Flame spray synthesis of visible light active nanocrystalline bismuth oxide based photocatalysts

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ABSTRACT

$BaBiO_3$ nanoparticles have been synthesized by dissolving Ba and Bi precursors in a suitable solvent and spraying into the high temperature acetylene flame using an atomizing gas. Resulting powders were characterized by nitrogen physisorption (measuring specific surface area), x-ray diffraction (phase composition), transmission electron microscopy (size, shape and morphology of the particles), whilst UV-vis diffuse reflectance spectroscopy analyzed with the Kubelka-Munk function has been used to study the visible light absorption of the photocatalyst and the optical band gaps. Specific surface area of the nanoparticles has been varied by changing the flow rate of the of the precursor solution that has significant influence on the combustion enthalpy density (CED) of the flame. Rate of degradation of formaldehyde under visible light illumination (>400 nm) has been used as the measure of the photocatalytic activity (PCA) of the particles whose specific surface area ranges from 5 to 50 m^2/g. Clear dependence of the specific surface area and crystallinity of the particles on the PCA has been observed which signifies the advantages of nanoparticles.

Keywords: nanoparticles, flame spray, photocatalysis, visible light, Barium oxide, bismuth oxide

INTRODUCTION

Photocatalysis phenomenon has attracted considerable interest in recent years because of its usage in water purification, environmental cleaning, solar energy conversion and generation of alternative energy resources. Development of a practical photocatalytic system focuses on the cost effectiveness of the process. Usage of the expensive solar concentrators and artificial UV irradiation for photocatalytic reactions has negative influences on the cost effectiveness. Instead, more practical and inexpensive step is to employ renewable solar energy as the illumination source to activate the photocatalyst for photocatalytic decomposition reactions. To date, TiO_2 has undoubtedly proven to be the most effective photocatalyst. However, owing to the large band gap of TiO_2, it is not suitable for the usage as visible light active photocatalyst. Narrow band gap (<2.6 eV) bismuth oxide based materials, MBi_2O_4 (M = Ba, Sr, Ca), has been reported [1] as an efficient visible light active photocatalysts and are synthesized by the conventional solid state reaction methods that leads to particles having very low specific surface area (<1 m^2/g). Since photocatalysis is a surface phenomenon, less surface area of the large particles hinders the number of active sites where the photocatalytic reaction can take place. Hence there is a need to synthesize the visible light absorbing photocatalysts with high specific surface area. In the present study, flame spray synthesis has been employed to synthesize $BaBiO_3$ nanoparticles. High temperatures prevailing in the flame result in the nanoparticles with high degree of crystallinity. Reduction of the particle size is also associated with the increased absorption of the visible light irradiation. Moreover, the ability of the synthesis of Ba-Bi-O nanoparticles by flame spray synthesis at high production rates has been shown.

EXPERIMENTAL PROCEDURE

Fig 1 shows the schematic of the experimental set-up of the flame spray synthesis. It consists of a syringe pump to feed the precursor mixture, an external mixing gas-assisted nozzle and the powder collection unit. Liquid precursor is stored in a separate vessel and the flow rate is adjusted with the syringe pump. The nozzle consists of a central opening (2.8 mm) incorporated in a capillary tube (1.05 and 1.59 mm internal and external diameter, respectively) through which the precursor and fuel mixture is fed to the flame. The spacing between the capillary tube and central opening is used to feed the atomizing gas (oxygen) that forms fine droplets of the liquid precursor mixture. The liquid is ignited by six supporting premixed flamelets produced by C_2H_2 (13 l/min) and O_2 (17 l/min). Openings (1.3 mm) contributing to the supporting flames are located at 3.25 mm from the centre of the nozzle and all gas

