



Cyclohexane photocatalytic oxidation on Pt/TiO₂ catalysts

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ABSTRACT

Gas-solid heterogeneous photocatalytic oxidation (PCO) of cyclohexane in humidified air over TiO₂ and Pt/TiO₂ catalyst was studied.

Pt/TiO₂ photocatalysts were synthesized by photodeposition method at different Pt loadings (0.5–2 wt.%). The addition of 0.5 wt.% Pt does not significantly modify the TiO₂ properties. The increase in Pt loading induces to an aggregation of metallic particles on TiO₂ surface.

The cyclohexane PCO was performed in a fluidized bed photoreactor at 60 and 100 °C. Pure TiO₂ was more active than 1 and 2 wt.% Pt/TiO₂ samples at 60 °C. Nevertheless, the conversion level increases with temperature on Pt/TiO₂ photocatalysts. The cyclohexane was mineralized into CO₂, water and low amount of CO. A beneficial effect of Pt addition was found, since total CO₂ selectivity was obtained. The Pt/TiO₂ photocatalysts prepared by photodeposition provide the total cyclohexane PCO without CO production. Photocatalysts deactivation was not observed in any performed test. Evidence of an opportune tuning of temperature is highlighted.

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1. Introduction

Due to their high toxicity, the so-called volatile organic compounds (VOCs) have attracted considerable attention in the last decades [1]. Cyclohexane belongs to VOCs and it is released into the environment as an air pollutant and contributes to the formation of photochemical smog. This chemical occurs naturally in crude oil and may be released to the environment from sites where petroleum products are refined, stored and used [2].

In the last years, heterogeneous photocatalysis has appeared as an efficient and environmentally-friendly remediation technology; thus, a wide variety of VOCs in gas phase are decomposed on the UV-irradiated TiO₂ surface under ambient conditions without any chemical additives [3]. It has been reported that cyclohexane may be oxidized by the active sites of the TiO₂ surface via oxidation of intermediate radicals under UV irradiation. Subsequently, these intermediates are decomposed to CO₂ and CO [1,4].

In general, during photocatalytic reactions there may be production of undesirable intermediates, which eventually may be even more toxic than the original compounds. For instance, the photodegradation of atrazine, a widely used herbicide, yields

undesirable cyanuric acid as final product when unmodified TiO₂ is employed as photocatalyst [5]. Therefore, a careful control of all reaction intermediates is needed to assure total degradation of toxic organic compounds by photocatalysis without the production of harmful by-products.

Deposition of noble metals (e.g. Pt, Au, or Rh) on TiO₂ has been intensively studied as a means for enhancing efficiency of this oxide in the PCO of organic compounds [6–10]. Pt deposition on TiO₂ has been reported to improve [11,12] or to be detrimental [13,14] on TiO₂ photocatalytic reactions depending on Pt loading, metal particle size, original source of TiO₂ and kind of substrates to be degraded [7,15]. So, the effects of surface platinization of TiO₂ in photocatalysis still need to be studied in order to understand them fully.

On the other hand, during the PCO of organic compounds photocatalysts deactivation can be often observed. The accumulation of stable intermediates on the TiO₂ surface may block the surface active sites and subsequently deactivate the photocatalyst. In order to solve this problem, some strategies have been studied, such as different reactor designs [4,16]. It has been shown that in benzene PCO with TiO₂ catalyst, the water vapor in the reaction gas can contribute to inhibit the formation of carbon deposits on the catalyst surface and accelerate their decomposition [17]. In fact, the deactivated TiO₂ catalysts are photochemically regenerated in the presence of water vapor and the carbon deposits were decomposed to CO_x.

In this work, the influence of deposited platinum on TiO₂ in the gas phase cyclohexane PCO has been studied. PCO reactions were

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performed at different temperatures using a gas-solid fluidized bed photoreactor. In order to reduce the catalyst deactivation water vapor was added in the gaseous stream sent to the reactor. The effect of platinum loading in the total oxidation of cyclohexane was also analyzed.

2. Experimental

2.1. Synthesis procedure

TiO₂ and Pt/TiO₂ samples were synthesized following a similar procedure described somewhere else [18]. Briefly, the TiO₂ was obtained by hydrolysis of titanium tetraisopropoxide (Aldrich, 97%) in isopropanol solution (1.6 M) by the addition of distilled water. The obtained powders were sulfated by immersion in 1 M sulfuric acid solution for 1 h and calcined at 650 °C for 2 h prior to metalization.

Platinum photodeposition was performed using aqueous solutions of H₂PtCl₆ (Aldrich 99.9%), nominal Pt loadings were 0.5, 1 and 2 wt.%. A suspension of TiO₂ containing isopropanol as sacrificial donor and the selected Pt concentration was illuminated under N₂ atmosphere during 120 min using an Osram Ultra-Vitalux lamp (300 W) with a sun-like radiation spectrum and a main emission line in the UVA range at 365 nm. The intensity of the lamp was 14 mW/cm². After photodeposition, the powders were recovered by filtration and dried at 110 °C overnight.

2.2. Characterization techniques

X-ray diffraction (XRD) was performed using a Siemens D-501 diffractometer with Ni filter and graphite monochromator using Cu K α radiation. Crystallite sizes were estimated from the line broadening of the main X-ray diffraction peaks by using the Scherrer equation. Peaks were fitted by using a Voigt function.

