

Chemistry

CHARACTERIZATION AND THERMAL TRANSFORMATION OF Fe(III) COPRECIPITATED WITH ALUMINIUM HYDROXIDE

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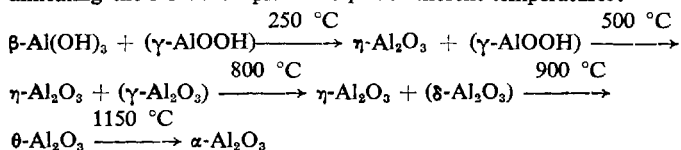
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Identification and characterization of iron (III) coprecipitated aluminium hydroxide system and its thermal products has been made using thermal analysis (DTA, TG and DTG), electron microscopy and infrared absorption spectroscopy. The thermal, structural and microstructural evidence so obtained and the Mössbauer characteristics indicate that the original coprecipitate consists of bayerite β -Al(OH)₃ as the main phase alongwith a small fraction of böhmite γ -AlOOH with trivalent iron ions incorporated in the octahedrally coordinated sites.

The following sequence of transformations was confirmed to occur on annealing the initial sample in steps at different temperatures:



Iron ions change the state of their coordination and occupy tetrahedrally coordinated positions in vacant lattice sites available in the spinel structure of η - and γ - alumina. Further, in samples annealed at 875 °C and 1200 °C a sixfold coordination is assumed by Fe³⁺ ions corresponding with the formation of θ - and α -Al₂O₃ respectively at these annealing temperatures. The η - and θ -forms of alumina were the principal intermediate phases which were formed fairly rapidly and their conversion to α -Al₂O₃ was shifted towards a lower energy as evidenced by the peak at 1090 °C in DTA curve for exothermic crystallization of corundum. Formation of a mixed oxide AlFeO₃ was not observed at any stage but incorporation of iron ions in alumina lattice resulted in disorder and local weakening of the structure as is reflected by a lower degree of crystallinity of the phases formed at different stages of phase transformations.

INTRODUCTION

BOTH in naturally occurring and synthetic iron aluminium mixed oxide hydrate systems, iron and aluminium ions are interchangeable over wide ranges of concentration. Recently Hill *et al.* (1978) have made studies of the Mössbauer effect and characterised the presence of fine particles of goethite, mixtures of hematite and goethite and aluminium substituted goethite phases in different bauxite specimens. Malden and Meads (1967) investigated iron ions present in gibbsite environment and reported preliminary Mössbauer data for these ions and compared them to the

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incorporation characteristics of iron ions in muscovite and kaolinite layered clay structures. Van Dijk (1978) investigated incorporation of iron ions as dilute impurity species in aluminium hydroxide samples during their precipitation, ageing and crystallization process.

In the studies reported here, identification and characterization of initial iron containing aluminium hydroxide and its thermal products has been made using thermal analysis (DTA, TG and DTG), electron microscopy and infrared absorption spectroscopy. The thermal, structural and microstructural evidence so obtained warranted a re-examination of the results of earlier Mössbauer spectroscopic studies reported by Saraswat *et al.* (1977). The results of additional Mössbauer data on samples annealed at 1200 °C are also presented in this paper with a view to explore the behaviour of iron ions held in the α -alumina phase formed at higher temperature.

MATERIALS AND METHODS

Freshly prepared 0.1M solution of ferric ammonium sulphate (A. R.) and aluminium sulphate (A. R.) were thoroughly mixed so that the atomic ratio of iron to aluminium was 3 : 97. Ammonium hydroxide was added to the vigorously stirred solution till pH 8.0 was indicated. The precipitate was washed and dried in air at room temperature for 24 hrs. Thermal products were obtained by subsequently annealing it at different temperatures in air for 24 hrs each.

Thermal curves (DTA, TG and DTG) of the gel were recorded on a Paulik Paulik Erdey Derivatograph model 1969 manufactured by MOM, Budapest. The IR spectra were obtained for samples in KBr discs. For electron optical experiments specimens were mounted onto a thin film of carbon black deposited on the 200 mesh copper grids and were studied with Philips EM-300 electron microscope using a 40 kV beam.

