Research Letter

Analysis of Polymorphic Nanocrystals of TiO$_2$ by X-Ray Rietveld Refinement and High-Resolution Transmission Electron Microscopy: Acetaldehyde Decomposition

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In this work, TiO$_2$ nanocrystals were synthesized by the sol-gel method. These materials were annealed at 200 and 500°C, and characterized by the XRD-Rietveld refinement, and by BET and TEM. As for the low-temperature-treated sample (200°C), nanocrystals with small crystallite sizes (7 nm) and high abundance of anatase, coexisting with the brookite phase, were obtained. Meanwhile, the sample annealed at 500°C showed an increased crystallite size (22 nm) and an important polymorphic increment. The sample annealed at 200°C showed a high activity in the photocatalytic decomposition of acetaldehyde.

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1. INTRODUCTION

TiO$_2$ is a material that is widely used in electronics, ceramics, catalysis, and pigment industries because of its optical and photocatalytic properties, which stem from the quantum size effect [1]. Likewise, TiO$_2$ has become a very important material due to its applications in different processes such as water purification; and more recently, in the control of air contaminant gases present in both indoor and outdoor environments, where the UV-light is the necessary energy source in the photocatalytic processes [2–4]. There are three types of TiO$_2$ crystalline structures: rutile, anatase, and brookite. Rutile is the only stable phase, whereas anatase and brookite are almost metastable at all temperatures. Nowadays, the challenge for many researchers, in order to obtain a photocatalytic material, is to control the following TiO$_2$ properties: the crystal size, anatase-rutile transition, surface area, hydroxylolation, and thermal stability [5]. According to some studies, the anatase phase is obtained at low temperatures, at around 350°C, which is useful for catalytic and industrial applications [6]. Recently, the effect of the brookite phase on the anatase-rutile transition in TiO$_2$ nanoparticles has been studied, where the proportion of brookite depends on both the method and conditions used [7]. For instance, by using either thermolysis or hydrothermal synthesis, it is possible to obtain brookite at high temperature, likewise, in some works, the role of brookite in the TiO$_2$ crystal size has been analyzed [8, 9]. Furthermore, both the TiO$_2$ nanocrystals and anatase-rutile transition phase have considerably attracted attention because of their special physical and chemical characteristics in photocatalytic applications; however, both characteristics depend on the preparation methods [10–12]. Through the sol-gel method, it is possible to obtain the smallest TiO$_2$ crystal size, which is a fundamental property to perform the near-visible UV photocatalytic reactions; that is why TiO$_2$ is a very useful material in a variety of applications such as the decomposition of both volatile organic compounds (VOCs) and gas-phase nitrogen oxides (NOx) [13, 14].

The aim of this work is the synthesis of TiO$_2$ nanocrystals by the sol-gel method, where these materials were annealed at 200 and 500°C, and characterized by the XRD-Rietveld refinement, nitrogen adsorption (BET) and high-resolution transmission electron microscopy (HRTEM) of polymorphic TiO$_2$ for their application as catalysts in the acetaldehyde photodecomposition through in situ microreactions photoassisted with UV light.
2. EXPERIMENTAL

The sol-gel TiO₂ nanocatalysts were prepared as follows: 36.67 mL of titanium (IV) isopropoxide (Aldrich, Mo, USA, 99.9%) were dissolved in 60 mL of 2-propanol (Baker 99.9%). The solution was set under constant stirring; and then, hydrochloric acid (Baker 36.5 vol.% in water) was added to adjust the reaction medium at pH 3. The hydrolysis of the preparations (with 2-propanol as solvent) was accomplished by adding 18 mL of bidistilled water (water/alkoxide ratio of 1:2). The solutions were then maintained under stirring and reflux until the gels were formed. Afterwards, the gels were dried at 70 °C for 12 hours; and then annealed at 200 and 500 °C for 4 hours, respectively, with a heating rate of 20 °C/min. The samples were labeled as TiO₂-P200 and TiO₂-P500.

