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Synthesis and comparison of the photocatalytic activities of flame spray pyrolysis and sol–gel derived magnesium oxide nano-scale particles

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ABSTRACT

In this study, nano-scale magnesium oxide particles were synthesized by means of flame spray pyrolysis and sol–gel techniques. Phase structures, morphologies, particle size, specific surface area and optical band gap were determined using an X-ray diffractometer (XRD), scanning electron microscope (SEM), particle size analyzer, Brunauer–Emmett–Teller (BET) specific surface area analyzer and UV diffused reflectance spectroscopy (UV DRS), respectively. In order to determine photocatalytic activity of the nano-scale particles, aqueous methylene blue (MB) solutions were employed. The photocatalytical degradation rates of MB solutions were determined through absorbance measurements performed via UV–vis spectrophotometer. Fourier transform infrared spectroscopy (FTIR) studies confirmed the formation –OH hydroxyl and other groups provide by MB solutions, after photocatalytic studies. It was found that both flame spray pyrolysis and sol–gel synthesized MgO nano-scale particles exhibited appreciable photocatalytic activity for the degradation of MB dye under UV light irradiation with small differences. Moreover, the effects of particle size and surface area on the photocatalytic properties were investigated in detail.

1. Introduction

Magnesium oxide (MgO) is a versatile oxide material with respect to its wide range of utilization, such as in catalysis, hazardous waste treatment, antimicrobial materials and refractory materials [1]. Recently, MgO has attracted tremendous attention on account of these immense applications. Particularly, in the field of catalysis, MgO has become a promising material in the roles of both catalyst and catalyst support in many organic reactions [2].

Over the past several years, numerous semiconductor metal oxides such as TiO_2, ZnO, WO_3, Fe_2O_3 and CuO were used as photocatalyst materials for the degradation of organic pollutants in water or air [3]. Among these oxides, MgO has received considerable attention about its photodegradation efficiency, thanks to its electronic structure and chemical properties [3,4]. Photocatalysis is a surface

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related process; therefore, structural, morphological and optical properties are critical parameters for controlling the photocatalytic activity of the synthesized materials [5].

In recent decades, many new techniques have been developed to synthesize nano-sized MgO, including the sol–gel (SG) method [6], thermal evaporation [7], flame spray pyrolysis (FSP) [8,9], and microwave-assisted synthesis [10]. The morphology and properties of the resulting MgO differ and depend on the synthesis route and processing conditions [2]. Among these, FSP and SG are promising techniques that enable the production of high purity nanosized powder with controlled particle size and crystallinity [11]. Generally speaking, during the flame spray process a flammable precursor solution where metal compounds are dissolved in an organic solvent is sprayed as micro droplets with high velocity oxygen and ignited with a premixed methane–oxygen supporting flame. These vapors condense to clusters and nanoparticles which form weak bounded agglomerates upon rapid cooling of the gas. This product can be collected on a filter and used as the calcined catalyst. This makes FSP a fast, one-step method for catalyst synthesis and can be extended by addition of further components in principle [12]. As for SG, it is advantageous in the synthesis of nano-sized materials due to the fact that it has the advantages of simple procedure, low crystallization temperature, and low cost. This technique involves a colloidal solution which transforms into gel, producing high purity and chemically homogeneous materials [2,13,14].

In this study, MgO nano-scale particles were produced by both SG and FSP methods. The fabricated nano-scale particles were used to grasp and investigate a deeper insight of the synthesis process for the first time for comparing in terms of particle size, surface morphology, and regarding photocatalytic efficiencies.

2. Experimental details

2.1. Nano-scale particle fabrication

In order to produce SG derived MgO nano-scale particles, precursor material magnesium ethoxide ($C_4H_{10}MgO_2$) was used. Methanol was utilized for both methods to dissolve the precursor and to obtain homogenous solution of the precursor as a solvent. A small amount of glacial acetic acid was added into the solution as a flux to hasten the transition of the liquid into a viscous polymeric structure and to facilitate gel formation under magnetic stirring. After that, the final homogeneous solution was obtained. This solution was kept at 80 °C for 30 min for the gelation process, then the obtained xerogel was dried at 100 °C for 4 h on a hot plate. Finally, the dry gel powder was eventually calcined at 500 °C for 4 h in air to obtain sol–gel-assisted crystalline nano-scale particles.

