PRECIPITATION OF ALUMINUM HYDROXIDE FROM SODIUM ALUMINATE, BY TREATMENT WITH FORMALIN, AND PREPARATION OF ALUMINUM OXIDE

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SUMMARY

Aluminum oxide has been prepared by thermal dissociation of aluminum hydroxide obtained by precipitation, with formalin, from sodium aluminate with Na_2O/Al_2O_3 molar ratio, M, between 1.5 and 2.0. The effect of aluminate molar ratio on the pore volume and specific surface area of the aluminum oxide was investigated. It was found that pore volume and specific surface area increased with decreasing Na_2O/Al_2O_3 molar ratio. Aluminum oxide of pore volume 0.60–0.63 $cm^3 g^{-1}$ and specific surface area 300–320 $m^2 g^{-1}$ was obtained from sodium aluminate with $M = 1.5$. It was found that the concentration of the sodium aluminate mother liquor affects the yield of aluminum oxide and the pore volume but does not significantly affect the specific surface area.

INTRODUCTION

The development of new methods for preparation of aluminum oxide with controlled structural properties has always been important, because active aluminum oxide is of great practical significance. Special demands are made of aluminum oxide as an adsorbent for chromatography [1–3] and as a carrier for catalysts. These materials are usually called 'active aluminum oxide'. For these applications it is very important to obtain aluminum oxide with reproducible porosity and reproducible adsorption and catalytic properties. The adsorptive and catalytic properties of aluminum oxide have been investigated in depth, and have been shown to depend on the method used to obtain the aluminum hydroxide from which the oxide is prepared [4,5]. Each stage of the synthesis of aluminum hydroxide has an important effect on the properties of active aluminum oxide.

At the precipitation stage the structure of aluminum hydroxide depends on medium pH, temperature, solution concentration, and other conditions [6].

Aluminum hydroxide is usually obtained by hydrolysis of aluminum salts, aluminates, and alcoholates, and from metallic aluminum. Methods of precipitation from salts by treatment with ammonia [7–9] and from sodium aluminates by treatment with acids or aluminum salts [10–13] are most often used [4–9]. Precipitation of aluminum hydroxide from sodium aluminates has also been achieved by passing carbon dioxide through aluminate solutions [14] or by priming the aluminate solution with particles of aluminum hydroxide [14–16].

Caustic aluminate liquors of different concentration have been prepared from different starting materials and by different methods [17,18]. Static light-scattering and in-situ X-ray diffraction experiments have been performed on these solutions. The results showed there was a definite correlation between method of liquor preparation, size of the initial species present in solution, and the resulting crystalline phase. Liquor prepared by the dissolution of gibbsite under atmospheric pressure crystallized only as gibbsite and contained species with radii >25 nm in the initial solution. Identical solutions prepared from gibbsite and subsequently heated to 160°C for 16 h furnished a mixed crystalline product of gibbsite and bayerite and contained species with radius <55 nm in the initial solution. Solutions prepared from aluminum metal behaved identically with solutions prepared from gibbsite with additional heating.

Observation of the sequential formation of low and high-density aluminum-containing clusters which subsequently grew into colloidal size $Al(OH)_3$ crystallites provided the first visual evidence of the nucleation behavior of unseeded, supersaturated sodium aluminate solutions initially containing $Al(OH)_4^-$ species [19].

The nature of the species in Al(III)-containing solution as function of NaOH and Al(III) concentrations, before $Al(OH)_3$ nuclei formation and growth, has been investigated by use of light scattering. A significant decrease in light scattering was observed for NaOH concentrations between 1.0 M and 2.5 M. Further increasing the NaOH concentration to 7.0 M had no significant effect on the light scattering of the species, irrespective of Al(III) concentration. This indicates that the Al(III)-containing species formed have less structure or are small, consistent with predominantly $Al(OH)_4^-$ monomers, and effectively form part of the solution [20].

The effect of impurities on nucleation processes and aluminum hydroxide precipitation have been discussed [21,22]. A process has been de-

veloped to remove humate from Bayer spent liquor using polymers of dial-lyldimethyl ammonium chloride (polyDADMAC). Results from precipitation tests showed that increasing the humate concentration does not adversely affect the yield of precipitated aluminum trihydroxide ($Al_2O_3 \cdot 3H_2O$) but that the presence of humate during precipitation causes a decrease in the average particle size of the precipitate [21]. The presence of sodium gluconate inhibitor extended the region over which homogeneous nucleation was dominant, but did not affect the measured value of the interfacial tension and hence the critical nucleus size.

