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Preparation and characterization of TiO_2/HZSM-11 zeolite for photodegradation of dichlorvos in aqueous solution

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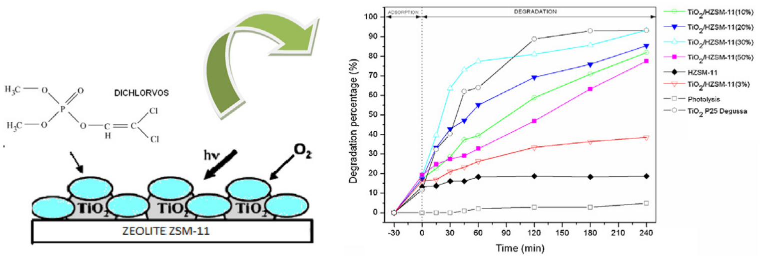
HIGHLIGHTS

- TiO_2/HZMS-11(30%) sample degraded efficiently aqueous solutions of dichlorvos.
- TiO_2/HZSM-11 samples did not show evidence of rutile phase.
- HZMS-11 (support) is not active by itself in the degradation of dichlorvos.
- The catalyst can be reused without activity loss during at least four cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

The TiO_2/HZSM-11 materials were synthesized using titanium isopropoxide as a TiO_2 precursor and HZSM-11 a medium pore size zeolite with high thermal and chemical resistance as support. The amount of titanium isopropoxide was varied in order to obtain TiO_2 concentrations of 3, 10, 20, 30 and 50 wt% in the final material. They were characterized by a series of complementary techniques: X-ray diffraction (XRD), ultraviolet–visible diffuse reflectance spectroscopy (DRS), transmittance Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The surface area of the TiO_2/HZSM-11 samples decreased with the increment of TiO_2 loading. As result of the increment of the calcination temperature from 450 to 800 °C an increase in the size of the anatase crystals was observed. However, the X-ray diffraction patterns of the solids only presented the characteristic peaks of the anatase phase. The catalytic activity of the materials in the photodegradation of Dichlorvos (DDVP) depended on the TiO_2 amount the thermal treatment temperature. The sample containing 30% TiO_2 calcined at 450 °C showed the best catalytic performance and it can be reused without noticeable activity loss during at least four cycles. The catalytic performance was similar to that of the P25 Degussa used as a reference but its separation, recovery and reuse was easier.

1. Introduction

In recent years, advanced oxidation processes (AOPs) have been proposed as innovative water treatment technologies. The rationale of these AOPs is based on the in situ generation of active species (i.e. H_2O_2, OH°, $O_2^{\circ -}$, O_3) for the mineralization of refractory organic compounds, water pathogens and disinfection by-products [1,2]. One of the most widely used processes is heterogeneous photocatalysis, which is the acceleration of a photoreaction by a

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catalyst, an attractive and efficient method for the degradation of environmental pollutants or nonbiodegradable toxics present in aqueous domestic, industrial or agricultural effluents.

Titanium dioxide (TiO_2) is 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 [3,4]. For most photocatalytic reaction systems it is generally accepted that the anatase phase has higher activity than rutile, and this enhancement in photoactivity has been ascribed to the higher Fermi level of anatase than that of rutile by about 0.1 eV [5].

However, there are certain limitations to using bulk TiO_2 in photocatalytic reactors, – for example, due to small size (about 4–30 nm) TiO_2 aggregates in a suspension that rapidly lose their effective surface area as well as their catalytic efficiency. Being nonporous, TiO_2 exhibits low adsorption ability for the pollutants, especially for the nonpolar organic compounds due to their polar surface [6].

The technical limitations of this method are the difficult separation of the catalyst, its reuse and low quantum efficiency [7].

To solve this, recent research has focused on different kinds of supports for dispersing titania catalysts, such as silica [8–10], alumina [11,12], activated carbon [13–15], clay and zeolites [10–12,16,17]. TiO_2 supported on an adsorbent provides higher specific surface area and facilitates more effective adsorption sites than bulk TiO_2 [8,13,16–18]. Recent research, has proposed the synthesis of a zeolite-supported Fe^{3+}-TiO_2 photocatalyst as an alternative to degrade dyes [19].

Zeolites have been investigated as potential supports for photocatalytic systems. They offer several distinct advantages over the other supports such as:

- They have cages and channels of the order of 4–14 Å that can confine substrate molecules to enhance the photocatalytic reactivity. TiO_2 can thus be supported on this zeolite matrix.
- Zeolites behave as electron donors and acceptors of moderate strength toward the guest species depending on the adsorption site [20].

