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The effect of Al^{3+} concentration on the properties of alumina powders obtained by reaction between aluminium sulphate and urea in boiling aqueous solution

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Abstract

Homogeneous precipitation of alumina precursors was carried out in boiling aqueous solutions that contained excess urea and 0.010–0.200 M Al^{3+}. The obtained precursor precipitates were dried for 2 h at 100 °C to yield precursor powders and the precursor powders were calcined for 2 h at 1000 °C to yield alumina powders. Precursor powders and alumina powders were investigated by X-ray diffraction (XRD), electron microscopy (EM), particle size distribution (PSD) analysis and nitrogen adsorption-desorption techniques for characterisation. Inspection of the XRD data showed that the precursor powders were amorphous in nature and the final product was δ-Al_2O_3. Investigation of the EM and PSD data of the powders showed that they contained unequally sized spheres and agglomerates. It was determined that, as the Al^{3+} concentration in the boiling aqueous solution increased, the number of 0.3–1.0 μm sized independent particles decreased and the sizes of agglomerates grew between 1.00–100 μm while their volume percentages increased from 50 to 80%. It was also observed that the specific surface areas of the alumina powders decreased from 98 $m^2\ g^{-1}$ to 54 $m^2\ g^{-1}$ and their specific micropore-mesopore volumes decreased from 0.31 $cm^3\ g^{-1}$ to 0.14 $cm^3\ g^{-1}$ as the Al^{3+} concentration in the boiling aqueous solution increased. It was observed that it was possible to prepare alumina powders that have different particle size distributions and different porosities by changing the Al^{3+} concentration while keeping the [urea]/[Al^{3+}] ratio constant at a value of 5.4 in the boiling aqueous solution. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Agglomeration; Al_2O_3; Porosity; Powders-chemical preparation

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1. Introduction

Alumina powders are extensively used in the production of ceramics, abrasives, medications, membranes, chromatographic column support materials, adsorbents and catalysts.[1,2] It was understood that commercial alumina powders produced by the conventional Bayer procedure did not possess the required characteristics for most of the application areas. Therefore, as was similarly done in the cases of other powders, other methods were developed to prepare alumina powders that possess the required characteristics.[3–5] Some of these non-conventional methods may be mentioned as hydrothermal synthesis,[6] microwave synthesis,[7] emulsion evaporation[8–10] and precipitation from solution.[11] In such methods, the required characteristics are obtained by controlling the crystal type, crystal size, particle shape, particle size distribution, agglomeration degree and porosity.[12–19]

In the method of precipitation from solution, the reactants may or may not be in the same phase before the precipitation begins. If they are in the same phase, the precipitation is homogeneous, otherwise, it is heterogeneous. Most often the homogeneous precipitation is preferred due to its more controllable behaviour.[20] Homogeneous precipitation of alumina precursors is carried out by heating the aqueous solution containing excess urea and an aluminium salt approximately up to its boiling temperature.[21–24]

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In previous studies, some of the required experimental conditions of homogeneous precipitation and their effects on most of the properties of the final product obtained were discussed. Nevertheless, the effect of Al^{3+} concentration used in the aluminium salt-urea aqueous solution on the properties of the resultant powders was not investigated systematically. In that respect, the aim of this study was to investigate solely the effect of Al^{3+} concentration used in the aluminium sulphate-urea reaction, on some of the properties of the resulting alumina powders by keeping all of the other parameters constant.

2. Materials and methods

$Al_2(SO_4)_3{\cdot}18H_2O$, $CO(NH_2)_2$, 65% HNO_3 (1.40 g cm^3) and 25% NH_3 (0.91 g cm^{-3}) (all analytical grade from Merck Company) were used. A 0.4 M $A1_2(SO_4)_3$ stock aqueous solution was prepared by $Al_2(SO_4)_3{\cdot}18H_20$. Since this salt is not very soluble, a small amount of 0.1 M HNO_3 was added to help its dissolution during the preparation of the stock solution.

