

Hydrolysis catalyst effect on the textural and structural properties of sol-gel mixed oxides TiO₂-CeO₂

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Sol-gel TiO₂-CeO₂ semiconductors were synthesized at pH 3 and 9 using titanium alkoxide as the initial reactant; and either nitric acid or ammonium hydroxide as hydrolysis agents. The gels annealed at 473, 673 and 873 K were characterized by nitrogen adsorption, X-ray diffraction and Raman spectroscopy. The surface fractal dimension, crystallite size, titanium deficiency and electron density were calculated by the Frenkel-Halsey-Hill method, Rietveld refinement, and Fourier electron density map, respectively. Mesoporous materials showing high specific surface areas (250-99 m²/g for pH 3 and 267-88 m²/g for pH 9) were obtained in both preparations. Anatase and anatase-cerianite crystalline phases were observed by X-ray diffraction in the samples prepared at pH 3 and pH 9 respectively. Nanocrystalline structures (from 7.1 to 43.6 nm) and an important titanium deficiency, depending on the synthesis conditions are reported. The Fourier electron density maps showed that for the semiconductors prepared at pH 3 the electron density was contracted in comparison with the samples synthesized at pH 9 where enlarged electron density maps were observed. A good agreement between the electron density maps and the surface fractal dimensions was obtained.

Key words: Titania-ceria solids, Titania-ceria electron density maps, Titania-ceria Raman spectra, Titania-ceria XRD, Rietveld refinement for titania-ceria.

Introduction

In the present study, the preparation by the sol-gel method of TiO₂-CeO₂ mixed oxides is reported. The selection of cerium oxide and titania was done because of the important role of the Ce³⁺/Ce⁴⁺ redox pair in heterogeneous oxidation catalytic reactions; and titania because of its photocatalytic oxidative properties [1-4]. The study was focused on investigating the effect of hydrolysis catalyst on the TiO₂ properties [5-8]. The characterization of the TiO₂-CeO₂ mixed oxides was performed in order to determine the main variables that control the texture and structure in semiconductors. The specific surface area, titania crystallite size, crystalline phase composition, interplanar distances, Ti⁴⁺ deficiency, microstrain and electron density map were evaluated. The correlation between these textural, structural and electron density properties is reported.

Experimental Procedure

Catalysts preparation

The sol-gel TiO₂-CeO₂ materials were synthesized at pH 3 and 9 under conditions similar to those reported by Yoldas [9, 10] using titanium alkoxide as reactant and

HNO₃ and NH₄OH as hydrolysis catalysts. The procedure was as follows: to a two neck flask containing an ethanol/water solution with a 16 : 8 molar ratio, either HNO₃ or NH₄OH was added to adjust the pH of the solutions to 3 and 9 respectively. Afterwards, to these solutions, the appropriate amount of cerium nitrate (Aldrich 99.9 %) was added to obtain a 10 wt% CeO₂ loading in the final solids. After this 1 mol of titanium n-butoxide (Aldrich 97%) was added dropwise to the reactant solution during 1 h. Then, the solution was set at reflux with vigorous stirring until a gel was formed. After gelling, the samples were dried in air at 373 K for 8 h and then, by using a thermal program rate of 2 K minute⁻¹ the samples were annealed at 473, 673 and 873 K for 4 hours.

Characterization

Adsorption measurements

The nitrogen adsorption isotherms were obtained at 77 K with an automatic Quantachrome Autosorb 3B instrument. Prior to the nitrogen adsorption all the samples were outgassed overnight at 573 K. The specific surface areas of the samples were calculated from the nitrogen adsorption isotherms using the BET method and the mean pore size diameter from the desorption isotherms using the BJH method [11].

Fractal dimension

The determination of the fractal dimension D_s was calculated from the adsorption-desorption isotherms data

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and using the Frenkel-Halsey-Hill equation, which is expressed as follows [12, 13]:

$$\ln(S^g) = \text{const} - (3 - D_s) \ln(\mu) \quad (1)$$

where S^g is the amount adsorbed at the relative pressure (P/P^0) at the absolute temperature (T) and μ is the adsorption potential which is defined as:

$$\mu = RT \ln\left(\frac{P^0}{P}\right) \quad (2)$$

Raman spectroscopy

The near-infrared Fourier transform Raman spectroscopic measurements were performed with a Thermo Nicolet ALMEGA dispersive Raman spectrometer equipped with a diode-pumped Nd:YAG laser with an emission wavelength of 1,064 nm. The beam was doubly focused on a sample mounted in a capillary tube. The light scattered at 90° over the sample was focused on the entrance slit of a double monochromator; and detected by a Peltier-cooled photomultiplier attached to a phonon counter.

