

Scientific paper

# Peptization and Al-Keggin Species in Alumina Sol

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Dedicated to the memory of Professor Ljubo Golič

## Abstract

A novel sol-gel proces for preparing alumina sol is reported in this article. Using this new method alumina sols can be prepared from inexpensive materials such as inorganic aluminium salts. Influence of the type and amount of acid (HCl(aq) and HNO<sub>3</sub>(aq)), used for aluminium hydroxide peptization, were investigated. <sup>27</sup>Al NMR, N<sub>2</sub> absorption (single-point BET), X-ray diffraction (XRD), infrared spectroscopy (IR) and dynamic thermoanalytical meauserments (TG) were used to detect the properties of the alumina sol and xerogel. The results of <sup>27</sup>Al NMR shows there are Keggin-Al<sub>13</sub><sup>7+</sup> species in the sol. Besides Al<sub>13</sub><sup>7+</sup> species some other reactive polymers with hexameric ring structure also exist in the sol. The results of this work show that the higher ratio  $n(\text{acid}) / n(\text{Al}(\text{OH})_3)$  (peptization ratio) leads to an increase in crystallinity and amount of water in the aluminium xerogel, and to a decrease in specific surface area. The results also show that the role of acid is not only as catalyst for peptizing, but also as reactant to react with aluminium hydroxide to produce the Al<sub>13</sub><sup>7+</sup> species, and other reactive aluminium polymers.

**Keywords:** Alumina, sol-gel, peptization

## 1. Introduction

Transition alumina-based compounds have a wide range of applications in many areas. Particularly as special hydrates, their application covers a variety of products such as chemicals, pharmaceuticals, catalysts, plastics and pigments, synthetic substitutes, papers and as alumina ceramics, refractories, insulators, abrasives, porcelain, electronics, etc.<sup>1,2</sup>

Their properties depend on preparation procedures and a thorough knowledge of hydroxide precursor is fundamental to obtain a pure, well defined and reproducible support. Boehmite  $\gamma\text{-AlO}(\text{OH})$  remains the most important precursor or intermediate for the synthesis of aluminas. The preparation of boehmite or pseudoboehmite can be performed by several ways and has been the subject of numerous papers. They can be sorted in three main preparation procedures, leading to different shapes, morphologies and surface properties:

1. Solid state decomposition of gibbsite or hydralgillite Al(OH)<sub>3</sub>,<sup>3</sup>

2. Precipitation in aqueous solution from acidic or basic aluminium solutions, with the control of the basic or acidic reactant,<sup>4,5</sup>

3. Sol-gel procedures, starting generally from aluminium alcoholates or aqueous aluminium solution, with possibility to obtain xerogels<sup>6</sup> or aerogels.<sup>7</sup>

The third method for preparation of xerogels or aerogels is interesting because it is a possibility for preparation of very pure and reproducible boehmite, with finely controlled procedures and steps, from hydrolysis of molecular precursors to the synthesis of "tailor made" materials.

The initial process in the sol-gel alumina synthesis is sol formation. The synthesis of boehmites by neutralization of aluminium salts has been extensively studied in the literature,<sup>8</sup> but only a few reports refer to the peptization of materials.<sup>9,10</sup>

The most cited process for making alumina sol, the precursor of the alumina materials, developed by Yoldas, is to hydrolyze aluminium iso-propoxide or sec-butoxide in a large excess of water in the presence of an acid catalyst with acid/Al mol ratio of 0.07.<sup>11,12</sup> The type of acid

was found to play a much more important role than the pH of the system. Complete peptization was observed when the concentration of HCl(aq), HNO<sub>3</sub>(aq) or HClO<sub>4</sub>(aq) varied between 0.03 and 0.1 acid/Al mol ratio. It appears that there are two requirements for the type of acid that have to be satisfied: the anion of the acid must be noncomplexing for aluminium ions, and the acid must be sufficiently strong to produce the necessary charge effect. The rate of peptization depends greatly on the heat treatment, higher temperatures and pressures enhance it.

