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Generalized preparation method and characterization of aluminum isopropoxide, aluminum phenoxide, and aluminum *n*-hexyloxide

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ABSTRACT

We report an optimized synthesis of aluminum *n*-hexyloxide (AH), aluminum phenoxide (APh) and aluminum isopropoxide (AIP) with high yields. Aluminum alkoxides, among other applications, are important starting materials to produce high surface area alumina catalyst supports for catalytic applications, such as hydrocracking and supported Fischer–Tropsch catalysts (FT). One mole of aluminum was reacted with excess alcohol in the presence of 0.001 mole mercuric chloride catalyst. All solid alkoxides were obtained in high yields (90–95%) and analyzed by ^{1}H NMR, ^{13}C NMR and ^{27}Al NMR, X-ray diffraction (XRD), ICP-MS and elemental analysis. Aluminum *n*-hexyloxide was synthesized and characterized for the first time. Results indicate that fresh AH, APh, and AIP have the same coordination number of aluminum, but AIP changes as it ages.

1. Introduction

Metal alkoxides are used to make Al_2O_3 (alumina) catalyst supports for a wide range of applications, including hydrocracking, hydrodesulfurization and Fischer–Tropsch catalysis (FT) [1–6]. Unlike metal nitrates and chlorides, metal alkoxides are easily purified; they hydrolyze to produce hydrated oxides with no anionic contaminations [7,8]. Properties of alumina, notably surface area and pore size, depend on a number of factors, including the nature of the aluminum alkoxide starting material [6–8]. Since the identity of the parent alkoxide influences the catalytic properties of the alumina support, it is important to develop an efficient method to synthesize different aluminum alkoxides.

The physical properties of metal alkoxides vary with the electronegativity and coordination number of the metal, as well as the nature of the attached alkyl group [7], where the identity of the parent alcohol influences the electronic and steric properties of the alkoxide. This, in turn, modifies the structure of the corresponding alkoxide [9].

Many studies have been performed focusing on the preparation of alumina with selected properties such as particle size, surface area, pore volume, and pore diameter, using aluminum isopropoxide [3,8,10–13], aluminum *sec*-butoxide [3,14–16], aluminum ethoxide [3], and aluminum phenoxide [9]. We have previously [17,18] designed nano alumina supports with high surface areas (150–350 m^2/g) and large pore sizes (13–20 nm) using various aluminum alkoxides. Here we report a generalized method to synthesize aluminum alkoxides, which can be employed as starting materials for the production of alumina based catalyst supports.

Aluminum alkoxides contain acceptor and donor centers and exist as monomers, dimers, trimers and tetramers with various coordination numbers. The oligomerization is inversely dependent on the steric demand of the R group attached to the oxygen [19]. Al^{3+} can form four-, five-, and six-coordinated complexes. The structure of aluminum ethoxide is polymeric, containing five-coordinated aluminum [20]. Aluminum tert-butoxide is dimeric containing aluminum with a coordination number of four [20]. Aluminum isopropoxide exists as a trimer in freshly prepared samples or as a tetramer in aged samples [20,21]. The coordination numbers of aged AIP can be six and four [22]. Aluminum phenoxide has been reported to be a trimer containing aluminum with coordination numbers of four and five. [23]. Different coordination numbers of aluminum are also reported in di-, tri-, tetra-, and polynuclear aluminum alkoxides [19,24–27].

Aluminum alkoxides can be produced without using a catalyst, but the reaction rates are very slow [28] and thus aluminum alkoxides are more efficiently formed using three equivalents of anhydrous alcohol with one equivalent of metal in the presence of 1 mol% mercury chloride $HgCl_2$ as catalyst (Eq. 1). [29] This reaction has been widely used to make simple alkoxides, including aluminum isopropoxide and aluminum ethoxide. In these cases, this route has become a well-known industrial process [7,28,30–32]. Tomar and Yoo [2,9] recently reported approaches to aluminum phenoxide and aluminum isopropoxide through this process as well.