Organophosphorous pesticides are comprised within the 10 most widely used pesticides all over the world. They have been used as an alternative to organochlorine compounds for pest control. However, they are considered as extremely toxic compounds acting on acetylcholinesterase [21]. Their presence as contaminants in aquatic environments may cause serious problems to human beings and other organisms. Dichlorvos (DDVP), an organophosphorous insecticide, is widely used for crop protection mainly in greenhouses and for controlling parasites and insects in houses, aircraft, and outdoor areas (as aerosols, liquid sprays) [22].

In the present work, we report for first time the synthesis of TiO_2 supported on HZSM-11 a medium pore size zeolite with high thermal and chemical resistance. The resulting TiO_2/ZSM-11 materials were characterized by a series of complementary techniques: X-ray diffraction (XRD), ultraviolet–visible diffuse reflectance spectroscopy (DRS), transmittance Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The materials were evaluated in the photodecomposition of the organophosphate pesticide dichlorvos.

2. Experimental

2.1. Materials

The ZSM-11 zeolite was prepared using the following reactants: sodium aluminate ($NaAlO_2$, Johnson Matthey Electronics), tetrabutylammonium hydroxide (TBAOH, Fluka), Silicic Anhydride (Fluka) and distilled water. For the supported catalysts, titanium (IV) isopropoxide (Aldrich chemistry, 97%) and ethanol (Cicarelli) were employed. P-25, standard TiO_2, was kindly supplied by Degussa. Dichlorvos (Pestanal, Fluka) was selected as the target organic pollutant.

2.2. Preparation of HZSM-11-supported TiO_2 catalyst

The parent Na-ZSM-11 zeolite (Si/Al = 17) was obtained by known methods of hydrothermal crystallization, using TBAOH as a structure directing agent [23]. The ammonium form of the zeolite (NH_4-zeolite) was prepared by ion exchange of the as-prepared Na-zeolite form with 1 M ammonium chloride solution at 80 °C for 40 h. Finally, NH_4-zeolite was dried at 110 °C, treated in a nitrogen flow at 500 °C for 8 h and then calcined in air at the same temperature for 10 h to obtain the HZSM-11 zeolite. The supported catalysts were prepared by taking an appropriate amount of titanium (IV) isopropoxide and zeolite in ethanol, which was mechanically stirred for 4 h at ambient temperature. Then the solvent was removed by rotary evaporation. The amount of titanium (IV) isopropoxide was varied with the purpose of generate in situ TiO_2 concentrations of 3, 10, 20, 30 and 50 wt% in the final solid, and they were denominated TiO_2/HZSM-11(3%), TiO_2/HZSM-11(10%), TiO_2/HZSM-11(20%), TiO_2/HZSM-11(30%) and TiO_2/HZSM-11(50%), respectively. The mixture was then dried at 110 °C and calcined in air at 450 °C. The catalyst TiO_2/HZSM-11(30%) was also calcined at 600 and 800 °C.

In order to compare the activity with the TiO_2/HZSM-11(30%), a physical mixture of P25/HZSM-11(30/70 wt%) was prepared. This mixture was calcined at 450 °C for 8 h.

2.3. 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 60° in steps of 0.05° with a count time of 2 s at each point. The mean crystallite size (d) of the corresponding phase was estimated using the Scherrer equation and silicon as standard for the correction of the instrumental broadening. It is worth noting that the Scherrer equation was used in order to perform a rough estimation of the crystallite size. BET surface area determinations were carried out with Micromeritics ASAP 2000 equipment. Infrared (IR) studies of TiO_2/zeolites 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. The morphological features of supported and unsupported catalysts were obtained using scanning electron microscopy (SEM, FEG-SEM Zeiss Sigma) using fine catalyst powder supported on carbon tape and coated with platinum. UV–vis diffuse reflectance spectra (UV–vis DRS) in absorbance mode were recorded using an Optronics OL 750-427 spectrometer in the wavelength range of 200–900 nm.

Ti, Si and Al content were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using a VARIAN, model VISTA MPX – CCD simultaneous ICP-OES. They are provided as supplementary material (Table S1).

2.4. Photocatalytic experiments

The photocatalytic degradation of DDVP was performed in aqueous medium in a batch reactor. A cylindrical Pyrex glass photochemical reactor of 18 cm × 8 cm (height × diameter), provided with water circulation arrangement to maintain the temperature in the range 25–30 °C, was used in all the experiments. The irradiation was carried out using 125 W high-pressure mercury lamp