

Basic aluminium succinate: An alumina precursor formed by precipitation from homogeneous solution

B S MARUTHIPRASAD[†], M N SASTRI[†], S RAJAGOPAL, K SESHAN,
K R KRISHNAMURTHY and T S R PRASADA RAO*

[†] School of Chemistry, Andhra University, Visakhapatnam 530 003, India
Research Centre, Indian Petrochemicals Corporation Ltd., Baroda 391 345, India

MS received 2 January 1988; revised 17 October 1988

Abstract. Precipitation from a homogeneous solution of aluminium nitrate by neutralisation using urea in presence of succinic acid leads to the formation of a well-defined alumina precursor, basic aluminium succinate, which on calcination yields microspheroidal γ -alumina with excellent free-flowing characteristics.

Keywords. PFHS: basic aluminium succinate; alumina precursor; microspheroidal γ -alumina.

1. Introduction

The nature and mode of formation of precursors of alumina is of paramount importance in achieving the desired characteristics for aluminas as supports for heterogeneous catalyst systems. In our efforts (Maruthiprasad 1985) to investigate the influence of precursor characteristics of the aluminas on the nature and activity of final catalysts, different methods of preparation were adopted. One of them was a PFHS (precipitation from homogeneous solution) method, wherein the alumina precursor was obtained by neutralisation of aluminium nitrate by urea hydrolysis, in the presence of succinic acid (method SA). Willard and Tang (1937), adopting the method of SA, had reported the formation of a basic aluminium succinate as a dense precipitate. However, the method remained only an analytical procedure for the estimation of aluminium. During studies on the preparation of aluminas by PFHS methods, detailed characterisation of the precursor obtained by SA was carried out, since the precursor on calcination at 773 K yielded microspheroidal alumina with small mean crystallite size (< 3 nm), narrow size distribution and excellent free-flowing characteristics.

2. Experimental

The precursor was prepared in the following manner. To a solution of 1.5 mol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 2.25 mol of succinic acid were added 300 g of urea. The solution

* For correspondence

was slowly heated to 363 K with constant stirring till the pH reached 7.0. The precipitate formed was filtered and dried at 373 K.

3. Results and discussion

Characterisation of the precipitate showed some interesting features (table 1). The X-ray diffractogram of the compound (figure 1a) does not correspond to any known aluminium trihydroxide or oxyhydroxide phases. The elemental analysis of this compound (table 1) shows a high percentage of carbon. Carbon, hydrogen and aluminium content values for the compound correspond to an empirical formula $\text{AlC}_4\text{H}_5\text{O}_5$. The absence of nitrogen indicates that the occlusion of nitrate ions and the presence of urea in the precipitate is highly unlikely. The IR spectrum (figure 1b) of the compound exhibits the characteristic bands of the succinate ion at 1595 and 1400 cm^{-1} . Presence of an -OH group is indicated by a broad band centred around 3450 cm^{-1} . Bands corresponding to the bending mode, which are expected at 1025 and 975 cm^{-1} for the -OH group are not seen, possibly because they merge with those of the succinate ion. Since the IR spectrum gives evidence for the presence of both succinate and -OH groups, the compound may be a basic aluminium succinate, $\text{Al}(\text{OH})(\text{C}_4\text{H}_4\text{O}_4)$. This is also in accordance with the elemental analysis of the compound (table 1). A DTA of the compound (figure 1c) exhibits an intense and broad exothermic peak around 813 K and the weight loss corresponding to this from TGA is 68.1%. The exothermic nature of decomposition rules out the presence of any hydroxide or oxyhydroxide. The presence of free succinic acid is most unlikely because neither DTA nor TG show any evidence for its melting or decomposition. The weight loss measurements are in accordance with the formula $\text{Al}(\text{OH})(\text{C}_4\text{H}_4\text{O}_4)$, i.e. basic aluminium succinate, if the end-product is assumed to be Al_2O_3 . This of course holds good since the end-product is found to be $\gamma\text{-Al}_2\text{O}_3$ by XRD analysis. The exothermic nature of the decomposition can be explained as follows. Decomposition of basic aluminium succinate is endothermic, as all decompositions are, but one of the products of decomposition, carbon monoxide, gets oxidised *in situ*, and this being a largely exothermic reaction, masks the endothermicity of decomposition and appears overall

Table 1. Characteristics of alumina precursor prepared by SA method.