$$Al + 3ROH \xrightarrow{0.01HgCl_2} Al(OR)_3 + 3/2H_2 \quad (1)$$

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The surface of elemental aluminum is covered by a oxide layer, thus it is thought $HgCl_2$ will activate this surface and accelerate the reaction kinetics [30]. The $HgCl_2$ initially reacts with aluminum to produce the Al^{3+} ion, which then reacts with the alcohol to form the alkoxide adduct. We have optimized the process by lowering the reaction time and the concentration of $HgCl_2$ to obtain improvements in yield, which now allows for a complete characterization of these useful products. Optimum conditions include use of excess alcohol and a lower amount of mercuric chloride catalyst [9,21,28,29]. The work presented herein includes a generalized preparation and characterization of divergent aluminum alkoxide structures including aluminum isopropoxide ($R = C_3H_7$), aluminum phenoxide ($R = C_6H_5$), and aluminum *n*-hexyloxide ($R = C_6H_{13}$). Notably, the approach allows for the first generalized synthesis and characterization of aluminum *n*-hexyloxide. Synthesis of aluminum *n*-hexyloxide from 1-hexanol is significant in that this alkoxide possesses low water, high stability, and efficient reactivity for the production of aluminum oxide nanomaterials. We selected aluminum isopropoxide, aluminum phenoxide, and aluminum *n*-hexyloxide, as a general representation of steric bulk effects since the A-values of the attached alkyl groups are different for each group. Isopropyl = 2.15 kcal/mol, phenyl = 2.7 kcal/mol, and ethyl (analogue of *n*-hexyl) = 1.75 kcal/mol [33]. The effect of ligand environment on the physiochemical properties of aluminum alkoxides influences the properties of the alumina [3,11,34]. The structure and properties of aluminas produced from these aluminum alkoxides with different steric characteristics can now be produced and studied using the reported method.

2. Experimental

2.1. Materials

The aluminum *n*-hexyloxide (AH) was prepared from the reaction of aluminum (granular, Spectrum, 99.6%) and 1-hexanol (anhydrous, Alfa-Aesar, 99.0%) in the presence of $HgCl_2$ (Fischer, 100.0%) as a catalyst. Aluminum phenoxide (APh) was prepared from aluminum (granular, Spectrum, 99.6%) and phenol (detached crystals, Alfa-Aesar, >99%) in the presence of $HgCl_2$ (Fischer, 100.0%) as catalyst and dried THF (EMD, 99.99%) as solvent. Aluminum isopropoxide (AIP) was prepared from aluminum (granular, Spectrum, 99.6%) and isopropyl alcohol (Sigma-Aldrich, >99.8%) in the presence of $HgCl_2$ (Fischer, 100.0%) as catalyst. HNO_3 (EMD, 70%-Omni Trace) was used to dissolve samples for the ICP-MS experiment.

2.2. Equipment

AH, AIP and APh were characterized by IR, XRD, NMR, ICP and elemental analysis. To obtain the IR spectra, nujol mulls of the solid alkoxides were analyzed with a Nicolet (Avatar 360) spectrophotometer. Elemental analysis was performed (Galbraith Laboratory) for AH, APh and AIP separately using a C, H, O combustion method. The structure of the synthesized alkoxids were determined by Powder X-ray diffraction (XRD) using a Panalytical X'Pert Pro X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm) at a scanning rate of 0.02 s^{-1} in the 2θ ranges from 10° to 90°. The XRD power source was (40 kV, 40 mA). ^{1}H NMR, ^{13}C NMR and ^{27}Al NMR were collected on a Varian NMR-S 500 MHz instrument using a pfg-enabled dual-broadband probe. The ^{1}H NMR, gCOSY, ^{13}C NMR and ^{27}Al NMR spectrum of aluminum isopropoxide (AIP) and aluminum *n*-hexyloxide (AH) were recorded with benzene-d6 as solvent. The spectrum of aluminum phenoxide (APh) was recorded with DMSO-d6 and methanol-d4 as solvent. All samples were prepared and measured at ambient temperature 25 °C. We used ICP-MS (Elan 6000, Perkin Elmer) to determine the levels of Hg impurity in the synthesized alkoxides. 2% nitric acid was used to dilute and dissolve the alkoxides followed by 30 min sonicating using a Branson 1510 sonicator.

Table 1
Synthesis conditions to produce APh, AH, and AIP.

Product	Aluminum mole	Alcohol mole	$HgCl_2$ mole	Reflux time (h)	Solvent
APh	1	4.3 (Phenol)	0.001	24	THF
AH	1	7.9 (Hexanol)	0.001	11	–
AIP	1	8.3 (Isopropanol)	0.001	9	–

2.3. Synthesis

2.3.1. General procedure

To ensure an anhydrous environment, solvent and alcohols were dried over molecular sieves. The flask was fitted with a condenser and a $CaCl_2$ tube. A sand bath and heat regulator were used to provide homogenous heating for the reactions. One mole of aluminum was treated with excess alcohol in the presence of catalytic mercuric chloride (0.001 mole) and refluxed. Vacuum distillation was applied to remove un-reacted alcohol and solvent in the case of APh and un-reacted alcohol in the case of AIP and AH. AIP was purified by further vacuum distillation. However, APh and AH were collected without further vacuum distillation since they were shown to decompose upon heating. Experimental conditions to synthesis aluminum alkoxides are shown in Table 1.