X-ray diffraction and Rietveld refinement

The X-ray diffraction patterns were obtained at room temperature with a Bruker Advance D-8 diffractometer with a Cu K α radiation and a graphite secondary beam monochromator. The intensities were obtained in the 2 theta ranges between 20 and 100° with a step of 0.05° and a measuring time of 0.5 s per point. The crystalline structures were refined using the computer program Rietica (DBW3.2) for X-ray and neutron powder diffraction patterns [14-17]. The titania tetragonal structure was refined using a tetragonal unit cell with the symmetry described by the space group I4₁/amd (Table 1 and Table 2) and the cubic cerianite by the group Fm3m [18]. For the peaks profile shapes we used the Voigt function and Cheby I polynomial with 6 terms. The values for titanium deficiency per unit cell (%) were calculated using the Wyckoff positions and the occupancies refined by Rietveld.

Microstrain

The microstrain for the samples was calculated by using the Williamson Hall method expressed in the following equation [19]:

Table 1. Atomic fractional coordinates of tetragonal anatase (space group I4₁/amd)

Atom	Site	x	y	Z
Ti	4a	0	0.75	0.125
O	8e	0	0.25	0.078

Table 2. Miller indices and interplanar distances for anatase

TiO ₂ (Anatase)	Miller indices			
	(101)	(004)	(200)	(105)
Interplane distance (nm)	0.3520	0.2378	0.1892	0.1699

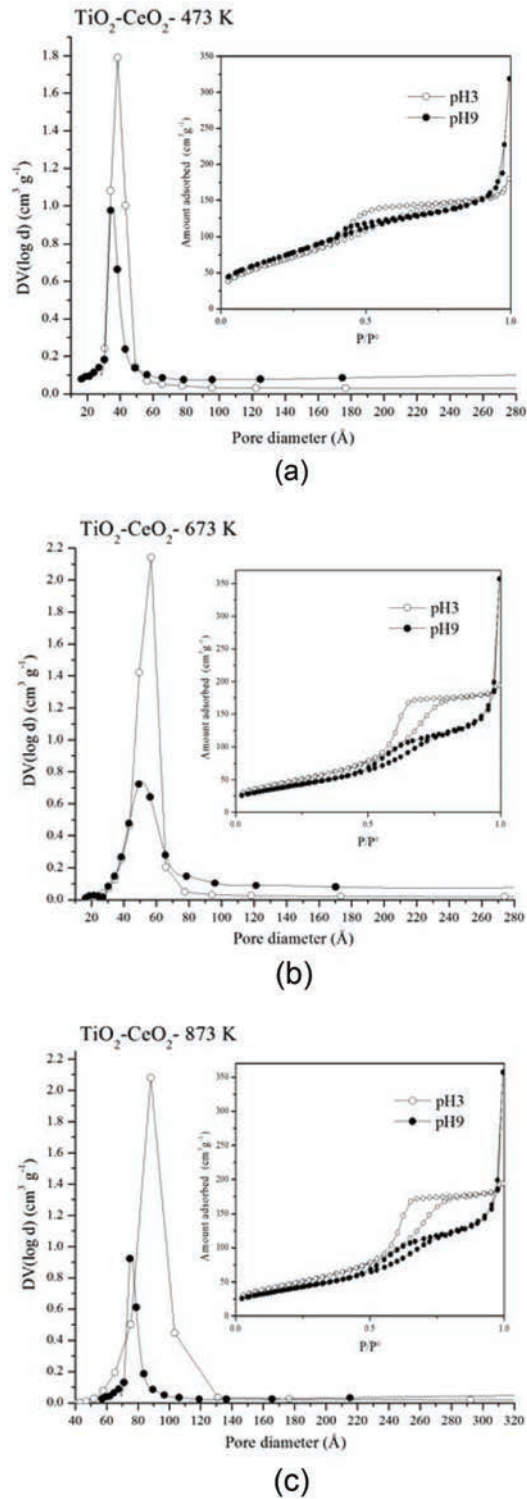


Fig. 1. Nitrogen sorption isotherms and pore size distributions of the TiO₂-CeO₂ materials.

$$\{\beta_{obs} - \beta_{ins}\} \cos \theta = \lambda / D_v + 4 \epsilon_{str} \{\sin \theta\} \quad (3)$$

where ϵ_{str} is the weighted average strain, β is the integral breadth of a reflection (in radians 2 θ) located at 2θ and D_v is the volume weighted crystallite size. The full-width half-maximum values used for this purpose were calculated by means of the PowderCell software [17].

The Cu K α radiation wavelength was $\lambda = 1.540598 \text{ \AA}$ with the Bragg diffraction angle in radians.