In this paper, a novel sol-gel process is reported for preparation of alumina sol from inexpensive materials such as inorganic aluminium salts. The influence of the type (HCl(aq), HNO<sub>3</sub>(aq)) and amount of acid used for aluminium hydroxide peptization was investigated. The boehmite was characterized by N<sub>2</sub> absorption (single point BET), X-ray diffraction (XRD), infrared spectroscopy (FT-IR), dynamic thermogravimetry (TG), and the sol was characterized by <sup>27</sup>Al NMR.

## 2. Experimental

Boehmite sols were prepared by peptization of freshly precipitated Al(OH)<sub>3</sub>, obtained by bubbling of NH<sub>3</sub> gas into AlCl<sub>3</sub> or Al(NO<sub>3</sub>)<sub>3</sub> (Merck, p. a.) aqueous solution (0.05 molar) until the pH 9. The product was filtered and rinsed with distilled water in order to exclude Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup> ions. Al(OH)<sub>3</sub>(s) was then suspended in distilled water, and various amounts of 1M HCl(aq) or 1M HNO<sub>3</sub>(aq) were added. The acid / Al mol ratio was 0.04, 0.1, 0.2, 0.4 respectively. The suspensions were heated to 70 °C and stirred with magnetic stirrer at this temperature for one hour in an open beaker in order to form the transparent sol. The final sol was transferred into the petrie dish and dried at 80 °C for 12 hours.

<sup>27</sup>Al NMR spectra of sol samples were recorded in a VARIAN NMR Unity Inova 300 upgrade spectrometer operating at 300 MHz. Chemical shifts were referenced to 0.1M AlCl<sub>3</sub>(aq) solution (pH = 1.0). BET surface area of aerogel particles was determined by N<sub>2</sub> adsorption-desorption at 77 K, using BET one point method. Measurements were made on a AREA-meter II Bb 226. All samples were previously desorbed at 100 °C under vacuum (10<sup>-6</sup> torr) for at least one hour before measurement.

The crystallinity of boehmite powder was determined using a Siemens D-5000 diffractometer with CuK<sub>α</sub> radiation in the range of 2θ = 5°–70° by a 0.04° step.

IR analysis was carried out using a Bruker 66 spectrometer in the range from 400 to 4000 cm<sup>-1</sup>, with samples prepared by the KBr method.

Dynamic thermoanalytical measurements were performed on a Mettler Toledo TGA/SDTA 851° instrument. TGA curves were run simultaneously on each 10 mg sample from 30 °C to 800 °C in an atmosphere of air using a heating rate of 4 K/min.

## 3. Results and Discussion

Before discussing the results, a few remarks should be made about the crystalline structure and preparation condition of the Al<sub>13</sub><sup>7+</sup> species. The tridecamer polyoxocation of aluminium [AlO<sub>4</sub>Al<sub>12</sub>(OH)<sub>24</sub>(OH<sub>2</sub>)<sub>12</sub>]<sup>7+</sup> can be prepared by base hydrolysis of [Al(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup> and has been isolated and characterized in the solid state by Johansson et al.<sup>13</sup> and in <sup>27</sup>Al NMR studies in solution by Akitt<sup>14</sup>. In tridecamer with Keggin structure the central tetrahedrally coordinated aluminium atom is surrounded by twelve edge-linked octahedrally coordinated aluminium atoms. The structure is shown in Fig 1.