Laser Raman spectra of the catalysts were obtained with a Dispersive MicroRaman (Invia, Renishaw), equipped with 785 nm diode-laser, in the range 100–2500 cm⁻¹ Raman shift.

Light absorption properties of the samples were studied by UV–vis spectroscopy using a PerkinElmer spectrometer Lambda 35. Band gaps values were calculated from the corresponding Kubelka–Munk functions, $F(R_{\infty})$, which are proportional to the absorption of radiation, by plotting $(F(R_{\infty}) \times h\nu)^{1/2}$ against $h\nu$.

BET surface area was carried out by N₂ adsorption at 77 K using a Micromeritics ASAP 2010 instrument.

Chemical composition and total platinum content of the samples were determined by X-ray fluorescence spectrometry (XRF) in a Panalytical Axios sequential spectrophotometer equipped with a rhodium tube as the source of radiation. XRF measurements were performed onto pressed pellets (sample included in 10 wt.% of wax).

Platinum particle sizes were studied by TEM, in a Philips CM 200 microscope. The samples were dispersed in ethanol using an ultrasonicator and dropped on a carbon grid.

X-ray photoelectron spectroscopy (XPS) studies were carried out on a Leybold–Heraeus LHS-10 spectrometer, working with constant pass energy of 50 eV. The spectrometer main chamber, working at a pressure $< 2 \times 10^{-9}$ Torr, is equipped with an EA-200 MCD hemispherical electron analyzer with a dual X-ray source working with Al K α ($h\nu = 1486.6$ eV) at 120 W and 30 mA. C 1s signal (284.6 eV) was used as internal energy reference in all the experiments.

2.3. Cyclohexane PCO

Photocatalytic tests were carried out feeding 30 L/h (STP) N₂ stream containing 200 ppm cyclohexane, 10 vol.% O₂ and adding

320 ppm of water in order to minimize catalysts photodeactivation. Two different temperatures were set for the photoreaction, 60 and 100 °C, and reaction pressure was 1 atm. Nitrogen was the carrier gas for cyclohexane and water vaporized from two temperature controlled saturators. The gas flow rates were measured and controlled by mass flow controllers (Brooks Instrument).

In this study, a fluidized bed photoreactor was used; this was designed for working with a gas flow rate in the range 20–70 L/h (STP) with a Sauter average diameter in the particles size range 50–100 μ m, assuring optimal fluidization. It was a two dimensional reactor with 40 mm \times 6 mm cross section, 230 mm height pyrex-glass walls, and a bronze filter (mean pores size 5 μ m) to provide a uniform distribution of fed gas. In order to decrease the amount of transported particles an expanding section (50 mm \times 50 mm cross-section at the top) and a cyclone specifically designed [19–21] are located on the top and at the outlet of the reactor, respectively.

The reactor was irradiated by UVA-LEDs matrices, emitting at 365 nm (light intensity: 90 mW/cm²). The catalytic bed was composed by 1.2 g of catalyst mixed with 20 g glass spheres in order to improve the fluidization properties.

The reactor inlet reactants and outlet products were analyzed by an on-line quadrupole mass detector (Quanta Fourier transform ion cyclotron resonance mass spectrometer, Siemens) and a continuous CO–CO₂ NDIR analyzer (Uras 10, Hartmann & Braun). UV-LEDs were switched on after complete adsorption of cyclohexane on catalyst surface.

3. Results and discussion

3.1. Characterization results

All the photocatalysts were widely characterized by different techniques. Some characterization results for the samples with the lower nominal content of Pt have been reported in a previous work [18]; therefore, here a summary of these results with the addition of the data corresponding to the catalyst with the higher content of Pt will be presented.

The XRD, Raman and N₂ adsorption analysis of the TiO₂ and Pt/TiO₂ samples indicate that the structural and textural properties of pristine TiO₂ were not altered by the addition of Pt, even for the highest nominal Pt percentage of 2 wt.%, as it can be observed in Table 1.

XRD spectra for the different samples are shown in Fig. 1. The only crystalline phase observed in all samples was anatase, with an

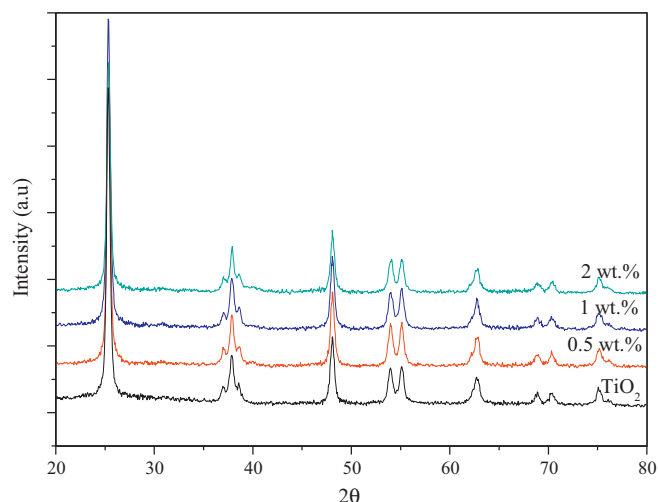


Fig. 1. XRD patterns for analyzed photocatalysts.

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