Electron distribution density

The electron density on a point (x, y, z) of the crystallite cell with volume V was calculated by Fourier series using the structural factors $F(h, k, l)$ [20]:

$$\rho(x, y, z) = V^{-1} \sum_h \sum_k \sum_l F(h, k, l) \exp[-2\pi i(hx + ky + lz)] \quad (4)$$

where (x, y, z) represents a vector r of real space, with one vector space (a, b, c) and (h, k, l) are the coordinates of one vector from the reciprocal space with base (a^*, b^*, c^*) , i.e., they are the coordinates from the diffraction plane that it is given by Bragg's Law. The electron density distribution in the base plane {slice 1 with $Z = 0$, i.e. face ba , with a set (hkl) as projection plane (001) } for both the TiO_2 and $\text{TiO}_2\text{-CeO}_2$ solids were calculated and delineated by the Rietica program from the XRD data [17].

Results and Discussion

Adsorption results

The nitrogen adsorption isotherms for the $\text{TiO}_2\text{-CeO}_2$ -pH 3 and $\text{TiO}_2\text{-CeO}_2$ -pH 9 samples annealed at different temperatures are presented in Fig. 1. It can be seen that the isotherms show hysteresis loops which are more evident for the samples prepared at pH 3. As the annealing temperature increases the hysteresis loop becomes more important. Inserted in the Fig. 1 we can see the pore size distributions for the different samples, a monomodal distribution can be seen in all of them [21]. The calculated specific surface areas are reported in Tables 3 and 4. The results show high specific surface areas for the pH 3 preparations ($250\text{-}99 \text{ m}^2/\text{g}$); and $267\text{-}88 \text{ m}^2/\text{g}$ for the samples prepared at pH 9. Such results indicate that the annealing temperature is the most important factor in the final textural properties of the solids. Meanwhile, the pH used for the preparation of the solids has only marginal effects on the specific surface area. In the same way the calculated mean pore size diameter showed important effects due to the thermal treatments. The mean pore size diameter increases from 3.5 to 9.0 nm for the pH 3 samples annealed at 473 and 873 K respectively; a similar behavior was also observed on the samples prepared at pH 9 where the mean pore size diameter increases from 3.3 to 7.4 nm