In order to have a quantitative reaction between urea and aluminium sulphate, urea has to be present in excess in the reaction medium. Therefore, as a first step for the preparation of aqueous solutions with desired aluminium sulphate-urea concentrations, a preliminary study was realized and the appropriate ratio of [urea]/[Al^{3+}] was determined as 5.4. To adjust the pH of the aqueous solutions, the pH value necessary for the precipitation of $Al(OH)_3$ was calculated from the following relationship:

$$pH = (1/3)p[Al^{3+}] - (1/3)pK_{sp} + pK_w \tag{1}$$

where $K_{sp} = 1.9\times10^{-33}$ is the solubility product constant of $Al(OH)_3$ and $K_w = 10^{-14}$ is the ionization constant of water. The stock $Al_2(SO_4)_3$ solution and solid urea were used to prepare aqueous solutions (0.8 dm^3) having different concentrations that satisfy the above ratio. Since the stock solution contained a certain amount of HNO_3, the prepared solutions were rather acidic. 0.1 M NH_3 solution was added drop by drop to adjust the pH of the solutions to the calculated value. It was assumed that this pH value did not change appreciably with temperature. It is necessary to mention that in aqueous solutions containing an Al^{3+} concentration larger than 0.200 M, a heterogeneous precipitation of the alumina precursor occurred during the addition of ammonia to adjust the pH of the solution. Therefore, solutions containing Al^{3+} concentrations larger than 0.200 M were not prepared. The codes, concentrations and adjusted pH values of the prepared aqueous solutions are given in Table 1.

Table 1
The codes, concentrations and adjusted pH values of the solutions which were heated and prepared for precipitation

Code	A010	A020	A050	A100	A150	A200
[Al^{3+}]/M	0.010	0.020	0.050	0.100	0.150	0.200
[urea]/M	0.054	0.108	0.270	0.540	0.810	1.080
pH	3.76	3.66	3.52	3.42	3.36	3.12

The solutions hence prepared were stirred continuously with a magnetic stirrer and heated up to their boiling temperatures and continued boiling for 2 h for complete precipitation of the precursor. The precursor precipitates were separated by filtration and were washed with distilled water until they were free of SO_4^{2-} and NO_3^-. Each experiment was repeated at least five times in order to obtain sufficient material for further experiments. The precursor precipitates obtained after each experiment were similar in character showing the reproducibility of the experiments. Therefore, the precursor precipitates obtained by using the same Al^{3+} concentration were mixed. Then, these precipitates were dried for 2 h at 100 °C and precursor powders were obtained. The precursor powders were calcined for 2 h at 1000 °C to yield fine alumina powders. The precursor powders and alumina powders carried the same codes corresponding to those of the solutions from which they were prepared. The X-ray diffraction patterns of both the precursor powders and alumina powders were recorded by a Rikagu D-max 2200 powder diffractometer with a Ni filter and CuK_α X-rays having 0.15418 nm wavelength. An electron microscope (LEO 435) was used to take the photographs of precursor and alumina powders. The specific outer surface areas i.e. apparent geometric areas and volumetric particle size distributions of the precursor powders and alumina powders were determined by a Mastersizer Instrument (Malvern Instruments, Model Micron) based on a light scattering technique. The adsorption and desorption of nitrogen on alumina powders, at liquid nitrogen temperature was investigated by a volumetric adsorption instrument. The instrument was constructed completely of Pyrex glass and connected to high vacuum.[25]

3. Results and discussion

3.1. Chemical reaction

The overall chemical reaction for homogeneous precipitation of the precursor $Al(OH)_3$ can be given as follows:

$$Al_2(SO_4)_3 + 3CO(NH_2)_2 + 12H_2O \rightarrow 2Al(OH)_3 + 3(NH_4)_2SO_4 + 3H_2CO_3$$

It was claimed that an intermediate compound, $Al_4(OH)_{10}\ SO_4$, which disappeared afterwards was also formed during the reaction.[24,26] CO_2 is continuously evolved since the boiling aqueous solution is acidic (pH≈3.5). The $(NH_4)_2SO_4$ and excess $CO(NH_2)_2$ which may be left in the filtered precursor precipitate are washed away during the subsequent washings of the precipitate.