The Mössbauer spectra of samples — unannealed and those annealed at various temperatures were recorded in transmission geometry on a constant acceleration velocity transducer coupled to ^{57}Co in Pd-matrix. Iron metal was used for velocity calibration and as the standard for the central shifts.

RESULTS AND DISCUSSION

Thermal (DTA, TG and DTG) Studies

Thermal curves of Fe(III) 3 atom per cent coprecipitated with aluminium hydroxide are shown in Fig. 1. An intense endothermic effect starting at 80 °C and continuing upto 300 °C having a peak at 175 °C is observed. Another endothermic effect starts above 340 °C showing a less pronounced peak at 430 °C. There is a large weight loss associated with both these endothermic effects and transformation to $\alpha\text{-Al}_2\text{O}_3$ is completed with a total weight loss of 40 per cent, instead of 34.6 per cent expected for stoichiometric conversion of $\text{Al}(\text{OH})_3$ to $\alpha\text{-Al}_2\text{O}_3$.

A weight loss of 30.1 per cent upto 400 °C followed by continuous weight losses of 3.25 per cent, 5.65 per cent and 1 per cent in temperature ranges of 400–500 °C, 500–900 °C and 900 to 1000 °C respectively has been shown by TG and DTG

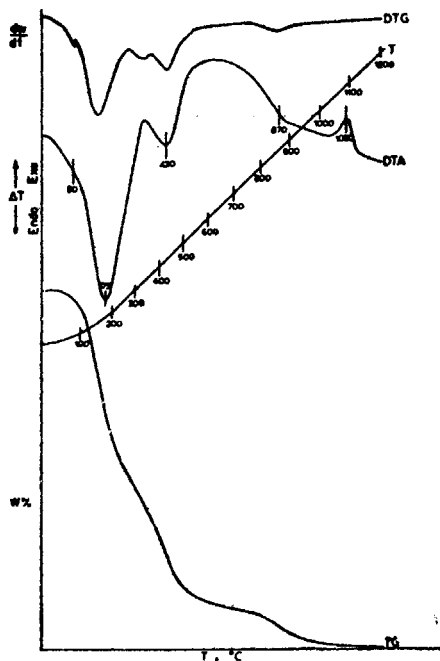


FIG. 1. Thermal curves of 3 atoms % Fe(III) coprecipitated with aluminium hydroxide.

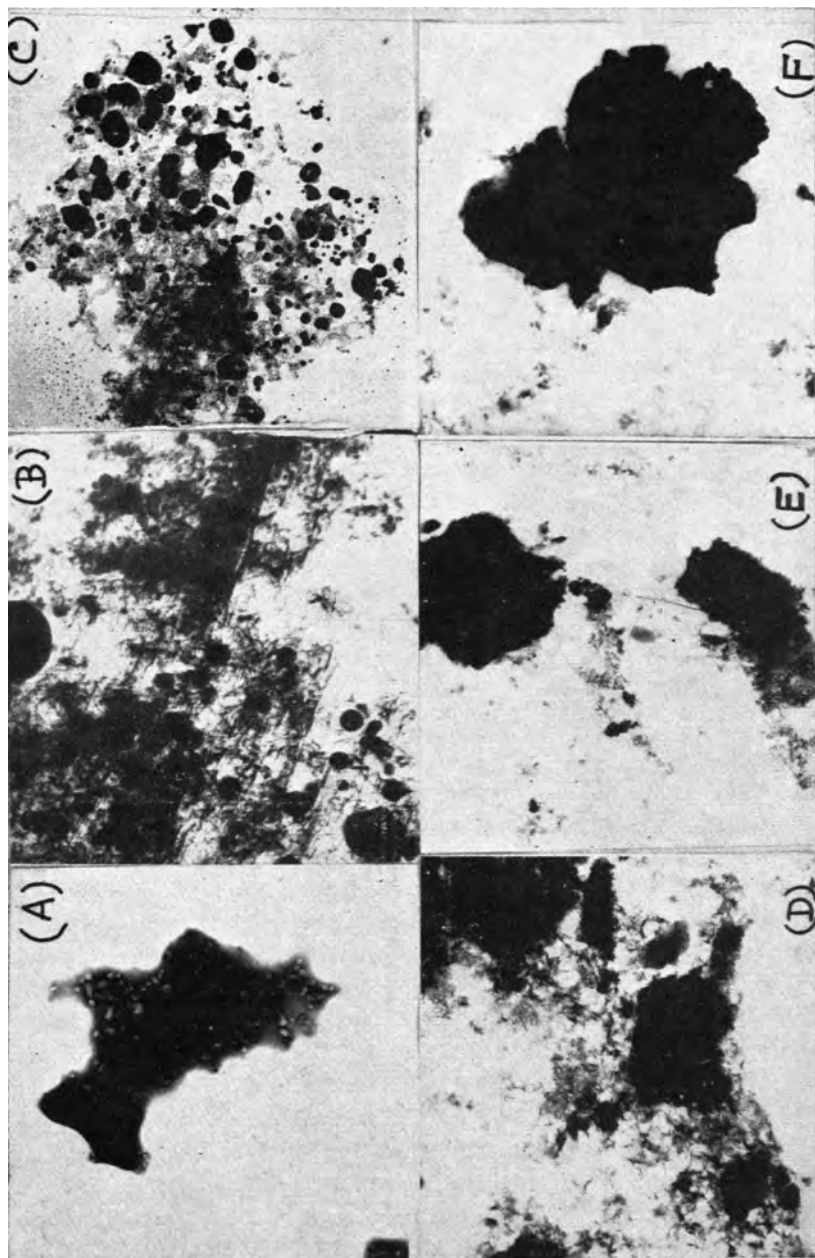
analyses. A pronounced hump exhibited by the DTA curve with an inflexion around 870 °C is due to the emergence of intermediate high temperature transitional alumina forms (Mackenzie & Berggren, 1970). Further, at 1090 °C, DTA and DTG curves indicate final higher temperature transformation of metastable alumina modifications to α -Al₂O₃ (Mackenzie & Berggren, 1970).

