Powder Technology 298 (2016) 42–49

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Synthesis and characterization of Al_2O_3 nanoparticles by flame spray pyrolysis (FSP) — Role of Fe ions in the precursor

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ARTICLE INFO

Article history:
Received 2 November 2015
Received in revised form 11 April 2016
Accepted 4 May 2016
Available online 6 May 2016

Keywords:
Flame spray pyrolysis (FSP)
θ-Al_2O_3
η-Al_2O_3
$FeAl_2O_4$
Lattice parameter
Fluoride removal

ABSTRACT

Iron doped aluminium oxide nanoparticles are of interest for number of applications (e.g. water treatment, catalytic conversion of exhaust gases) due to their high surface area, hardness, catalytic and magnetic properties. In the present study, flame spray pyrolysis (FSP) was employed for the synthesis of Fe/Al_2O_3 nanoparticles. Precursor solutions of aluminium acetylacetonate (0.2 mol·L^{-1}) and ferrocene (0 to 0.2 mol·L^{-1}) in toluene were used to synthesise pure and iron (Fe) doped Al_2O_3. The particle composition and morphology were studied and effect of iron concentration was analysed. It was found that in the absence of the iron precursor, FSP produced a mixture of two Al_2O_3 polymorphs: θ-Al_2O_3 and η-Al_2O_3. The addition of ferrocene as an iron precursor was found to suppress formation of θ-Al_2O_3. At an iron molar concentration of 0.2 mol·L^{-1} mainly hercynite, $FeAl_2O_4$, was observed. Furthermore, increasing the iron concentration caused a linear shift of the X-ray diffraction peaks from positions corresponding to η-Al_2O_3 to those of $FeAl_2O_4$. This indicates the formation of a solid solution ($Fe_xAl_2O_{3+x}$) at intermediated concentrations. It was also found that the primary particle size, which was below 10 nm, did not significantly change with the increased iron concentration and was comparable to the mean crystallite size indicating that size of these single crystalline primaries is determined by the synthesis process rather than the chemistry of the product. However, the hydrodynamic size was around 180 nm indicating that the particles are agglomerates in the water suspension. Additionally, zeta potential of the nanoparticles was found to decrease slightly with increasing iron content, though in all cases it was above 50 mV. Finally, the potential of synthesized nanoparticles was examined for the removal of fluoride because fluoride causes harmful health effects to human health at elevated concentrations. The results of fluoride removal using synthesized nanoparticles produced in this study showed that the highest fluoride removal efficiency was observed for the sample having no iron content.

1. Introduction

In recent years, synthesis of nanomaterials has attracted wide attention due to their excellent properties and numerous applications in different fields [1,2]. Many methods exist for the synthesis of nanoparticles such as chemical vapour deposition [3], physical vapour deposition [4], sol-gel [5], microwave assisted synthesis [6], grinding [7] and flame spray pyrolysis (FSP) [8–10]. The use of the FSP method has been expanded in the recent years because it can produce large quantities of metal oxide nanoparticles with high purity and higher surface area compared to some conventional methods (e.g. sol-gel) [11–13]. Furthermore, FSP is fast, one-step and low-cost synthesis method [1,11,12]. There are several inter-related stages in the formation of nanoparticles by FSP such as precursor dispersion, droplet evaporation, combustion, nucleation, condensation, coagulation, sintering, aggregation and agglomeration [1,14].

Metal oxide nanoparticles offer unique structural properties such as core shell, and wide range of potential application [15–17]. Chemical and physical properties of metal oxide nanoparticles produced by FSP depend on the synthesis conditions and properties of the precursor solution (e.g. solvent, solutes) [18]. In the synthesis, precursor droplets are dispersed with oxygen and ignited with a premixed methane-oxygen flamelet [19,20]. This results in the formation of a high-temperature flame, with temperatures in excess of 3000 K [21]. Within the flame the organometallic precursors decompose and the organic compounds undergo complete combustion, forming carbon dioxide and water

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http://dx.doi.org/10.1016/j.powtec.2016.05.003

Table 1
Molar rations of precursors and production rates in the experiments.

No.	Precursor compounds	Concentration ($mol \cdot L^{-1}$)		Volume of toluene (mL)	Feeding rate ($mL \cdot min^{-1}$)	Production rate ($g \cdot h^{-1}$)
		Al $(C_5H_7O_2)_3$	$Fe(C_5H_5)_2$			
S1	Al $(C_5H_7O_2)_3$	0.2	0	250	5	0.368
S2	Al $(C_5H_7O_2)_3 + Fe(C_5H_5)_2$	0.2	0.1	250	5	0.397
S3	Al $(C_5H_7O_2)_3 + Fe(C_5H_5)_2$	0.2	0.2	250	5	0.399

vapour. The chemical modification of aluminium-iron oxide nanoparticles can be used to further improve the particles properties and provide additional functionalities like magnetic or catalytic properties [9,22]. In addition, iron oxides have shown to improve the removal of negatively charged species (e.g. fluoride) from water [23]. Previous researches have shown that synthesized nanoparticles from mixed metal oxide have better properties than metal oxide alone [24,25].