EXPERIMENTAL

Sodium aluminate solutions were prepared by dissolution of aluminum hydroxide in 35% sodium hydroxide solution ($d = 1.38$ g cm^{-3}) at 95°C. Three sodium aluminate samples with different M values (= Na_2O/Al_2O_3 ratio) were obtained: $M = 1.5$, containing 628 g L^{-1} $Al(OH)_3$; $M = 1.67$, containing 564 g L^{-1} $Al(OH)_3$; and $M = 2.0$, containing 471 g L^{-1} $Al(OH)_3$. Aluminum hydroxide ($Al(OH)_3$) was obtained by adding formalin to the sodium aluminate solution with constant and thorough stirring, at room temperature or at boiling point, over periods of 5–30 min. Aluminum hydroxide precipitated between 5 and 40 min after addition. The precipitate was separated from the mother liquor by filtration and rinsed with distilled water until pH 7.0–7.5. The precipitate obtained was dried on the filter by washing with acetone and then by heating in a muffle furnace at 250°C.

The volumes of the sodium aluminate and formalin solutions were the same in all experiments (each 100 mL).

Specific surface area was determined by BET using an Accusorb 2300A (Micrometrics, USA) instrument. Sorption pore volume was measured by means of benzene-vapor sorption according to a technique described elsewhere [23]. To determine adsorption pore volume a sample of the adsorbent (0.2 g) was weighed in a closed weighing vessel then placed in a desiccator containing benzene. Adsorption pore volume values were calculated on the basis of the maximum amount of benzene adsorbed according to the formula:

$V_p = (m_{max} - m_0)/m\rho_b$

where m is the weight of the sample, m_0 the weight of the vessel plus sample, m_{max} the weight of the vessel plus sample and adsorbed benzene, and ρ_b the density of benzene (at 20°C $\rho_b = 0.878$ g cm^{-3}).

All reagents used were 'chemically pure' grade.

Preparation of Octadecyl Methacrylate–Methyl Methacrylate Prepolymer

Octadecyl methacrylate (ODMA; 10.0 g), a solid at room temperature, and dicumyl peroxide (DCP; 0.25 g) were dissolved in methyl methacrylate (MMA; 10.0 g), heated under reflux for 3 h, then cooled. The resulting oligo-ODMA–MMA co-polymer (0.25:0.75) was soluble in *n*-pentane [24].

Coating of Alumina Supports

Alumina beads (5.0 g) of 4 μm average particle size and 0.54 cm^3 g^{-1} pore volume were added to a solution of the prepolymer (1.0 g) and DCP (40 mg) in 15 mL solvent. The solvent was then removed by rotary evaporation. The dry powder thus obtained was placed in a hermetically closed container and subjected to thermal treatment. The temperature was initially increased to 100°C during the course of an hour, kept at this temperature for another hour, heated to 130°C during the course of an hour, and kept at this temperature for an additional hour. The adsorbent obtained was rinsed with a hot dimethylformamide–toluene, then with ethanol, and then dried with acetone on the filter. Final drying was performed in an oven (120°C, 2 h). The amount of the polymer component was determined gravimetrically (from adsorbent mass values before and after baking at 800°C for 4 h.

DISCUSSION

Apparently, fixing a constant pH throughout the whole system without local irregular precipitation of the aluminum hydroxide mainly depends on homogeneous (uniform) distribution of the precipitating agent. This is problematic when applying commonly used reagents (see Introduction), because the 'pH factor' of the precipitator comes into action at once, and pH values can change from pH 5.5 to pH 12.0. The optimum pH during precipitation of aluminum hydroxide is within the range 8.7–9.3 [5,6].

