

Heteroleptic Derivatives of Aluminium(III) as Precursors for Nano-Al₂O₃: A Study on the Influence of Ligands on Morphology of Alumina

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Three metalloorganic derivatives of aluminium(III) [(CH₃COCHCOOCH₃)Al(OC₆H₄CH=NC₆H₄O)(EtOH)] (1), [(CH₃COCHCOCH₃)₂Al(*o*-MeC₆H₄O)]₂ (2) and Al(O^{*i*}Pr)₃ (3) were exploited as precursors of alumina through well-established sol-gel hydrolytic pathway. The resultant white alumina powders (a), (b) and (c) were characterized by FTIR, powder XRD, TEM and EDX analyses. Formation of pure alumina was confirmed through EDX and FTIR techniques. The powder XRD patterns of alumina samples established their existence in γ -phase. The morphological examination of all oxidic ceramics through TEM illustrated that the alumina powders (a) and (b) were fine and discrete nanorods whereas alumina powder (c) was highly agglomerated with irregular morphology.

Keywords: Aluminium, Alumina, Metalloorganic complexes, Alkoxides, Nanoparticles, Sol-gel method.

INTRODUCTION

Nanostructured Al₂O₃ was significantly utilized in orthopedics, dental restoratives, catalysis, electrochemical sensors, water repellent surface modifiers, ceramic and corrosion resistant coatings, electronics, wear resistant paints, refractory materials due to its biocompatibility, Lewis acidity, hydrophobicity, wear resistance, band gap, corrosion resistance and high strength [1-12]. The aforesaid applications of nano-sized alumina could be greatly attributed to its enhanced optical, mechanical, thermal, electrical and chemical properties.

There are several well established techniques like flame spray pyrolysis, double hydrolysis, chemical vapour deposition, laser ablation, precipitation, combustion, hydrothermal synthesis and sol-gel synthesis reported for the synthesis of alumina in nanoscale [13-20]. Amongst these, sol-gel is far advantageous while synthesizing nano-Al₂O₃ from heteroleptic metalloorganic complexes of aluminium due to the prospect of directing the hydrolysis and condensation steps, which govern the morphology of aluminium oxide.

Aluminium alkoxides like Al(O^{*i*}Pr)₃, Al(O^{*n*}Bu)₃ and Al(OEt)₃ were commonly utilized precursors of nano aluminium oxide

through sol-gel hydrolytic pathway [21,22]. The most common problem encountered while synthesizing nano alumina by sol-gel pathway using these aluminium alkoxides was precipitation instead of gelation due to irrepressible hydrolysis of alkoxy groups resulting undesirable coarse Al₂O₃ [23]. The rate of hydrolysis and condensation of parent aluminium alkoxides could be retarded predominantly by modifying the electronic environment around the metal by substituting existing alkoxy groups using various chelating ligands through alcohol elimination reactions [24]. The chelating agents often utilized in replacing rapidly hydrolyzable alkoxy groups were diols, oximes, amino-alcohols, Schiff's bases, carboxylic acids, β -diketones, pyrazolyl phenolates, β -ketoesters, etc. [25-34]. The varied kinetics of the resultant complexes towards hydrolysis and condensation during sol-gel processing determines the morphology of the alumina obtained.

In the current study, so as to witness the impact of the modified hydrolysis rates of aluminium alkoxides on the morphology of alumina, synthesis of alumina nanoparticles from [(CH₃COCHCOOCH₃)Al(OC₆H₄CH=NC₆H₄O)(EtOH)], [(CH₃COCHCOCH₃)₂Al(*o*-MeC₆H₄O)]₂ and aluminium(III) isopropoxide is tried through prominent sol-gel method.

EXPERIMENTAL

$\text{Al}(\text{O}^i\text{Pr})_3$ was procured from Avra Synthesis Pvt. Ltd. India. FTIR spectra of alumina powders were recorded with Shimadzu IR Affinity 1 spectrometer in the range of 4000-400 cm^{-1} . The powder XRD patterns of alumina samples were recorded on D8 Advance X-ray diffractometer from Bruker. EDX coupled JEM 2100 HRTEM by JEOL was used for elemental analyses and in capture of TEM images.

