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Barium hexaaluminate nanowhiskers synthesized by novel sol–gel process in reverse micellar media†

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Barium hexaaluminate (BHA) synthesized by coupling of sol–gel process in reverse microemulsions shows a unique nanowhisker morphology and high surface area, which are retained after calcination at 1300 °C.

Design of novel materials with controlled shape, size, morphologies and microstructure has emerged as an interesting area of research. Of these, the one-dimensional (1-D) nanomaterials are especially interesting due to their physical and chemical properties arising as a result of the nanoscale dimensions and preferential growth in particular directions.[1–2] These one-dimensional nanoscale structures like nanowhiskers, nanowires, nanorods *etc.*, are essentially, single crystals, free from any lattice defects and form as a result of anisotropic crystal growth in the reaction media.The synthesis of 1-D nanostructures in reverse micellar media,[3] molten salt synthesis in microemulsions,[4] surfactant assisted solid-state reactions[5] and surfactant assisted hydrothermal synthesis[6] are currently of considerable interest.

Barium hexaaluminate ($BaO{\cdot}6Al_2O_3$ (BHA)) is a potential high-temperature combustion catalyst because of of its excellent thermal stability and high catalytic activity for methane combustion.[7–11] But the conventionally sol–gel prepared BHA crystallizes above 1300 °C compared to 1500 °C when synthesized by a solid state reaction (SSR) route.[7] Crystallisation at such high temperatures is accompanied by particle growth, agglomeration and presintering of the grains, which greatly reduces the surface area of BHA. BHA nanoparticles synthesized in microemulsions[12,13] possess superior chemical homogeneity, so crystallization occurs at lower temperatures (1100 °C) and hence, grain growth at higher temperatures is suppressed owing to the anisotropic crystal growth of BHA.[7,14] Also, the microemulsion-derived BHA nanoparticles have much lower light-off temperature of 590 °C compared to 710 °C of conventionally-prepared BHA.[13]

In all routes reported to date for the synthesis of BHA,[7–13] alcoholic solutions of Ba and Al isopropoxides were used as precursors, wherein barium isopropoxide was synthesized by refluxing barium metal with isopropanol under an inert atmosphere. This method is not suitable for the commercialization of BHA as an industrial catalyst owing to the high cost and instability of barium alkoixide. The primary objective of the present work was to identify and use non-alkoxide barium precursors that would lead to homogeneous, ultrafine and high surface area BHA powders. Here, we report a novel method to synthesize BHA nanowhiskers by using the inherent characteristics of microemulsions and advantages of the sol–gel process.

Reverse microemulsions were prepared using 52 wt% cyclohexane as the oil phase, 33 wt% Triton X-100–*n*-hexanol as surfactant cosurfactant mixture (surfactant : cosurfactant ratio of 2 : 1 by weight) and 15 wt% aqueous phase. Two microemulsions, each with different aqueous phases, 0.5 M barium acetate and 6.0 M NH_4OH, were prepared. A suspension of aluminium isopropoxide (AIP), in toluene was prepared by refluxing at 80 °C for 8 hours. All chemicals were GR grade (E-Merck, India) and used as received without further purification. Water used was doubly distilled and deionized. The two microemulsions were mixed slowly under inert atmosphere, while introducing the AIP suspension simultaneously under stirring. The precipitated powders were recovered by centrifugation after 3 hours of aging and oven dried at 110 °C for 10 hours. The resulting white fluffy precursor powder was heat-treated at different temperatures ranging from 400–1300 °C in flowing air to study the microstructural and phase development.

The TG-DTA of microemulsion-derived nanopowders (not shown here), taken at a heating rate of 10 °C min^{-1} (TG/DTA 32, Seiko, Japan) shows that the amorphous nanopowders crystallized at around 1170 °C (exothermic peak), as compared to 1100 °C reported in an earlier microemulsion method.[13] The TG shows a three-step weight loss; (i) at 200–270 °C due to the removal of ammonium acetate formed after hydrolysis of barium acetate (sharp endothermic DTA peak), (ii) at 270–380 °C (broad exothermic DTA peak) due to the removal of surfactant and other organics, and finally (iii) dehydroxylation weight loss at 380–560 °C.