2.3.2. Aluminum n-hexyloxide (AH)

Al (1 mole) was added to excess 1-hexanol (7.9 mole) and (0.001 mole) $HgCl_2$ in a flask. The mixture was refluxed for 11 h under N_2 atmosphere with stirring then the solution was allowed to cool overnight without stirring. Since AH decomposed on vacuum distillation, it was collected from the top layer of the flask and vacuum filtered with a Buchner funnel using filter paper (Fischer, P_4). ^{1}H NMR (C_6D_6): δ 0.8 (t, 3H, JCH = 6.97, 7.22 Hz, CH_3), 1.1 (m, 6H, CH_2), 1.3 (m, 2H, CH_2), 3.2 (m, 2H, CH_2). ^{13}C NMR (C_6D_6): δ 13.87 (s, CH_3), 22.64 (s, CH_2), 25.44 (s, CH_2), 31.62 (s, CH_2), 32.77 (s, CH_2), 62.34 (s, CH_2). ^{27}Al NMR (C_6D_6): δ 56.5 (s, 4 or 5 coordinated Al). XRD (γ alumina at 1000 °C): 2θ 25.7, 35.2, 37.9, 43.5, 52.6, 57.6, 60.1, 61.5. IR (nujol, Al–O–C, cm^{-1}): 1055.80 cm^{-1}.

2.3.3. Aluminum phenoxide (APh)

Al (1 mole) was added to excess phenol (4.3 mole), in 2 L dried THF (solvent) and (0.001 mole) $HgCl_2$ in a flask [9]. The mixture was refluxed for 24 h under a N_2 atmosphere with stirring. Solvent and alcohol were removed by vacuum distillation. Aluminum phenoxide was not extracted by further vacuum distillation since it decomposes on heating and was collected from the flask [9]. ^{1}H NMR (DMSO and methanol): δ 6.73 (m, 3H, CH), 7.12 (m, 2H, CH). ^{13}C NMR (DMSO and methanol): δ 115.55 (s, 2H, CH), 119.22 (s, 2H, CH), 129.77 (s, ^{1}H, CH), 157.63 (s, qC). ^{27}Al NMR (DMSO and methanol): δ 56.5 (s, 4 or 5 coordinated Al). XRD (γ and α alumina at 1000 °C): 2θ 25.7, 35.2, 37.9, 43.5, 52.6, 57.6, 60.1, 61.5, 19.5, 32, 37.7, 39.5, 45.8, 60.5. IR (nujol, Al–O–C, cm^{-1}): 1070.75 cm^{-1}.

2.3.4. Aluminum isopropoxide (AIP)

Al (1 mole) was added to excess isopropyl alcohol (8.3 mole) and (0.001 mole) $HgCl_2$ in a flask. The mixture was refluxed for 9 h under N_2 atmosphere with stirring. Afterward, vacuum distillation was applied to remove the un-reacted alcohol. Further

