Preparation of lanthanum-β-alumina with high surface area by a homogeneous precipitation method for use as catalyst support

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Samples containing mixtures of 5 mol % La₂O₃ and 95 mol % Al₂O₃ were prepared by homogeneous precipitation method with or without the presence of various anions, and calcined at different temperatures in the range of 873-1473 K. Sample prepared by urea hydrolysis in the absence of anions, and calcined at about 1273 K results in the formation of pure lanthanum-β-alumina (LBA) with high surface area. However, in the presence of additive anions, the formation of LBA is retarded.

In recent years, immense attention has been paid to prepare thermally stable catalyst support materials with high surface area for catalytic combustion at high temperature. Among several support ceramic materials, viz., γ-Al₂O₃, SiO₂, TiO₂, CeO₂, MgO and mixtures thereof, lanthanum-β-alumina (LBA) is considered to be the most promising one because of its high thermal stability. Various approaches to the preparation of β and β⁺-alumina have been reported in literature. A β-alumina compound containing lanthanum was first observed by Roth and Hasko. Dexpert-Ghys et al. have reported that the LBA phase exists over the composition range (and ratio) La/Al = 1/11 to 1/14. They prepared the material by firing lanthanum oxide and alumina powder. Ropp and Carroll have observed that LBA is formed via LaAlO₃ at temperature higher to 1673 K by firing a mixture of La₂O₃ to Al₂O₃ (ratio = 8.3:91.7) for 24 h. They found that the formation rate is extremely slow below 1773 K. For the first time Kato et al. have prepared LBA (La₂O₃ 11-14 Al₂O₃) by calcining lanthanum and aluminium hydroxides (2 to 10 mol % of La₂O₃ in Al₂O₃) at a lower temperature of 1473 K.

The fact that urea decomposes to CO₂ and NH₃ when its solution is heated has been exploited for the homogeneous precipitation of various hydrated precipitates. The advantage of using urea is the uniform rise in pH which is in contrast to the situation during the rapid addition of a base, where local supersaturation is very high. Slow controlled increase in pH enables controlled nucleation, growth of precipitate particles and their agglomeration. In this paper, the preparation of LBA by homogeneous precipitation method and its characterisation have been reported. For the purpose of comparison, samples have also been prepared by coprecipitation method and are characterised.

Experimental Procedure

Mixtures of aluminium and lanthanum hydroxides were prepared from 0.168 M Al(NO₃)₃ and 0.0088 M La(NO₃)₃ solutions by precipitation from homogeneous solution (PFHS) technique in the presence and absence of additive anions. Precipitation was carried out in a three-necked 2 dm³ round bottomed flask (reaction vessel), one neck of which was connected to a condenser, a thermometer was inserted through the second neck and the third neck was used as a sample port to measure the pH of the solution. Aluminium nitrate (6.80 g), lanthanum nitrate (1.84 g) and 75 g urea were dissolved in about one dm³ distilled water in a beaker. The pH of the solution was adjusted to 3.0 with ammonia (1:1) and the total volume was made up to 1.5 dm³ and transferred to the reaction vessel. The reaction vessel was heated on a rotamantle maintained at 363-368 K. During hydrolysis, the solution was stirred using a magnetic stirrer and the pH of the solution was measured from time to time till it reached 9.2 ± 0.3. At this pH, the reaction vessel was removed from the heating mantle and cooled under running water to arrest the reaction. The precipitate was filtered, washed thoroughly with distilled water until the washings were free from nitrate, and air dried at 383 K in an oven for 24 h. Similar procedure was followed for preparation of a number of samples in the presence of following additives: formate, succinate and sulph-
ate in order to see their effect on the formation of LBA.

In all these cases, the concentration of the additive anion in the solution was kept 1M. For the purpose of comparison, two more samples were prepared by coprecipitation method using ammonia or sodium hydroxide solution, keeping all other experimental conditions same. The samples thus prepared by adding sodium hydroxide and ammonia and urea hydrolysis in absence and in presence of formate, succinate and sulphate were identified by serial numbers 1,2,3,4,5 and 6, respectively. The dried samples were calcined in a muffle furnace at different temperatures in the range of 873-1473 K. The X-ray diffraction (XRD) patterns of the calcined powders were taken on a Philips semiautomatic X-ray diffractometer with an auto-divergent slit and a graphite monochromator using CuKα radiation, operated at 20 kV and 20 mA. The characteristic reflection peaks (d-values) were matched with published data files for identification of phases. The particle morphology of the samples was examined under a scanning electron microscope (SEM). The secondary images were recorded on a SEM (Jeol, Japan) operated at 25 kV. The specific surface area of the powders was measured using a Micromeritics high speed surface area analyser (Model 2202, USA) by adsorption of nitrogen at liquid nitrogen temperature (77 K).