Characteristics	Properties
Phase composition (by XRD)	100% Basic aluminium succinate
Crystallite size ^a (nm)	6-80
Infrared spectroscopy	Characteristic bands of succinate ion at 1595 and 1400 cm^{-1}
Morphology ^b	Highly porous and microspheroidal in nature
Elemental analysis	
Aluminium (wt%)	16.9
Carbon (wt%)	30.0
Hydrogen (wt%)	3.13
Sodium (ppm)	205
Potassium (ppm)	147
Nitrogen (ppm)	nil

^a X-ray line broadening analysis; ^b Scanning electron microscopy.

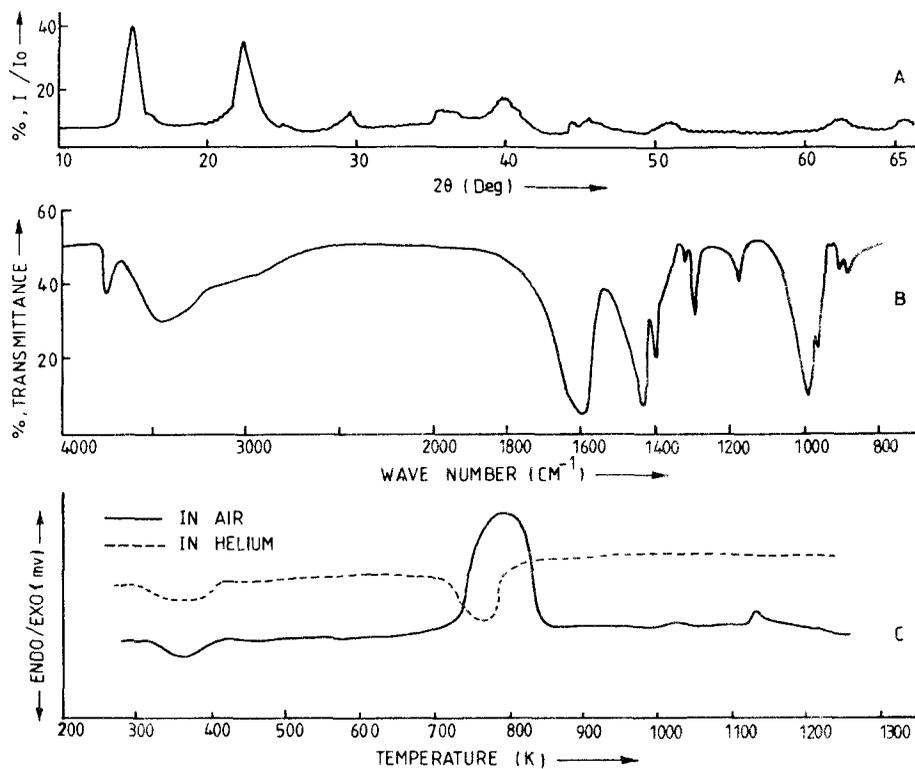


Figure 1. X-ray diffractogram (A), IR spectrum (B) and DTA curve (C), for basic aluminium succinate.

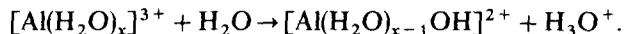


Figure 2. Morphology of basic aluminium succinate.

as an exothermic peak. DTA in a nonoxidising/inert atmosphere (figure 1c), does show the endothermic nature.

The compound formed therefore is a basic aluminium succinate $\text{Al}(\text{OH})(\text{C}_4\text{H}_4\text{O}_4)$. The XRD pattern of this compound has not been indexed yet and is therefore given in figure 1a. SEM photographs (figure 2) clearly reveal the microspheroidal nature which

is retained even after calcination at 773 K. The use of basic aluminium succinate as a precursor for preparation of active alumina has also been recently reported by Sivaraj *et al* (1986). Precipitation of the succinate can be envisaged on the basis of equilibrium for the first dissociation of aluminium ion



Since the conjugated acid of the base used here has a greater dissociation constant, the equilibrium for the aluminium cations will be forced to the right. Since a large excess of anion (succinate) is present, basic salt of the aluminium precipitates at this stage.

References

- Maruthiprasad B S 1985 *Studies on alumina and alumina-supported catalysts prepared by PFHS*, Ph D thesis, Andhra University, Waltair
- Shivaraj Ch, Prabhakara Reddy B, Rama Rao B and Kanta Rao P 1986 *Appl. Catal.* **24** 25
- Willard H H and Tang N K 1937 *Ind. Eng. Chem. Anal. Ed.* **9** 35