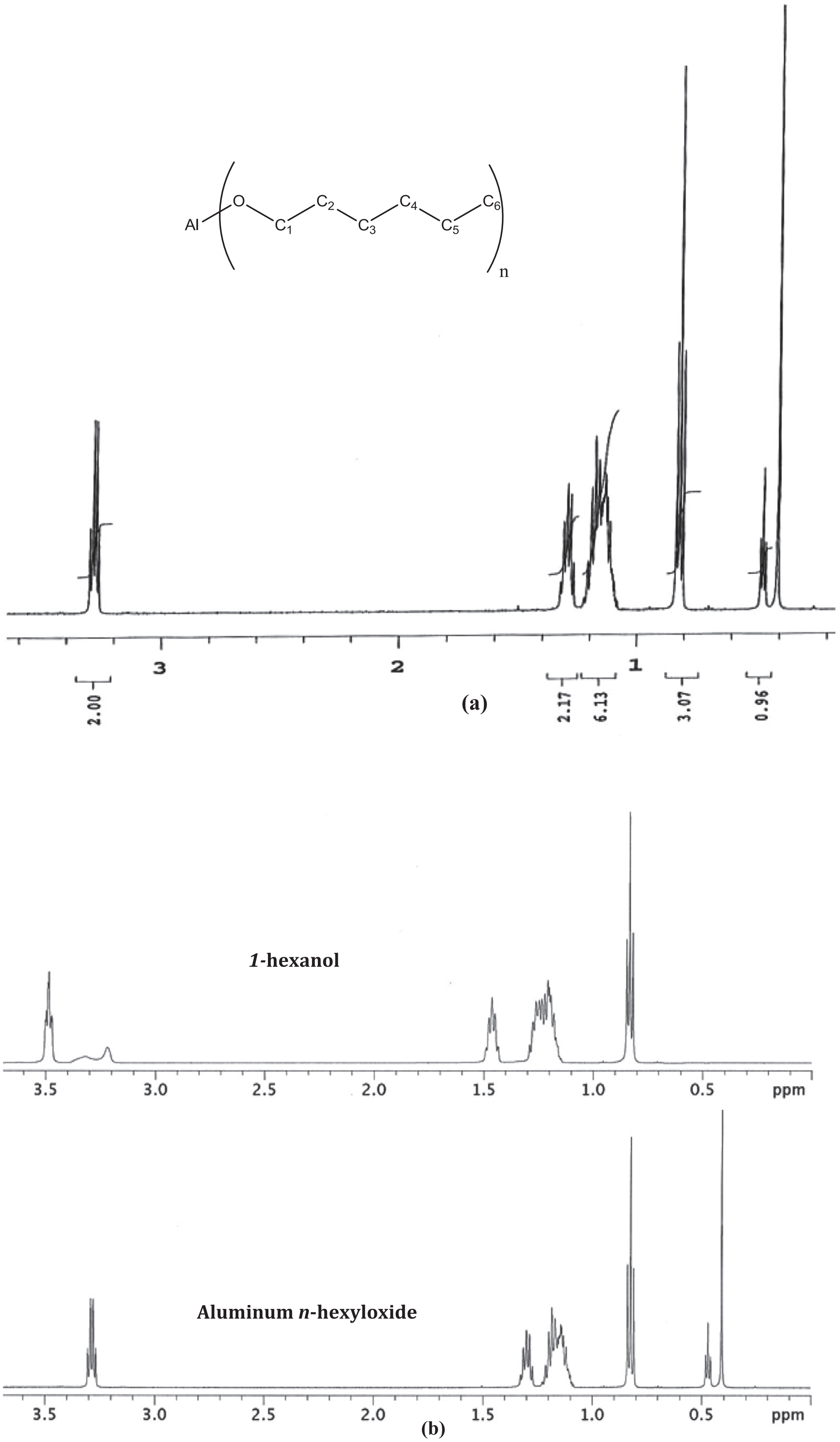

Fig. 1. (a)^{1}H NMR of aluminum *n*-hexyloxide, and (b) ^{1}H NMR of aluminum *n*-hexyloxide and 1-hexanol comparison.

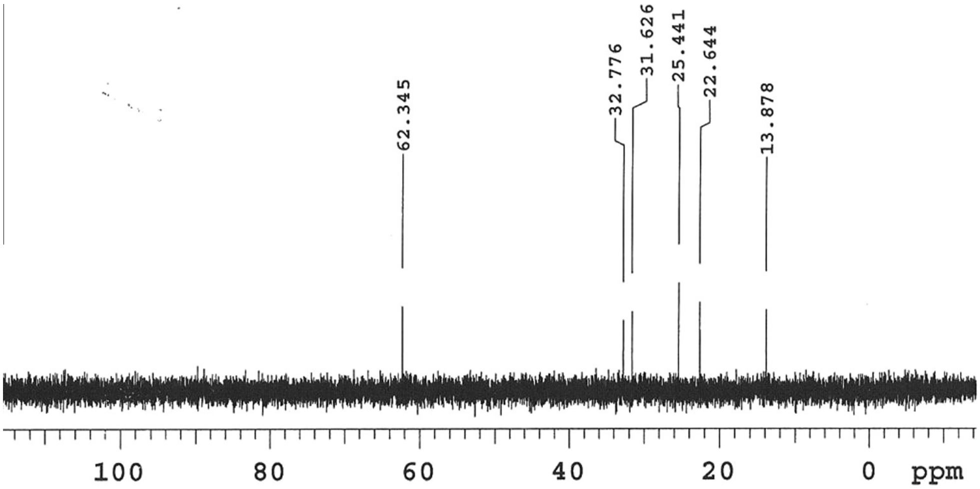

Fig. 2. ^{13}C NMR of aluminum *n*-hexyloxide ^{13}C NMR.