The Powder X-ray diffraction (PW 1730, Philips, Holland) was taken using Ni-filtered Cu–Kα radiation (λ = 1.5418 Å) at 30 kV and 20mA and a scan rate of 2° min^{-1} 2θ (not shown here). XRD of the as-synthesized precursor and powder calcined at 800 °C for 4 hours show that the nanopowders are amorphous. The 1100 °C and 1300 °C calcined powders show the characteristic XRD peaks[7,13] of single phase BHA without any intermediate and $BaCO_3$ phase formation. The XRD of BHA synthesized by conventional SSR route, by heating a mixture of barium acetate and AIP to 1300 °C for 6 hours, shows impurity peaks of $BaCO_3$ and alumina, formed as intermediate reaction products.

Fig. 1 shows the ^{27}Al solid-state magic-angle spinning NMR (Avance 500 MHz, Bruker) of the samples. The Al in precursor powder is predominantly 6-coordinated (δ_{iso} = 8.31 ppm) with OH^- and O^{-2}. Further, the 4-coordination as AlO_4 species increases with rise in calcination temperature. The fully crystallised BHA phase calcined at 1300 °C shows prominent shifts for AlO_4 (δ_{iso} = 66.39 ppm) and AlO_6 (δ_{iso} = 9.25 ppm) as expected from its crystal structure. No chemical shift due to AlO_5 polyhedra could be detected in any of these samples which proves the nanowhiskers have a defect β-alumina structure‡ (not magnetoplumbite like Ca, Sr, Pb or La hexaaluminates) as recently proved.[14] The SSR-synthesized BHA shows a higher

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† Electronic supplementary information (ESI) available: DTA and XRD plots of the BHA nanopowders and the mechanism of formation of BHA nanowhiskers. See http://www.rsc.org/suppdata/cc/b3/b303815g/

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(downfield) shift of AlO_6 coordination (δ_{iso} = 13.00 ppm) and a split AlO_4 shift, one due to the BHA phase (δ_{iso} = 66.86 ppm) and other due to some amorphous or transition alumina (δ_{iso} = 73.89 ppm). It also shows sharp spinning side bands (shown as * in Fig. 1) due to the α-alumina impurity (as seen in the XRD) on either sides. The sidebands produced by the defect β-alumina structure of BHA are very broad and diffuse, and are also very weak in intensity.

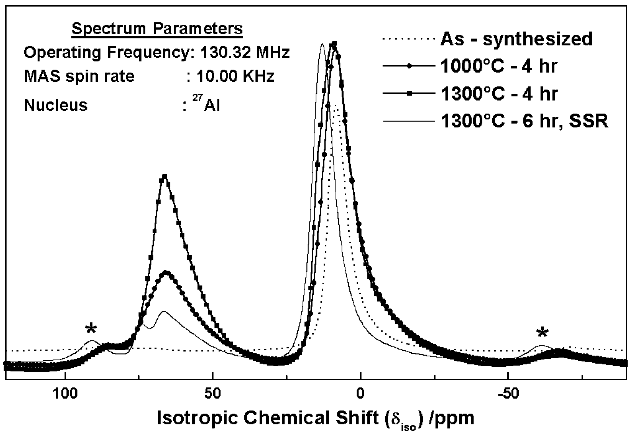

Fig. 1 ^{27}Al solid-state MAS-NMR of BHA nanowhiskers.

The transmission electron microscopy (JEM 1200 EX, JEOL, Japan) measurements were done at an accelerating voltage of 100 kV by dispersing the samples ultrasonically in isopropanol and then depositing them on a polymer-coated copper grid. TEM of the as-synthesized precursor (Fig. 2) shows agglomerates of amorphous nanowhiskers. The individual nanowhiskers are 1–5 nm in diameter and 10–50 nm in length. The TEM micrograph of the nanopowder calcined at 1300 °C (Fig. 3) shows the agglomerated nanowhiskers, which have grown in size. The BET surface area of as-synthesized powder was measured to be ~315 $m^2 g^{-1}$, and after heat treatment to 1300 °C for 4 hours, it retained a high surface area of ~90 $m^2 g^{-1}$, consistent with the earlier reported works.[13] This retention of high surface area by BHA is due to highly anisotropic crystal growth of BHA,[14] the crystal growth along [001] being suppressed strongly, and also due to the lowering of crystallization temperature to 1100 °C. Due to the high surface area of BHA nanowhiskers, they can be used as a high temperature catalyst for methane combustion.[7–13]