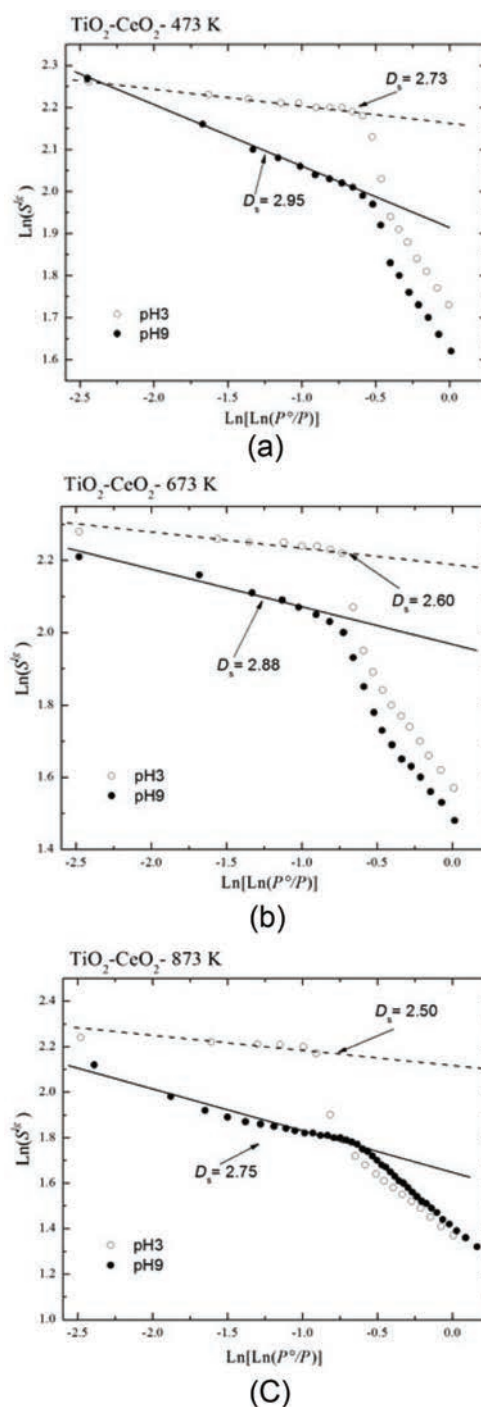


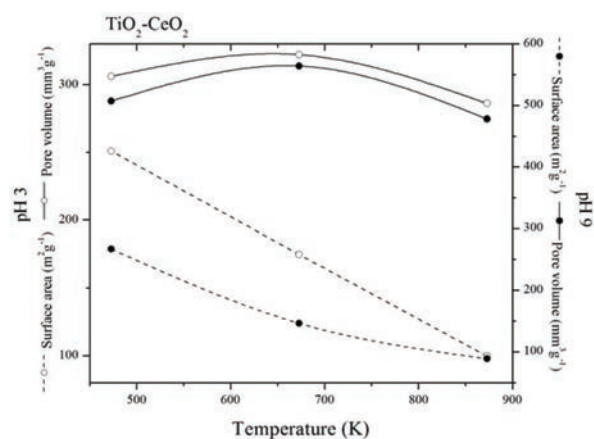
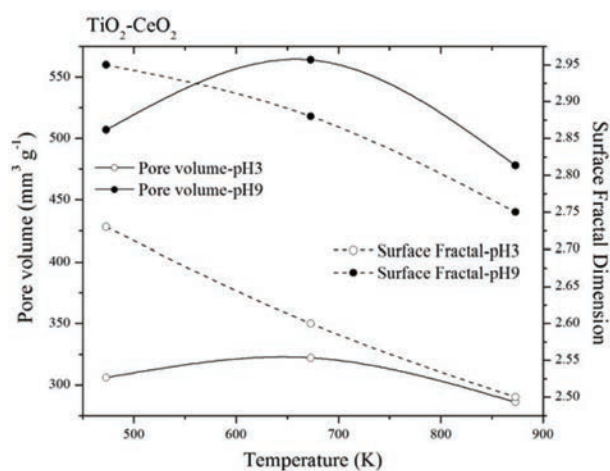
Fig. 2. Frenkel-Halsey-Hill fractal analysis of the desorption isotherms of the $\text{TiO}_2\text{-CeO}_2$ materials. (a) $\text{TiO}_2\text{-CeO}_2$ -pH 3 and pH 9 at 473 K, (b) $\text{TiO}_2\text{-CeO}_2$ -pH 3 and pH 9 at 673 K and (c) $\text{TiO}_2\text{-CeO}_2$ -pH 3 and pH 9 at 873 K.

Table 3. Specific surface area, pore volume, mean pore size and surface fractal dimension for the $\text{TiO}_2\text{-CeO}_2$ -pH 3 sample annealed at different temperatures

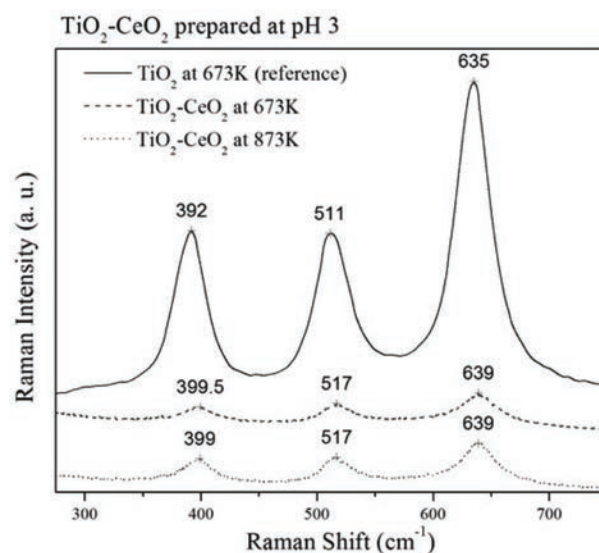
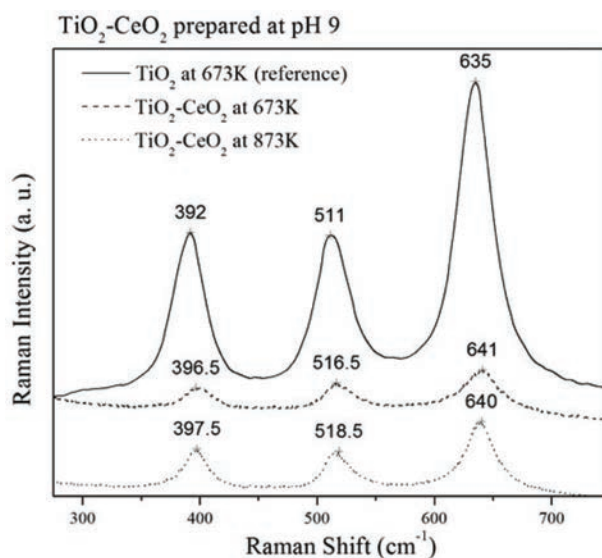
Substrate	Surface area (m^2g^{-1})	Pore volume ($\text{mm}^3 \text{g}^{-1}$)	Mean pore size (nm)	Surface Fractal Dimension
$\text{TiO}_2\text{-CeO}_2$ -pH 3 473 K	250	306	3.5	2.73
$\text{TiO}_2\text{-CeO}_2$ -pH 3 673 K	174	322	5.4	2.60
$\text{TiO}_2\text{-CeO}_2$ -pH 3 873 K	99	286	9.0	2.50