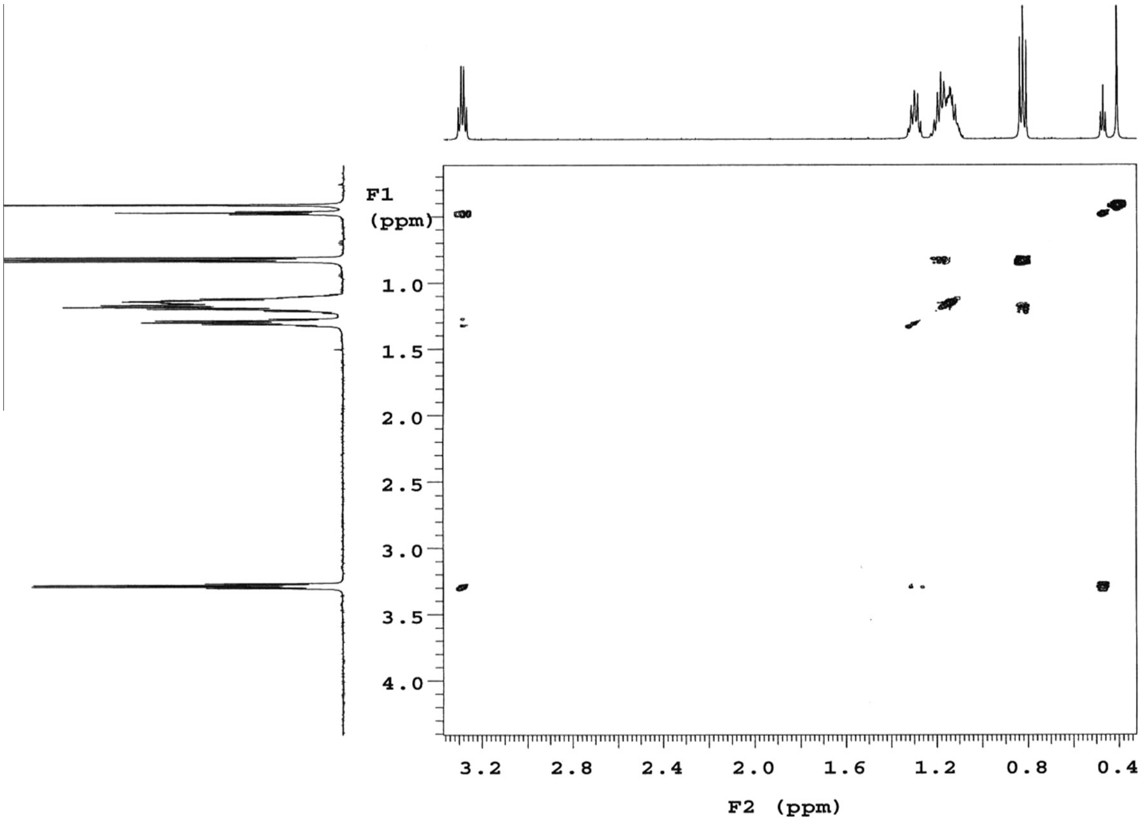

Fig. 3. gCOSY of aluminum *n*-hexyloxide.

vacuum distillation was applied to collect the viscous AIP from the flask. Freshly prepared AIP was aged to a white powder after 2 days. ^{1}H NMR (C_6D_6): δ 0.92 (d, 3H, JCH = 4.39 Hz, terminal-CH_3), 1.66 (d, 6H, JCH = 6.23 Hz, bridge-CH_3), 4.4 (h, 2H, terminal-CH), 4.6 (h, 2H, bridge-CH). ^{27}Al NMR (C_6D_6): δ 56.5 (s, 4 coordinated Al), 3.5(s, 6 coordinated Al). XRD (γ alumina at 1000 °C): 2θ 25.7, 35.2, 37.9, 43.5, 52.6, 57.6, 60.1, 61.5. IR (nujol, Al–O–C, cm^{-1}): 1033 cm^{-1}.

3. Results and discussion

Since the derivates of metal and alcohols are sensitive to trace amounts of water and decompose to alcohol and water, all steps were performed under an inert nitrogen atmosphere. Reaction times and reactant concentrations were varied to improve the yields. Aluminum *n*-hexyloxide was obtained in 95% yield. Aluminum phenoxide was synthesized in 90–95% yield and aluminum isopropoxide was produced in 95% yield. Some alkoxides (such as AH and APh) decompose without melting at high temperature but others can sublime without decomposition (such as AIP) [9].

3.1. FTIR

Fig. S1 shows the FT-IR spectra for AIP, AH, and APh. The absorption peaks in IR spectra confirm conversion of the alcohol peak around 3500 cm^{-1} to alkoxide peaks. The Al–O–C bond stretch of aluminum alkoxides appears at 1030–1080 cm^{-1} and the Al–O–Al bond shows absorption between 945 to 980 cm^{-1} as reported earlier [9,28,35].