3.2. Crystal structure

Firstly, the XRD patterns of the precursor powders (A010–A200) that are not shown here were investigated and it was observed that they were amorphous in nature. Previous studies report that the precursor precipitates obtained by the reaction of aluminium salt with urea yields boehmite upon prolonged refluxing at higher pH values i.e. 7.2 to 9.2.[26–28]

Secondly, the XRD patterns of the powders obtained after calcination of the precursor powders at 1000 °C, for 2 h (A010–A200) were investigated in detail by comparing the results with other literature data.[29,30] It was determined that these powders were δ-Al_2O_3. It was also observed that these powders were all very similar to each other. The XRD patterns of the A050 powder thus obtained is shown in Fig. 1 as an example.

It is known that as the investigated crystals get smaller, the XRD peaks get wider. The relationship between the average crystal size (L) and full width at half-maximum peak height (FWHM) in terms of radians is given as follows by the Scherrer formula[31]

$$L = 0.9\lambda/(\mathrm{FWHM})\cos\theta \qquad (2)$$

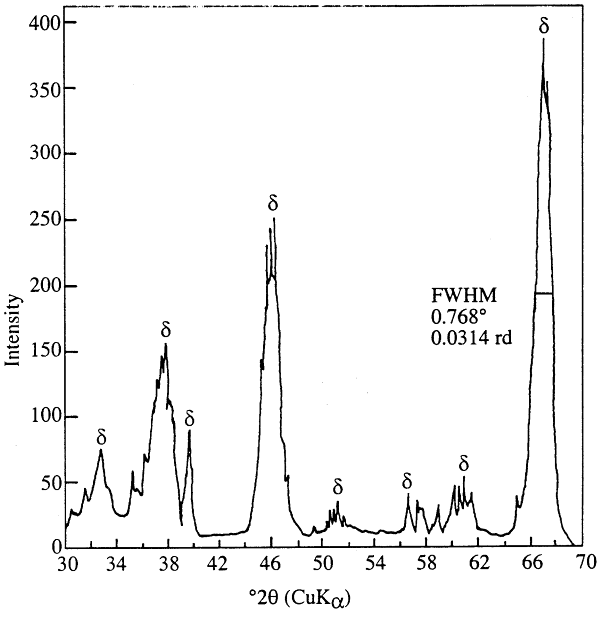

Fig. 1. The XRD pattern of the A050 powder.

where λ is the wavelength of the X-rays and θ is the diffraction angle. The average sizes of the δ-Al_2O_3 crystals was calculated as $L\approx12$ nm by using $\theta = 33.520°$ and FWHM $= 0.768° = 0.0134$ rd values of the 440 highest intensity peak in the XRD patterns.

3.3. Particle shapes and sizes

The inspection of EM photographs showed that the particles were spherical and there were not appreciable differences between the photographs of precursor powders and alumina powders. Therefore, it can be stated that considerable shape differences did not occur during the calcination stage in which the transformation of the precursor powders to alumina powders occurred. It was also observed that the sizes of agglomerates grew as the concentration of Al^{3+} increased and most of the spherical particles that had diameters larger than 1 µm were agglomerates, but it was not possible to determine exactly the sizes of agglomerates from the EM photographs. The EM photographs of the alumina powders A050 and A150 are shown as an example in Fig. 2.

The PSD curves of both the precursor powders and alumina powders were investigated in detail to obtain information about the sizes of agglomerates. The