Synthesis: Heteroleptic derivatives of aluminium(III) **1** and **2** were synthesized as reported earlier [35,36]. In brief, complex **1** was synthesized by adding ethanolic solution of Schiff's base 2-[[[(2-hydroxyphenyl)imino]methyl]phenol and a dry benzene solution of methyl acetoacetate to one more anhydrous benzene solution of $\text{Al}(\text{O}^i\text{Pr})_3$ in 1:1:1 stoichiometry. Precursor **2** was synthesized by reacting *tris*(isopropoxy)-aluminium(III) with acetylacetonate and *o*-cresol using moisture free benzene as solvent in 1:2:1 stoichiometry.

Transformation of $[(\text{CH}_3\text{COCHCOOCH}_3)_2\text{Al}(\text{OC}_6\text{H}_4\text{-CH=NC}_6\text{H}_4\text{O})(\text{EtOH})]$ (1**) to nano Al_2O_3 by sol-gel:** Precursor **1** (3 g) was added to 30 mL of dry 2-propanol and few drops of conc. HCl was added while the solution was under gentle heating and stirring. The resultant clear solution was added with 0.2 mL of mixture of H_2O -PrⁱOH (1:5) and stirred for 4 h. As immediate gel formation was not achieved, a surfeit of water-isopropanol mixture was added occasionally in diminutive quantities and stirred uninterrupted for 48 h to corroborate complete hydrolysis. The gel attained was dried for 12 h in a preheated oven (maintained above 100 °C) and the subsequent xerogel was triturated and frequently washed using water and acetone. Finely ground xerogel was sintered over a muffle furnace at 900 °C for 4 h to produce white alumina (**a**). Similar synthetic procedure has been followed in transforming precursors **2** and **3** into alumina (**b** and **c**), but no acid catalyst was added and the gelation was immediately formed.

RESULTS AND DISCUSSION

Controlled hydrolysis of complexes **1**, **2** and **3** was achieved by adding 0.2 mL of water-isopropanol solvent mixture (1:5) to their discrete clear solutions in anhydrous isopropyl alcohol. Gel formation was quick in case of complexes **2** and **3**. On the other hand, gelation was achieved through addition of acid catalyst along with prolonged stirring and heating while hydrolyzing precursor **1**. Complete hydrolysis of complexes **1**, **2** and **3** was ensured by addition of surplus of water-isopropanol concoction. The gel obtained for all the three samples were dried to xerogels in hot oven (>100 °C). The resultant creamy white powders were washed with water and acetone for several times to ensure removal of inorganic and organic impurities. Lastly, the samples were sintered in a muffle furnace at 900 °C to obtain alumina powders **a**, **b** and **c**.

FTIR analysis: Occurrence of wide and strong absorption peaks around 518 cm^{-1} in the FTIR spectra of all the three alumina samples undoubtedly indicates the stretching of aluminium and oxygen bond in Al_2O_3 .

XRD studies: The diffraction patterns of the alumina powders obtained through sintering at 900 °C (Fig. 1) were

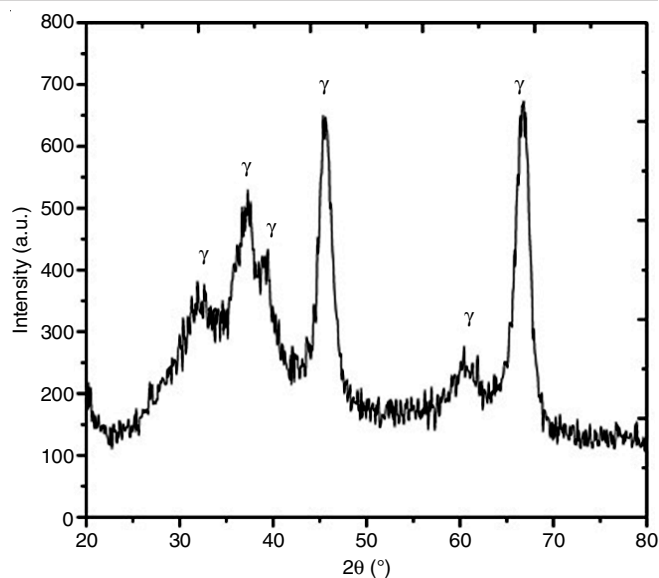


Fig. 1. X-ray diffraction of alumina (**a**) sintered at 900 °C

compared with the standard (JCPDS file No. 10-0425) and confirmed as γ -alumina [37]. The 2θ values were observed at 32.3° (220), 37.3° (311), 39.2° (222), 45.6° (400), 60.7° (511) and 66.7° (440) (Fig. 1).

