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Original Research Paper

Optimization of a nanoparticle ball milling process parameters using the response surface method

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ABSTRACT

Nanocrystalline TiO_2-CeO_2 powders were synthesized from their TiO_2 and CeO_2 oxides using mechanical ball milling process. The response surface method is applied to identify optimal parameters for the synthesis of TiO_2-CeO_2 photocatalyst. Analysis of variance and main effect plot are used to determine the significant parameters and set the optimal level for each parameter. Regression analysis showed good agreement of experimental data with the second-order polynomial model with a coefficients of determination: $R^2 = 0.991$, $R^2_{Adj.} = 0.940$ and $R^2_{Pred.} = 0.983$. Under optimal experimental conditions of TiO_2:CeO_2 weight percentage ratio 71:29, milling speed 200 rpm, and milling time 115 min the highest photodegradation efficiency was achieved. On the basis of the above statistical analysis, it was found that the band gap energy of TiO_2-CeO_2 nanoparticles decreases with the increase of the milling speed and milling time with constant TiO_2:CeO_2 weight percentage ratio. Obtained results suggest that mechanical ball milling process is a rapid, efficient and low energy consumption method to synthesize TiO_2-CeO_2 photocatalyst.

1. Introduction

Titanium dioxide (TiO_2) based materials have shown great potential as powerful photocatalysts for various significant reactions, because of their chemical stability, non-toxicity and high reactivity [1–4]. Also, titanium dioxide is well known and important n-type semiconducting material for the degradation of a vast number of organic pollutants under UV light irradiation due to its relatively wide band gap (anatase phase: 3.2 eV and rutile phase: 3.0 eV) [5]. These processes are based on the irradiation of the semiconductor with light energy that is greater than its band gap, generating electron/hole pairs that initiate a heterogeneous photocatalytic reaction. However, a high rate of recombination between excited electron / hole pairs limits the photocatalytic activity [6,7]. To overcome these limitations coupling of TiO_2 with other metal oxides such as WO_3 [8], SnO_2 [9], ZrO_2 [10] and Fe_2O_3 [11] was widely investigated. Especially, CeO_2 has attracted a lot of attention due to its optical and catalytic properties associated with the redox pair Ce^{3+}/Ce^{4+} [12–14]. In addition, CeO_2 increases the specific surface area and diminishes the crystallite size [14] supporting the stability of the anatase phase [15]. Coupled TiO_2-CeO_2 nanocomposites also feature a specific electron transfer process that increases the production of the electron/hole pairs and improves the photocatalytic activity [16].

Many techniques have been applied for preparing of TiO_2 and TiO_2-CeO_2 powders such as: sol–gel synthesis [17], hydrothermal synthesis [18], co-precipitation method [19] and flame spray pyrolysis [20]. These conventional methods predominantly included multi step procedures, demanded the utilization of toxic metal–organic precursors, and expensive equipment. Also, long processing times are required, which is detrimental for industrial fabrication purposes [21]. Therefore, the mechanochemical process has gained importance over conventional synthesis, and it yielded large quantities of desired product at ambient conditions within a very short processing time [22].

Alongside, present day industrial applications demand comprehensive theoretical simulations before actual experimental design. A central composite design (CCD) is the most commonly used response surface designed experiment. CCD are a factorial or fractional factorial design with center points, augmented with a group

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of axial points (also called star points) that let an estimation of curvature. The design and statistical analysis of experiments have resulted in development of the response surface modeling (RSM) used for process optimization and prediction of the interaction between variables, reducing the number of runs and consequently, the cost of experiments [23]. Main objective of this method is to attain maximum performance by finding the appropriate operating point. A second-order response surface model has been used to develop an equation for predicting selected process response, based on the data collected with statistical design of experiments [24]. The analysis of variation (ANOVA) shows extent of agreement i.e., how the observed data fit into the assumed second-order RSM model. Moreover, the RSM model allows process optimization with limited number of experimental data. Desirability is simply a mathematical method to find the optimum. The goal of optimization is to find a good set of conditions that will meet all the goals, not to get to a desirability value of 1.0.

In this study, an environmentally friendly and sustainable approach, dry reactive milling, was employed to synthesize TiO_2-CeO_2 nanopowders using the CCD design of experiments. The effects of selected process variables (TiO_2:CeO_2 weight percentage ratio, milling speed, and milling time) on TiO_2 phase composition, microstrain, and crystallite size have been discussed. The main objectives were to optimize the nanoparticle ball milling process and investigate the parameters that influence the photodegradation efficiency. The optimal conditions of ball milling process were also demonstrated from the model obtained via experimental data.