In order to perform the XRD, a D500 Siemens with a copper tube and Kα radiation of 1.5405, operating at 35 KeV and 15 mA, was used. The intensities were determined in the 2θ interval ranging from 20° to 80°. To refine each spectrum, the Rietveld analysis was applied by using the full prof software by Rodríguez Carbajal [15]. The crystal size was determined by the Rietveld refinement and Scherrer equation [16]. The determination of the surface area was size was determined by the Rietveld refinement and Scherrer full prof software by Rodríguez Carbajal [15]. The crystal spectrum, the Rietveld analysis was applied by using the

\[ \text{size} = \text{Scherrer constant} \times \frac{\lambda}{\beta \cos \theta} \]

where \( \lambda \) is the wavelength of the X-ray radiation, \( \beta \) is the full width at half maximum (FWHM), and \( \theta \) is the Bragg angle. The crystal size was determined by the Rietveld refinement and Scherrer equation [16]. The characterization parameters of each crystalline structure and their average crystallite size were obtained from the corresponding Rietveld refinement. The HRTEM digital images were obtained using a CCD camera and the Digital Micrograph Software from Gatan. In order to prepare the materials for observation, the powdered samples were ultrasonically dispersed in ethanol and supported on holey carbon-coated copper grids. From the obtained micrographs, the average particle size was calculated by the surface/volume equation [17]. The photocatalytic activity tests for the TiO₂-P200, TiO₂-P500 samples, and the witness (Degussa P25) were carried out in experimental equipment at microreaction level. A quartz cell was used as a photoreactor with a 365-UV lamp (UVP-light-sources) with an intensity of 100 μW/cm². The tests were carried out by using acetaldehyde (CH₃CHO) with a concentration of 300 ppmv; and 2% of oxygen.

3. RESULTS AND DISCUSSION

By the XRD and Rietveld refinement, the phases and structures formed in each of the TiO₂ samples were determined using the unit cells and known space groups (Table 1) [18]. In the sol-gel TiO₂ catalysts, the three known titania phases, anatase (tetragonal), rutile (monoclinic), and brookite (orthorhombic), were obtained (Figure 1). The TiO₂-P200 sample was less polymorphic (anatase-brookite phases) than the TiO₂-P500 sample (anatase-brookite-rutile phases). The anatase-rutile transition was determined as a function of the thermal treatment, where an appreciable percentage of anatase was observed in the sample prepared at high temperature (TiO₂-P500); likewise, only in this sample appears the rutile phase. With regard to the TiO₂-P200 sample, anatase and brookite phases with small crystal sizes were found, which could give specific photocatalytic properties because of the nanometric-crystal size/phase ratio (Figure 1) [19]. The characterization parameters of each crystalline structure and their average crystallite size were obtained from the corresponding Rietveld refinement. By the Rietveld refinement, the TiO₂-P200 sample showed the following phase compositions: anatase (62.88%) and brookite (37.1%); whereas in the TiO₂-P500 sample, its phase composition was anatase (82.67%), brookite (14.9%), and rutile (2.43%) (Table 1). According to these results, we can see that the handling of both the hydrolysis degree and pH in the sol-gel method enabled us to synthesize TiO₂ anatase at low temperature (200 °C) since the anatase phase transformation by other methods occurs at 450 °C [5, 19].

Both the anatase and brookite found in the TiO₂-P200 sample showed a very small crystallite size (≈6 nm); and on the other hand, the TiO₂-P500 sample showed a little anatase-rutile transition due to the thermal treatment (anatase 82.67% and rutile 2.43%), which suggests that the