Use of formalin as precipitating agent enables moderate and better target-oriented precipitation of aluminum hydroxide from sodium aluminate with different values of the Na_2O-to-Al_2O_3 ratio. Formalin was chosen as precipitating agent on the basis of several considerations. When formalin is used as precipitating agent, precipitation does not occur immediately but after a definite period of time during which reaction between the for-

malin and the alkali occurs–precipitation of aluminum hydroxide from aluminate solutions by formalin proceeds because of partial neutralization of the alkali. As a result there is an induction period which enables uniform distribution of the precipitating agent throughout the whole volume of the system. For this reason nucleation and further precipitation of $Al(OH)_3$ occur without formation of new growth centers. The induction period observed before precipitation of the aluminum hydroxide from sodium aluminate solutions by formalin can be from five to forty minutes, depending on the quantity of formalin added and the temperature of the mixture. This period enables homogeneous distribution of the precipitating agent throughout the system.

It is possible to fix the final pH of the medium, to avoid sharp changes, by varying the quantity of formalin added. Fixing of the final pH of the system is by completion of the above neutralization reaction. It is impossible to avoid large local variation of pH during precipitation of aluminum hydroxide by acids and, as mentioned above, pH differences in different regions at the moment of addition of the acid can fluctuate within the pH range 5.5–12.0. Such conditions during aluminum hydroxide precipitation do not enable preparation of aluminum hydroxide with reproducible properties. Reducing the pH results in more homogenous systems but it is still impossible to achieve system uniformity, without local precipitation of $Al(OH)_3$, by use of other types of precipitating agent.

Accurate fixing of the pH of the medium during precipitation of aluminum hydroxide is very important and enables the preparation of aluminum hydroxide with specified structural properties. The precipitating agent suggested–formalin–satisfies all the demands indicated. It has also been shown by microscopy studies that precipitation of aluminum hydroxide by addition of formalin furnishes powders without agglomerates and with good filtration properties. Aluminum hydroxide precipitated at pH deviating from the target values was difficult to filter and rinse free from Na^+ ions. At lower pH a finely dispersed precipitate was formed, which blocks the pores of filter paper or filter fabric. Increasing the pH to >10 impedes rinsing. Filtration of aluminum hydroxide samples precipitated by addition of formalin can be achieved in 5–10 min.

The dependence of aluminum oxide pore volume on baking temperature is depicted in Fig. 1. The aluminum oxide content of the sodium aluminate solutions was varied; the amounts of Al_2O_3 used to prepare samples 1 to 6 were 8.0, 8.0, 11.0, 13.0, 11.0, and 13.0%, *m/m*, respectively.

Before addition of the formalin the sodium aluminate was diluted with distilled water.
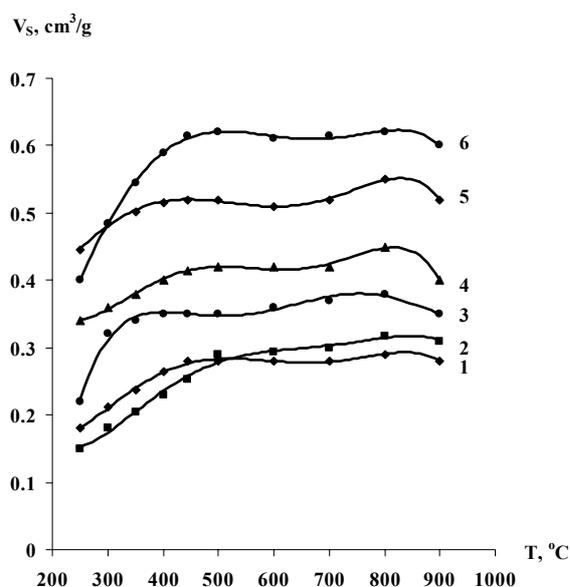
Fig. 1

Dependence of Al_2O_3 pore sorption volume on thermal treatment temperature. For samples 1, 3, and 4 the molar ratio, M, was 1.67; for samples 2, 5, and 6 M was 1.50

It is apparent from Fig. 1 that pore volume depends on thermal treatment temperature for all the aluminum oxide samples. An increase in pore volume was observed over the temperature range 250–400°C, then the increase in pore volume became insignificant in the temperature range 400–700°C. Within the temperature range 700-800°C pore volume again increased and the maximum pore volume was observed near 800°C. Further increasing the baking temperature led to a decrease in pore volume.

