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Preparation of Al_2O_3–SiO_2 fine particles by CVD method in tube flow reactor

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Abstract

The aim of this study was the synthesis of mixed or coated multicomponent alumina–silica particles by chemical vapour deposition method in a tube flow reactor. The particles were produced by simultaneous thermal decomposition of aluminum tri-*sec*-butoxide and tetraethylorthosilicate in one reactor. The particle production was monitored by Differential Mobility Particle Sizer, composition of particles was analysed by energy dispersive X-ray analysis, morphology by scanning/transmission electron microscopy and crystallinity by selected area electron diffraction. In dependence on experimental conditions, the particles produced were either alumina particles with intermixture of silica, or they were coated by silica, or it was a mixture of particles of various compositions. The particles were often agglomerates of the primary nanoparticles and were partially crystalline.

Keywords: CVD; SEM/TEM; Aluminum tri-*sec*-butoxide; Tetraethylorthosilicate

1. Introduction

Ultrafine powders are finding a great number of uses, especially in the technology of high performance materials, medicine, catalysis, etc. Mixed metal oxides have proven especially useful in the preparation of ceramic powders and glasses. Synthesis of spherical colloidal particles of mixed silica–alumina by the liquid phase hydrolysis in the presence of sulfate ions has been reported by Nishikawa and Matijević [1]. In our previous works, we prepared silica [2] and alumina [3] fine particles by chemical vapour deposition (CVD) method in a tube flow reactor using tetraethylorthosilicate (TEOS) and aluminum tri-*sec*-butoxide (ATBO) as precursors. While ATBO decomposes very easily already at 200 °C and in the presence of traces of water vapour or oxygen at even lower temperature [4], the pyrolysis of TEOS in an inert atmosphere requires temperature above 700 °C [5]. In this work, the synthesis of mixed alumina–silica particles by simultaneous decomposition of ATBO and TEOS in a tube flow reactor is presented.

2. Experimental

The use of glass as a construction material in thermal processes is limited up to temperatures slightly above 500 °C. ATBO used as precursor for alumina particle formation decomposes at much lower temperature in an inert atmosphere, and presence of oxygen in the carrier gas has no effect on particle production [3]. But TEOS decomposes within this temperature limit only in the presence of oxygen in the reaction mixture [2,5], so that we had to use air as a main part of the carrier gas.

2.1. Apparatus

Experiments were performed using an apparatus shown in Fig. 1. Particles were synthesised in an externally heated

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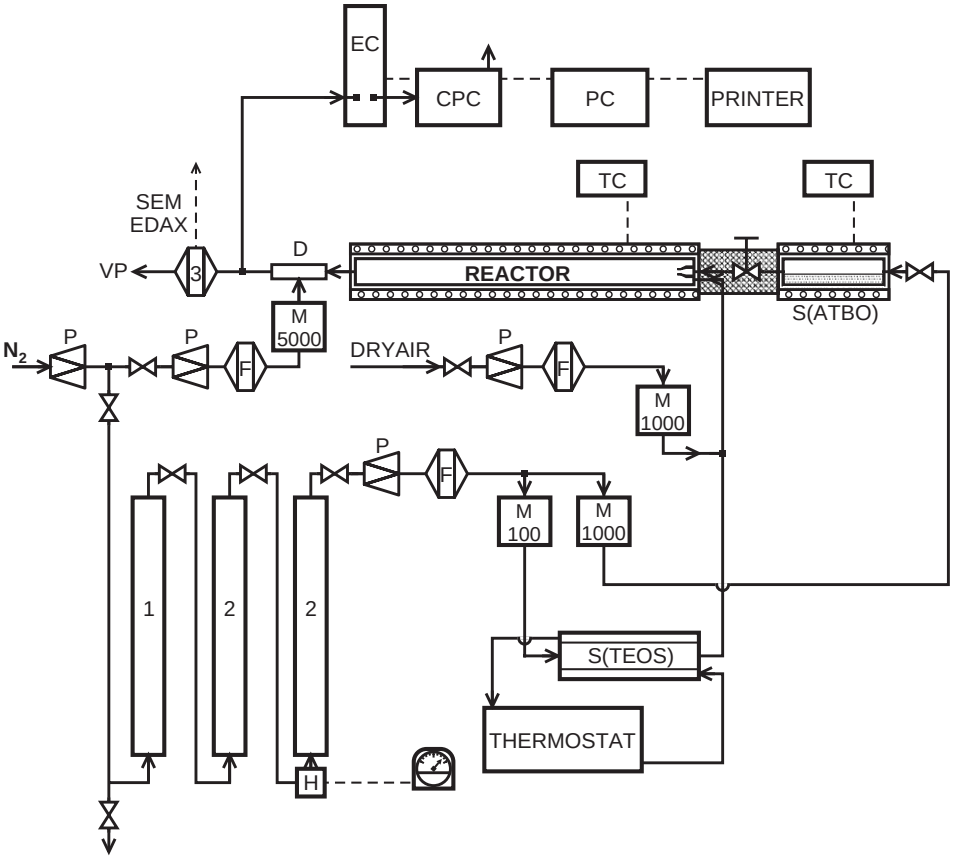