Table 4. Specific surface area, pore volume, mean pore size and surface fractal dimension for the $\text{TiO}_2\text{-CeO}_2\text{-pH 9}$ sample annealed at different temperatures

Substrate	Surface area (m^2g^{-1})	Pore volume (mm^3g^{-1})	Mean pore size (nm)	Surface Fractal Dimension
$\text{TiO}_2\text{-CeO}_2\text{-pH 9 473 K}$	267	507	3.3	2.95
$\text{TiO}_2\text{-CeO}_2\text{-pH 9 673 K}$	146	564	4.4	2.88
$\text{TiO}_2\text{-CeO}_2\text{-pH 9 873 K}$	88	478	7.4	2.75

**Fig. 3.** Pore volume and surface area of the $\text{TiO}_2\text{-CeO}_2$ samples as a function of the annealing temperature.**Fig. 4.** Pore volume and surface fractal dimension of the $\text{TiO}_2\text{-CeO}_2$ samples as a function of the annealing temperature.

at annealing temperatures of 473 and 873 K respectively. The dependence between the specific surface and the mean pore size diameter as a function of the annealing temperature is illustrated in Fig. 1. On the other hand, the fractal dimension (D_s) calculated from the adsorption-desorption isotherms is illustrated in Fig. 2. [22, 23]. The calculated results reported for the various samples in Tables 3 and 4 show that in these materials the fractal dimension diminishes with the annealing temperature and this diminution is more important for the solids prepared at pH 3. The diminution of D_s with the increasing annealing temperatures implies that the wall pores of the solids were smoothed by sintering effects (Figs. 3 and 4)

**Fig. 5.** Raman spectra for the TiO_2 and $\text{TiO}_2\text{-CeO}_2\text{-pH3}$ materials annealed at different temperatures.**Fig. 6.** Raman spectra for the TiO_2 and $\text{TiO}_2\text{-CeO}_2\text{-pH 9}$ materials annealed at different temperatures.

[24, 25]. It can also be seen in Tables 3 and 4, that the fractal dimension values are smaller for the solids prepared at pH 3 ($2.50 < D_s < 2.73$) than those obtained on the solids prepared at pH 9 ($2.75 < D_s < 2.95$). Thus the roughness of the surface exposed by the samples prepared at pH 9 is higher than that exposed by the materials prepared at pH 3.

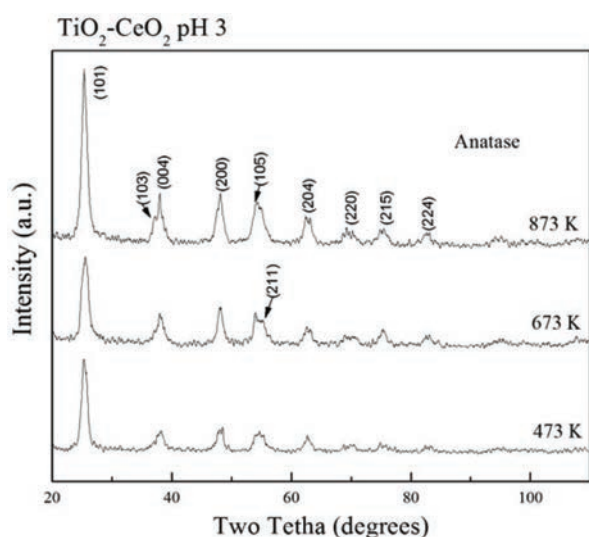


Fig. 7. X-ray diffraction patterns of the $\text{TiO}_2\text{-CeO}_2\text{-pH 3}$ materials annealed at different temperatures.

Raman spectroscopy

The Raman spectra for the TiO_2 (sol-gel reference) $\text{TiO}_2\text{-CeO}_2\text{-pH 3}$ and $\text{TiO}_2\text{-CeO}_2\text{-pH 9}$ materials in the $300\text{--}750\text{ cm}^{-1}$ region are presented in Figs. 5 and 6. In the Raman spectra the peaks at 392 , 511 and 635 cm^{-1} assigned to the anatase crystalline phase can be clearly seen in all the samples [26]. However, they appear shifted to a higher energy in the ceria-containing solids. The shift of the anatase peaks in the Raman spectra can be taken as a proof of the perturbation of the Ti-O-Ti bonds by the insertion of Ce^{4+} into the titania network forming some Ti-O-Ce-O-Ti bonds [27]. Since the shift is of the same order in both titania-ceria preparations, we can say that the insertion of Ce^{4+} into the anatase structure is independent of the pH used for the gelling of the titanium alkoxide.

