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Research Paper

One step hydrothermal synthesis of TiO_2 with variable HCl concentration: Detailed characterization and photocatalytic activity in propene oxidation

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ABSTRACT

TiO_2 materials have been prepared by a novel one-step hydrothermal synthesis method at mild conditions (low temperature and time) using titanium tetraisopropoxide as precursor and HCl solutions of different concentration, ranging from 0.5 to 12 M. A detailed physico-chemical characterization has been done, putting especial attention to the quantification of crystallinity and surface OH content. All the obtained samples have high surface areas (100–135 m^2/g), small anatase crystal size (8–11 nm) and high crystallinity (around 80%). The concentration of the HCl used in the synthesis has a significant effect on the two first mentioned parameters and on the proportion of crystalline phases (anatase-brookite-rutile) developed. There is a good correlation between the amount of hydroxyl surface groups and the specific surface area (S_{BET}), but regarding surface density of OH groups there are, as well, some differences between samples (the samples with higher OH surface densities are those prepared with less concentrated HCl solutions).

Most of the prepared photocatalysts are more active than commercial TiO_2-P25 in the gas phase oxidation of propene at low concentration. The best photocatalytic performance is found for samples prepared with 0.5 and 0.8 M HCl, what can be explained by a suitable combination of properties: high surface area and developed porosity, high surface OH groups' content and density and large proportion of anatase with small crystal size.

1. Introduction

TiO_2 materials have appealed considerable interest as photocatalysts for many applications, among which the decomposition of harmful organic pollutants can be pointed out [1–3]. TiO_2 photocatalysts show outstanding properties like excellent oxidative capability, chemical stability, low price, non-toxicity and biocompatibility [4–6]. For this reason, an intense research is being devoted to develop simple and suitable synthesis methods to obtain TiO_2 with improved photocatalytic efficiency, and to broaden the knowledge of how the physical and chemical properties of TiO_2 determine its photocatalytic activity [7–11].

It is known that the reagents and conditions used in the TiO_2 synthesis strongly determine the key physical and chemical properties of the photocatalysts. In particular, the main properties relevant to the catalytic performance are: surface area, crystalline structure and crystalline phases present, surface chemistry and optical behavior [12–15].

It is usually accepted that the larger the surface area, the higher the catalytic activity, in accordance with the superficial reactions involved in the photocatalytic process [16]. However, in materials like TiO_2, the surface area is strongly linked with the degree of crystallinity and crystal size and, in general, large surface areas correspond to materials with relatively low crystallinity and/or small crystal size [16]. Therefore, because these two properties of TiO_2 (large surface area and amorphous contribution) have, in principle, opposite effects in the photocatalytic performance, a proper balance of them should be considered as the most suitable situation.

Together with the degree of crystallinity, the presence of different crystalline phases is a crucial and controversial parameter that affects the photocatalytic performance of TiO_2 in different applications. On one hand, crystalline TiO_2 seems to be more effective than amorphous titania to prevent recombination of electrons (e^-) and holes (h^+) [17]. Maybe because of that, most references just deal with the characterization of crystalline TiO_2, setting aside the analysis of the amorphous contribution, leaving unregarded the degree of crystallinity and the fact that amorphous titania could have some positive influence [17–22]. On the other hand, while in some works anatase is considered as the most photoactive TiO_2 crystalline phase [23–25], other published papers state that materials containing different TiO_2 polymorphs (mainly anatase with some rutile) are more active in oxidation processes

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[26–29]. This synergistic positive effect of mixed phases has been attributed to a lower electron-hole recombination rate [30,31], and/or to particular defects in the rutile/anatase interface in which charge transfer complexes would be favorable [32].

Although brookite is frequently encountered as a by-product in TiO_2 photocatalysts prepared by sol-gel or hydrothermal methods [33], it is less studied than anatase and rutile. In general, data about pure brookite are lacking mainly because of the difficulty of synthesizing this metastable phase with a high purity, being brookite the least known TiO_2 photocatalyst [34]. In recent years, several studies have dealt with the behavior of brookite in photocatalytic oxidation applications [34,35], but its role has not been clearly stated yet.

Surface chemistry of TiO_2 has received much less attention than its crystallinity. Some studies report that surface $-OH$ groups play an important role in the activity [36,37], acting as capture centers for the photoexcited electrons [38] and preventing recombination of electrons and holes [18,39]. It has also been published that adsorbed water and hydroxyl groups can react with generated holes to produce hydroxyl radicals [30], which are powerful oxidants in the degradation of organic compounds [37]. The OH concentration depends on the surface area, but it also seems to be related with the TiO_2 phases and degree of crystallinity [28,40]. In contrast with what happens with other parameters, there is not a widely accepted standard method to characterize and quantify the surface chemistry of TiO_2.

As mentioned above, the preparation procedure strongly determines the TiO_2 physical and chemical properties, but it must be noted that the available methods have different degrees of complexity and cost. The sol-gel synthesis is widely employed due to the inexpensive equipment required, the low temperatures used and the high homogeneity and purity of the obtained product [41–46]. In contrast, hydrothermal (HT) techniques have been much less used. They are recently becoming interesting tools for advanced nanomaterials' synthesis and potential methods for preparing highly crystalline TiO_2 [12,47,48]. However, they are more complex because two steps and the use of surfactants and co-surfactants [49–51] or organic solvents, like *n*-hexane or cyclohexane [50–52], are usually involved.

