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TiO_2 nanoparticle layer formation on ceramic support, a statistical approach to control influential synthesis parameters

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ABSTRACT

TiO_2 nanoparticles were synthesized by sol–gel method and they were coated on alpha-alumina supports to form ultra fine layer of nanosized TiO_2. The effect of synthesis parameters; molar ratio of surfactant/precursor, refluxing temperature and refluxing time, calcination temperature and time was simultaneously investigated on crystallite size, crystalline phase content, specific surface area and photocatalytic activity of the product, using a statistical approach. The powder samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and Brunauer–Emmett–Teller technique (BET). The results revealed positive effect of refluxing temperature on the crystallite size and crystallinity, while a negative effect was observed on the anatase phase content. The anatase phase content was enhanced by increasing the reflux time. Increasing calcination temperature and calcination time resulted to the higher crystallite size and relative crystallinity but lower anatase phase content. Application of surfactant improved specific surface area and pore size of the crystals. The optimal synthesis conditions to achieve maximum content of anatase phase, surface area and minimum crystallite size were found to be equal molar ratio of surfactant/precursor, refluxing temperature of 60 °C, reflux time of 6 h, calcination temperature of 550 °C and calcination time of 2 h. The optimal gel product was applied for preparing TiO_2 thin films by spraying the gel content on the alpha-alumina support. The photocatalytic behavior of the coated films was examined in photocatalytic degradation of acetaldehyde in gas phase batch reactor under UV irradiation and a reduction of 61% was observed for only 0.01 g coated TiO_2 film on the ceramic support.

1. Introduction

Among the various numbers of photocatalysts, TiO_2 holds one of the most important places due to its high photocatalytic activity, either as powder or as coatings. The preferential use of TiO_2 in the photocatalytic degradation of volatile organic compounds (VOCs) is because it is relatively inexpensive, highly stable chemically, and the photogenerated holes are highly oxidizing [1,2]. In addition, photogenerated electrons are reducing enough to produce superoxide from dioxygen [3] thus; TiO_2 has gained much attention as the material of choice for environmental applications such as air purification [4], water treatment [5] and self-cleaning [6] recently. TiO_2 photocatalyst is used either as free-standing particulates or as a coating on a support. Using finely powdered TiO_2 particles suspended in contaminated water or gaseous medium, may prove useful but is rather commercially unavailable and may be costly. In addition, use of these nanosized particles in continuous medium is impossible because it may cause water and air pollution. Coated catalyst configurations, on the other hand, eliminate the need for catalyst filtration and centrifugation [7,8]. Previous studies have revealed that the physical and chemical characteristics, as well as the performance of nanostructured TiO_2 strongly depend on its crystalline structure, morphology, and dimension [9–11]. It has been reported that the photocatalytic activity of TiO_2 highly depends on its crystallite size, surface area, crystalline structure and synthesis procedure [11,12].

Among different methods of synthesis, sol–gel is one of the most appropriate technologies. The interest in the use of sol–gel process is due to its good homogeneity, ease of composition control, low processing temperature, coating large areas, low equipment cost and good optical properties [13,14]. In particular, the sol–gel method is efficient in producing thin films on various supports. This method provides fine control of the physical and chemical properties of the TiO_2 crystalline phase and as a result improves its photocatalytic activity [15]. In addition, high-purity products can be synthesized at low temperatures and homogeneous multi-component systems can be obtained by mixing precursor solutions, which allows for easy chemical doping of the materials prepared, and the activity of titanium dioxide powders and thin films highly depends on the synthesis procedure.

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Nomenclature

C	Final concentration (ppmv)
C_0	Initial concentration (ppmv)
Cal.Temp.	Calcinations temperature (°C)
Cal.Time	Calcinations time (h)
FID	Flame Ionization Detector
ppmv	Parts per million by volume
prec.	Precursor
R.Temp.	Refluxing temperature (°C)
R.Time	Refluxing time (h)
surf.	Surfactant
TTIP	Titanium tetraisopropoxide
UV	Ultraviolet

This paper reports a study of the correlation between the photocatalytic activity and morphological properties of synthesized TiO_2 nanoparticles and nanofilms synthesized by sol–gel method. In this study, influential synthesis parameters were investigated with a statistical approach to prepare nanosized TiO_2 powders with desired properties. The powders were synthesized in different refluxing and calcination times and temperatures. 1,4-butandiol was used as a surfactant to enhance specific surface area, which was not previously used, according to the literature survey. The effect of synthetic parameters has been derived quantitatively on crystallite size, relative crystallinity and phase contents of the products by a linear model and the optimal condition has been derived to approach to the least crystallite size, highest surface area and the maximum content of anatase phase. The optimum product was coated as thin film on alpha-alumina supports by spraying the prepared sol and the photocatalytic activity of TiO_2 thin films and powders were investigated by the degradation of acetaldehyde as a model feed.