IR and Electron Microscopy Studies

Some representative IR spectra and electron microphotographs of initially coprecipitated samples and of those annealed at different temperatures are shown in Fig. 2 and in Plate I respectively. IR spectra of the initial samples (Fig. 2-A) show bands around 980 cm⁻¹ and 1080 cm⁻¹ in the region characteristic of Al-OH bending vibrations. Bands in the stretching vibration region for OH groups and absorption bands at 1640 cm⁻¹ indicate presence of water molecules. Further, the bands appearing at 980 and 1080 cm⁻¹ are to be identified (Dorsey, 1966) with the presence of bayerite β -Al(OH), alongwith a small amount of bohmite, γ -AlOOH. Weak and poorly defined bands in the region 1410–1450 cm⁻¹ and at 840 cm⁻¹ indicate presence of CO₃⁻ in the sample. These features result from atmospheric CO₂-adsorption by the aluminium hydroxide precipitates.

Conical and wedge shaped aggregates formed by a large number of platelets arranged perpendicular to the longitudinal directions of the serrated triangular somatoids are observed in electron microphotographs of the original precipitate. These features depict the characteristic crystal morphology of the bayerite phase

PLATE—I



Crystal morphology and microstructure of thermally treated 3 atoms % Fe (II) coprecipitated with $\text{Al}(\text{OH})_3$
 Heat treatment : (A) None (B) 300 °C (C) 350 °C (D) 375 °C and (F) 400 °C for 24 hours each.
 Magnifications : (A) 70,000 (B) 1,14,000 (C) 33,000 (D) 42,000 (E) 42,000 (F) 42,000