Comparison of data on the effect of thermal dissociation conditions used to prepare aluminum oxide from aluminum hydroxide on the specific surface area of the alumina [13], and on the pore volume obtained by us, shows that both specific surface area and pore volume tend to increase in the temperature range 250–750°C. The specific surface area of aluminum oxide samples decreases as temperature is increased within the temperature range 750–1100°C. The pore sorption volume acquires its maximum value within the range 750–800°C and begins to decrease as baking temperature is increased within the temperature range 800–1100°C.

The experimental points given in Fig. 1 were verified by repeating the synthesis of aluminum oxide 3–5 times. Relative standard deviations did not exceed 5–8%.

Dependence of aluminum oxide (baked at 500°C) pore sorption volume on the concentration (g per 100 mL) of the sodium aluminate solution used for precipitation is depicted in Fig. 2. Three types of sodium aluminate were studied; Na_2O-to-Al_2O_3 ratios, M, were 1.50, 1.67, and 2.0 for samples 1, 2, and 3, respectively. It is apparent from Fig. 2 that increasing pore volumes are observed as values of M are reduced and as the concentration of the sodium aluminate solution is increased, i.e. with sodium aluminate solutions of decreasing alkalinity aluminum oxide samples with higher pore volume are obtained. This is because sodium aluminate solutions with lower M values are more inclined to nucleation than aluminate solutions with higher M values. It is important to note that $Al(OH)_3$ precipitation from sodium aluminate solutions with $M = 1.50$ and 1.67 occurs at room temperature whereas the same process occurs only under the action of heat for sodium aluminate with $M = 2.0$.
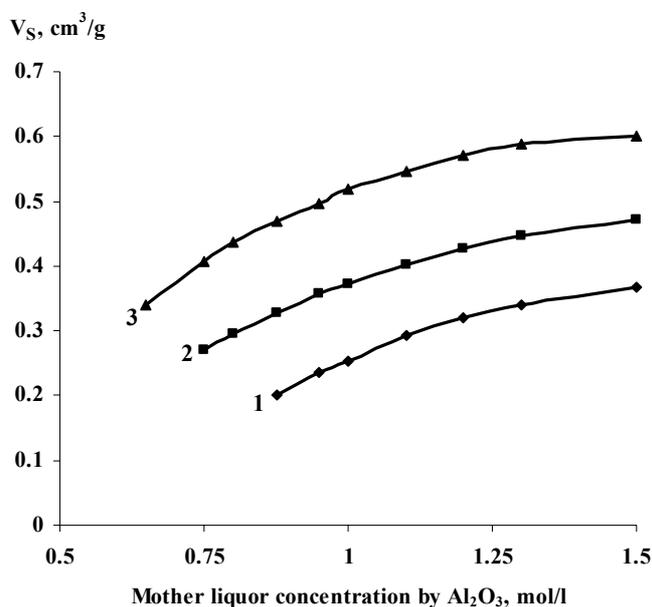
Fig. 2

Dependence of Al_2O_3 pore volume on the concentration of the sodium aluminate solution. Na_2O-to-Al_2O_3 ratios, M, were 1.50, 1.67, and 2.0 for samples 1, 2, and 3, respectively

For lower M values, i.e. lower alkali content, the possibility of appearance of new growth centers increases and, therefore, a larger number of seeds forms in such systems and, naturally, more dispersed particles form when using sodium aluminate with higher M values. Apparently, the exact rate of formation of seed-growth centers determines the increase in pore sorption volume. During this process the possibility of formation of particles of heterogeneous size increases and, as is usually observed, chaotic packing of heterogeneous particles results in greater pore volume. The dependence of $Al(OH)_3$ yield on the concentrations of sodium aluminate, formalin, and water is presented in Fig. 3. Two sodium aluminate solutions were studied–M = 1.50 and 1.67 for samples 1 and 2, respectively.
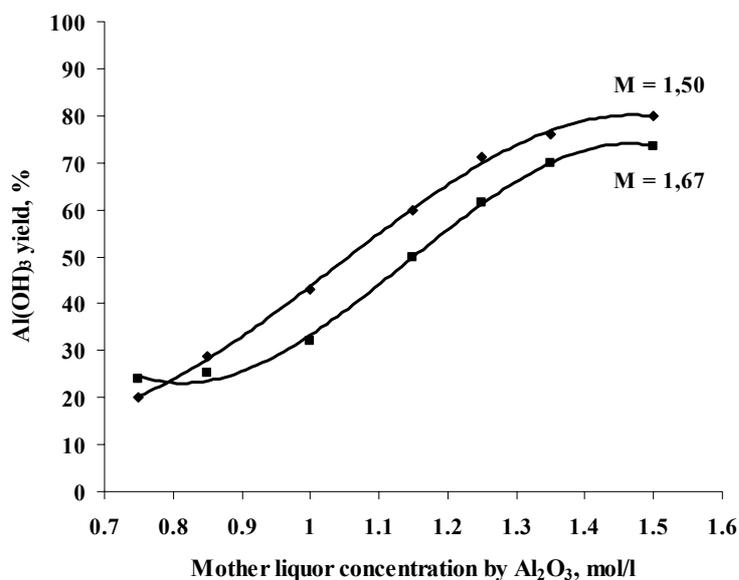
Fig. 3