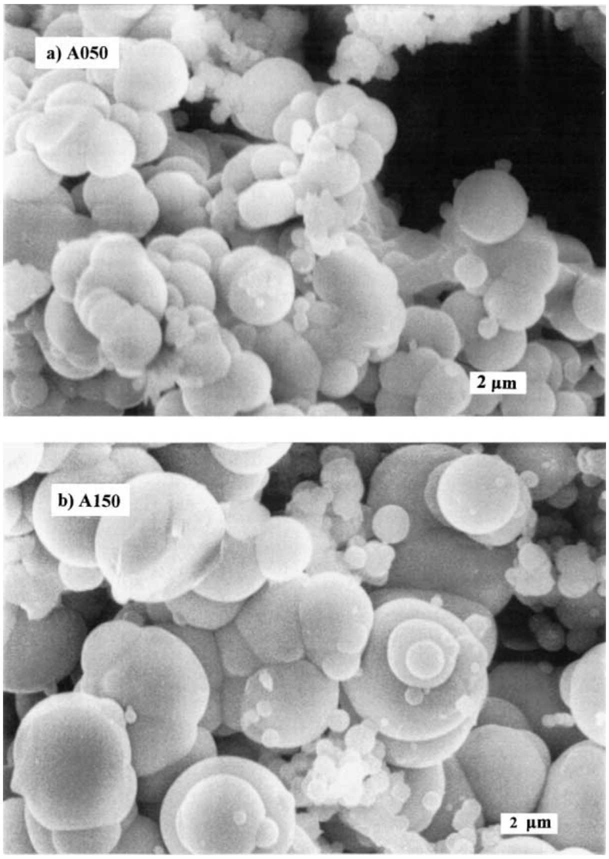

Fig. 2. The electron microscopy photographs of the (a) A050 and (b) Al50 powders.

volumetric particle size distribution curves of A050 and A200 coded precursor powders and alumina powders are shown in Fig. 3 as an example. In the vol.%-*D* and [d(vol.%)/d*D*]-*D* curves, the first distribution observed between $0.3 < D < 1.0$ μm belongs to independent spherical particles and the second distribution observed between $1 < D < 100$ μm belongs to agglomerates. In these figures, it can be clearly observed that although the precursor powder and alumina powder couples do not coincide exactly they show a very similar particle size distribution. So, the observations derived from EM photographs and PSD curves support each other. In addition, a comparison of volumetric particle distribution curves of different powders that resulted from solutions with different Al^{3+} concentrations such as in Fig. 3a and b revealed that as the concentration of Al^{3+} in the solution increased, the sizes of independent particles stayed the same but their numbers decreased. On the other hand, agglomerates grew in size and their numbers increased. Therefore, it can be stated that as the concentration of Al^{3+} used in the reaction increases the agglomeration degree of the powders increases.

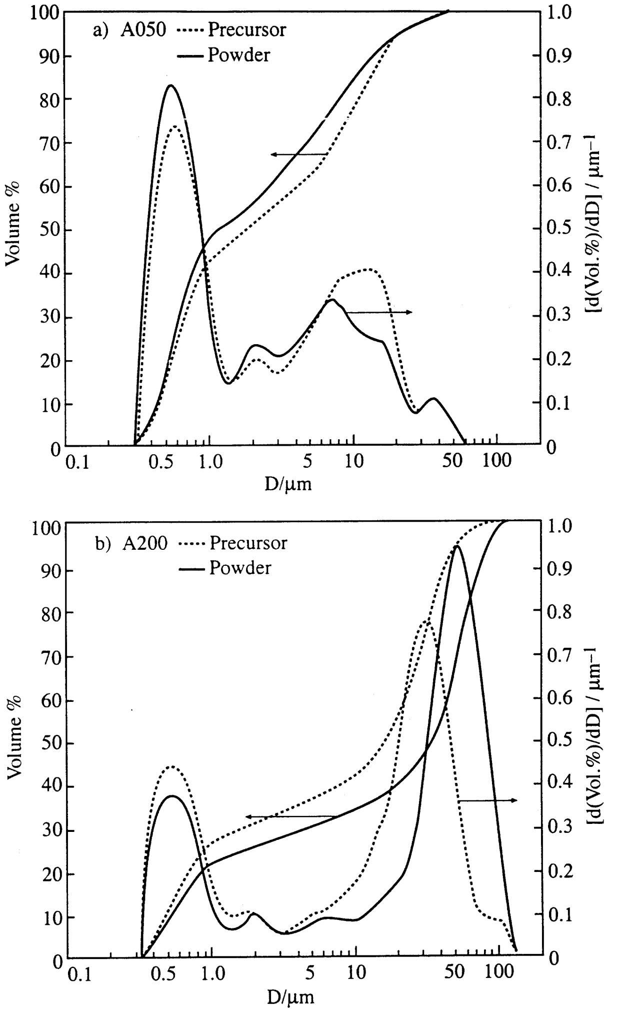

Fig. 3. The vol.%-*D* and [d(vol.%)/d*D*]-*D* particle size distribution curves of the (a) A050 and (b) A200 samples.