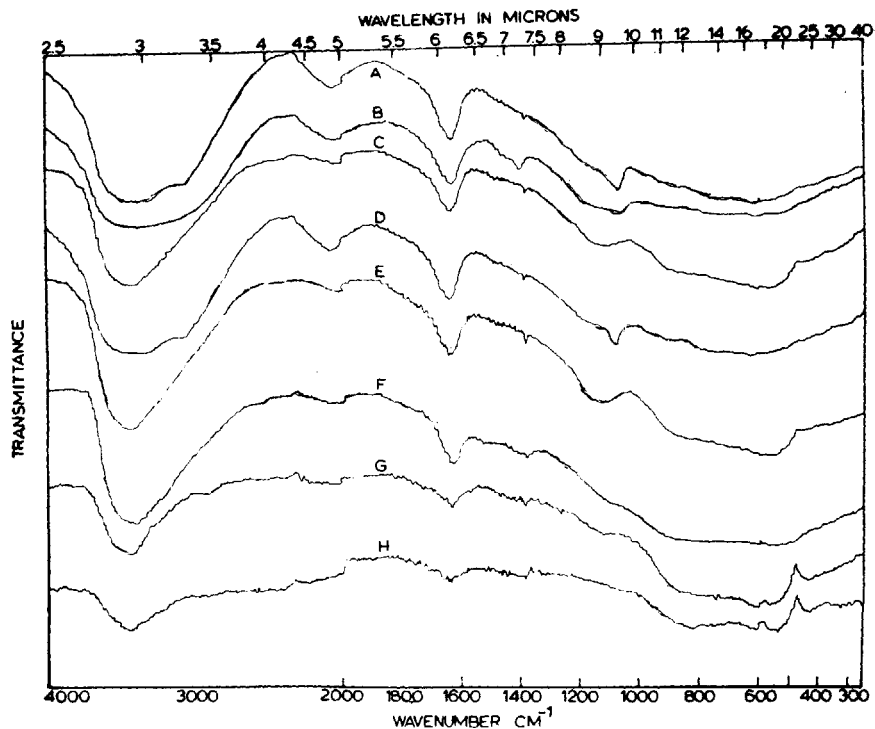


FIG. 2. Infrared spectra of Fe(III) 3 atom % coprecipitated with aluminium hydroxide (A) and its thermal products obtained on annealing at (B) 100 °C, (C) 200 °C, (D) 350 °C, (E) 400 °C, (F) 550 °C, (G) 600 °C, (H) at 700 °C for 24 hours.

(Mackenzie *et al.*, 1969) which is the main product formed. Presence of some distinct fibrous habits developed around the periphery of conical aggregates of bayerite and of some fibrillar particles in the sample again suggest that initial aluminium hydroxide precipitate also consists of a small fraction of bohmite (γ -AlOOH) phase.

IR and electron microscopic evidence obtained from samples annealed at different temperatures may be presented as follows: IR spectra of samples annealed at 250 °C show a broad band below 970 cm^{-1} extended to 500 cm^{-1} and centered at 820 cm^{-1} . These features arise from the partial conversion of bayerite into η -alumina (Newsome *et al.*, 1960; and Lyon, 1962). Infrared spectra of samples annealed at 350 °C and 450 °C gets improved exhibiting more pronounced features but position of bands remains more or less the same as that of the sample annealed at 250 °C. These features are to be ascribed to the removal of gross lattice imperfections and better crystallization of η -Al₂O₃ on annealing the sample at a higher temperature. Further as may be seen from an increase in the intensity of the absorption and at 1080 cm^{-1} for samples annealed at 250, 350 and 450 °C conversion of a part of bayerite under the influence of intergranular hydrothermal conditions (Newsome *et al.*, 1960; and Lyon 1962) that set in the sample on annealing in earlier stages results in formation of some bohmite.

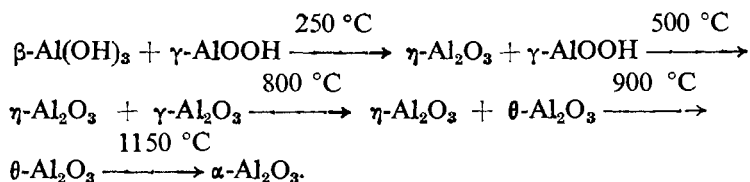
In the samples annealed at 500 °C, all the bohmite component completely disappears and a broad band below 1000 cm^{-1} is observed due to the formation of highly developed crystals of η -alumina alongwith some γ - Al_2O_3 (Newsome *et al.*, 1960; and Lyon, 1962). In samples annealed at 600 and 700 °C a progressive sharpening of bands around 825, 740, 670, 630, 580, 520 and 430 cm^{-1} is observed indicating further removal of remnant lattice imperfections of η - Al_2O_3 and γ - Al_2O_3 both of which persist at these temperatures.