Fig. 1. Scheme of the apparatus: (1) deoxidiser, (2) dryer, (3) Millipore filter or electrostatic precipitator, (CPC) condensation particle counter, (D) diluter, (EC) electrostatic classifier, (F) filter, (H) humidity sensor, (M100, M1000) electronic mass flow rate controllers, (P) pressure reducing valve, (PC) personal computer, (S) saturator, (TC) temperature controller, (VP) vacuum pump.

tube flow reactor of the length 55 cm and ID 2.7 cm. The deoxidised (1), dry (2) and particle free nitrogen, used as a carrier gas, was saturated by ATBO vapour in an externally heated saturator (S_{ATBO}). Saturated carrier gas was then fed axially into the centre of the reactor through a nozzle. Another stream of nitrogen was saturated by TEOS vapour, mixed with the stream of air and fed into the reactor coaxially with the stream saturated by ATBO. Particle-laden gas leaving the reactor was cooled in a diluter (D) by mixing it with additional stream of nitrogen. Flow rates of individual gas streams were controlled by electronic mass flow meters Tesla 306 KA/RA and the temperatures of the ATBO saturator and the reactor by electronic temperature controllers RLC T48. The temperature of the TEOS saturator was maintained at the value 20 °C by a thermostat. Samples of particles were collected on Millipore filters or deposited onto Cu or carbon coated Cu grids with a point-to-plate electrostatic precipitator and before subsequent examination they were sputtered by a thin layer of graphite.

2.2. Particle characterisation

The particle size distribution was monitored with a Differential Mobility Particle Sizer (DMPS, TSI 3932C), consisting of Electrostatic Classifier (TSI 3071) and Condensation Particle Counter (TSI 3022). Particle morphology was analysed by scanning/transmission electron microscopy (SEM/TEM), *JEOL-2000FX* and crystallinity by selected area electron diffraction (SAED). Energy dispersive X-ray analysis (EDAX) of chemical composition of some samples was performed on the microprobe *Philips JXA 50A*.

2.3. Experimental conditions

On the basis of our previous investigations [2,3], we selected a set of experimental conditions suitable to preparation of both silica and alumina particles by decomposition of TEOS and/or ATBO vapour. They are: reactor temperature T_R 500 °C, residence time in the reactor RT_R 16.5 s (flow rate at standard conditions Q_R 400 cm^3/min), concentrations c_{TEOS} $3.9\cdot10^{-6}$ mol/l, c_{ATBO} $2.2\cdot10^{-8}$ mol/l, $c_{O2}\geq15\%$ vol., and temperatures of TEOS and ATBO saturators 20 and 55 °C, respectively. The particle production was then investigated in dependence on: c_{TEOS} from 0 to $1.2\cdot10^{-5}$ mol/l, c_{ATBO} from 0 to $2.4\cdot10^{-8}$ mol/l, T_R from 450 to 510 °C and RT_R from 11.1 to 33.4 s. For comparison, we also tested different arrangement of the inlet section of the reactor when the stream saturated by TEOS was fed into the reactor through the ATBO saturator.