3.2. NMR

The aluminum *n*-hexyloxide ^{1}H NMR (Fig. 1a) spectrum shows a triplet at 0.8 ppm due to a methyl group (C_6), a multiplet at 1.1 ppm due to (C_4,C_5,C_3), a multiplet at 1.3 ppm due to C_2 and a doublet of a triplet at 3.2 ppm due to C_1 attached to oxygen. The triplet appearing at 0.47 ppm was unexpected. Both the *J*-splitting in the ^{1}H NMR and the cross-peaks in the gCOSY show that this peaks are correlated with the signal at 3.2 ppm (Figs. 1 and 3). Given the relative intensity of 2:1 and the fact that this is coupled with C_1 suggests that there is a hydrogen attached to the oxygen of each alkoxide. This is not a signal from water as that appears at 0.41 in benzene-d6 and water would not show *J*-coupling to the methylene at C_1. This is also not free 1-hexanol in solution; as Fig. 1b compares aluminum *n*-hexyloxide and 1-hexanol in benzene-d6. The C_1, C_2 and C_3 hydrogens of aluminum *n*-hexyloxide are clearly shifted upfield due to the interaction of the oxygen atom with the aluminum. Furthermore, the alcohol peak in 1-hexanol is shifted approximately 3 ppm downfield relative to the hydroxyl peak in aluminum *n*-hexyloxide. Aluminum *n*-hexyloxide ^{13}CNMR shows peaks at 13.87, 22.64, 25.44, 31.62, 32.77 and 62.34 ppm corresponding to all six carbons in the alkyl chain (Fig. 2).

The aluminum phenoxide ^{1}H NMR shows two peaks with relative intensities of 3:2 at 6.73 and 7.12 ppm, respectively. The signal at 6.73 ppm corresponds to the meta C_3 and para C_4 hydrogens. 7.12 ppm corresponds to the ortho C_2 which is consistent with previously reported spectra [9]. Signals at 2.483, 3.498 and 4.077 were due to solvents (Fig. S2). Aluminum phenoxide ^{13}C NMR shows four peaks at 115.55, 119.22, 129.77 ppm due to C_2, C_3 and C_4 carbons and one peak at 157.63 due to quaternary carbon C_1. Signals at 47.9 and 39.9 are due to solvents (Fig. S3). The ^{1}H NMR of freshly distilled aluminum isopropoxide showed a doublet at 1.04 ppm due to CH_3 and a heptet at 3.8 ppm due to the CH group. The alcohol signal comes at 3.4 ppm (Fig. S4). Aged aluminum isopropoxide ^{1}H NMR showed two high field doublets at 0.92 and 1.66 ppm due to the terminal and bridged CH_3 respectively and two lower field heptets at 4.4 and 4.6 ppm due to terminal and bridged CH respectively. Signals at 3.6, 1.2 and 1.3 result from residual isopropyl alcohol (Fig. S5).

Aluminum phenoxide, freshly prepared aluminum isopropoxide, and aluminum *n*-hexyloxide ^{27}Al NMR all showed one broad peak at 50 ppm that is consistent with tetra and penta-coordinated Al (Fig. 4). The lack of an intense signal at 3.50 ppm is consistent with the absence of hexa-coordinated Al in these structures. Aged aluminum isopropoxide ^{27}Al NMR showed one broad peak at 50 ppm that indicates tetra-and penta-coordinated Al. The sharp signal at 3.50 ppm (Fig. 5) indicates the presence of hexa-coordinated aluminum (octahedral environment) [20,36].

All measurements indicate that synthesized aluminum alkoxide with Al(OR)$_3$ units oligomerized differently. Aluminum coordination number is 4 (Fig. 6a) or 5 (Fig. 6b) in APh, AH, and fresh AIP. However, the coordination number of freshly distilled AIP

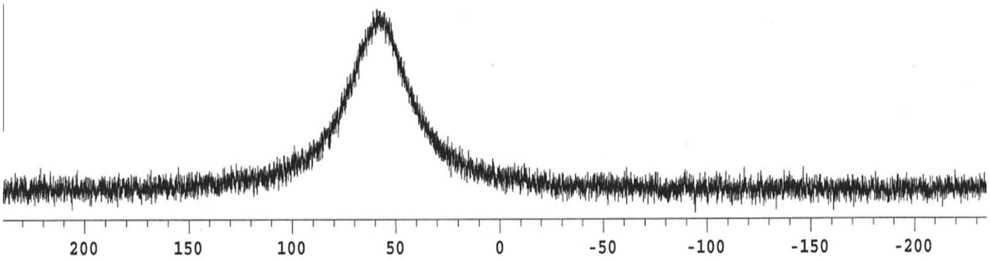

Fig. 4. ^{27}Al NMR of aluminum phenoxide, freshly prepared aluminum isopropoxide and aluminum *n*-hexyloxide.