Bands characteristic of η -alumina persist and some weak intensity peaks at 880, 810 and 755, 725 cm^{-1} also emerge in samples annealed at 800 °C. These bands indicate (Newsome *et al.*, 1960; and Lyon, 1962), formation of a small amount of δ - Al_2O_3 . Absorption at 815, 760 and 720 cm^{-1} become progressively sharpened in samples annealed at 900 and 950 °C owing to the formation of θ -alumina (Newsome *et al.* 1960; and Tartre, 1967) which correspond to the temperature range between the descending slope of the hump centered around 870 °C and the exothermic peak at 1090 °C shown by the DTA curve.

In samples heated to 1150 and 1200 °C bands below 910 cm^{-1} centered at 720 cm^{-1} and strong bands near 650 and 600 cm^{-1} and a peak at 450 cm^{-1} are obtained (Newsome *et al.*, 1960; and Tartre, 1967) indicating the crystallization of α - Al_2O_3 . Electron microscopic examination of annealed samples supplement and confirm the results of i.r. and thermal analysis. In samples annealed at 350 °C, it is indicated that a small part of bayerite undergoes decomposition with development of internal steam pressures (Lippens, 1961; and Lippens & De Boer, 1964) leading to the formation of hydrothermal fibrillar bohmite while much of the bayerite gets converted to highly amorphous to microcrystalline sheets of η -alumina. Granular fibres of bohmite completely disappear and plates giving smooth lath shaped surfaces are observed due to formation of some γ - Al_2O_3 in samples annealed at 500 °C. η -alumina which is the main phase in the samples annealed at 500 °C undergoes crystallization with a drop in surface area at this stage and persists in samples annealed upto 800 °C. However, γ -alumina component gets converted into δ - Al_2O_3 on annealing at 800 °C. Particles with well developed rod like morphology observed in samples annealed at 900 °C correspond (Lippens, 1961; and Lippens & De Boer, 1964) to the formation of theta-alumina which persists in samples annealed upto 950 °C. Samples annealed at 1050 °C and 1100 °C and above give sharp symmetric diffraction patterns identifiable with the formation of hexagonal α - Al_2O_3 in massive form.

DISCUSSION

Foregoing results of thermal, IR, and electron microscopic studies of Fe(III) 3 atom per cent coprecipitated with aluminium hydroxide and its thermal products indicate the following transformation sequence :



Taking into account these findings, it is all the more justified to re-examine the earlier reported results of a Mössbauer spectroscopy study by Saraswat *et al.* (1977) in the light of the new evidence obtained on the nature and extent of phase transitions taking place in the system subjected to annealing at different temperatures. For unheated samples and for those annealed at different temperatures upto 1200 °C, Mössbauer spectra invariably consist of a well resolved quadrupole split doublet pattern both at 300 and 77K. Characteristic feature of the resonance lines and Mössbauer parameters indicate changes in electronic environment and coordination symmetry of iron ions variously held in alumina lattice. From an analysis of Mössbauer spectra recorded at 300 and 77K, at different stages of phase transformations the state of iron ions in different phases may be inferred as follows :

(i) For Fe(III) 3 atom per cent coprecipitated with aluminium hydroxide, Mössbauer parameters are typical of iron in Al^{3+} -octahedra substituting for Al^{3+} ion (Malden & Meads, 1967; Saraswat *et al.*, 1977; and Dijk, 1978) and characterize iron atoms present in high spin ferric state in distorted octahedral sites, available in both bayerite $\beta-Al(OH)_3$, and bohmite. In samples annealed upto about 200 °C, the Mössbauer spectra and parameters show very little changes in them. This apparently indicates that no significant changes occur virtually in the bonding and symmetry of iron ions.

(ii) Annealing at 350 °C for 24 hrs results in a pronounced dehydroxylation and collapse of lattice habits of bayerite giving a highly amorphous η -alumina phase known to have a strong one dimensional disorder in stacking of the cubic close packed array of oxygen layers and with highly perturbed and asymmetric lattice surfaces (Lippens & Steggarda, 1970). Observed broadening of resonance lines and exceptionally lowered resonance effect magnitude in Mössbauer spectra of the sample indicate a distinct loosening of lattice at this stage. Further, for these samples both at 300 and 77K, is observed a very large quadrupole splitting of magnitude 1.079 mm/sec and 1.058 mm/sec respectively (cf. Saraswat *et al.*, 1977). These features alongwith the isomer shift values characterize (Malathi *et al.*, 1971; and Bancroft, 1973) iron ions in trivalent state and tetrahedral coordination to oxygen and are thus consistent with the substitutional incorporation of iron ions in vacant tetrahedral lattice sites available in the defect spinel structure of η -alumina.