For each Al^{3+} concentration (i) the volumetric agglomeration percentages corresponding to the inflection points at around $D = 1$ μm in the vol.%-*D* graphs were noted (ii) the average sizes of independent particles and agglomerates corresponding respectively to the maximum points which appeared at the left-hand side and right-hand side in the [d(vol.%)/d*D*]-*D* graphs were noted. The variations of volumetric agglomeration percentages (a), average sizes of independent particles (b) and average sizes of agglomerates (c) were plotted as a function of Al^{3+} concentration and are collectively shown in Fig. 4. In this figure, it can be clearly observed that as the Al^{3+} concentration increased between 0.010–0.200 M, the average sizes of independent particles stayed constant around 0.6 μm whereas, the average sizes of agglomerates grew from 7 to 56 μm and the volumetric agglomeration percentage increased from 50 to 80%. A parallel variation between average agglomeration sizes and volumetric agglomeration percentages as a function of Al^{3+} concentration was also observed. This observation verifies again the above statement which indicates that the agglomeration degree of the powders increases as the concentration of Al^{3+} used in the solution increases.

3.4. Adsorptive properties of the powders

The specific surface areas (*A*) of the alumina powders were calculated according to the Brunauer–Emmett–Teller (BET) procedure[32,33] by using the data of adsorption of nitrogen on the powders at 77 K. The relative equilibrium pressure of adsorption is defined as

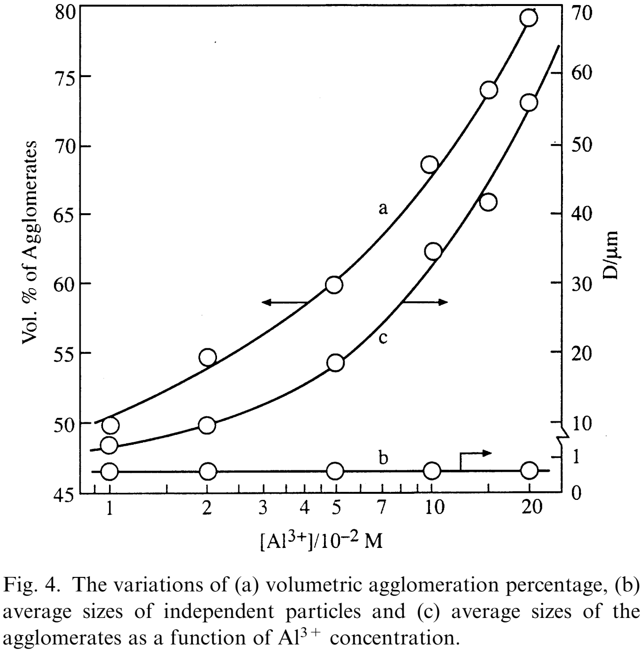

Fig. 4. The variations of (a) volumetric agglomeration percentage, (b) average sizes of independent particles and (c) average sizes of the agglomerates as a function of Al^{3+} concentration.