<table>
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<th>Sample</th>
<th>Structure</th>
<th>Phase (%)</th>
<th>Crystal size (nm)</th>
<th>Scherrer crystal size (nm)</th>
<th>Phase</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
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<td>18.26</td>
<td>Brookite</td>
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<td>0.5210546</td>
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<tr>
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<td>20.5</td>
<td>22.04</td>
<td>Anatase</td>
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<td>0.9506104</td>
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<tr>
<td></td>
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<td>13.1</td>
<td>34.02</td>
<td>Brookite</td>
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<td></td>
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<td>34.7</td>
<td>27.14</td>
<td>Rutile</td>
<td>0.4591337</td>
<td>0.4591337</td>
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small crystallite size controls the anatase-rutile transition and its stability; likewise, the synthesis method enabled us to obtain brookite at low temperature [9]. According to Zhang and Banfield, the particle size plays an important role in the phase stability; for instance, anatase is more thermodynamically stable at sizes below 11 nm; and brookite is stable for crystal sizes between 11 and 35 nm [20]. It is known that the brookite-rutile transformation is faster than the anatase-rutile transformation, where there is an effect related with the pressure on the small anatase crystallites; such a case could promote the formation of a rutile nucleus at short transition-temperature periods; but in this work, even at high temperatures, the anatase-rutile transition does not occur; therefore, probably, the anatase-rutile transition could be modified when the grain size was small enough (Table 1), (Figure 1) [21, 22].

The structure of the polycrystals, the interplanar distances, and the TiO$_2$-P200 and TiO$_2$-P500 samples were determined by HRTEM. Figures 2 and 3 show the typical HRTEM images for the TiO$_2$-P200 sample with a morphology characteristic of the tetragonal structure. The inset corresponds to the fast Fourier transform (FFT) or digital diffractogram. The diffraction spots correspond to the interplanar distance $d_{110} = 0.323$ nm of the tetragonal TiO$_2$ (anatase phase). The distribution of the crystal size is shown in Figure 4; the average nanometric size of the crystals is around 7 nm; and the standard deviation is 1.32 nm; these results confirm the presence of nanostructured TiO$_2$.

Figure 5 shows an image of the TiO$_2$-P500 sample and the corresponding FFT. The HRTEM image of the TiO$_2$ particle was identified as the anatase phase with zone axis [112]. The average nanometric size of the crystals is 17 nm. Likewise, Figure 6 shows the image of a single crystal of the TiO$_2$-P500 sample, with a morphology characteristic of the TiO$_2$ tetragonal structure, which corresponds to the anatase phase. The morphology of the TiO$_2$ nanostructured materials is equiaxial with a zone axis of [010]. The effect of the calcination temperature on the surface area in the samples is very important; for instance, in the TiO$_2$-P200 sample, this value is tripled (189 m$^2$/g) with respect to that in the TiO$_2$-P500 sample (60 m$^2$/g). There is also an effect
on the TiO₂ crystal size, which was more than doubled as a consequence of the sinterization process (Table 1).

The textural and morphological properties showed by the sol-gel TiO₂ catalysts could be related to their activity in the acetaldehyde decomposition. In the TiO₂-P200 sample, a conversion higher than 95% was obtained after 150 minutes, meanwhile the TiO₂-P200 sample reached a conversion near to 70% in the same period of time (Figure 7). It is important to note that the sol-gel catalysts were more active than the P-25 commercial titania, which reaches only 30% of conversion in 150 minutes. In our opinion, the high activity of the TiO₂-P200 sample can be attributed to (i) the presence of the anatase-brookite phase; (ii) the presence of an important abundance of brookite; (iii) the small particle sizes which were three times smaller than those obtained in the TiO₂-P500 sample (Table 1). According to the CH₃COH mineralization, assisted with a lamp near the UV-vis (365 nm), showed by the sol-gel TiO₂ catalyst, it could be considered as a good option to be applied in both indoor and outdoor pollution control.

4. CONCLUSIONS

By varying the sol-gel parameters, it was possible to obtain less polymorphic TiO₂ at low temperature, since the TiO₂-P200 sample only showed two phases (anatase and brookite) and a small crystal size (≈7 nm) whereas the TiO₂-P500 sample showed the three main structures (tetragonal, orthorhombic and monoclinic), likewise a bigger crystal size (>22 nm). In the same way, by handling the sol-gel method parameters, it was possible to increase the surface area (189 m²/g). The TiO₂ with less polymorphism and small crystal size showed high photoactivity in the acetaldehyde decomposition; therefore, these two variables could play a major role in photocatalysis.

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