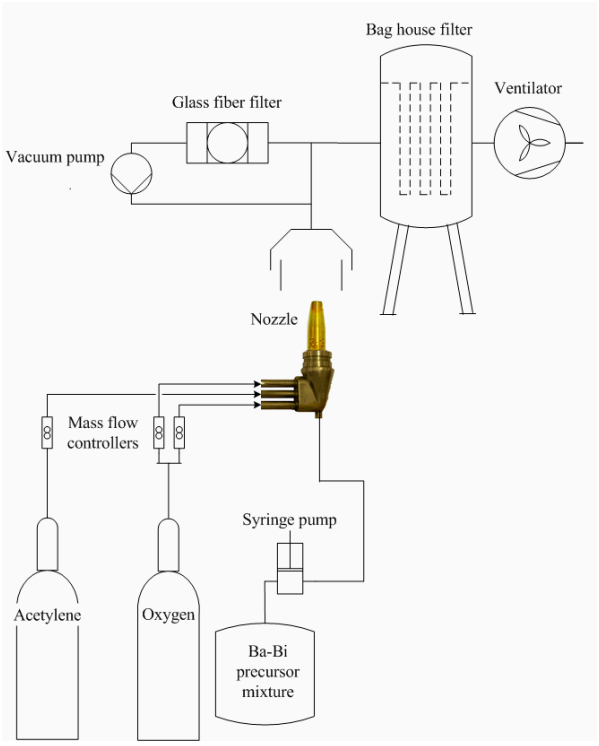

Fig. 1: Experimental set-up for the synthesis of $BaBiO_3$ nanoparticles

flow rates are controlled by the mass flow controllers (Bronkhorst HI-TEC, Netherlands). Due to the high exit velocities of the process gases, particles are collected in a bag house filter (Friedli, Switzerland) and the representative samples of about 1 g are collected on a glass fiber filters (Type GF50, Schleicher and Schuell, Germany), via a by-pass, using a vacuum pump.

As a precursor source of Bi, bismuth nitrate pentahydrate ($Bi(NO_3)_3$. $5H_2O$, purity>98.5%, Sigma Aldrich, Switzerland) was used by dissolved in water with 15 vol% HNO_3. Barium acetate [$Ba(CH_3COO)_2$] was used as a precursor source for Ba and was dissolved in distilled water. The CED in this study is defined as the ratio of the total liquid precursor mixture plus acetylene-oxygen combustion enthalpy to the total gas flow in the system. Changing the combustion enthalpy density is associated with the variation of oxygen concentration (Lambda, λ) in the process. Lambda is defined as the ratio of the actual fuel-to-oxygen ratio of the reactants to the stoichiometric fuel-to-oxygen ratio.

CHARACTERIZATION

The specific surface area (SSA) of the product powder was determined from a five-point N_2 adsorption isotherm obtained from BET (Brunauer–Emmett–Teller) measurements using a Beckman-Coulter SA3100. Prior to BET analysis, the powder samples were degassed at 200°C for 180 min under flowing N_2 atmosphere to remove adsorbed H_2O from the surface. Assuming monodisperse, spherical primary particles, the BET- equivalent primary particle diameter d_{BET} is calculated by

$$d_{BET} = \frac{6}{(\rho_B) * SSA}$$

Where ρ_B– density of $BaBiO_3$ (7.88 g/cm^3). The primary particle size, shape and morphology of the particles were investigated by transmission electron microscopy (TEM). Powder samples were dispersed in isopropanol (purity > 99.5%, Fluka, Switzerland) and a few drops of the dispersion were allowed to dry on carbon-coated copper grids (Plano GmbH, Germany). The TEM analysis was performed on a Philips CM30 electron microscope operating at 300 kV.

X-ray diffraction (XRD) was used for identification of the crystal phases and determination of the average crystallite size. Diffraction measurements were performed with a PANalytical PW 3040/60 X'Pert PRO instrument using Ni-filtered Cu-Kα radiation of wavelength 1.5418 Å. A 2θ scan range from 5 to 80°, a scanning step size of 0.01° and a scintillation counter detector was used. Curve fitting and integration was carried out using proprietary software from Philips X'Pert high score plus.

The PCA of the as-synthesized powders was evaluated by the degradation of the formaldehyde using TL 20W visible light lamps (Philips, λ_{max} – 450 nm, 400-500 nm range).

