PREPARATION OF γ-ALUMINA FROM ALUMINUM AMINOALKOXIDES

MOSTAFA M. AMINI, S. JAVAD S. SABOUNCHEI*, FATEMEH MIRNAJAFI*, MAHDI MIRZAEE, MAASOMEH SHARBATDARAN

Department of Chemistry, Shahid Beheshti University, Tehran 1983963113, Iran *Department of Chemistry, Bu-Alisina University, Hammedon, Iran

E-mail: m-pouramini@cc.sbu.ac.ir

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New aluminum aminoalkoxides, $Al(OCH_2CH_2OCH_3)_2(OCH_2CH_2NH_2)$ (1) and $Al(OCH_2CH_2OCH_3)(OCH_2CH_2)_2NH$ (2), were synthesized from aluminum 2-mehoxyethoxide by alcohol exchange method and after characterization by infrared, mass, 'H and ²⁷Al NMR spectroscopes have been used as precursors for the preparation of γ -alumina by conventional and hydrothermal hydrolysis. The hydrolysis process revealed that the precursors are significantly less sensitive to hydrolysis than the parent aluminum alkoxides. Thermal analysis indicates that the gel prepared from hydrothermal hydrolysis losses about 65% weight upon heating to 800°C. The X-ray diffraction shows that in the conventional and hydrothermal hydrolysis of (1) and (2) pseudoboehmite phase forms and converts to fine γ -alumina by calcination at 800°C. The scanning electron microscopy shows that the alumina prepared by hydrothermal hydrolysis is more uniform than the powder obtained from conventional one. The prepared aluminum aminoalkoxides have good potential for casting monolithic gel by sol-gel process.

INTRODUCTION

The synthesis of materials with tailored properties is one of the most active areas of material science [1, 2]. Among so many materials, y-alumina due to the significant application in catalysis, electronic and ceramic industry has been studied extensively [3]. Various processes have been employed for the preparation of high quality alumina, including sol-gel processing from aluminum alkoxides. The advantage of sol-gel route for the synthesis of alumina, such as high surface area, purity, narrow size and pore distribution, with respect to conventional routes is well established [4, 5]. The commercially available aluminum alkoxides are very sensitive to moisture and in order to be used as a precursor for preparation of alumina, a chelating agent for control of hydrolysis-condensation and improving quality of alumina is require [6,7]. It is well known that the coordination number of aluminum atom in aluminum alkoxides increases by introducing chelating agent and consequently rate of hydrolysis-condensation decreases and that reflect on the properties of final materials. However, large amount of carbon in the precursor gels, as shown by thermal analysis [8], will prevent from complete crystallization of alumina at lower temperature; and calcination at higher temperature will led to aggregation or phase transformation. Furthermore, trace amount of carbon residue in the final product can have negative impact on quality of powder, which will be an obstacle for the preparation of high quality materials for advanced technology. In similar context, modification of aluminum alkoxides with externally chelating agents for stabilization of sol and fabrication of alumina thin films is not suitable.

The aim of this work is to use internally coordinated aluminum aminoalkoxides instate of commercially available aluminum alkoxides, in order to reduce the rate of hydrolysis, and explore possibility for the preparation of transparent gel and fabrication of monolithic part by conventional hydrolysis or preparation of high quality alumina by hydrothermal route, which is not accessible from commercial precursors.

EXPERIMENTAL

Synthesis of precursors

All manipulations were carried out under dry nitrogen atmosphere using standard Schlenk line technique [9]. Monoethanolamine, diethanolamine, 2-methoxyethanol and aluminum 2-butoxide were obtained from Merck. Due to the hydroscopic nature of monoethanolamine and diethanolamine, they dried and distilled over potassium. Aluminum 2-methoxyethoxide was prepared from aluminum 2-butoxide and 2-methoxyethanol by alcohol exchange method [10] in benzene and purity of it was established by spectroscopic techniques.

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Alcohol exchange method also was used for the preparation of aluminum aminoalkoxides. In a typical reaction, aluminum 2-methoxyethoxide was refluxed with one mole equivalent of mono- or diethanolamine in benzene and then benzene and 2-methoxyethanol was removed by isotropy with benzene to furnish a white solid.

$Al(OCH_2CH_2OCH_3)_2(OCH_2CH_2NH_2)$ (1)

White solid, m.p. 82-83°C. FT-IR (CH₂Cl₂, cm⁻¹) 3254 m, 3150 m, 2874 s, 1840 m, 1453 v, 1092 s, 836 m, 677 v, 587 vw. Mass spectra data: m/e 181 [(M-2C₂H₄)]⁺. ¹H NMR (500 MHz, chloroform-d) δ 2.7 (s, NH₂), 3.2-3.6 (m, OCH₃, CH₂O, CH₂N), 3.7-3.9 (m, AlOCH₂). ²⁷Al NMR (500 MHz, Chloroform-d) δ 15.2 and 69.9.