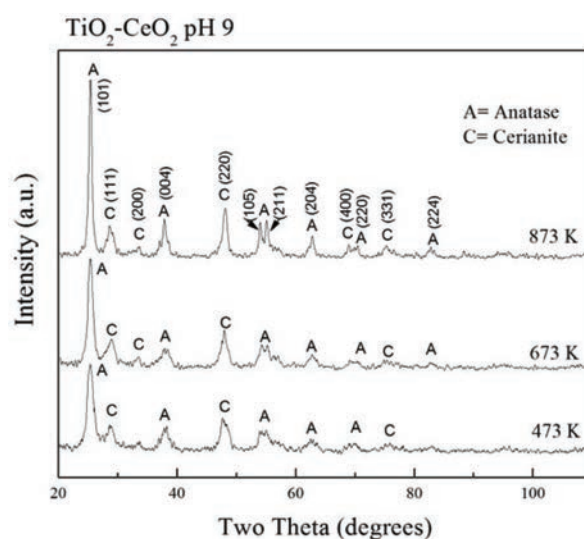


Fig. 8. X-ray diffraction patterns of the $\text{TiO}_2\text{-CeO}_2\text{-pH 9}$ materials annealed at different temperatures.

Phase concentration, crystallite size, interplane distances, occupancy and microstrain

The X-ray diffraction patterns for the sol-gel samples synthesized at pH 3 and pH 9 annealed at 473 , 673 and 873 K are shown in Figs. 7 and 8. For the pH 3 preparation only the peaks corresponding to the anatase phase can be seen, in this preparation the anatase phase was strongly stabilized. However, for the samples prepared at pH 9 the anatase phase as well as the formation of cerianite can be observed. These results show that the effect of the pH on the preparation of the titania-ceria mixed oxides, if any, is related to modifications in the structural properties of the solids. The parameters characterizing the crystalline structure of the solids were calculated by Rietveld refinement and reported in Tables 5 and 6 [28]. For the

Table 5. Rietveld refinement results for the $\text{TiO}_2\text{-CeO}_2\text{-pH 3}$ sample annealed at different temperatures

Substrate (anatase)	Crystallite size (nm)	$d_{(h\ k)}$				$*O_{Ti}$	$[V_{Ti}^{+4}]$	$\varepsilon_{str}(\%)$
		$d_{(101)}$	$d_{(004)}$	$d_{(200)}$	$d_{(105)}$			
$\text{TiO}_2\text{-CeO}_2\text{-pH 3 473 K}$	8.9 (7)	0.3518	0.2367	0.1895	0.1694	0.069 (18)	44.8	3.06
$\text{TiO}_2\text{-CeO}_2\text{-pH 3 673 K}$	21.0 (10.3)	0.3520	0.2373	0.1895	0.1697	0.097 (9)	22.4	2.99
$\text{TiO}_2\text{-CeO}_2\text{-pH 3 873 K}$	43.6 (2)	0.3520	0.2375	0.1895	0.1698	0.100 (21)	20.0	2.00

The number in parenthesis corresponds to the standard deviation; d : interplanar distance (nm)

O_{Ti} : Titanium occupancy; $[V_{Ti}^{+4}]$: Titanium deficiency per unit cell (%)

*The Ti occupancy for stoichiometric composition is 0.125.

ε_{str} : microstrain

Table 6. Rietveld refinement results for the $\text{TiO}_2\text{-CeO}_2\text{-pH9}$ annealed at different temperatures (anatase)

Substrate (anatase)	wt (%)	Crystallite size (nm)	$d_{(h\ k)}$				$*O_{Ti}$	$[V_{Ti}^{+4}]$	$\varepsilon_{str}(\%)$
			$d_{(101)}$	$d_{(004)}$	$d_{(200)}$	$d_{(105)}$			
$\text{TiO}_2\text{-CeO}_2\text{-pH 9 473 K}$	75.0	7.1 (19)	0.3524	0.2428	0.1898	0.1696	0.113 (11)	9.6	1.68
$\text{TiO}_2\text{-CeO}_2\text{-pH 9 873 K}$	89.0	21.0 (7)	0.3515	0.2372	0.1892	0.1696	0.103 (12)	17.6	1.63

The number in parenthesis corresponds to the standard deviation; d : interplanar distance (nm)

O_{Ti} : Titanium occupancy; $[V_{Ti}^{+4}]$: Titanium deficiency per unit cell (%)

*The Ti occupancy for stoichiometric composition is 0.125.