Dependence of yield of precipitated $Al(OH)_3$ on the concentration of the sodium aluminate solution. Na_2O-to-Al_2O_3 ratios, M, were 1.50 and 1.67 for samples 1 and 2, respectively

It follows from Fig. 3 that the yield of precipitated aluminum hydroxide depends on the final concentration (as Al_2O_3) of sodium aluminate in the solution. The increasing yield of aluminum hydroxide with decreasing M values can be explained on the basis that rapid seed formation at low M values (alluded to above) leads to precipitation of larger amounts of aluminum hydroxide, i.e. the amount of aluminum hydroxide precipitated is proportional to the number of seed-growth centers formed. Although

the yield of precipitated aluminum hydroxide can be increased by increasing the amount of formalin added, it is necessary to remark that the final pH of the system will be determined by the amount of formalin added to the sodium aluminate solution and this will affect the filtration properties of the aluminum hydroxide. Thus, increasing the amount of formalin leads to a reduction of the pH of the system and an increase in the yield of precipitated aluminum hydroxide, but its filtration properties become worse, as a direct result of the formation of more highly dispersed particles. Rinsing of the samples of aluminum hydroxide obtained is also severely impeded.

Specific surface areas of different samples of aluminum oxide prepared by thermal dissociation of aluminum hydroxide precipitated from sodium aluminate solutions of different M value are presented in Table I.

Table I

Conditions used and properties of aluminum hydroxide (oxide) samples

Sodium aluminate		Reaction mixture (mL)			Sodium aluminate solution concentration (g L^{-1})	Specific surface area (m^2 g^{-1})
Concentration (g L^{-1})	Na$_2$O/Al$_2$O$_3$	Sodium aluminate	Water	Formalin		
628	1.50	100	430	100	100	318 ± 22
628	1.50	100	300	100	126	290 ± 20
628	1.50	100	100	100	209	320 ± 21
564	1.67	100	200	100	141	160 ± 10
564	1.67	100	333	100	106	175 ± 11
471	2.00	100	0	100	236	130 ± 8
471	2.00	100	0	100	236	133 ± 7

It is apparent from the table that specific surface areas of aluminum oxide samples are higher when aluminate solutions with lower M values are used. This is because species size in sodium aluminate solutions must be larger to be 'stable' and insoluble in alkaline medium. On the other hand, in systems with lower M values a larger number of such particles are present and, correspondingly, their size is smaller. As a result aluminum oxide samples prepared from sodium aluminate with lower M values have a comparatively higher specific surface area. It has been reported [20] that signifi-

cantly increased light scattering was observed when the NaOH concentration was increased from 1.0 and 2.5 mol L^{-1}. This confirms the assumption that species size must be larger in sodium aluminate solutions with higher M values.