2. Materials and methods

2.1. Materials

Titanium tetraisopropoxide ($Ti(i\text{-}C_3H_7O_2)_4$, Panreac, 97% pure), Isopropyl alcohol (C_3H_7OH, Merck, 99.8% pure), Nitric acid (HNO_3, Merck, 65% pure), 1,4-Butanediol ($C_4H_{10}O_2$, Merck 98% pure), and acetaldehyde (CH_3CHO, Merck, 99% pure) were used as received. In this study commercial TiO_2 powder, P25, manufactured by Aldrich Company was used as an index for comparing the properties of synthesized samples. Commercial titanium dioxide's crystallite size was determined about 25 nm and its crystalline phase was consisted of 85% anatase and 15% rutile with a total specific surface area of 50 m^2g^{-1}. The XRD pattern and SEM image of P25 are shown in Figs. 1 and 2, respectively.

2.2. Preparation of TiO_2 nanopowder

For preparing the titanium dioxide powders, a sol–gel system was prepared where 5 ml of titanium tetraisopropoxide was added to 10 ml of isopropyl alcohol. This mixture was added drop wise to the solution of 200 ml deionized water and 1.5 ml 1,4-butanediol under vigorous stirring. The pH of the solution was adjusted with nitric acid at 1.5. The final mixture maintained under magnetic agitation at a speed of 1000 rpm while refluxing at 60 or 80 °C for 6, 12 or 24 h to obtain a homogeneous suspension. The resulting mixture was kept tightly closed and aged at room temperature for over 24 h until the mixture changed to a transparent solution. Then the samples were dried in air at 110 °C for 6 h and calcined at 250 to 650 °C for 2 or 10 h with a heating rate of 2.5 °C min^{-1} in a Furnace. The experimental conditions for preparation of TiO_2 samples are given in Table 1.

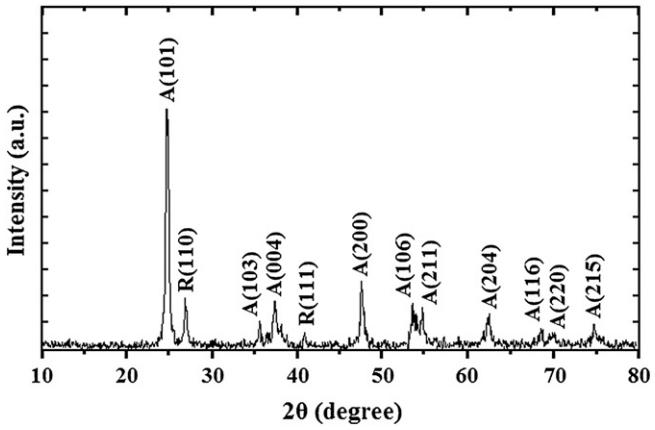

Fig. 1. XRD pattern of P25.

2.3. Preparation of TiO_2 thin film

After studying the synthesis parameters of TiO_2 nanoparticles, the sol needed for the thin film deposition was prepared at optimal condition and uniform TiO_2 films were prepared by spraying the transparent sol over the outer surface of the tubular alpha-alumina ceramic supports (inner diameter: 9 mm, outer diameter: 13 mm, length: 30 mm, mean pore size: 200 nm). Then the deposited film was dried in air at 110 °C for 6 h. The spraying and drying sequence was repeated two and five times to prepare two different coated film samples. The prepared samples were calcined in air at 550 °C for 2 h with a heating rate of 2.5 °C min^{-1} in a Furnace.

2.4. Characterization techniques

The X-ray diffraction (XRD) patterns of the TiO_2 samples were collected with a Siemens D5000 diffractometer using CuKα radiation in angular domain of $20<2\theta<80$. The morphology of the TiO_2 samples was investigated by field emission scanning electron microscopy (FE-SEM) with a Camscan NV2300 and Hitachi-F4160. Powder surface area was determined from N_2 gas-adsorption data using Brunauer–Emmett–Teller technique (BET) with Belsorb II.

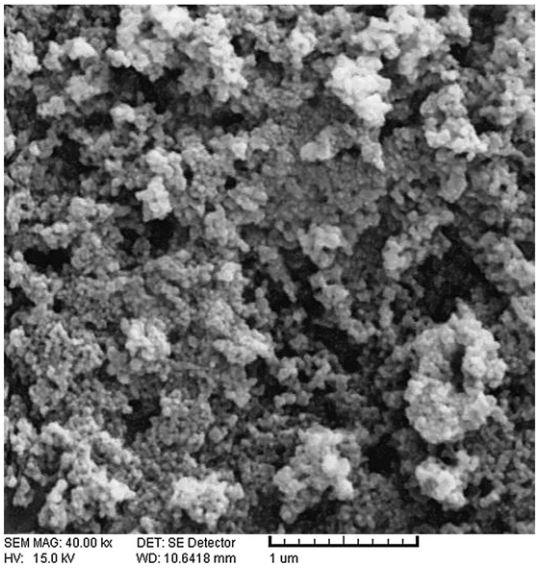

Fig. 2. SEM image of P25.