The water : alkoxide ratio used in the present work is 10 : 1 as compared to that in the previous work by Zarur *et al.*[13] of 100 : 1. The low water : alkoxide ratio is the governing factor for precursor nanopowder shape, size and agglomeration, apart from factors like aging time, microemulsion composition and water : surfactant molar ratio. On the addition of AIP–toluene to the microemulsion mixture, AIP starts to hydrolyze whereas toluene (which itself acts as an oil phase) is in equilibrium with the w/o microemulsion, hence forming a Winsor II type phase system. The formation of nanowhiskers (initially as xerogels in the reverse micelles) could be partly due to the fact that Triton X-100 forms non-spherical micelles in cyclohexane[16] and thus acts as a soft template for the formation of nanowhiskers[1,15,17] as a result of nucleation and growth of BHA precursor particles in these rod-like or cylindrical micelles. Many ceramic nanowhiskers and nanorods have been prepared in a Triton X-100–cyclohexane system.[18] The other prominent reason for nanowhisker morphology of BHA could be due to the highly anisotropic crystal growth of the BHA precursor[7,13,14] inside the micellar cores during aging, and later during heat treatment of the precursor. This nanowhisker morphology was retained on calcination, the whiskers growing larger in size, as expected.

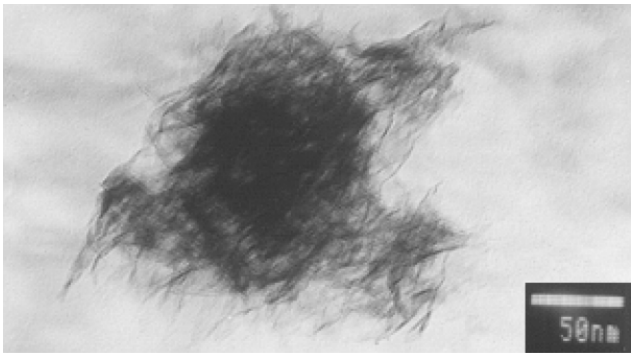

Fig. 2 TEM image of BHA as-synthesized precursor nanowhiskers.

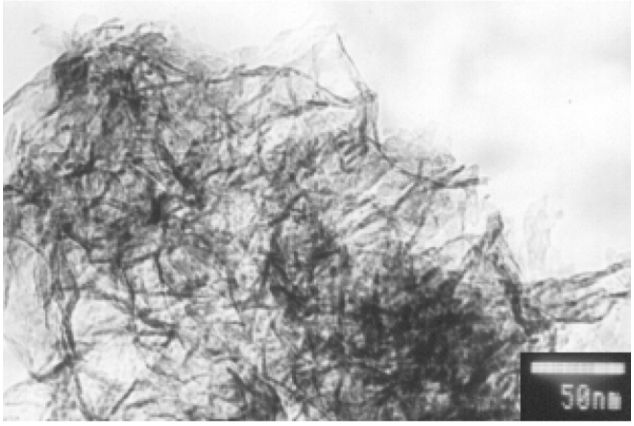

Fig. 3 TEM image of BHA precursor nanowhiskers calcined at 1300 °C for 4 hours.

The experimental results confirm the formation of BHA in reverse micellar media by coupling of the sol–gel process. The method is being generalised for syntheszing nanowhiskers of other ceramics after appropriate modifications.

Notes and references

‡ BHA exhibits hexagonal symmetry and belongs to space group $P6_3/mmc$.[14] The reported δ_{iso} values for AlO_6, AlO_5, and AlO_4 polyhedras are 0–20 ppm, 20–45 ppm, and 45–80 ppm, respectively.

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