$p/p^{\circ} \equiv x$, where p is the adsorption equilibrium pressure and p° is the vapour pressure of liquid nitrogen at 77 K. The BET equation can be given as follows:

$$x/n(1-x) = 1/n_{\mathrm{m}}c + [(c-1)/n_{\mathrm{m}}c]x \quad (3)$$

where n_{m} is the monomolecular capacity and c is a constant. Straight lines which obey the BET equation were plotted in the relative equilibrium pressure interval, $0.05 < x < 0.35$. The constants n_{m} and c were determined by solving the simultaneous equations obtained from the slopes and intercepts on the vertical axis of the BET straight lines. The specific surface area (A) was calculated from the following equation

$$A = n_{\mathrm{m}} N_{\mathrm{A}} a_{\mathrm{M}} \quad (4)$$

where the area that a nitrogen molecule occupies is given by $a_{\mathrm{M}} = 16.2 \times 10^{-20}$ m^2 and the Avogadro constant is $N_{\mathrm{A}} = 6.02 \times 10^{23}$. The specific outer surface areas (S) of the alumina powder particles were directly read by the Malvern instrument used for PSD analysis. It is known that when the relative equilibrium pressure is 0.96, the micropores whose widths are smaller than 2 nm and mesopores whose widths vary between 2–50 nm are compeletely full.[34–36] Therefore, the adsorption capacity which corresponds to the liquid nitrogen volume which is not desorbed from the alumina powders at a relative equilibrium pressure of 0.96 was taken as the specific micropore-mesopore volume (V). Hence, the V values were calculated by using the desorption data determined at this relative equilibrium pressure.

The variations of A, S and V values were plotted as a function of Al^{3+} concentration and are shown in Fig. 5. It can be clearly observed from this figure that as the Al^{3+} concentration increased from 0.010 to 0.200 M the A values decreased from 98 to 54 m^2 g^{-1} and the S values decreased from 6 to 2 m^2 g^{-1}. Therefore, it can be stated that the outer surfaces of the alumina powder particles are very small compared to their inner surfaces resulting from the micropore and mesopore walls. In the above mentioned Al^{3+} concentration interval, it can also be observed that the V values decreased from 0.31 to 0.14 cm^3 g^{-1}. Therefore, it can be stated that as the Al^{3+} concentration used in the reaction increases, the porosity of the resultant alumina powders decreases.

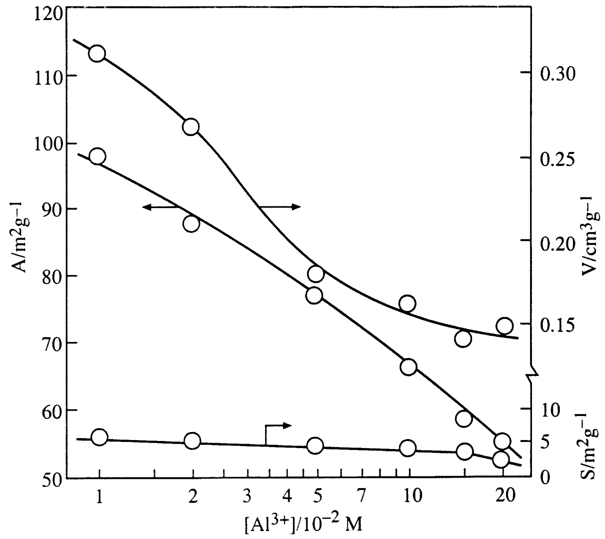

Fig. 5. The variations of the specific outer surface area (S), specific surface area (A) and specific pore volume (V) as a function of Al^{3+} concentration.

4. Conclusion

In this study that uses the method of homogeneous precipitation from solution to prepare fine alumina powders, it was observed that it was possible to prepare mostly agglomerated δ-Al_2O_3 powders by adjusting the concentration of Al^{3+} in the $Al_2(SO_4)_3$ and $CO(NH_2)_2$ boiling aqueous solution. It was determined that the agglomeration degree of the alumina powders increased, their porosities decreased and the agglomerates grew in size as the Al^{3+} concentration in the aqueous solution was increased while the $[Al^{3+}]/[\text{urea}]$ ratio was kept constant at 5.4. Therefore, it can be concluded that it is possible to prepare alumina powders possessing some required characteristics such as a certain degree of porosity or agglomeration etc. by adjusting the Al^{3+} concentration in the method of homogeneous precipitation from solution. Hence, the alumina powders thus obtained and which possess the required characteristics may be used in the production of abrasives, column support materials, catalyst beds, filters and ceramics.

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