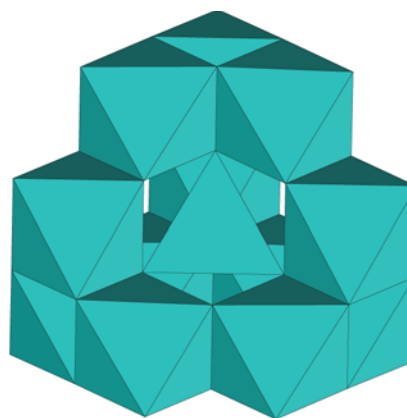
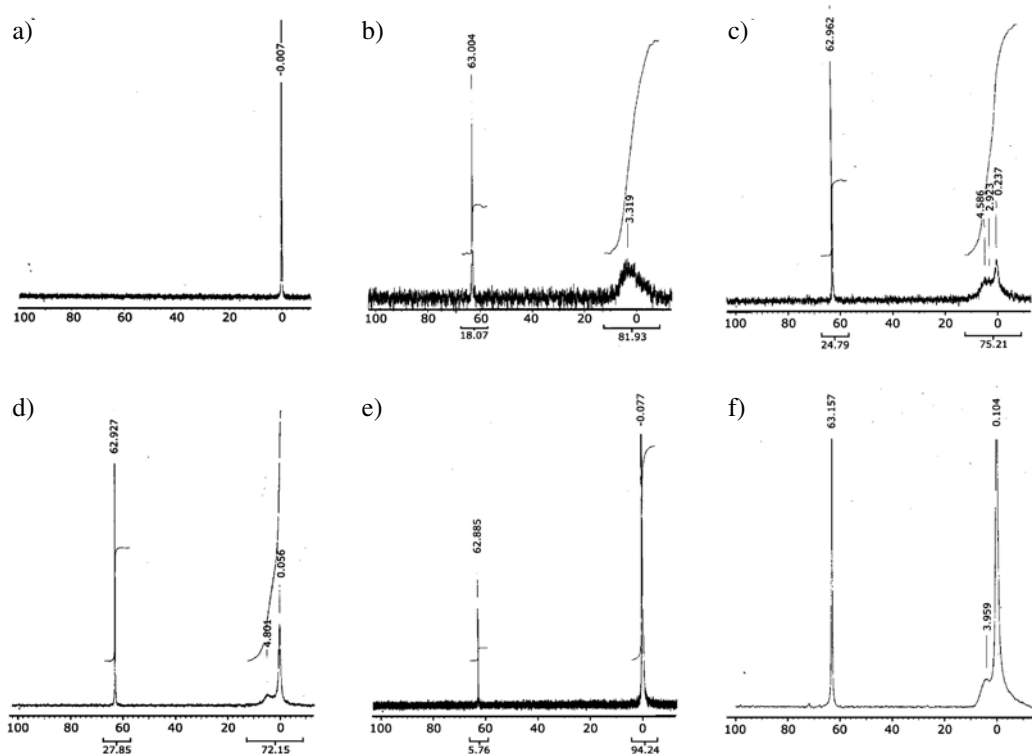


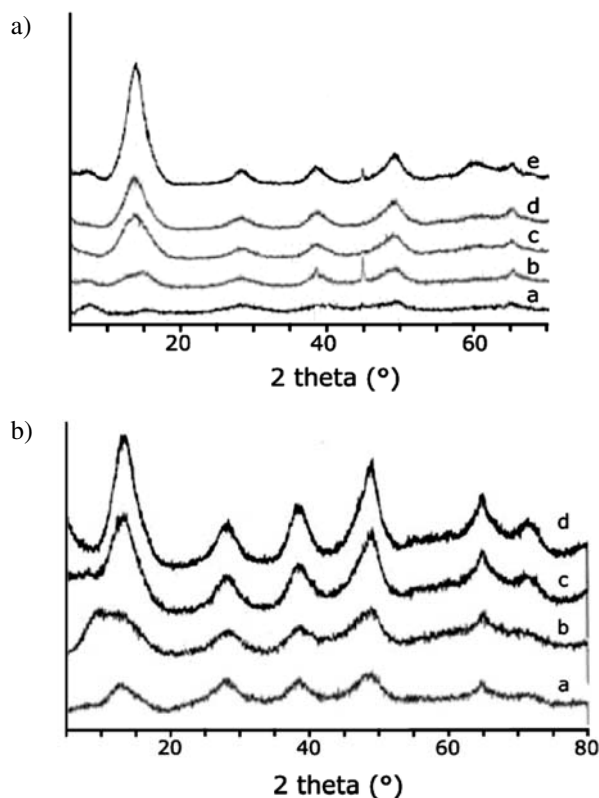
Figure 1. The Al<sub>13</sub> unit characterized by Johansson et al<sup>13</sup>