This paper reports the FSP synthesis of aluminium oxide and iron (Fe) doped aluminium oxide nanoparticles. The effect of different molar ratios of iron doping on the particle properties were studied. The structure and physico-chemical properties of produced powders were characterized with the zeta potential, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Brunauer-Emmett-Teller (BET) methods. In addition, the efficiency of the synthesized particles for the removal of fluoride from aqueous solution was also studied. Fluoride was selected as a model pollutant in this study because elevated concentrations (higher than 1.5 $mg \cdot L^{-1}$) of fluoride in drinking water cause harmful health effects to humans such as, skeletal fluorosis, causing debilitating bone structure disease, as well as discoloration and mottling of teeth, cancer or adverse effects on the brain and kidney [26]. High fluoride concentrations in drinking water have affected millions of people globally and for this reason, endemic fluorosis has been a considerable worldwide health problem [27]. Although, many materials have been examined for the removal of fluoride, but, the use of metal nanoparticles is of great interests because of a number of key physico-chemical properties of nanoparticles (e.g. larger surface area than bulk particles, enhanced reactivity and self-assembly).

2. Materials and methods

2.1. Materials

Table 1 compiles the information regarding the precursors, molar ratios and solution feeding rates in each experimental set up. Three precursor solutions were prepared for FSP synthesis (S1, S2, and S3). The used organometallics were aluminium acetylacetonate (ReagentPlus®, 99%, Sigma-Aldrich, USA) and Ferrocene (98%, Sigma-Aldrich, Germany). To evaluate the effect of precursor solution molar ratios on the characteristics of synthesized powder, the organometallic precursors were dissolved with different molar ratios in toluene (Analytical grade, 99.6%, Scharlau, Spain) according to the Table 1. The actual mass ratio of Fe:Al varied from 0 to 2.1. Thus, the estimated mass ratio of $FeO:Al_2O_3$ was between 0 and 1.4 accordingly.

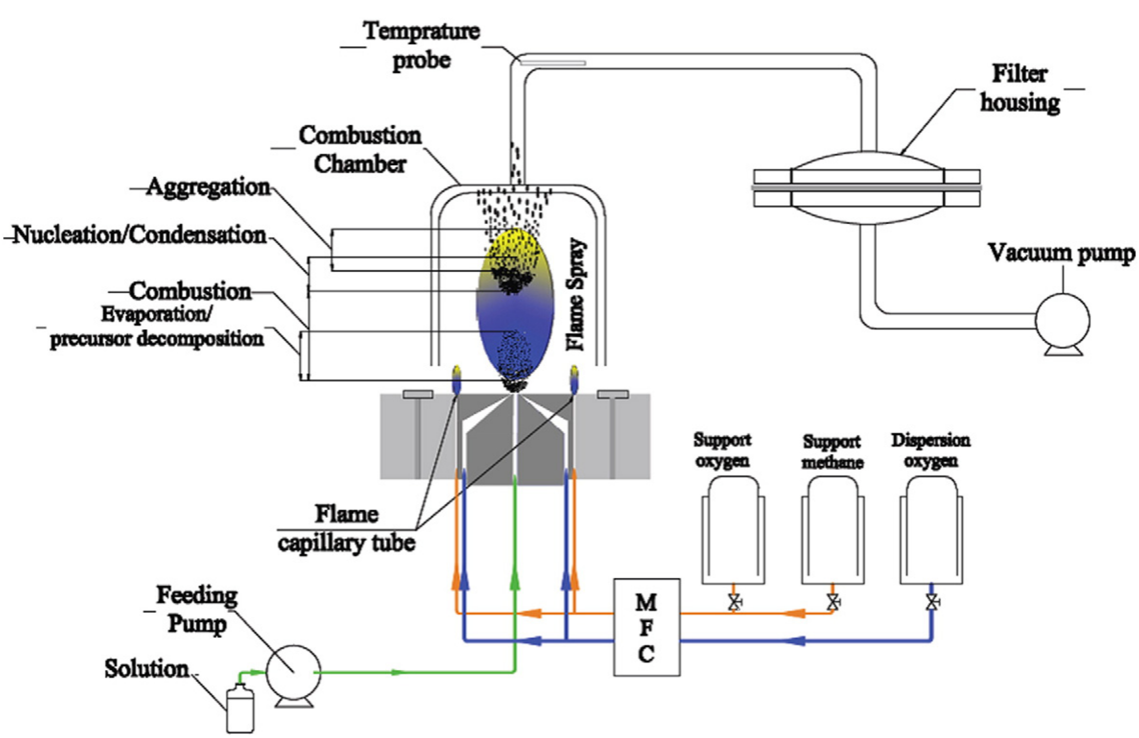

Fig. 1. Schematic of the flame spray pyrolysis system used in this study and the particles production process (MFC — mass flow controller).