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In situ generated TiO_2 over zeolitic supports as reusable photocatalysts for the degradation of dichlorvos

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ABSTRACT

Materials based on titania supported on zeolitic matrices (HBETA, HY and HZSM5) were synthesized by in situ generation of TiO_2. The supported catalysts characterized by XRD indicate the presence of the anatase phase alone. The materials were also characterized by FTIR, S_{BET}, and UV-VIS DRS. A high TiO_2 content produced lower degradation, due to the presence of TiO_2 particle aggregates of greater size on the zeolite matrix surface, as evidenced by the calculated crystal size. TiO_2/HBETA(20%) presented more activity than TiO_2 supported on the other matrices due to higher adsorption of dichlorvos on HBETA. It has more surface area and a lower band gap value too, which makes it more effective. The mineralization degree is lower than the degradation percentage due to the formation of organophosphorous intermediates that are less toxic than the starting material. The complete degradation and mineralization of the pollutant was obtained in 360 and 540 min of reaction with TiO_2/HBETA(20%), respectively. This catalyst resulted in degradation percentages close to that of commercial TiO_2 P25. The main advantage of supported catalysts is their easy separation and reuse, in this case resulting in a very low activity loss during eight cycles. These materials present suitable properties to be used as catalysts in the photocatalytic treatment of wastewater that contains pesticide dichlorvos in water.

1. Introduction

The increasing demand and shortage of clean water sources due to the rapid development of industrialization, population growth and long-term droughts have become an issue worldwide. With this growing demand, various practical strategies and solutions have been adopted to yield more viable water resources [1].

In recent years, an alternative to conventional methods for the decontamination of water has been provided, which is known as "Advanced Oxidation Processes" (AOPs) and is based on the generation of very reactive species such as hydroxyl radicals that quickly and nonselectively oxidize a broad range of organic pollutants [2]. One of these AOPs that has attracted special attention is heterogeneous photocatalysis, employing UV–Vis light as energy source and a solid catalyst as active site for water detoxification. Indeed, the subject has become an area of intensive research. The main advantage of photocatalysis over conventional water treatment methods is that a wide range of organic compounds can be completely mineralized, leading to the formation of carbon dioxide, water, and inorganic mineral salts [3]. The generated $OH^{\bullet}$ radicals interact with organic pollutants, leading to progressive degradation that is followed by complete mineralization. Among these heterogeneous photocatalysts, TiO_2 has been considered as a promising one for the remediation of wastewater treatment [4–7]. TiO_2 is presented as one of the most appropriate semiconductor materials to be employed as a photocatalyst due to its high activity in the photodegradation of organic compounds, low cost, low toxicity, and chemical stability [8].

The main drawbacks of TiO_2 catalysts are the need for complex filtration procedures and the high turbidity that decreases the radiation flux. The practical applications of TiO_2 are limited because

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of the problems of low recovery efficiency of TiO_2 fine particles, fast recombination rate of the photogenerated electron–hole pair, and a low quantum yield in the photocatalytic reactions in aqueous solutions [9].

Such problems have motivated the development of supported photocatalysts in which TiO_2 is immobilized on different adsorbent materials. Immobilizing TiO_2 on substrates such as a glass matrix, optical fiber and stainless steel plate eliminates the problem of agglomeration, although the photocatalytic efficiency of immobilized TiO_2 is less than that of the suspended TiO_2 particles [10]. Besides, the specific surface area also decreases due to the fixing of TiO_2 on nonporous supports, which reduces the adsorption capacity. For photocatalytic decomposition of a target compound, its adsorption on the TiO_2 surface is essential prior to the surface reaction. Furthermore, organic pollutants generally occur in low concentrations (ppm level or below) and pre-concentration of the substrates on the surface where photons are absorbed is a desirable feature for effective photodegradation [11].

The supports should withstand reactive oxidative radical attack during illumination, have long-term stability, prevent TiO_2 leaching during light irradiation, and have the ability to delocalize electrons. Many reported studies deal with the immobilization of TiO_2 over different inert porous supports [10,12–23]. In this context, zeolites have attracted greater attention due to their adsorption capacity, which helps in pooling the pollutants to the vicinity of the TiO_2 surface and also leads to faster degradation [7,23,24].

Zeolites are microporous crystalline aluminosilicates with structural features, such as the ability to trigger photoinduced electron donor and acceptor reactions, which make them attractive hosts for photochemical applications [25,26]. Furthermore, zeolites delocalize band-gap excited electrons of TiO_2 and minimize electron–hole recombination. Due to these interesting properties, zeolites are attractive catalyst supports in the treatment of pesticide-contaminated water. TiO_2 supported on zeolites, which have large surface area and light transparent nature, increases the adsorption capacity, and the uniform diffusion of pesticide pollutants leads to efficient degradation [27].

