Low temperature preparation of β -alumina by an alkoxide route⁺

M K DONGARE* and A P B SINHA

National Chemical Laboratory, Pune 411 008, India

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Abstract. β -alumina has been prepared by the thermal decomposition of a mixture of sodium and aluminium isopropoxides followed by heating up to 1000°C. It has been found necessary to use sodium isopropoxide in excess (25–30%) for the complete formation of β -alumina at 1000°C. On the other hand one obtains a mixture of β -alumina and α -alumina when the starting materials are taken in the stoichiometric ratio $\text{Na}_2\text{O}:11\text{Al}_2\text{O}_3$. DTA, TG and DTG studies of a mixture of sodium and aluminium isopropoxide showed β -alumina formation at 1000°C.

Keywords. β -alumina; sodium isopropoxide; aluminium isopropoxide; low temperature preparation.

1. Introduction

β -alumina refers generally to either of the two closely related compounds, β -alumina $\text{Na}_2\text{O}:11\text{Al}_2\text{O}_3$ and β'' -alumina $\text{Na}_2\text{O}:5\text{Al}_2\text{O}_3$ with layer structures (Beevers and Brohault 1936). β -aluminas are excellent sodium ion conductors which makes them technically important in applications such as thermoelectric generators and the experimental high energy density sodium sulphur battery (*Science* 1966; Kumer and Weber 1968; Huggins 1975).

The formation of β -alumina can be accomplished by heating Na_2CO_3 (or NaNO_3 or NaOH) with any one of the modifications of Al_2O_3 or its hydrates at 1400–1500°C (Kumer 1976). However, many problems are encountered with this method e.g. contamination during pulverising, high sintering temperature and associated undesirable grain growth. β -alumina has an appreciable Na_2O equilibrium vapour pressure which leads to its decomposition to α -alumina in flowing air or reducing atmosphere at this temperature. Because of this, precautions such as heating in covered or sealed platinum vessels must be taken to prevent loss of Na_2O . The synthesis of β -alumina at lower temperature is therefore very desirable.

Metal alkoxides $\text{M}(\text{OR})_n$ [M —metal atom with valence n and R —alkyl group $\text{C}_x\text{H}_{2x+1}$] have proved to be very useful metal organics in the preparation of ultrafine and highly reactive metal oxide precursors for solid state synthesis (Mazdiyasi *et al* 1967). Ultrafine aluminium oxide powder has been prepared by controlled hydrolysis or sol gel technique using aluminium alkoxide as the starting material (Yoldas 1982, 1986). Thin films of β -alumina have also been prepared by a controlled hydrolysis of sodium and aluminium isopropoxide (Yoldas and Partlaw 1980). In this method the water/alcohol ratio, dilution, pH and temperature are the critical factors which determine the nature of the metal oxides.

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*For correspondence.

The metal oxides decompose at lower temperature (300–400°C) to give metal oxides of submicron size and high reactivity (Dongare and Sinha 1984). We have studied the preparation of β -alumina using metal alkoxides by a thermal decomposition technique. The present paper reports the results of our study.

2. Experimental

2.1 Preparation of aluminium isopropoxide

Aluminium isopropoxide was prepared by following the method established earlier (Bradley *et al* 1953). 27.5 g of clean aluminium foil was reacted with 300 ml of anhydrous isopropyl alcohol in the presence of 0.5 g of mercuric chloride. Initially the reaction was slow but became very vigorous after some time. It was necessary to cool the flask in ice water. When the reaction slowed down the mixture was refluxed for 10–12 hr. The unreacted isopropyl alcohol was removed under reduced pressure and the residue was vacuum distilled at 150°C. The compound obtained was characterised by elemental analysis and IR spectroscopy.

2.2 Sodium isopropoxide

Sodium isopropoxide was prepared by reacting freshly cut sodium metal with anhydrous isopropyl alcohol. The excess alcohol was removed under reduced pressure and the compound obtained characterised by elemental analysis and IR spectroscopy.

2.3 Thermal analysis

DTA, TG and DTG analyses were carried out in a dry nitrogen atmosphere using a Hungarian derivatograph, Paulik–Paulik and Erdy (mom Budapest). A sample of alkoxide (200 mg) was taken in a platinum crucible and heated at the rate of 4°C/min. Fine powdered Al_2O_3 was used as the reference material. For the analysis of decomposition products an all-glass apparatus (Dongare and Sinha 1982) was used. The compound was placed in a glass flask in a dry nitrogen atmosphere and heated to 150–200°C in an oil bath. The evolved liquid and gases were condensed in two cold traps, one cooled to 0°C and the other to liquid nitrogen temperature. The compound was further heated at higher temperatures using electrical heating and the evolved liquid and gases were collected in the cold traps. Gas and liquid products were identified by using gas chromatography and mass spectrometry (CRC 21:110 B).