Results and Discussion

The XRD patterns of the samples calcined at 873 to 1473 K for 3 h are shown in Figs 1-4. Samples calcined at 873 K are found to be almost amorphous except one or two broad peaks at 2θ=46° and 67° indicating the formation of γ-Al2O3. The crystalline nature of the samples improved at 1073 K in all cases except for those prepared by homogeneous precipitation (HP) in the absence of additive anions and ammonia addition methods. The latter sample still contained γ-Al2O3. Broad XRD peaks of samples 1,4,5 and 6 calcined at 1073 K are ascribed mostly to γ-Al2O3 and lanthanum aluminate (LaAlO3). The formation of quasi-amorphous LBA is clearly evident from the XRD patterns (Fig. 3) of samples 1,2,3 and 4 calcined at 1273 K. This is probably, the transition state of LBA at a lower temperature (1273 K) before being converted to poorly crystallised form at 1473 K. XRD peaks ascribed to α-Al2O3 are observed in samples prepared by HP method in presence of succinate, whereas, in the presence of sulphate, characteristic peaks of LBA appear along with a few peaks denoting α-Al2O3. It can be concluded that γ-Al2O3 phases formed by urea hydrolysis in presence of succinate are stable up to 1073 K and transform to α-Al2O3 at 1273 K. Samples 2 and 3 calcined at 1473 K show characteristic lines of pure LBA whereas those of samples 4 and 6 indicate the presence of a mixture of α-Al2O3 along with LBA besides traces of other oxides in case sample 6. The peaks ascribed to LBA are broad and less intense (Figs 3 and 4) and this could be interpreted in terms of its poor crystallinity and small crystallite size. While sample 1 contains mostly LBA be-
sides traces of $\alpha$-$\text{Al}_2\text{O}_3$, $\theta$-$\text{Al}_2\text{O}_3$ and $\text{LaAlO}_3$. Sample 5 mostly contains a mixture of $\alpha$-$\text{Al}_2\text{O}_3$ and $\text{LaAlO}_3$. It may be inferred that the presence of additive anions during hydrolysis retard the formation of LBA due to the strong adsorption of the anions on the surface of the hydroxide precursors.$^{15,16}$ Fig. 5 shows the variation in specific surface area of the products prepared by various methods and calcined for 3 h at different temperatures in the range of 873-1473 K. Samples, 2, 3, 4, 5 and 6 had the highest surface area when calcined at 1073 K while for sample 1 the peak is reached at 873 K. The surface area decreases with increase in calcination temperature beyond 1073 K. The relatively high surface area exhibited by sample 2 and 3 at all calcination temperatures indicates that these samples are thermally more stable than the other samples. The surface area of the samples prepared in the absence of anions is higher compared to those prepared in the presence of anions. This could be explained in the light of the adsorption of these anions on the surface of the precipitated particles thereby blocking the micropores of the particles, but the decrease in surface area at higher calcination temperatures could be due to the combined effect of the formation of mesopores and sintering. From Figs 3 and 5, it can be concluded that homogeneous precipitation method yields products with large surface areas facilitating the formation of LBA at relatively low calcination temperature. The formation of LBA retards the grain growth of $\text{La}_2\text{O}_3$-$\text{Al}_2\text{O}_3$ particles and this property imparts better thermal stability. Kato et al.$^5$ have concluded that the retardation of sintering is caused by the formation of LBA. Similar observations, on the retardation of sintering by the addition of 2 to 10 mol % $\text{La}_2\text{O}_3$ to $\gamma$-$\text{Al}_2\text{O}_3$, have also been made by others.$^5,12$
Fig. 6a—Scanning electron micrograph of sample prepared by HP method, calcined at 1473 K

Fig. 6a shows the micro-structure of LBA prepared by homogeneous precipitation method (sample 3) and the magnified view of the sample shows the porous nature of the particles which corroborates the surface area data. The SEM photograph (Fig. 6b) shows that the particles of the sample prepared in the presence of sulphate ion are either spheroidal or tending to achieve the spherical shape but remain in the form of aggregates. Furthermore, the particles are almost uniform in both shape and size and the average particle size of these samples are in the range of 15-25 μm.

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References