Results and discussion

Characterization:

BET

Fig 2 shows the specific surface area (SSA) of the WO_3/TiO_2 nanocomposites synthesized as a function of flow rate of the precursor solution. From the figure it is apparent that the SSA of the $BaBiO_3$ particles decreased with increasing flow rate of the precursor. The temperature of the flame increases with the increasing the flow rate of precursor that enhances the combustion enthalpy density (CED) [2]. An increase in the flame temperature and combustion enthalpy density enhances the sintering rate of the particles facilitating them to grow to large sizes and concomitantly decrease the SSA. In addition, decrease of precursor concentration in the flame reduces the initial particle number concentration, resulting in lower coagulation rates and smaller primary particles. This is similar to the conven-

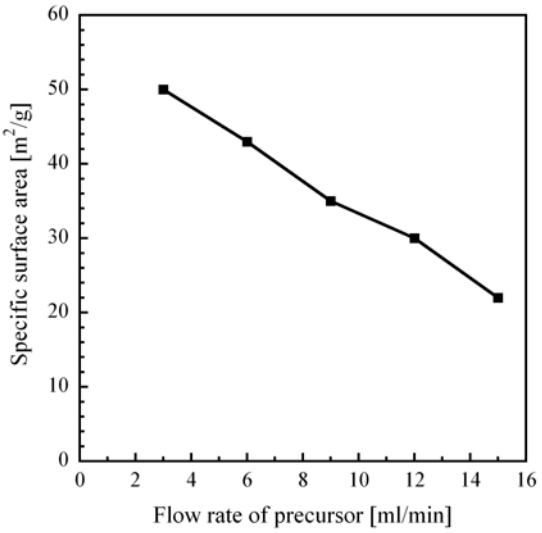

Fig. 2: Specific surface area (SSA) of the $BaBiO_3$ nanoparticles synthesized with various flow rates of precursor solution.

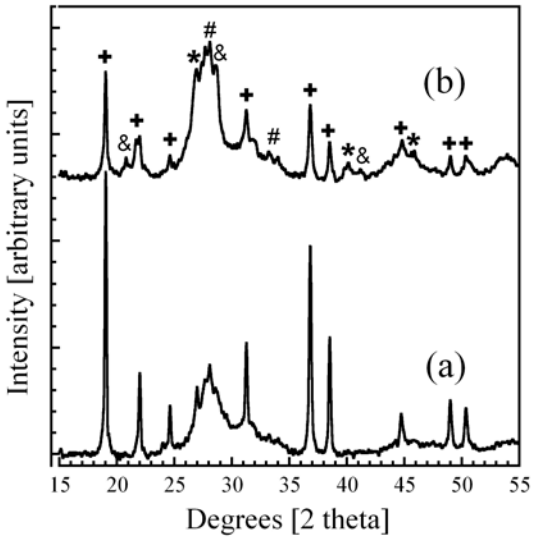

Fig. 3: XRD pattern of the particles synthesized with 6 ml/min precursor flow rate, (a) using water as the solvent to dissolve the Ba and Bi precursors and (b) water mixed with organic solvent to dissolve the precursors. Symbols +, *, # and & corresponds to $Ba(NO_3)_2$, $BaCO_3$, Bi_2O_3 and $BaBiO_3$ phases, respectively.

tional flame aerosol process where the surface area of the particles decreases with increasing temperature as reported by several authors [3, 4]. It is also in agreement with other FSP studies reported earlier. [5, 6]

XRD

Fig. 3a and 3b shows the XRD pattern of the particles synthesized using water and the mixture of water plus organic solvent, respectively as the solvent for the Ba and Bi precursors. The melting point of bismuth nitrate pentahydrate and barium acetate is 30 and 460°C, respectively [7]. XRD pattern of the particles synthesized using only water as the solvent shows several undecomposed products of barium, i.e. $Ba(NO_3)_2$ and $BaCO_3$. In addition weak reflections corresponding to $BaBiO_3$ is also seen suggesting that the Ba and Bi precursors did not decompose homogeneously. Water cools the high temperature flame drastically and sufficient heat is not available to completely decompose the high melting point barium acetate precursor. Presence of the individual peaks of Bi_2O_3 suggests that the entire bismuth nitrate has been decomposed. Hence it can be said that, only the decomposed Ba-acetate precursor contributed to the formation of $BaBiO_3$ phase.

Fig. 3b shows the XRD pattern of the particles synthesized by using an organic solvent in addition to the water used for dissolving the Ba and Bi precursors. Reflections corresponding to the $Ba(NO_3)_2$ phase has been significantly reduced and intensity of the reflections corresponding to $BaBiO_3$ phase increased. Usage of more amount of heat generating organic solvent assists in the complete decomposition of barium acetate precursor and resulting in the formation of the stoichiometric $BaBiO_3$ phase. Also the SSA of the stoichiometric $BaBiO_3$ particles is significantly higher than the particles synthesized by the partial decomposition of the precursor mixture.