Morphological studies: The morphological investigations of alumina samples through TEM analysis indicated formation of alumina powders (**a**) and (**b**) in nanoscale whereas alumina powder **c** was highly agglomerated and resembled flakes in appearance. Al_2O_3 (**a**) nanoparticles produced from complex **1** appeared as spherical and rod shaped discrete particles ranging from 3.2 nm to 54.6 nm and the average was found to be 21.3 nm (Fig. 2). Alumina nanopowder (**b**) derived from precursor **2** was irregularly spherical in shape and the size ranges from 21.61 to 94.67 nm with an average size of 62.7 nm (Fig. 3). On the other hand, aluminium triisopropoxide (**3**) yielded bulky, extremely agglomerated alumina (**c**) particles with irregular morphology (Fig. 4). The extraordinary purity of the alumina samples was proved by the EDX mappings.

Conclusion

In the present investigation, three different aluminium(III) complexes with variety of electronic and steric environments were tested as precursors for nano alumina through sol-gel technique. Highly moisture stable heteroleptic Al(III) complex (**1**) with tridentate Schiff's base and bidentate β -ketoester resulted in fine and discrete nano alumina (**a**) with average grain size of 21.3 nm. Moderately moisture stable modified Al(III) alkoxide (**2**) with strong β -diketonate and bridged cresol modifiers resulted in nano-aluminium oxide (**b**) with a mean size of 62.7 nm. Unmodified, highly moisture sensitive $\text{Al}(\text{O}^i\text{Pr})_3$ (**3**) resulted in coarse oxidic ceramic powder (**c**). Thus, the significance of the modifiers in altering the hydrolytic susceptibility of aluminium alkoxides is clearly demonstrated.

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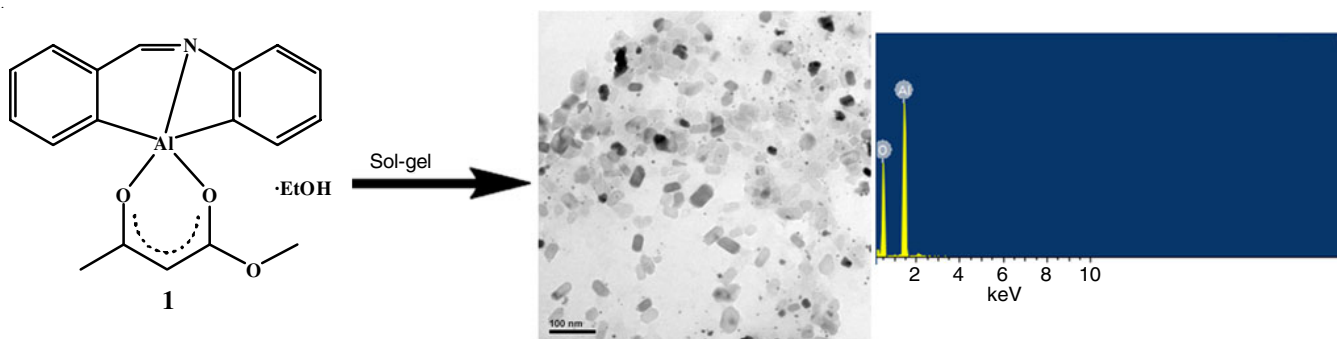


Fig. 2. Transformation of $[(\text{CH}_3\text{COCHCOOCH}_3)\text{Al}(\text{OC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{O})(\text{EtOH})]$ to nano Al₂O₃