$Al(OCH_2CH_2OCH_3)(OCH_2CH_2)_2NH(2)$

White solid, m.p. 102°C. FT-IR (CH₂Cl₂, cm⁻¹) 3256 m, 3155 m, 2875 s, 1455 v, 1231 s, 836 m, 677 v, 587 vw. Mass spectra data: m/e 205 (M⁺), 177 [(M-C₂H₄)]⁺. ¹H NMR (chloroform-d) δ 2.8 (b, NH), 3.2-3.6 (m, CH₂O, OCH₃, CH₂N), 3.6-4.2 (OCH₂). ²⁷Al NMR (500 MHz, chloroform-d) δ 23.3.

Hydrolysis of aluminum aminoalkoxides

Conventional hydrolysis

A 0.25 M solution of aluminum aminoalkoxide in 2-methoxyethanol were hydrolyzed by a mixture of water and 2-methoxyethanol (1/10) in several stages with vigorously stirring. Solution remained clear up to addition of 18 mole equivalents of water to alkoxides ratio. Solution was refluxed for two hours and then was cast in a beaker and transparent monolithic gel was prepared.

Hydrothermal hydrolysis

For hydrothermal assisted hydrolysis, aluminum aminoalkoxides were diluted with 2-methoxyethanol to 50% and then was loaded to a glass container and transferred into a 300 ml stainless steel autoclave chamber. The gap between autoclave chamber and glass container was covered with 50 ml of distilled water and then autoclave tightly was closed in order to prevent from escape of water from autoclave during heating and then was hea-ted to 200°C. After twenty-four hours, autoclave was cooled and dry powder was collected and characterized.

Characterization techniques

X-ray diffraction (XRD) patterns of powder were collected on a Phillips PW-1730 diffractometer with Cu K α radiation. Thermal analysis was carried out in a Rheometric Scientific STA-1500 with heating rate of 10°C/min in air. Electron microscopy was performed on

a Phillips XL-30 scanning electron microscope (SEM). For observation of morphology by SEM, powders were coated with gold/palladium. Specific surface areas were measured using BET method on a Quantasorb instrument at 77 K by nitrogen adsorption (S_{BET}). Infrared spectra were recorded (KBr pellets) on a Bomem MB-Series FT-IR spectrophotometer working at a resolution of 4 cm⁻¹. Mass spectra were obtained on a Shimadzu QP-1100 EX spectrometer at 20 eV. ¹H and ²⁷Al NMR data were recorded on a Bruker Avance DRX 500 MHz spectrometer.

RESULTS AND DISCUSSION

The new precursors that used for the preparation of y-alumina have been characterized by infrared, ¹H and ²⁷Al NMR spectroscopes. Incorporation of alkanolamines into aluminum alkoxide was established by appearance of amine protons in 1H NMR spectra in addition to change of 27Al NMR spectra after introducing mono- and diethanolamine. Qualitative observation made during the initial experiment indicated that the new precursors are significantly less sensitive to hydrolysis than the parent aluminum alkoxide. For instance solution of (1) remains transparent up to addition of 12 mole equivalents of water, where as the parent aluminum alkoxide, Al(OCH₂CH₂OCH₃)₃, produce opaque gel by addition of only six mole equivalents of water. Interestingly, aluminum aminoalkoxide with diethanol-amine substitution, (2), shows even less sensitivity to hydrolysis than monoethanolamine derivative, (1), by accepting 18 mole equivalents of water and remaining transparent. The higher stability toward hydrolysis is attributed to coordination of amine group to aluminum atom. The results are in good agreement with ²⁷Al NMR chemical shifts, which shows aluminum atom of (2) in solution is only five coordinate, whereas for (1) four and five coordinated aluminum atoms exist simultaneously in solution, which four coordinated aluminum atom is the dominate species [11]. The unusual stability of these aluminum aminoalkoxide precursors make them good candidate for casting monolithic gel and possibly for preparation of monolithic alumina. The monolithic gel that obtained from hydrolysis of precursor (2) by 18 mole equivalents of water after drying for several weeks in room temperature is shown in figure 1.



Figure 1. Picture of a monolithic gel prepared from hydrolysis of compound (2).

X-ray diffraction

The X-ray diffraction pattern of sample obtained from hydrothermal hydrolysis of (2) depicted in figure 2. Sample display five weak reflections at 14.4, 28.7, 38.2, 46.0 and 49.4 which are assigned to (020), (120), (031), (131) and (051) reflection of pseudoboehmite, respectively [12]. Interestingly, comparison of XRD results of materials obtained from hydrothermal hydrolysis of (1), (2) and aluminum 2-butoxide (table 1) indicate that introducing amine group to aluminum alkoxides; prevent material from complete conversion to beohmite and lead to the formation of pseudoboehmite phase. By taking into account the coordination of amine to aluminum, slow hydrolysis for aluminum alkoxides are expected [13]. XRD pattern of powder obtained from hydrothermal hydrolysis of (1) similarly showed formation of pseudoboehmite. Ironically, the X-ray diffraction patterns of gels prepared form conventional hydrolysis of (1) and (2) similarly showed formation of pseudoboehmite phase, which converted to fine γ -alumina by calcination at 800°C.