As for FSP derived nano-scale particles, the same solution was fed into the precursor syringe of flame spray pyrolysis equipment (Np10, Tethis, Milan/Italy). In a typical run of the flame spray reactor, the liquid precursor solution was fed into the center of a methane/oxygen flame by a syringe pump with a feed rate of 5 mL/min and dispersed by oxygen to form the fine spray. At the nozzle, the pressure drop at the capillary tip was kept constant at two bars by adjusting the orifice gap area. The spray flame was ignited by a smaller flame ring issuing from an annular gap. This premixed methane/oxygen supporting flame was kept constant with a flow rate of 5 L/min and fuel/oxygen ratio of 0.5 methane (1.5 L/min)/oxygen (3.0 L/min). A sintered metal plate ring provided an additional oxygen sheath flow (5 L/min) surrounding the supporting flame. Nano-scale particle products were collected on a cellulosic filter with the aid of a vacuum pump [15]. The setup of the flame spray pyrolysis system was demonstrated on the left-hand side of Fig. 1 to compare the routes of FSP and SG.

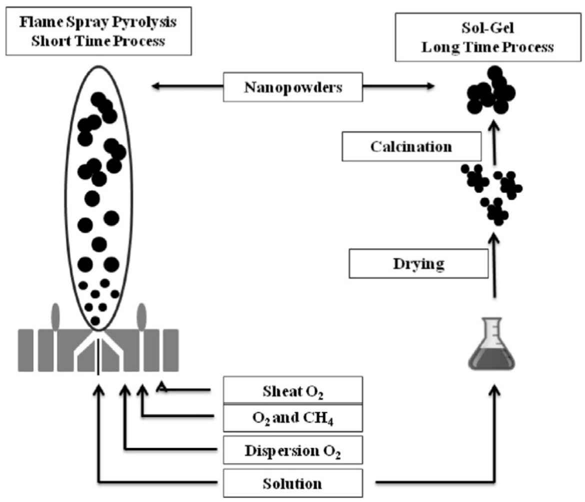

Fig. 1. Illustration of SG and FSP methods.

2.2. Characterization

Phase identification and crystal structures of samples were carried out through a Thermo Scientific ARL X-ray diffractometer (XRD) which works with voltage and current settings of 40 kV and 30 mA, respectively, and uses Cu-K_α radiation (1.5405 Å). XRD datum were recorded in the interval $20^\circ \leq 2\theta \leq 90^\circ$ with a scanning speed of 2°/min. SEM images of the MgO nano-scale particles were obtained with the help of a Philips XL 30S FEG scanning electron microscope operating at an accelerating voltage of 20 kV. MgO nano-scale particles were homogenously dispersed in pure water to determine the average particle size distribution (APS) using a particle size analyzer (Zetasizer Nano ZS, Malvern Instruments, Worcestershire, U.K.), which uses light scattering technique to measure hydrodynamic size of nanopowders. Specific surface area values were calculated using a surface area analyzer (Nova 2200e, Quantachrome Instruments, Boynton Beach, FL) using Brunauer, Emmett, and Teller (BET) analyzer under N_2 adsorption at −196 °C. The nano-scale particles were outgased for 18 h at 300 °C to remove any moisture and adsorbed volatile contaminants. Optic band gaps of the MgO nano-scale particles were detected by UV diffused reflectance spectroscopy (UV-DRS) using a (Thermo Scientific Evolution 600) model in the wavelength range of 100–400 nm. Fourier transform infrared spectroscopy (FTIR) studies were carried out using (Thermo scientific Nicolet I10) device in order to evaluate whether or