In both methods, the nature and concentration of the acid hydrolysis medium used seem to play a substantial role in controlling the morphology and crystal structure of the synthesized TiO_2 [26,49–62]. Nitric, sulfuric, acetic or hydrochloric acids have been used [52,61,62], and it has been found that not only the acid concentration, but also the nature of the anion counterpart affects the nucleation process, the crystal growth and the morphology of TiO_2. It has been reported that SO_4^{2-} and CH_3COO^- anions could retard the formation of rutile [52,61], whereas this phase is easily formed in HNO_3 or HCl media [52,61,62]. Besides, the presence of Cl^- anions seems to lead to smaller TiO_2 crystals [61] and the use of hydrochloric acid has the advantage of its lower price.

In this context, the present study focuses on the synthesis of TiO_2 photocatalysts by a one-step hydrothermal process at low temperature and short time using aqueous HCl solutions as hydrolysis media. The investigated variable is the concentration of the HCl solution. Special attention has been paid to the characterization of the prepared materials, particularly because properties like the degree of crystallinity and the surface chemistry are not considered in many studies; and aspects like the detailed distribution of crystalline phases and their role in photocatalysis are sometimes controversial.

The catalysts have been tested in the gas phase photocatalytic oxidation of propene at low concentration, 100 ppmv, trying not only to develop effective photocatalysts for this reaction, but also to determine the role of the TiO_2 properties on their catalytic performance. Propene has been selected as a representative substance of VOCs (Volatile Organic Compounds). It is present in vehicle emissions, in many industrial effluents, such as those of petrochemical plants, foundry operations and others [63,64], and it is also an important component of tobacco smoke [65,66]. The test is carried out at low propene concentration because this is usually the case for VOCs in gas effluents and the implementation of efficient removal techniques is difficult and costly in these conditions [67].

2. Experimental

2.1. Materials

Titanium (IV) tetraisopropoxide (TTIP, 97%) was purchased from Sigma-Aldrich. Absolute ethanol (C_2H_6O, 99.8%) and hydrochloric acid (HCl, 37%) were supplied by Panreac. All reactants have been used without further purification. A commercial TiO_2 material, P25 from Evonik (previously Degussa), has been used as reference photocatalyst.

2.2. Preparation of TiO_2 materials

TiO_2 was prepared by hydrothermal synthesis using a procedure adapted from the sol-gel method described by Wang et al. [56]. In a typical synthesis, 4 ml TTIP and 20 ml ethanol were stirred at room temperature for 1 h, and then a mixture of HCl solution (4 ml of 0.5, 0.8, 1, 3, 5, 7 or 12 M concentration) and ethanol (10 ml) was added dropwise. The mixture was continuously stirred for 1 h, and then it was transferred to a 50 ml Teflon-lined stainless steel autoclave, which was heated in an oven at 180 °C for 12 h and then cooled down to room temperature. Afterwards, the solid was filtered, dried at 100 °C for 12 h and, finally, heat treated in air in a muffle at 5 °C/min up to 350 °C, for 2 h.

The synthesized materials are named TiO_2-xM, where x refers to the molar concentration of the HCl solution used. Note that the acid concentration in the synthesis pot is about 10 times lower (i.e. if 4 ml of 12 M HCl solution are used, considering that the total volume is 38 ml, the HCl concentration in the synthesis medium is 1.27 M). [HCl] has been used as an abbreviation of HCl solution concentration in some parts of the manuscript.

2.3. Characterization

Porous texture was characterized by N_2 adsorption at −196 °C in a volumetric Autosorb-6 B apparatus from Quantachrome. The samples were previously degassed at 250 °C for 4 h. The BET equation was applied to the nitrogen adsorption isotherms to get the apparent BET surface areas (S_{BET}). The Dubinin–Radushkevich equation was applied to the N_2 adsorption data to determine the total micropore volume (V_{DR} N_2, pores with size < 2 nm) [68]. The mesopore volume ($V_{mesopore}$ $2\text{ nm} < \o < 50\text{ nm}$) was calculated as the difference between the volume of N_2 adsorbed at $P/P_0 = 0.9$ and $P/P_0 = 0.2$, expressed as a liquid [69]. The total pore volume (V_T) was determined from the volume of nitrogen adsorbed at a relative pressure of $P/P_0 = 0.99$.

The percentage of crystalline TiO_2, phase composition and crystallite size were determined by X-ray diffraction (XRD) at room temperature. Details on the method used for the determination of the percentage of crystallinity and phase compositions are explained in the XRD results section. The XRD patterns were recorded both for TiO_2 samples and for mixtures of these samples and CaF_2 (50%, w/w), using the equipment Miniflex II Rigaku (30 kV/15 mA) with Cu Kα radiation and a scanning rate of 2°/min, in the 2θ range 6–80°. The average crystallite size, referred to as crystal size, was calculated by the Scherrer equation (Eq. (1)) [70]:

$$B = \frac{K\lambda}{\beta cos\theta} \tag{1}$$

where B is the average crystallite size (nm); λ is the wavelength of the radiation used (0.1540 nm for Cu Kα), K is the Scherrer constant (K = 0.93) [70], β is the full width at half maximum intensity (FWHM) and θ is the angle associated to the main peak of the studied phase (these peaks are those at 2θ values of 25.3, 27.5 and 30.8° for anatase, rutile and brookite, respectively).