Increasing pesticide application and improper wastewater disposal methods contaminate water resources and severely affect the ecology as well as the environment [24]. Insecticides are considered accumulative and toxic compounds. Their presence as contaminants in aquatic environments may cause serious problems to human beings and other organisms [28]. The migration of pesticides to groundwater and surface water has become an issue of great concern, and numerous incidents of contamination have been documented in developed countries [29]. Organophosphorous pesticides such as methyl parathion and dichlorvos are commonly used in Third-World countries like India where there are poor environmental controls for increasing agricultural productivity and they are detected in various environmental matrices such as soil, water and air because of their widespread use [30,31].

In the present work, we attempted to combine the well-known photocatalytic properties of TiO_2 and the properties of zeolites as TiO_2 supports to synthesize heterogeneous photocatalytic materials. They were prepared by impregnation of titanium (IV) isopropoxide onto three different zeolites (HBETA, HY and HZSM5) and characterized by a series of complementary techniques: X-ray diffraction (XRD), transmittance–Fourier transform infrared spectroscopy (FTIR), and UV–visible diffuse reflectance spectroscopy (DRS). The materials were evaluated in the photodecomposition of organophosphate pesticide dichlorvos. To the best of our knowledge, this is the first time that these materials have been successfully synthesized and tested in the photodegradation of this pollutant.

2. Experimental

2.1. Preparation of photocatalysts

The supports employed were BETA, ZSM5 and Y zeolites. Zeolite HY was provided by Aldrich; the other zeolites were synthesized by means of the hydrothermal crystallization method using tetrapropylammonium hydroxide (TPAOH, Fluka) for the ZSM5 structure [32] and tetraethylammonium hydroxide (TEAOH, Merck) for the BETA structure [33] as directing agents. The ammonium forms of zeolite were prepared by ion exchange of the as-prepared Na-zeolite form with 1 M ammonium chloride solution at 80 °C for 40 h. The HBETA and HZSM5 were obtained by means of a thermal treatment under nitrogen flow for 8 h at 500 °C and then calcinations in air at the same temperature for 10 h. The catalysts supported on zeolitic matrices (HBETA, HY and HZSM5) were prepared by using an appropriate amount of titanium (IV) isopropoxide (Aldrich chemistry, 97%) and zeolite matrix in ethanol (Cicarelli), which was mechanically stirred for 4 h at ambient temperature. Then the solvent was removed by rotary evaporation. In the HBETA matrix, the amount of titanium (IV) isopropoxide was varied with the purpose of generating in situ TiO_2 concentrations of 5, 10, 20, and 30 wt% in the final solid. The mixture was then dried at 110 °C and calcined in air at 450 °C. They were denominated TiO_2/HBETA(5%), TiO_2/HBETA(10%), TiO_2/HBETA(20%) and TiO_2/HBETA(30%). In order to compare the activity, TiO_2/HY(20%) and TiO_2/HZSM5(20%) were prepared with 20 wt% of TiO_2 in the final solid in HY and HZSM5, respectively. P25 standard TiO_2, which was included for comparison with the supported catalyst, was kindly supplied by Degussa.

2.2. Characterization

The powder XRD diffraction patterns of the materials were collected on a PANalytical X'pert PRO diffractometer equipped with Cu Kα (1.54 Å) in the range of 2θ from 5 to 50° (for HBETA and HY) and 5–60° (for HZSM5) in steps of 0.05° with a count time of 2 s at each point. The crystallite size (Dc) of the new crystalline phase was estimated by XRD using the Scherrer equation. BET surface area determinations were carried out with Micromeritics ASAP 2000 equipment. Infrared (IR) studies were performed on a JASCO 5300 FTIR spectrometer. The spectra in the lattice vibration region were performed using KBr 0.05% wafer technique and they were carried out from 1800 to 400 cm^{-1} in 16 consecutive registers of 4 cm^{-1} resolution each. UV–visible diffuse reflectance spectroscopy (DRS) in absorbance mode was recorded using an Optronics OL 750-427 spectrometer in the wavelength range of 200–900 nm.

The Si/Al relation of HBETA and HZSM5 zeolites was determined by atomic absorption in a Perkin Elmer Analyst 800 spectrometer after the digestion of the samples by microwave in a Milestone ETHOS 900 digester. In order to determine the Bronsted/Lewis acid site relation and concentration of acidic sites of the zeolitic matrices, pyridine (Py) adsorption experiments were carried out on self-supporting wafers (8–10 mg/cm^2) using a thermostated cell with CaF_2 windows connected to a vacuum line. Pyridine (3 Torr) was adsorbed at room temperature and desorbed at 400 °C and 10^{-4} Torr for 1 h. The Bronsted/Lewis relation was calculated from the maximum intensity of the adsorption bands at 1545 cm^{-1} and 1450–1460 cm^{-1}, for Bronsted and Lewis sites, respectively, and quantified using the literature data of the integrated molar extinction coefficients [34], which are independent of the catalysts or strength of the sites.