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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 crystallite size, anatase-rutile transition, surface area, hydroxylation, 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.

TABLE 1: DRX-Rietveld refinement, phase concentration, and crystal size of the sol-gel TiO_2 samples.

Sample	Structure	Phase (%)	Crystal size (nm)	Scherrer crystal size (nm)	Phase	a (nm)	b (nm)	c (nm)
TiO_2-P200	Tetragonal	62.88	6.9	7.03	Anatase	0.3790926	0.3790926	0.9495732
	Orthorhombic	37.12	6.0	18.26	Brookite	0.9167624	0.5416461	0.5210546
TiO_2-P500	Tetragonal	82.67	20.5	22.04	Anatase	0.3786167	0.3786167	0.9506104
	Orthorhombic	14.90	13.1	34.02	Brookite	0.9142567	0.5442068	0.5191934
	Monoclinic	2.43	34.7	27.14	Rutile	0.4591337	0.4591337	0.2951845

2. EXPERIMENTAL

The sol-gel TiO_2 nanocrystal-catalysts 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 TiO_2-P200 and TiO_2-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 performed by means of the nitrogen physisorption in an ASAP-2000 Micromeritics equipment. The high resolution transmission electron microscopy (HRTEM) was performed in a JEOL JEM-2200FS microscope with a Schottky-type field gun, working at 200 kV. The point resolution was of 0.19 nm; and the information limit was better than 0.10 nm. 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 TiO_2-P200, TiO_2-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/cm^2. The tests were carried out by using acetaldehyde (CH_3CHO) 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 TiO_2 samples were determined using the unit cells and known space groups (Table 1) [18]. In the sol-gel TiO_2 catalysts, the three known titania phases, anatase (tetragonal), rutile (monoclinic), and brookite (orthorhombic), were obtained (Figure 1). The TiO_2-P200 sample was less polymorphic (anatase-brookite phases) than the TiO_2-P500 sample (anatase-bookite-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 (TiO_2-P500); likewise, only in this sample appears the rutile phase. With regard to the TiO_2-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 TiO_2-P200 sample showed the following phase compositions: anatase (62.88%) and brookite (37.1%); whereas in the TiO_2-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 TiO_2 anatase at low temperature (200°C) since the anatase phase transformation by other methods occurs at 450°C [5, 19].

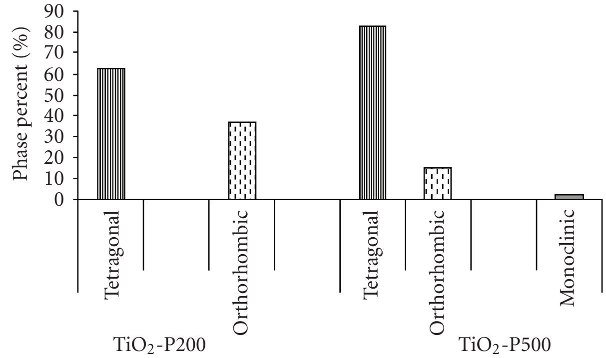

FIGURE 1: XRD-Rietveld refinement concentration for each structure in the sol-gel TiO_2 samples.

Both the anatase and brookite found in the TiO_2-P200 sample showed a very small crystallite size (≈6 nm); and on the other hand, the TiO_2-P500 sample showed a little anatase-rutile transition due to the thermal treatment (anatase 82.67% and rutile 2.43%), which suggests that the

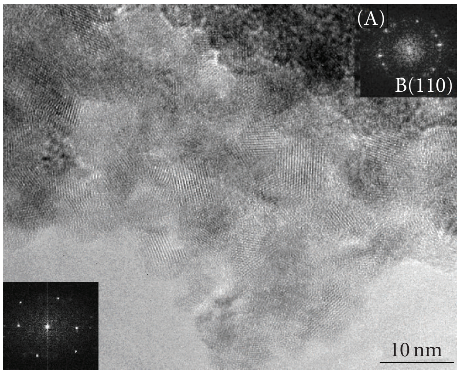

Figure 2: Polymorphic nanocrystals of TiO_2-P-200. (A) Diffraction.

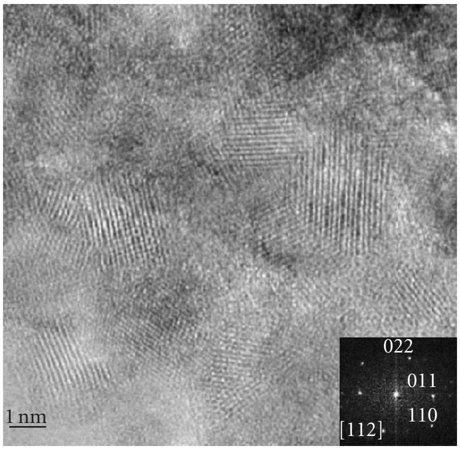

Figure 3: Details of TiO_2-P-200 nanocrystals.