ε_{str} : microstrain

acid preparation it can be seen in Table 5 that the crystallite sizes increase with the annealing temperature. However, the site is always within the nanosize range (8.9, 21 and 43.6 nm) for annealing temperatures of 473, 673 and 873 K respectively. As for the titanium deficiency per unit cell (%) it can be seen that the highest titanium deficiency (44.8%) corresponds to solids showing the smallest crystallite size (8.9 nm). As the crystallite size increases (21 to 43.6 nm) the titanium deficiency (22.4 and 20.0%) as well as the microstrain (3.06 to 2.00 %) of the solids diminishes.

On the other hand, for the solids prepared at pH 9 the crystallite sizes calculated for the anatase phase were 7.1, 15.0 and 21.0 nm for annealing temperatures of 473, 673 and 873 K respectively. They were smaller than those obtained with the pH 3 preparation (Tables 5 and 6), however an opposite behavior was observed in these solids since as the crystallite size increases, the titanium deficiency increases as well as 9.6, 12.4 and 17.6% for 473, 673 and 873 K of annealing temperature respectively. The microstrain calculated for the different samples is smaller and then it could be considered as constant and independent of the annealing temperature. It must be noted that the calculated results for the pH 9 preparation were done from the X-ray data and Rietveld refinement for the anatase phase, however in the X-ray diffraction spectra an important formation of cerianite is observed. In Table 7 the relative abundance of the cerianite phase as well as its crystallite size are reported. A diminution of the nanosized (5.7 to 8.0 nm) cerianite relative abundance from 25 to 11 wt% as the temperature increases from 473 to 873 K is observed. These results confirm that the effects of the gelling pH on the preparation of titania-ceria solids are mainly related to their structural properties [29].

Electron density distribution

Point defects in a nanocrystalline TiO_2 semiconductor are formed during the annealing of the samples, x cation vacancies were created and led to the formation of a non stoichiometric $\text{Ti}_{1-x}\text{O}_2$ semiconductor. During the annealing the point defects are created by a change in the position of the Ti^{4+} which migrates through the interstitial sites (a Frenkel defect) to occupy lattice vacancies. They can also be formed by the migration of the Ti^{4+} from the bulk lattice sites (Schottky defect) to the lattice sites on the surface of the crystal [27, 30]. This cation migration generates a reposition on the charge distribution in the crystal, which can be illustrated by the Fourier map

Table 7. Rietveld refinement results for the $\text{TiO}_2\text{-CeO}_2$ -pH 9 sample annealed at different temperatures (cerianite)

Substrate (cerianite)	wt (%)	Crystallite size (nm)
$\text{TiO}_2\text{-CeO}_2$ -pH 9 473 K	25.0	5.7 (25)
$\text{TiO}_2\text{-CeO}_2$ -pH 9 873 K	11.0	8.0 (29)

The number in parenthesis corresponds to the standard deviation.

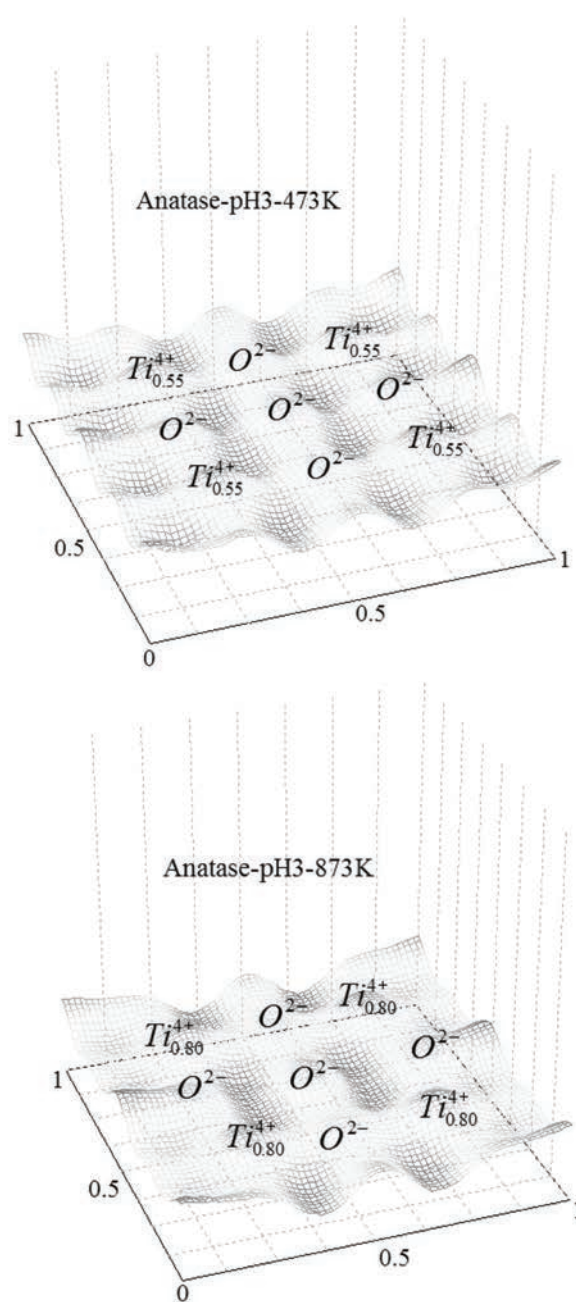


Fig. 9. Electron density distribution maps of the $\text{TiO}_2\text{-CeO}_2$ -pH 3 sample annealed at different temperatures.

showing the electron density of a segment of the unit cell, in this case, that of the anatase phase [31, 32].