2. Materials and methods

2.1. Mechanochemical synthesis of TiO_2-CeO_2 nanopowders

Commercially available TiO_2 powder (>99% purity, Alfa Aesar GmbH & CoKG) and CeO_2 powder (99.9% purity, Johnson Matthey-Alfa Product) were used as starting materials. TiO_2-CeO_2 nanopowders were synthesized in the absence of solvent via mechanochemical process using a high energy ball mill (Fritsch planetary mill Pulverisette 7 premium line). Milling was done at atmospheric conditions in a silicon nitride (syalon, Si_3N_4) vial (volume of 80 cm^3) using 25 silicon nitride balls with 10 mm of diameter, keeping powder sample to ball mass ratio at about 1:10 throughout the experiment. Quantity of powder used in each run was 4.87 g. Effect of mechanochemical synthesis conditions on the obtained nanopowders was studied by varying milling time (15–141 min), milling speed (150–400 rpm), and TiO_2:CeO_2 weight percentage ratio (90:10–40:60). All samples were calcined at 500 °C for 2 h, which resulted in the formation of TiO_2-CeO_2 photocatalysts.

2.2. Materials characterization

The phase structure of samples was analyzed by X-ray diffraction method (XRD), using a Rigaku Ultima IV diffractometer in Bragg-Brentano geometry, with Ni-filtered CuK_α radiation (40 kV, 40 mA, λ = 1.54178 Å). Structural and microstructural parameters of the TiO_2-CeO_2 samples were estimated by the Williamson-Hall (WH) plots [25].

The microstructures of TiO_2-CeO_2 nanopowders were examined by Scanning Electron Microscope (SEM) JEOL 840A, Oxford Instruments INCAPentaFET x3 system. The accelerating voltage used was 20 kV.

UV–Vis diffuse reflectance spectra (DRS) of catalysts were obtained using UV–Vis spectrophotometer (Specord M40 Carl Zeiss). In order to understand the reason for band gap narrowing of pure and CeO_2 doped TiO_2 sample, band gap energies were calculated from the equation:

$$Eg = \frac{1240}{\lambda} \quad (1)$$

where Eg is the band gap (eV) and λ (nm) is the wavelength of the absorption edges in the spectrum. The reflectance measurements were converted to absorption spectra using the Kubelka-Munk function, F(R). The absorbance F(R) can be expressed as $F(R) = (1\text{-}R)^2/2R$, were R represents the reflectance. Band gap energy was estimated by plotting $[F(R_\infty)]^\eta$ as a function of the photon energy ($h\upsilon$). The best linear relation was obtained for $\eta = 1/2$ indicating that direct allowed transitions are responsible for the measured optical band gap.

2.3. Photocatalytic tests

The photocatalytic degradation of methyl orange (MO) was carried out in an open cylindrical thermostated Pyrex cell of 6.8 cm in diameter, corresponding to the surface area accessible to the light of 36.3 cm^2. The experiments were performed with 100 mL of solution containing 8 mg/L MO added to 100 mg of TiO_2-CeO_2 samples. Irradiation of the solution was performed under the UV lamp (Solimed BH Quarzlampen), with a power consumption of 300 W, housed 25 cm above the top surface of the solution. Illumination intensity on the top of the photocatalytic reactor was 850 lx. Prior to illumination, the suspensions were magnetically stirred in the dark for 30 min to achieve adsorption–desorption equilibrium. Aliquots of suspensions were collected at different time intervals for a total of 150 min. The aliquots were filtered through a 0.20 μm syringe membrane filter into standard quartz cuvettes with an optical path of 1 cm and directed to UV–Vis spectrometer (Thermo Electron Nicolet Evolution 500) to check the degradation of MO via its absorption peak at 464 nm. These absorption data were used in the determination of degradation of MO through comparison with the absorbance at a certain time as a percentage of the initial absorbance.

The efficiency of the MO photodegradation (η) was calculated using the following equation [26]:

$$\eta = \frac{(C_0 - C)}{C_0} \times 100 \quad (2)$$

where C_0 represents the initial concentration and C represents the concentration after t minutes of photocatalysis.

2.4. Design of experiments

RSM is derived from mathematical and statistical techniques. This method can be used for studying the effect of several factors at different level and their influence on each other [23]. The 3-factor, 5-level CCD, which is a widely used form of RSM, was chosen to identify major parameters influencing MO degradation efficiency and the interactions among following parameters: TiO_2:CeO_2 weight percentage ratio, milling speed, and milling time. These parameters are denoted as X_1, X_2, and X_3 respectively. For statistical calculations, the variables was coded as according to the following equation:

$$x_i = \frac{X_i - X_0}{\Delta x} \quad (3)$$

where x_i is the dimensionless coded value of each independent variable, X_0 is the value of X_i at the center point, and Δx is the step change value.

A design of 17 experiments was formulated for three factorial (2^3) designs and three replicates at the central points, four star

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