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Original Research Paper

Structure–activity relationship of nanosized porous PEG-modified TiO_2 powders in degradation of organic pollutants

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ABSTRACT

This study aims to gain insights in structure–activity relationship of TiO_2 photocatalysts. For this purpose photocatalysts were synthesized via classical sol–gel method using titanium isopropoxide as a precursor and polyethylene glycols (PEGs) of different molecular mass ($M_n = 200, 600, 2000, 10{,}000$) as a template agents. Incorporating PEG into TiO_2 network enhanced not only catalyst porous structure, but also increased the fraction of anatase phase. The use of low-molecular-weight PEGs resulted in catalysts with increased anatase content and enlarged specific surface area. The catalyst photoactivity was estimated through degradation of organic pollutants: Reactive Black 5, arylazo pyridone dye and phenol. The results revealed that the photoactivity was following the same order independently of target pollutant: $TiO_2/P600 > TiO_2/P200 > TiO_2/P2000 > TiO_2/P10000 > TiO_2$. BET surface area and anatase fraction, rather than pore diameter or pore volume, were found to be predominant catalyst property determining the activity for particular reaction system. The existence of synergistic effect between anatase and rutile phases was confirmed for the most active catalysts $TiO_2/P200$ and $TiO_2/P600$. These catalysts showed similar activity in dye degradation, while $TiO_2/P200$ displayed significantly lower activity in phenol degradation, which was attributed to its lower sorption capacity and lower UV light utilization. The difference in the reactivity between investigated pollutants was discussed in relationship with their size, structure and sorption ability.

1. Introduction

Heterogeneous photocatalysis has gained increasing interest in the last four decades, especially in the field of solar water splitting and purification of air and water [1]. Nanosized metal oxides, typically semiconductors are usually used as photocatalysts [2]. The photoactivity of semiconductors is controlled by several processes: (i) the light absorption properties, (ii) the energy of the band gap between the valence band and the conduction band, (iii) the electron–hole recombination rate, (iv) the absorption of the reactants and finally (v) reduction and oxidation rates on the surface by the electrons and holes [3]. These processes depend on the chemical composition and the physicochemical properties of the oxide materials, such as: textural properties, morphology, crystallinity, crystallographic form and crystallite size. Fundamental understanding of the factors affecting photocatalytic process is therefore useful to produce more active catalysts and to provide improved procedure for catalyst preparation.

Among different photocatalysts (TiO_2, ZnO, Fe_2O_3, CdS, ZnS), TiO_2 has received special attention due to the stability of its chemical structure, biocompatibility, physical, optical, and electrical properties [1–5]. TiO_2 can exist in three crystallographic forms: anatase, rutile and brookite. While some research groups found that anatase is the most active phase [6–9], other studies reported that mixture of anatase and rutile phases is more effective than pure anatase form [10–12]. The higher activity of mixed phases has been attributed to favorable anatase/rutile constellation, which leads to rapid electron transfer from rutile to anatase, thus lowering electron (e^-)/hole (h^+) recombination.

Textural properties also exert a great influence on the catalyst photoactivity.

Increasing the surface area generally increases the amount of the substrates adsorbed, which therefore, enhances the reaction of e^- and h^+ with the substrates. On the other hand, higher surface area leads to faster e^-/h^+ recombination, which causes reduction of the reaction rate. Thus, the specific surface area has dualistic effect

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on photoactivity: when the surface reaction predominates the recombination, the photocatalyst of larger surface area is better and vice versa [3,13]. Additionally, internal diffusion of pollutant molecules and accessibility of catalytic sites are highly dependent on pore diameter and only molecules whose dimensions are less than critical can reach the pores and react there.

Among different methods that have been used for producing solid inorganic materials, sol–gel technique enjoys the advantages of low cost, simple and inexpensive equipment and possibility for producing unique metastable structure at low reaction temperatures with excellent chemical homogeneity [14,15]. The sol–gel preparation process for TiO_2 involves the reactions of hydrolysis and polycondensation, usually of titanium alkoxide, to form oxopolymers, which are transformed into an oxide network [14]. The relative rates of hydrolysis and polycondensation strongly affect the structure and properties of TiO_2 and different organic additives have been used to control the reactivity of the precursors [16–19]. Condensation process is further accomplished by gelization, which is followed by calcination. Calcination is important not only for removing organic compounds, but also for completion of crystallization. The drawback of calcination treatment at high temperature is that it results in dramatic growth of particle size, i.e. drop in surface area and porosity, which can diminish the efficiency of photocatalysis [20]. Much effort has been exerted to achieve highly crystallized materials with retained surface area and porosity. One of the attractive method to retain the catalyst porous structure after calcination is to use organic templates during catalyst synthesis, such as polyethylene glycol (PEG) [21–25], Pluronics triblock copolymer P123 [26,27], polystyrene [28] or biocomposite gel [29]. Decomposition of polymers during thermal treatment can lead to generation of porous structure, thus improving the textural properties of the catalysts. Guo et al. [22] found that porosity of the TiO_2 films could be significantly enhanced with the use of PEG template. The authors observed that higher PEG molecular weight led to larger pore size and specific surface area. Wang et al. [21] used PEG molecules during synthesis of TiO_2 film on Al_2O_3, not only to enlarge the specific surface area, but also to inhibit the macroscopic cracking. Sun et al. [23] used different PEG (average molecular mass = 400, 2000, 6000, 20,000) as templating agents to synthesize PEG modified TiO_2 photocatalysts. The authors inferred that PEG molecular weight is crucial factor for enlargement of surface area and suppression of crystal growth. In the work of Chang et al. [25], the introduction of PEG enhance the textural properties of synthesized TiO_2–$InVO_4$, but also promote anatase to rutile transformation.