The Fourier maps for the titania-ceria semiconductors annealed at the selected temperatures of 473 and 873 K are presented in Figs. 9 and 10 for the acid and basic preparations respectively. For the pH 3 preparations, a contracted electron density map can be seen in both samples, which is in agreement with the fractal dimension values of 2.73 (473 K) and 2.5 (873 K) reported in Table 3. On the other hand, for the semiconductors prepared at pH 9 enlarged electron density maps are observed in both samples. Moreover, an important roughness of the surface can be observed. For these samples the highest surface

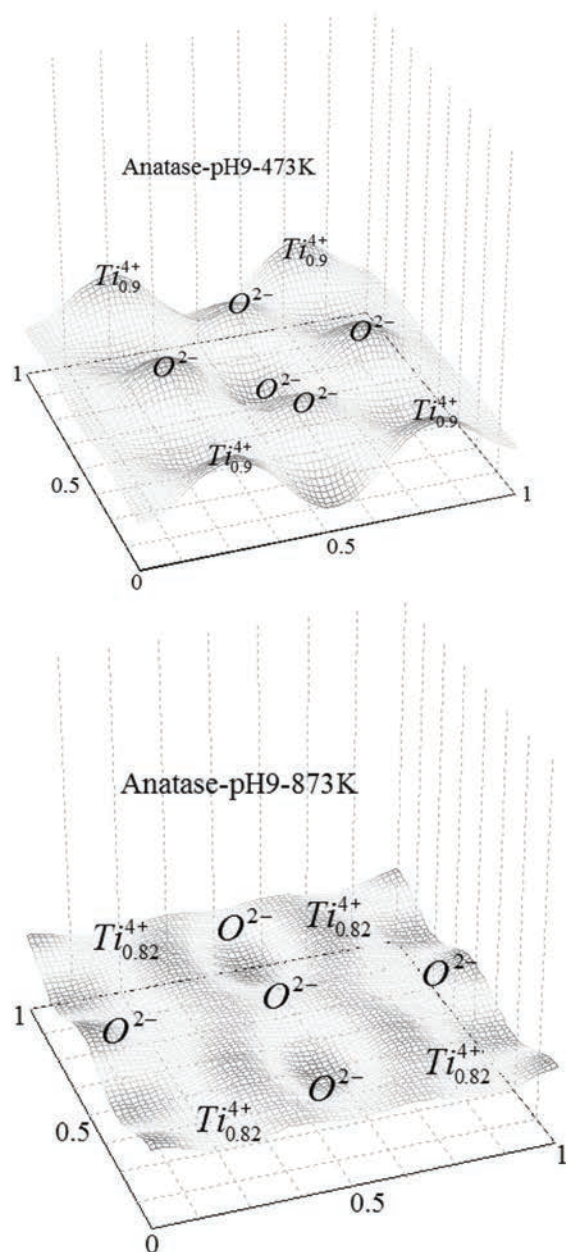


Fig. 10. Electron density distribution maps of the $\text{TiO}_2\text{-CeO}_2\text{-pH 9}$ sample annealed at different temperatures.

fractal dimension 2.95 and 2.75 (Table 4) were obtained. These results showed the importance of the electron density maps for they help to appreciate the big differences in the electron distributions on the anatase surface, which strongly depends on the preparation conditions of the semiconductors.

Conclusions

In $\text{TiO}_2\text{-CeO}_2$ semiconductors prepared by the sol-gel method the pH of the gelling conditions is an important factor which induces significant differences in the textural and structural properties of the solids. It is shown that the mean pore size for the sample prepared at pH 3 is

narrowed and bigger than that obtained in the sample prepared at pH 9. Anatase was the only crystalline phase observed by X-ray diffraction in the acid preparation, whereas in the basic one, anatase and cerianite coexist. In both preparations nanocrystalline anatase was obtained. Depending on the synthesis conditions the number of titanium deficiencies per unit cell was strongly modified. The Fourier electron density maps showed that a contracted electron distribution was obtained with the acid synthesis. Meanwhile with the basic conditions an enlarged electron distribution and important surface roughness were observed.

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