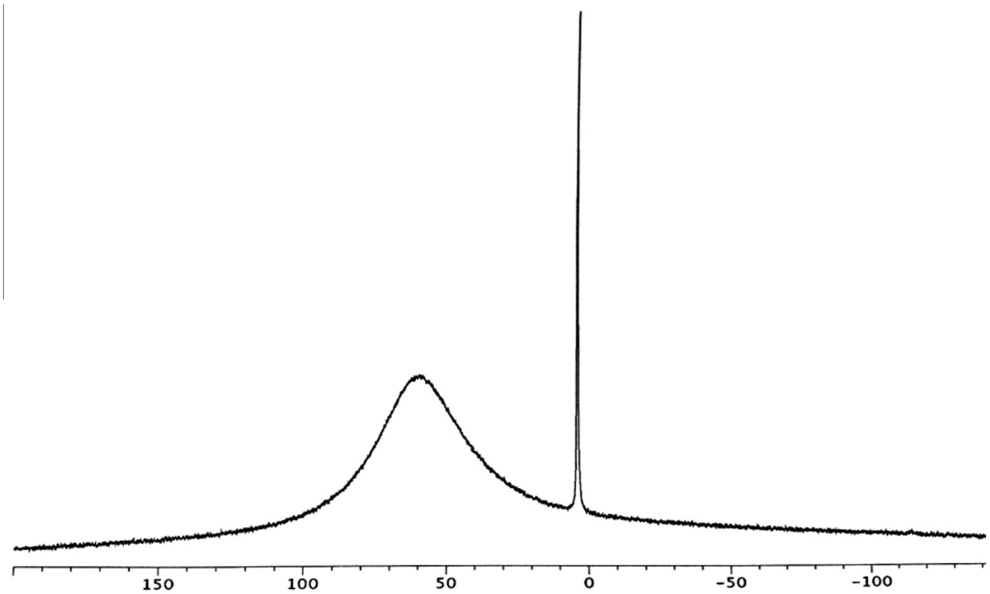

Fig. 5. ^{27}Al NMR of aged aluminum isopropoxide.

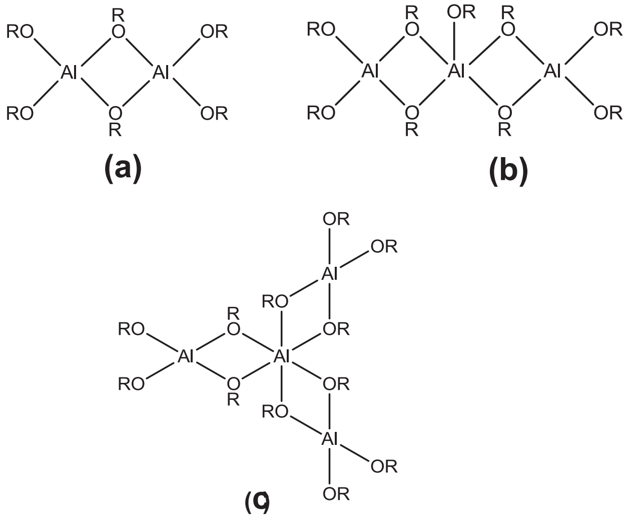

Fig. 6. (a) 4-coordinated aluminum (b) 5-coordinated aluminum (c) 6-coordinated aluminum.

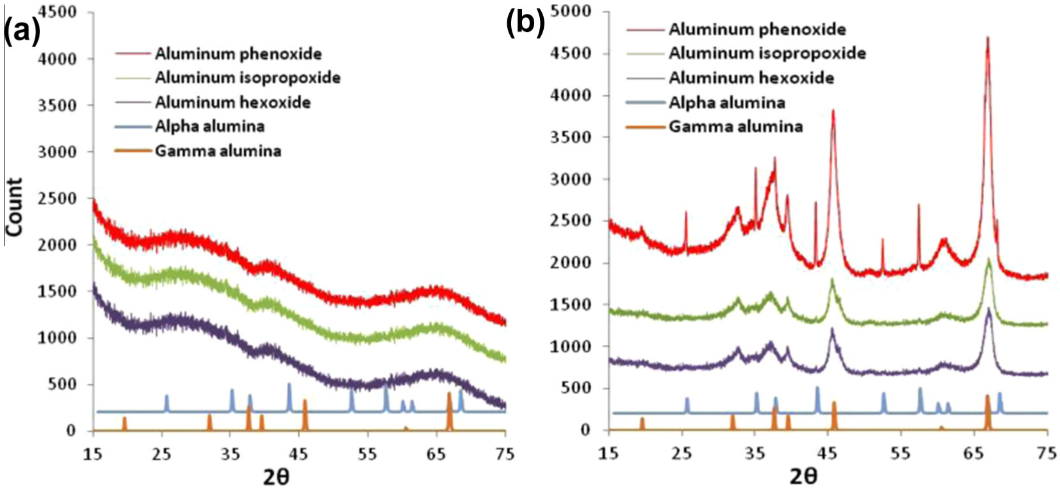

Fig. 7. X-ray diffraction patterns of (a) APh, AH, and AIP calcined at 550 °C (b) APh, AH, and AIP calcined at 1000 °C.