TEM

Fig. 4 shows the TEM image of the $BaBiO_3$ particles synthesized with 6 ml/min flow rate of the precursor mixture. Particles have aggregated morphology with the sinter necks in between.

PHOTOCATALYTIC ACTIVITY

Fig. 5 shows the degradation behavior of the formaldehyde using visible light irradiation. No detectable degradation of formaldehyde occurs without $BaBiO_3$ or with visible light irradiation alone. The degradation behavior is studied by gas chromatography. Figure 5 shows the photocatalytic activity of the $BaBiO_3$ particles synthesized at various flow rates of the precursor mixture. The degradation is compared with the commercial Degussa P25-TiO_2 which shows

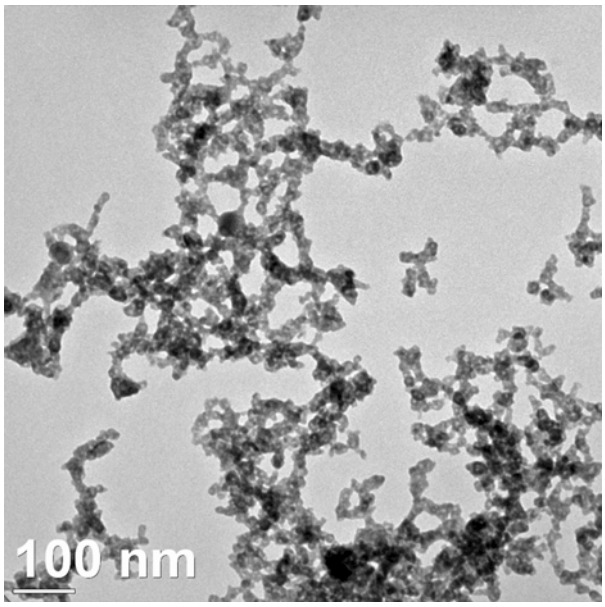

Fig. 4: TEM image of the $BaBiO_3$ particles

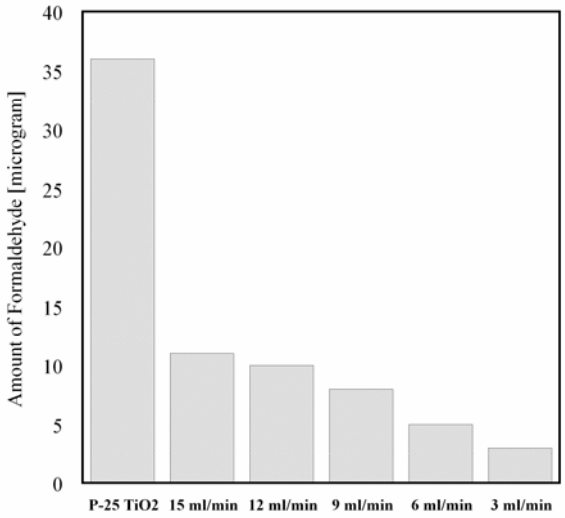

Fig. 5: Degradation profile of the formaldehyde after the visible light irradiation for 3 hours.

excellent activity towards the degradation of formaldehyde under UV irradiation. However, under the visible light irradiation P25 TiO_2 shows poor activity due to its inability to absorb visible light by virtue of its wide band gap [8]. PCA of the $BaBiO_3$ particles increased with the decrease of the precursor flow rate. As shown in the previous sections, synthesis of the particles with decreasing the precursor mixture flow rate accompanied with the increase of the SSA. Clear dependence of the specific surface area of the particles on the PCA has been observed which signifies the advantages of nanoparticles. Photocatalysis being a surface phenomenon, improvement in the PCA is attributed to the increased number of active sites where the photocatalytic reaction can take place.

CONCLUSIONS

Crystalline nanoparticles of $BaBiO_3$ have been successfully synthesized by flame spray synthesis. Influence of the melting points of the individual solid precursors to produce the mixed oxides is shown. As-synthesized $BaBiO_3$ nanoparticles shows activity towards the degradation of the formaldehyde under the visible light irradiation and the activity increases with the decrease of the particle size.

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