In this work we studied the aluminium species in the sol by <sup>27</sup>Al NMR. Fig 2 shows the spectra of sol peptized with HCl(aq) or HNO<sub>3</sub>(aq) at different peptization ratios. The <sup>27</sup>Al NMR for a solution of [Al(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup> ions exhibits a sharp intensive peak at 0 ppm assigned to octahedrally coordinated aluminium atoms (Fig 2.a). As the peptization ratio decreases, the octahedrally coordinated aluminium atoms are converted into dimer and tridecamer (Fig 2, b-e). Our studies have shown that aluminium sol have the following chemical shifts: sharp peak of monomer, [Al(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup>, at 0 ppm; broad peak of dimer [(OH<sub>2</sub>)<sub>4</sub>Al(OH<sub>2</sub>)<sub>2</sub>Al(OH<sub>2</sub>)<sub>4</sub>]<sup>4+</sup>, at about 5 ppm; and sharp peak of tridecamer, [AlO<sub>4</sub>Al<sub>12</sub>(OH)<sub>24</sub>(OH<sub>2</sub>)<sub>12</sub>]<sup>7+</sup>, at 62 ppm. This is in accord with previous <sup>27</sup>Al NMR studies.<sup>15–18</sup>

The spectra of sol peptized with HNO<sub>3</sub>(aq) (Fig 2,f) and the spectra peptized with HCl(aq) (Fig 2,d) are very similar to each other. Thus, two points of the <sup>27</sup>Al NMR results deserve special comment. First, the tridecamer polyoxocations of aluminium can be prepared by adding a suitable amount of acid to the aluminium hydroxide suspension, besides by base hydrolysis of aluminium salts in aqueous solutions. Another point is that the ratio of tridecamer species to other aluminium species is greatly affected by the peptization ratio in the range studied. Upon decreasing the peptization ratio, the octahedrally coordina-



**Figure 2.**  $^{27}\text{Al}$  NMR spectra of different sol samples: a) solution of  $[\text{Al}(\text{OH}_2)_6]^{3+}$ , b) to e) sol peptized with HCl, peptization ratio 0.04, 0.1, 0.2, 0.4, f) sol peptized with  $\text{HNO}_3$ , peptization ratio 0.2.



**Figure 3.** X-ray diffraction patterns of gel powders: A) sol peptized with  $\text{HNO}_3(\text{aq})$ , peptization ratio: a) to e) 0, 0.04, 0.1, 0.2, 0.4 B) sol peptized with  $\text{HCl}(\text{aq})$ , peptization ratio: a) to d) 0.04, 0.1, 0.2, 0.4

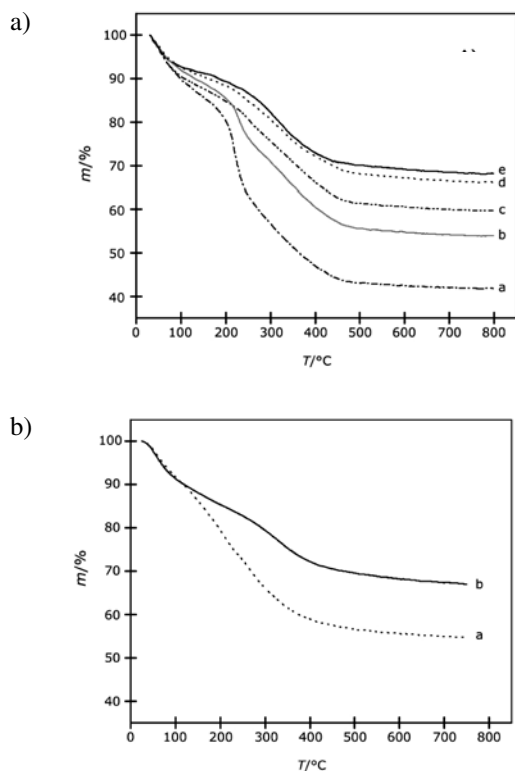
ted aluminium atoms are converted into dimer and tridecamer.

Diffraction patterns of alumina gel powders as a function of peptization ratio are shown in Fig 3. All peaks correspond to boehmite and pseudo-boehmite phase according to ASTM 212307 cards. Samples exhibit a pronounced diffraction line broadening due to small crystallite size.

In these XRD patterns the differences can be observed, compared to the crystallinity of powders. For sol obtained by  $\text{HCl}(\text{aq})$  and  $\text{HNO}_3(\text{aq})$  peptization respectively, the crystallinity increases with increasing peptization ratio. This suggests that the amount of acid added for peptization plays an important role not only for the stabilization of sol, but also influence the crystallinity of powders.