2.4 β -Alumina preparation

Aluminium isopropoxide and sodium isopropoxide were dissolved in isopropyl alcohol in the desired molar ratio. The solution was taken in a silica tube reactor. Since the alkoxides are extremely sensitive to moisture the entire procedure was conducted in a pure, dry, nitrogen atmosphere (see figure 1). The solution was first

Figure 1. Assembly for the preparation of β -alumina. (1) N_2 drying assembly, (2) reaction tube, (3) furnace, (4) cold trap and (5) drying tube.

refluxed in an atmosphere of dry nitrogen at 75°C for 2 hr. The solvent (alcohol) was then removed slowly by increasing the temperature of the external furnace. When the isopropyl alcohol was completely removed the temperature of the furnace was further increased slowly up to 400°C to decompose the alkoxides. The product obtained was taken out and further heated at $700\text{--}1000^\circ\text{C}$ in air for 2 hr. The compound thus obtained was characterised by X-ray powder diffraction using a Philips PW 1730 X-ray diffractometer with Cu-K_α radiations.

3. Results and discussion

The derivatogram of aluminium isopropoxide is given in figure 2. The derived data are given in table 1.

The liquid and gaseous products evolved during a separate decomposition run in the glass unit were identified by gas chromatography and mass spectrometry and the results are given in table 2.

The first weight loss of 40% in TG with an endotherm in the DTA is due to the loss of four propylene molecules from one dimer molecule (Mehrotra 1954) of the isopropoxide. The second exotherm in the DTA with the weight loss of 20% in TG is due to the loss of two molecules of isopropyl alcohol. The aluminium oxide hydroxide formed decomposes to aluminium oxide by losing one mole of water in the subsequent step. The discrepancy in the weight loss in the second decomposition step (i.e. 20% weight loss instead of 28%) is possibly due to the overlap of the second and third exotherms which makes it difficult to determine the correct value. The final compound is amorphous alumina which on heating to 700°C gives α -alumina. On the basis of these results the following possible mechanism for the thermal decomposition of aluminium isopropoxide is proposed.

The mechanism given here differs from that given by Garson *et al* (1963) in which

Figure 2. DTA, TG and DTG curves of aluminium isopropoxide.

Table 1. Data obtained for aluminium isopropoxide.

Nature of the peak in DTA	Temp. range (°C)	Peak temp. (°C)	Wt. loss in TG as % of the original wt.	No. of steps in DTG	Product evolved (quantity, mol)
Endotherm	40–200	160	40	1	C_2H_6 (4)
Exotherm	200–250	245	20	1	C_3H_7OH (2)
Exotherm	250–300	260	13	1	H_2O (1)
Total			73		

Table 2. Products obtained in the decomposition of aluminium isopropoxide.

Decomposition temp.(°C)	Products collected in trap (1) at 0°C	Products collected in trap (2) at liquid nitrogen temperature
20–200	—	C_3H_6
200–350	C_3H_7OH	C_3H_6

six possible reactions are proposed. The derivatogram of the mixture of sodium and aluminium isopropoxide [7:93 wt. %] dissolved in isopropyl alcohol and then partially decomposed at 250°C is given in figure 3. The weight loss in TG in the temperature range of 100–530°C is due to the decomposition of aluminium isopropoxide with one endotherm and one step in DTG. The second exotherm observed in the DTA in the temperature of 700–1000°C without any appreciable weight loss in TG curve shows the compound formation.

The X-ray diffraction pattern of aluminium oxide obtained from thermal decomposition of aluminium isopropoxide at 400°C shows no diffraction lines

Figure 3. DTA, TG and DTG curves of mixture of $\text{Na}_2\text{O} + \text{Al}_2\text{O}_3$ obtained from alkoxides.

suggesting that the material is noncrystalline. This powder when heated at 700°C for 1 hr showed the formation of α -alumina. The X-ray diffraction pattern of the material obtained from the thermal decomposition of the alkoxides at 1000°C containing sodium ions to give a sodium:aluminium oxide ratio of 1:11 is shown in figure 4a. It is observed that a mixture of β -alumina and α -alumina is formed. When sodium isopropoxide is taken in excess over the required stoichiometric value [25% excess], the X-ray diffraction pattern of the compound obtained at 1000°C shows the formation of pure β -alumina (see figure 4b). This is in agreement with the earlier reports that β -alumina has an appreciable Na_2O vapour pressure which leads to its decomposition to α -alumina in flowing air. The excess sodium isopropoxide used in this preparation compensates for the loss of Na_2O leading to the formation of β -alumina.

It can be inferred from the above results that β -alumina is formed at 1000°C by the thermal decomposition technique when metal alkoxides are used as starting materials. Sodium isopropoxide should be used in excess (25–30%) in order to get pure β -alumina.

Thermal decomposition of metal alkoxide gives metal oxide of submicron size and of very high reactivity which is responsible for the improved equilibrium conditions for β -alumina formation at lower temperature. This technique is simple as compared to hydrolytic decomposition or the sol-gel technique in which a critical control on reaction parameters is needed as well as requiring large volumes of volatile solvents, which causes large volume shrinkage. Thermal decomposition of metal alkoxides is a very promising method for the preparation of submicron-size

Figure 4. X-ray diffraction patterns of (a) $\text{Na}_2\text{O}:11\text{Al}_2\text{O}_3$ and (b) $\beta\text{-Al}_2\text{O}_3$

and highly reactive metal oxides, useful for the preparation of bulk materials or thin films of metal oxides at lower temperatures.

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