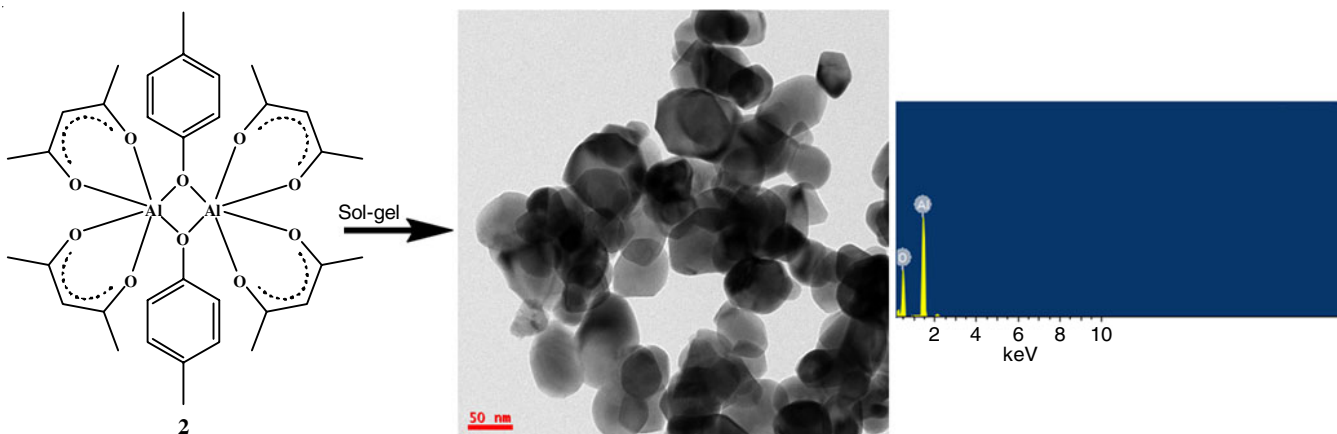


Fig. 3. Transformation of $[(\text{CH}_3\text{COCHCOCH}_3)_2\text{Al}(o\text{-MeC}_6\text{H}_4\text{O})_2]$ to nano Al₂O₃

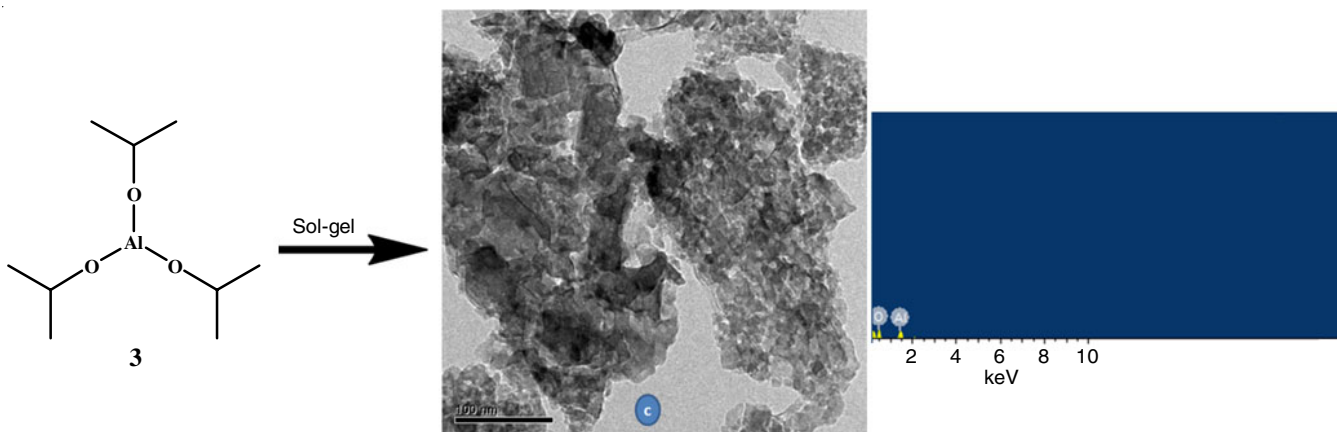


Fig. 4. Transformation of Al(OⁱPr)₃ to alumina

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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