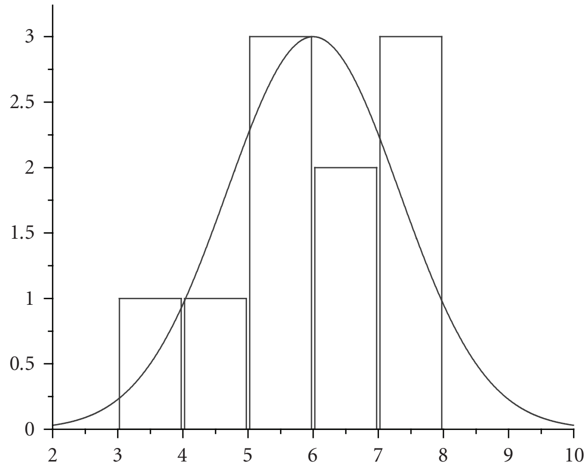

Figure 4: Average crystal size (SD = 1.32 nm) of sol-gel TiO_2 samples.

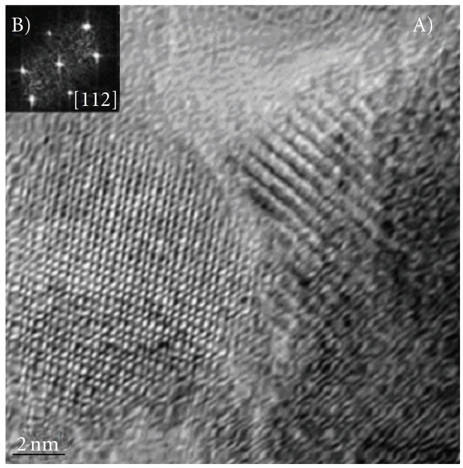

Figure 5: (A) Nanocrystals of TiO_2-P-500. (B) Diffraction pattern of the TiO_2.

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 policrystals, 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 diffractrogram. 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

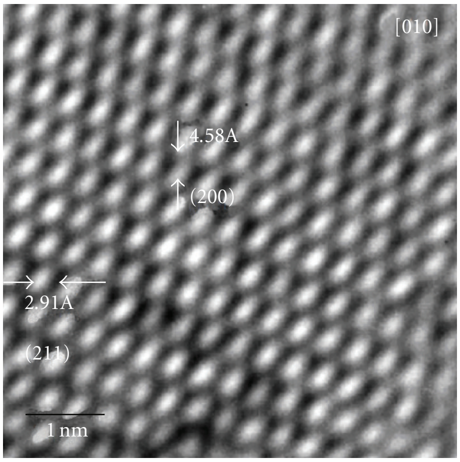

FIGURE 6: Details of nanocrystal of TiO_2-P-500.

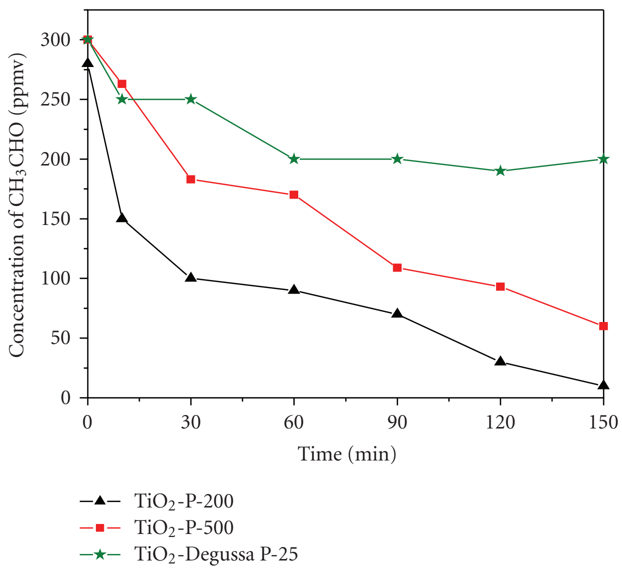

FIGURE 7: Acetaldehyde conversions as a function of time for the TiO_2 samples.

on the TiO_2 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 TiO_2 catalysts could be related to their activity in the acetaldehyde decomposition. In the TiO_2-P200 sample, a conversion higher than 95% was obtained after 150 minutes, meanwhile the TiO_2-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 TiO_2-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 TiO_2-P500 sample (Table 1). According to the CH_3COH mineralization, assisted with a lamp near the UV-vis (365 nm), showed by the sol-gel TiO_2 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 TiO_2 at low temperature, since the TiO_2-P200 sample only showed two phases (anatase and brookite) and a small crystal size (≈7 nm) whereas the TiO_2-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 m^2/g). The TiO_2 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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