(iii) On annealing at 650 °C crystallization of a more ordered and dense packed η -alumina takes place with removal of lattice imperfections. However, simultaneously formation of some small amount of well defined γ -alumina phase also occurs which possesses a fairly ordered cubic close packed oxygen lattice with strongly distorted tetrahedral sites (Lippens & Steggarda, 1970). In these structurally more inhomogeneous lattice sites available in the mixture of η - and γ -alumina modifications as may be seen from an increase in broadening of resonance lines, in resonance effect magnitude and from increased quadrupole splitting, iron ions remain tetrahedrally coordinated with an improved coupling with inhomogeneous but better crystallized environment,

(iv) In the samples annealed at 875 °C, a sharp doublet with significant diminution in quadrupole splitting and somewhat covalent isomer shifts is observed.

Thermal, IR and electron microscopy show that at this stage, structural inhomogeneities disappear and a complete recrystallization of α - and γ - aluminas to monoclinic θ -alumina modification takes place. In accordance with the Mössbauer studies, corresponding, to these changes, a well defined environment is indicated for iron ions which take up distorted octahedral coordinated sites in θ -alumina. The observed reduction in line width and an increase in resonance effect magnitude indicate that iron ions are quite uniformly incorporated in θ -alumina.

(v) In samples annealed at 1200 °C, cubic close packing of oxygen ions changes to stable hexagonal close packing with simultaneous rearrangement in the distribution of cations because of the formation of α -Al₂O₃ from the precursor θ -Al₂O₃. An increased degree of ordering and local densification achieved at this stage in the host lattice is accompanied by having more uniform distribution of iron ions and more covalent component for Fe³⁺- oxygen bond for iron impurity species held in corundum lattice. The evidence for such a description comes from the observation of a narrow linewidth and an increased resonance effect magnitude in the Mössbauer spectra by the sample. Mössbauer parameters : I. S. = 0.23 mm/s and 0.38 mm/s, with respect to iron and Q. S. = 0.45 mm/s and 0.43 mm/s respectively at room temperature and liquid nitrogen temperature characterize iron ions occupying trigonally distorted octahedral lattice sites in α -Al₂O₃.

Lastly, it is in place to mention the effect of iron ions on the phases formed and phase transitions observed during the formation of iron doped α -Al₂O₃ from the Fe(III) coprecipitated with aluminium hydroxide. The effect of Fe in solid solution in γ -Al₂O₃ on the rate of conversion to α -Al₂O₃ as studied by Bye and Simpkin (1974) have indicated that additions of Fe₂O₃ progressively reduce the temperature necessary to produce corundum structure. Studies on the effect of iron oxide on the sintering kinetics of α -Al₂O₃ have also been made by Rao and Cutter (1973) and it has been concluded there that sintering rate of iron doped α -Al₂O₃ increases with increase in total iron content.

Studies presented here however involve a fixed initial concentration (3 atom per cent) of iron ions coprecipitated with aluminium hydroxide which was annealed in steps at different temperatures to finally yield iron doped corundum lattice. Apparently, by increasing the rate of conversion, iron displaces the start of crystallization of α -phase towards a lower temperature at 1090 °C (cf. 1250 °C for pure samples), as evident from the thermal analysis curve. The η - and θ - forms of Al₂O₃ were the principal intermediate phases produced that contain Fe³⁺ in solid solution. Initially present small bohmite and hydrothermally formed bohmite phase also give rise to γ - and certain δ -alumina in small amounts. Considering rather sluggish nature of these transformations, it may be said that intermediates were formed relatively rapidly and the rates of their conversion to α -Al₂O₃ were increased by the addition of iron atoms. Crystal morphology and microstructure discerned from electron microphotographs and I. R. spectra respectively, suggest a reduction of crystallinity of the phases formed. This is because of the increase in the disorder and local weakening of the structure consequent to the substitutional incorporation of iron in the lattice.

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