the electropositive nature of carbon of carbonyl; (2) Alcoholic hydroxyl and $CH_3SO_3^-$ groups coordinate with Al^{3+} ; (3) Due to the activation of acid and alcohol by coordinating unsaturated Al^{3+} , water can be more easily produced and removed from the reaction system. The aluminum salt with the less-nucleophilic $CH_3SO_3^-$ anion is more electrophilic, which promotes the desired reaction through higher Lewis acidity.

After reaction, the catalyst separated by decantation without any treatment for recycling purposes. It can be seen from figure 4 that the catalytic activity of the recovered $[Al(H_2O)_6][MS]_3$ is practically the same as that of the fresh catalyst after recycling five times. The reusability of $[Al(H_2O)_6][MS]_3$ precursor and $Al_2(\mu-OH)(MS)_5$ is excellent and the esterification yield is very high.

3.6. Catalytic ketalization by [Al(H₂O)₆][MS]₃ and Al₂(µ-OH)(MS)₅

The ketalizations of cyclohexanone with glycol catalyzed by $[Al(H_2O)_6][MS]_3$ precursor and $Al_2(\mu$ -OH)(MS)_5, respectively, were investigated. The catalytic activity is excellent and the ketalization yield is 100%. $[Al(H_2O)_6][MS]_3$ precursor is soluble in the reaction mixture at the initial stage of the reaction, however, the catalyst is gradually precipitated as a solid along with water-separating. In case of the $Al_2(\mu$ -OH)(MS)_5, the catalyst is insoluble in the reaction mixture throughout the reaction stage. The reusabilities of $[Al(H_2O)_6][MS]_3$ precursor and $Al_2(\mu$ -OH)(MS)_5 were carried out for four cycles, which did not show significant loss of catalytic activity (figure 5).

3.7. Catalytic tetrahydropyranylation of alcohol by Al₂(µ-OH)(MS)₅

For the catalytic tetrahydropyranylation of *n*-butyl alcohol with DHP in dichloromethane at room temperature, $Al_2(\mu$ -OH)(MS)_5 exhibits the highest catalytic activity (100% yield) among various aluminum salts (table S4). Compared with $Al_2(\mu$ -OH)(MS)_5, the yield by $[Al(H_2O)_6][MS]_3$ is only 40%, demonstrating that the alcohol and DHP can be easily activated by anhydrous $Al_2(\mu$ -OH)(MS)_5 at room temperature [40]. The aluminum salt with the less-nucleophilic CH₃SO₃⁻ anion is more electrophilic, which promotes the desired reaction through stronger Lewis acidity.

After reaction, the Al₂(μ -OH)(MS)₅ catalyst can be separated by decantation without any treatment for recycling. The reusability of Al₂(μ -OH)(MS)₅ was investigated in catalysis of tetrahydropyranylation under the same condition. Figure 6 shows that the catalytic activity of Al₂(μ -OH)(MS)₅ decreases slightly during five runs, which may be due to the hygroscopicity of Al₂(μ -OH)(MS)₅ at ambient conditions.

4. Conclusion

The crystal structure, thermal decomposition mechanism and catalytic properties of [Al(H₂O)₆][MS]₃ have been studied, and catalytic properties of its decomposition intermediate Al₂(µ-OH)(MS)₅ have also been determined. A pure phase of [Al(H₂O)₆][CH₃SO₃]₃ was well defined by single-crystal X-ray diffraction measurements, TG, IR, NMR and PXRD. The intermediate dehydration product between 265-365°C is Al₂(µ-OH)(MS)₅, which contains two Al ions, five $CH_3SO_3^-$ and a bridging OH group. $Al_2(\mu-OH)(MS)_5$ is strongly hygroscopic, transformed to moisture sorption product $[Al_2(\mu-OH)(H_2O)_{10}][MS]_5$. The catalytic activity and reusability of both [Al(H₂O)₆][MS]₃ precursor and Al₂(µ-OH)(MS)₅ are excellent for the esterification and ketalization reactions by continuously removing the produced water. As for the tetrahydropyranylation of alcohols in dichloromethane, $Al_2(\mu-OH)(MS)_5$ exhibits very high catalytic activity compared with $[Al(H_2O)_6][MS]_3$ under the same reaction conditions. It can be inferred that CH₃SO₃ group is easier to replace by other ligands due to weaker coordination with Al than water molecules. These observations clearly show that Al^{3+} is the active site for the catalytic reactions. As a consequence, the hexaaquaaluminum methanesulfonate, which can be converted into an active $Al_2(\mu$ -OH)(MS)₅ catalyst, may be a promising Lewis acid catalyst precursor in acid catalyzed organic reactions.

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Empirical formula	$C_3H_{21}AlO_{15}S_3$
Formula weight	420.36
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ /c
a/Å, α/°	16.5119(15), 90
b/Å, β/°	6.4294(6), 118.629(6)
c/Å, γ/°	17.7145(14), 90
Volume/Å ³	1650.7(3)
Z	4
$\rho_{calc}/g \cdot cm^{-3}$	1.691
Absorption coefficient (μ/mm^{-1})	0.572
<i>F</i> (000)	880
Crystal size/mm ³	0.130×0.130×0.120
2θ range for data collection/°	2.304-26.087
Index ranges	-20≤h≤20, -7≤k≤7, -21≤l≤21
Reflections collected	26322
Independent reflections	3253
Data / restraints / parameters	3253 / 0 / 203
R _{int}	0.1115
Goodness-of-fit on F^2	1.061
Final <i>R</i> indexes $[I > 2 \operatorname{sigma}(I)]^a$	$R_1 = 0.0332 \text{ w} R_2 = 0.0886$
Final <i>R</i> indexes [all data]	$R_1 = 0.0378 \text{ w} R_2 = 0.0923$
Extinction coefficient	0.0066(6)

Table 1. Crystal data and structure refinement of [Al(H₂O)₆][MS]₃.

^{*a*} R= $\sum |F_0 - F_c| / \sum |F_0|$, wR₂=[$\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2$]^{1/2} where F_0 , F_c are the experimental structure factor and structure factor; S=[$\sum w(F_0 - F_c)^2 / (m-n)$]^{1/2} where 'm' is the number of reflections and 'n' is the total number of parameters refined.

Figure captions

Figure 1. The view of local coordination environment of Al^{3+} cation and hydrogen bond of the compound $[Al(H_2O)_6][MS]_3$ (dotted lines represent hydrogen bond, hydrogen in CH₃SO₃ is omitted).

Figure 2. The TG/DTG curves of [Al(H₂O)₆][MS]₃.

Figure 3. FTIR spectra of the $[Al(H_2O)_6][MS]_3$ (a) and its calcination product at 265 °C for 5 h (b).

Figure 4. Reusability of [Al(H₂O)₆][MS]₃ precursor and Al₂(µ-OH)(MS)₅ on esterification.

Figure 5. Reusability of $[Al(H_2O)_6][MS]_3$ precursor and $Al_2(\mu$ -OH)(MS)₅ catalyzed ketalization reaction.

Figure 6. Reusability of $Al_2(\mu$ -OH)(MS)₅ catalyzed tetrahydropyranylation of *n*-butanol with DHP.

265~365 °C → $Al_2(\mu$ -OH)(MS)₅ + 5H₂O + MSH $2 [Al(H_2O)_6][MS]_3 -$ **365~520 °C** amorphous Al_2O_3 + trace $Al_2(SO_4)_3$