Typical TG curves are reported in Fig 4. The thermogram profiles could be divided into three main regions. The first region finishes at about 200 °C. It accounts for 10–15% of the mass loss. The second region ends before 500 °C. It represents the major part of the mass loss, about 20–40%. The last region appears as a continuous mass loss, and stop at about 800 °C. It only corresponds to about 2% of the mass loss.

These kind of curves have often been reported in the literature.<sup>16,17</sup> The first region has been attributed to the desorption of physically adsorbed water, the second region to the conversion of boehmite into  $\gamma$ -alumina, and the last step to the elimination of residual hydroxyl groups. For the given samples, the change of the mass loss induced by heating have been followed. Because this mass loss



**Figure 4.** TG patterns of the alumina xerogels: A) Al-hydroxide peptized with  $\text{HNO}_3$ , peptization ratio: a) 0.4, b) 0.2, c) 0.1, d) 0.04, and e) without peptization; B) Al-hydroxide peptized with  $\text{HCl}$ , peptization ratio: a) 0.4, and b) 0.04.

is essentially from the loss of water and in order to help the interpretation of the experimental data we converted the sample mass loss into  $N(\text{H}_2\text{O})$ , where  $N(\text{H}_2\text{O})$  represents the number of water molecules in the sample for  $\text{Al}_2\text{O}_3$  formula. Thus for anhydrous boehmite,  $\text{AlOOH}$ ,  $N(\text{H}_2\text{O}) = 1$ , while  $N(\text{H}_2\text{O}) = 0$  per  $\alpha\text{-Al}_2\text{O}_3$ . The results are reported in Table 1.

**Table 1.** Effect of peptization ratio on the  $N(\text{H}_2\text{O})$  of xerogel.

Peptization ratio	$N(\text{H}_2\text{O})$	
	$\text{HCl}$	$\text{HNO}_3$
0.00	2.4	2.4
0.04	2.6	2.7
0.1	⋮	3.6
0.2	⋮	4.6
0.4	4.5	7.7

The results show that  $N(\text{H}_2\text{O})$  increases with the higher peptization ratio. It is also obvious that the higher  $N(\text{H}_2\text{O})$  is obtained when  $\text{HNO}_3(\text{aq})$  is used as peptizing agent.

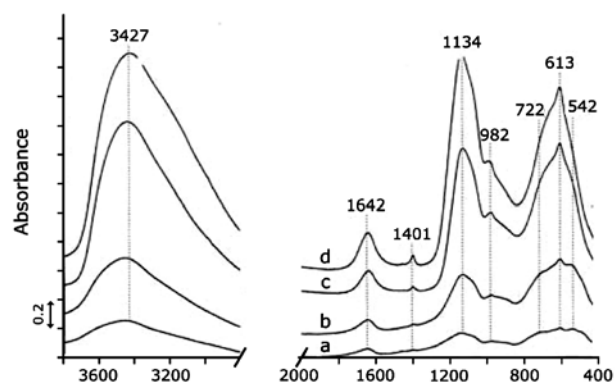
Specific surface areas of the xerogels are shown in Table 2. As it can be seen from the results, the continuous changes of the peptization ratio lead to discontinuous changes of the specific area of aluminium xerogels. There is

clear absence of simple additivity in the influence of this factor on the sol and gel formation processes. It is also obvious that a higher specific surface area value is obtained when  $\text{HCl}(\text{aq})$  is used as the peptization agent. It is also evident that a higher concentration of acid generally leads to the lower specific area, which agrees with the data presented in the paper of R. I. Zakharchenya<sup>21</sup>.