increases to six (Fig. 6d) as the alkoxide ages [37]. Aged AIP with high donor properties of oxygen of the alkoxy group (–OR) allows for formation of an oxygen bridged or polymeric structure with the attached oxygen functionality adopting a tetrameric structure. When the R group decreases donor-acceptor properties it leads to lower coordinated structures.

3.3. XRD

Fig. 7 shows the XRD patterns of alumina samples obtained by calcinations of the synthesized aluminum alkoxides at different temperatures. Fig. 7a shows powder X-ray diffraction patterns of aluminum phenoxide after calcination at 550 °C for 2 h. The peaks for all the calcined aluminum alkoxides are very broad, indicating that they are not highly crystalline. The particle sizes for these aluminas are less than 2 nm, based on the calculation from peak broadening using Scherrer formula [38]. Fig. 7b shows powder X-ray diffraction patterns of aluminum phenoxide at 1000 °C is crystalline with a pattern consistent with standard γ and α-alumina. XRD patterns of synthesized aluminum *n*-hexyloxide and aluminum isopropoxide after calcination at 1000 °C are crystalline, with a pattern consistent with standard γ-alumina. The particle sizes for these aluminas are less than 5 nm, based on the calculation from peak broadening using Scherrer formula [36]. All patterns were compared to an XRD standard patterns for α and γ alumina in the International Centre for Diffraction Data (ICDD) database software. Characteristic peaks of γ and α alumina (JCPDS ID card: 00029-0063) and (JCPDS ID card: 00001-1296), respectively, are seen in all patterns

Table 2
Mercury impurity in synthesized aluminum alkoxides.

Sample	Found, ppm
Aluminum isopropoxide	0.00
Aluminum Phenoxide	0.31
Aluminum hexoxide	0.42

3.4. ICP

It has been previously reported that ICP is a suitable technique for elemental analysis of aluminum isopropoxide [39]. Our experiments show that no mercury is detected in any sample (Table 2).

Table 3
Elemental analysis of synthesized and commercial aluminum isopropoxide.

Sample	C found	C calculated	O found	O calculated	H found	H calculated
Commercial AIP Alfa-Aesar (98%)	38.02	52.93	13.52	23.50	7.31	10.36
Synthesized AIP	39.14	52.93	15.82	23.50	8.70	10.36

3.5. Elemental analysis

Aluminum *n*-hexyloxide elemental analysis mass%: C calculated: 65.42; Found: 58.66. H calculated: 11.89; Found: 11.37. O calculated: 14.52; Found: 12.87. Aluminum phenoxide elemental analysis mass%: C calculated: 70.58; Found: 65.25. H calculated: 4.94; Found: 5.49. O calculated: 15.67; Found: 14.72. Aluminum isopropoxide elemental analysis mass%: C calculated: 52.93; Found: 39.14. H calculated: 10.36; Found: 8.7. O calculated: 23.50; Found: 15.82. The elemental analysis (C, H, and O) of synthesized aluminum alkoxides does not in agree well with the calculated C, H, and O values. To confirm purity, we compared synthesized aluminum alkoxides with available high purity commercial aluminum alkoxides. The results, as given in Table 3, show that elemental analysis of our synthesized aluminum alkoxides is closer to the calculated data than commercial aluminum alkoxides. Elemental analysis of metal alkoxides are often less accurate due to problems with stability and incomplete combustion.

4. Conclusions

We have developed a generalized reaction conditions employing excess alcohol and low catalyst loading (1 mole aluminum, excess alcohol and 0.1 mole% $HgCl_2$) to produce high yields (90–95%) of various aluminum alkoxides. Aluminum *n*-hexyloxide (AH), aluminum phenoxide (APh) and aluminum isopropoxide (AIP) were synthesized through this process. Aluminum *n*-hexyloxide was also synthesized and characterized for the first time using this approach. XRD data confirmed that nano γ- and α-alumina were produced using the synthesized alkoxides. ^{27}Al NMR, ^{13}C NMR, gCOSY and ^{1}H NMR spectra provide evidence for the structures of APh, AH, AIP. APh and AH structures do not aggregate. On the other hand, AIP tends to aggregate and forms tetrameric structures when aged. These alkoxides are currently being evaluated for use as starting materials to make high surface area catalyst nanomaterials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.06.019.

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