Nitrogen adsorption isotherms on aluminum oxide samples prepared by thermal treatment at 500°C of aluminum hydroxide obtained from the sodium aluminates with $M = 1.5$, 1.67, and 2.0 are presented in Fig. 4.
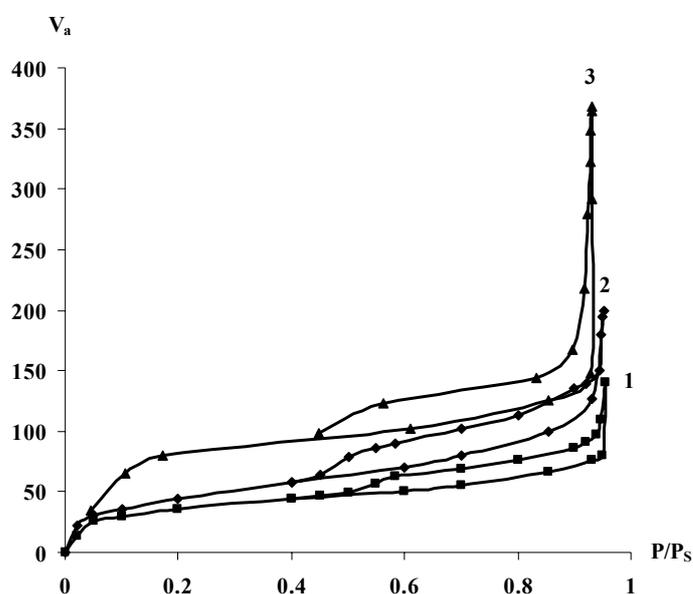
Fig. 4

Nitrogen adsorption isotherms obtained for aluminum oxide samples prepared from sodium aluminate with Na_2O-to-Al_2O_3 ratios, M, of 1.50, 1.67, and 2.0 (samples 1, 2, and 3, respectively)

A chromatogram obtained from a test mixture containing uracil, phenol, benzene, and toluene on a column packed with the hybrid adsorbent Al_2O_3 + ODMA + MMA is presented in Fig. 5. Chromatographic investigations were performed with a Waters HPLC system (model 626 pump, model 600 controller, and model 486 tunable absorbance detector). Evidently aluminum oxide may be modified by a C_{18} group-containing copolymer and the adsorbent thus obtained may be successfully used as a packing material for RP-HPLC.
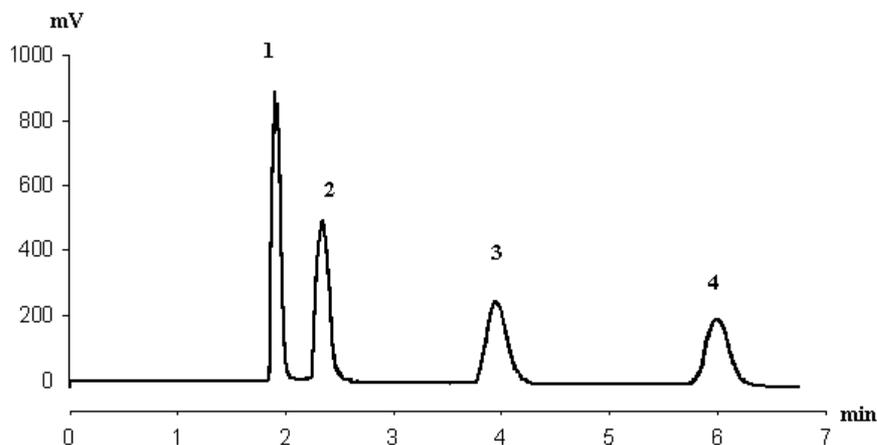
Fig. 5

Chromatogram obtained from uracil (1), phenol (2), benzene (3), and toluene (4) on a 150 mm × 4.6 mm column packed with Al_2O_3 + ODMA + MMA. The mobile phase was 50:50 acetonitrile–water and detection was by UV absorption at 254 nm

CONCLUSION

Formalin can be used as a precipitating agent in the preparation of aluminum hydroxide from sodium aluminate solutions (Na_2O-to-Al_2O_3 ratio 1.5–2.0). Use of formalin enables precipitation of aluminum hydroxide to be conducted under more closely controlled conditions, because of the induction period (5–40 min) of the formalin–alkali reaction. This ensures uniform distribution of the precipitator throughout the system.

It has been suggested that aluminum oxide samples with higher pore volume and specific surface area can be obtained from sodium aluminate solutions with lower Na_2O-to-Al_2O_3 molar ratios. The Na_2O-to-Al_2O_3 molar ratio and the final aluminum hydroxide content of the sodium aluminate solution also affect the pore volume and the yield of the aluminum oxide.

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