**Table 2.** The specific surface area ( $S_m$ ) in  $\text{m}^2/\text{kg}$  of the Al – xerogels

Peptization rate	$S_m \text{ m}^2/\text{kg}$	
	$\text{HCl}(\text{aq})$	$\text{HNO}_3(\text{aq})$
0.00	160858	160858
0.04	190757	104567
0.1	143627	24289
0.2	80430	15383
0.4	90478	81645

The IR spectra of different aluminium xerogels are shown in Fig 5. On the basis of the characteristic IR bands<sup>22–25</sup> all spectra show bands for nanocrystalline boehmite and amorphous product. There are prominent –OH stretching and bending modes associated with the interlayer hydrogen bonds of the structure. All products exhibit a broad band near 3100–3700 and 1642  $\text{cm}^{-1}$ , attributed to stretching and bending modes of adsorbed water.



**Figure 5.** IR spectra of the alumina xerogels: sol peptized with  $\text{HCl}$ , peptization ratio: a) 0.1, b) 0.2, c) 0.4, d) 0.04.

The peak at 1642  $\text{cm}^{-1}$  corresponds to water of hydration, the band at 3700–3200  $\text{cm}^{-1}$  to stretching vibration of the –OH group connected to Al cation, the band at 1134–1050  $\text{cm}^{-1}$  to symmetrical bending (O)H...O–H vibrations. The other vibration bands at 900–400  $\text{cm}^{-1}$  do not really match tetrahedral coordination Al–O stretching modes, hence, the site symmetry for the amorphous product was probably ill defined. However, recently some studies proposed Al atom pairs formation.<sup>24</sup> In this case, the proposed assignment for 613  $\text{cm}^{-1}$  band could corres-

pond to a 4–4 pair, whereas the band at  $982\text{ cm}^{-1}$  is near the suggested assignment for a 6–6 pair.

The peak intensity at  $1642\text{ cm}^{-1}$  generally increases with increasing peptization ratio, confirming that increasing acid content for peptization causes increase of inter-layer water content. This is in agreement with TG-results, which show that  $N(\text{H}_2\text{O})$  increases with the increasing peptization ratio.

## 4. Conclusion

A novel sol-gel process has been developed, in which the alumina sol can be prepared from inexpensive materials such as inorganic aluminium salts. The amount and type of acid ( $\text{HCl}(\text{aq})$  or  $\text{HNO}_3(\text{aq})$ ) added for peptization of aluminium hydroxide affect the amount of water in prepared gel as well as the specific surface area of the gel powder.  $^{27}\text{Al}$  NMR characterization shows that  $\text{Al}_{13}^{7+}$  species exist in the aluminium sols. Besides the  $\text{Al}_{13}^{7+}$  polymers, some other reactive polymers with six-membered ring structure were also detected in the mixture. The role of the acid in this work is not only for peptizing, but also for reacting with amorphous aluminium hydroxide to produce  $\text{Al}_{13}^{7+}$  ions as well as other reactive polymers. The different peptization ratio leads to the different amount of water in xerogel structure and changes the crystallinity of xerogel powders.

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## Povzetek

V prispevku smo opisali nov postopek priprave aluminijevega sola iz anorganskih aluminijevih soli. Vpliv različnih množin kislin ( $\text{HCl}(\text{aq})$  in  $\text{HNO}_3(\text{aq})$ ) na potek peptizacije aluminijevega hidroksida smo ugotavljali v Al-solu z  $^{27}\text{Al}$  NMR spektrometrijo, z merjenjem aktivne površine pripravljenih xerogelov, z enotočkovno BET metodo, z uporabo rentgenske praškovne difrakcije, infrardeče spektroskopije in termogravimetrije. Iz rezultatov  $^{27}\text{Al}$  NMR spektrometrije smo ugotovili, da so v pripravljenih Al-solih prisotne  $\text{Al}_{13}^{7+}$  zvrsti. V solih so prisotne tudi druge različne Al-polimerne strukture. Ugotovili smo, da razmerje množina kisline/množina  $\text{Al}(\text{OH})_3$  (delež peptizacije) pri pripravi sola odločilno vpliva na porazdelitev aluminija v različnih Al-zvrsteh v solu. Večji delež peptizacije povzroči manjšo kristaliničnost, večjo vsebnost vode in manjšo specifično površino kserogelov. Kislina pri peptizaciji ni samo katalizator, je tudi reagent, ki med peptizacijo reagira z aluminijevim hidroksidom in nastali produkti odločilno vplivajo na nadaljnji potek priprave in lastnosti kserogelov.