In the current study nanosized TiO_2 with variable anatase/rutile ratio and appropriate microstructure characteristics and morphology were obtained by using PEG templates of different molecular mass. The relationship between physico-chemical properties and photoactivity of synthesized catalysts was discussed by obtained structure–activity correlation. The investigation was specially focused on: (i) the effects of PEG molecular mass on structural and textural properties of TiO_2 particles toward better understanding the pore structure and crystal phase formation (ii) the main catalyst properties that determine the photoactivity for particular reaction system (iii) the difference in the reactivity between investigated pollutants.

2. Experimental

2.1. TiO_2 synthesis

Titanium isopropoxide (M = 284.2, $Ti(OC_3H_7)_4$; TTIP; 97%, Aldrich), ethanol (M = 46.07, CH_3CH_2OH; EtOH; 99.5%, Aldrich), diethanolamine (M = 105.14, $NH(CH_2CH_2OH)_2$; DEA; 99%, Alfa Aesar), polyethylene glycol (M_n = 200, 600, 2000 and 10,000; $H(OCH_2CH_2)_nOH$; PEG, Alfa Aesar) and distilled water were used as the starting materials. 3.73 mL of TTIP were dissolved in 10.0 mL of anhydrous ethanol and 1.3 g of DEA at room temperature for 2 h (solution A). DEA was used as sol stabilizer, in order to restrain the rapid hydrolysis. Meanwhile, 35.0 mL of anhydrous ethanol were mixed with 3.75 mL of water to prepare solution B. Solution A was subsequently added dropwise to solution B under vigorous stirring within 20 min. After that, 1.0 g of PEG was added to the solution and the solution was stirred for another 40 min. The stabilized sol was aged for 12 h at room temperature followed by sol–gel conversion. After that the gel was dried in an oven for 12 h at temperature of 80 °C. Finally, the dried gel was calcined in air stream using a multi-segment programmable tube furnace (Carbolite 12/75/700 CTF). The furnace temperature was increased at a ramp of 3 °C/min to the final temperature of 550 °C and held at this value for 4 h. The samples were cooled down naturally in the furnace to room temperature. The synthesized samples were designated as TiO_2/PX, where X denotes the molecular mass of the used PEG. For comparative study, the control unmodified TiO_2 was prepared without the use of the template by the same sol–gel method described above.

2.2. Catalyst characterization

Nitrogen adsorption–desorption isotherms were determined on Sorptomatic 1990 Thermo Finnigan automatic system using nitrogen physisorption at −196 °C. Before measurement the samples were outgassed at 130 °C for 3 h. Specific surface area of the samples (S_{BET}) was calculated from the nitrogen adsorption isotherms according to the Brunauer, Emmett and Teller method [30]. Pore diameter, pore volume distribution, and porosity were determined by mercury intrusion porosimetry on Pascal 140/440, Thermo Scientific. Powder X-ray diffraction patterns were measured on a Riga diffractometer using Cu Kα radiation (λ = 1.5418 Å) at room temperature operated at 35 kV and 20 mA (scanning step: 0.02° per second). For mineralogical identification from XRD data JCPDS (Joint Committee on Powder Diffraction Standards) mineral powder diffraction data bases was used incorporated within computer-based search-match programs PCPDFWIN and Powder Cell 2.4 [31]. Diffuse reflectance UV–Vis (DR UV–Vis) spectra were recorded on Nicolet Evolution 500, Thermo Electron Corporation. The surface morphology of the TiO_2 powders was examined by scanning electron microscopy (SEM, JEOL JSM-6610LV). Diffuse Reflectance Infrared Transform Spectroscopy (DRIFTS) of the samples were recorded in the region of 4000–400 cm^{-1} using a Thermo Nicolet 6700 FTIR spectrometer at spectral resolution of 8 cm^{-1} with a Collector II Diffuse Reflectance Accessory.

2.3. Photocatalytic activity determination

The photocatalytic behavior of prepared catalysts was tested in aqueous solutions by decomposition of the following pollutants: (i) synthesized arylazo pyridone dye – 5-(4-sulphophenylazo)-6-hydroxy-4-methyl-3-cyano-2-pyridone [32], (ii) commercial dye – Reactive Black 5 and (iii) phenol (Table 1).

Photocatalytic tests were performed in an open cylindrical thermostated Pyrex cell of 250 mL capacity. The photocatalytic material (0.15 g) was dispersed in a pollutant solution (150 mL, 2.8×10^{-5} mol/L) using magnetic stirrer. The irradiation was performed using Osram Ultra Vitalux lamp, with a power consumption of 300 W, housed 50 cm above the top surface of the pollutant solution. The emission spectrum of the lamp simulates solar radiation. During irradiation, the suspension was exposed to air, but without additional aeration. In order to remove the catalyst, after predetermined periods of time, aliquots were centrifuged for 10 min at the rate of 17,000 rpm, and analyzed by