Figure 2. XRD pattern of powder prepared from hydrothermal hydrolysis of compound (2).

Table 1. Summary of XRD analysis of materials obtained from hydrothermal hydrolysis of aluminum alkoxides.

Precursor	Before calcination	After calcination
Aluminum butoxide	Boehmite	γ-alumina
(1)	Pseudoboehmite	γ-alumina
(2)	Pseudoboehmite	γ-alumina

Thermal analysis

Thermal analysis of product obtained from hydrothermal hydrolysis of aluminum aminoalkoxide, (2), is shown in figure 3. The TGA curve shows that the sample losses about 20 % weight upon heating to 200°C. This weight loss accompanied by an endothermic peak in DSC curve indicates that the weight loss is due to the elimination of physically adsorbed water and possibly dehydroxylation. The distinct exothermic peak in DSC curve centered at 310°C with weight loss of about 43 % in TGA curve is attributed to combustion of carbonaceous materials that remained in the gel due to the incomplete hydrolysis. It should be noted that weight loss due to the combustion of carbonaceous materials relatively is high and clearly demonstrate low susceptibility of aluminum aminoalkoxide to hydrolysis.



Figure 3. TGA/DSC curves of sample obtained from hydrothermal hydrolysis of compound (2).

Infrared spectroscopy

Due to the overlap of stretching vibration peak of NH with OH starching vibration peak of boehmite, formation of boehmite phase that obtained from hydrothermal hydrolysis of (1) and (2) was ambiguous from their infrared spectra; contrary to powder obtained from hydrothermal hydrolysis of aluminum alkoxides without amine functional group [14]. Furthermore, the infrared spectra of materials that obtained from conventional hydrolysis differ from materials prepared by hydrothermal hydrolysis.

Scanning electron microscopy

Morphologies of materials obtained from hydrothermal and conventional hydrolysis are investigated by scanning electron microscopy. The SEM micrographs of powders that prepared by hydrothermal and conventional hydrolysis of compound (1), after calcination at 800°C, are shown in figures 4a and 4b, respectively. The alumina prepared by hydrothermal hydrolysis is more uniform, and average particle size of alumina that obtained by hydrothermal and conventional hydrolysis is about 50 nm and 75 nm, respectively. The particle sizes to some extent are in agreement with the values, 35 and 50 nm, calculated from surface areas (181 and 120 m^2/g , respectively). It seems that hydrothermal hydrolysis of aluminum aminoalkoxide resulted to the formation finer powder. The difference in morphologies of two alumina can be attributed to two distinct mechanisms, however, further work is needed in order to reach a solid conclusion.





Figure 4. SEM micrographs of a) hydrothermal processed sample b) conventional processed sample.

CONCLUSIONS

In this paper the possibility of utilizing modified aluminum alkoxides as precursors in casting monolithic gel by conventional hydrolysis, and also in preparation of fine nanoparticles alumina by hydrothermal hydrolysis is demonstrated. The new aluminum alkoxides are comparatively less hydrolysable than their parent alkoxide and no special precaution is needed for their handling; in contrast to parent aluminum alkoxides. The less susceptibility of new aluminum aminoalkoxides is attributed to the connectivity of amine group to aluminum atom according to the ²⁷Al NMR data.

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PŘÍPRAVA γ-ALUMINY Z AMINOALKOHOLÁTŮ HLINITÝCH

MOSTAFA M. AMINI, S. JAVAD S. SABOUNCHEI*, FATEMEH MIRNAJAFI*, MAHDI MIRZAEE, MAASOMEH SHARBATDARAN

Department of Chemistry, Shahid Beheshti University, Tehran 1983963113, Iran *Department of Chemistry, Bu-Alisina University, Hammedon, Iran

Nové aminoalkoholáty hlinité, Al(OCH₂CH₂OCH₃)₂ (OCH₂CH₂NH₂) (1) a Al(OCH₂CH₂OCH₃)(OCH₂CH₂)₂NH (2), jsme připravili z 2-metoxyetanolátu hlinitého metodou výměny alkoholu a po jejich charakterizaci IČ, hmotovou, ¹H a ²⁷Al NMR spektroskopií jsme z nich připravili γ-aluminu konvenční a hydrotermální hydrolýzou. Ukázalo se, že prekursory jsou podstatně méně citlivé k hydrolýze než původní alkoholáty hlinité. Termická analýza odhalila, že gely připravené hydrotermální hydrolýzou ztrácejí asi 65% hmotnosti při zahřátí na 800°C. Podle rtg difrakce (1) a (2) přechází konvenční a hydro-termální hydrolýzou na pseudoboehmit a ten se transformuje na jemně krystalickou γ-aluminu žíháním na 800°C. Řádkovací elektronová mikroskopie ukázala, že alumina připravená hydro-termální hydrolýzou má stejnorodější částice než získaná konvenční cestou. Připravené aminoalkoholáty hlinité by byly vhodné na odlévatelné monolitické gely připravené metodou sol-gel.