



Ecofriendly liquid phase oxidation with hydrogen peroxide of 2,6-dimethylphenol to 2,6-dimethyl-1,4-benzoquinone catalyzed by TiO₂–CeO₂ mixed xerogels

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ABSTRACT

Titania–ceria mixed xerogels were prepared with 10% (w/w) CeO₂ and different pH values during the sol–gel process. The gels were dried in air and calcined at different temperature. Moreover, a sample without cerium, 100% (w/w) TiO₂, was prepared to be kept as reference material. The prepared solids were characterized by means of XRD, SEM, DRS, FT-IR, TEM and EDX. Their textural properties were determined by adsorption–desorption isotherms of N₂ at 77 K.

The xerogels were tested as catalysts in the liquid phase oxidation of 2,6-dimethylphenol at 20 °C, using ethanol as solvent and aqueous hydrogen peroxide as a clean oxidizing agent. The 2,6-dimethyl-*p*-benzoquinone yield achieved was of 85–96% using the mixed xerogels as catalysts, and of 49% when the catalyst of titania without cerium was used. The best performance was achieved by the mixed xerogel synthesized at pH 4 and calcined at 200 °C; 100% of conversion of 2,6-dimethylphenol and 96% of yield in 2,6-dimethyl-*p*-benzoquinone were obtained in this case after 6 h of reaction. The reactions were again carried out with the catalyst recovered after its first use. Only a light yield decrease, lower than 2%, was observed.

The use of an ethanol–water mixture as solvent (35:65% (v/v)) in the reaction was studied in order to make the reaction more environmentally friendly. Total conversion of the initial reactant, after 4 h of reaction at 20 °C, with 70% yield in 2,6-dimethyl-*p*-benzoquinone (2,6-DMBQ), was observed. Under these conditions a red by-product, insoluble in the reaction solution, was formed. This by-product was isolated and characterized and it was possible to identify it as 2,6-DMBQ dimmer (3,3',5,5'-tetramethyl-4,4'-diphenquinone). This by-product was observed in very few amounts when ethanol (96% (v/v)) was used as solvent.

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1. Introduction

Titania (TiO₂) is widely used in the field of heterogeneous catalysis [1]. It has been demonstrated that it is a solid whose catalytic properties may be modified by a supported cation. It is usual to add other atoms to titania, such as cerium, in order to improve its properties, for example its structural stability. Pure and stoichiometric titania changes its stoichiometry when it is doped with a cation having a valence different than 4⁺, or when the titanium valence is reduced from 4⁺ to 3⁺.

The chemical and electronic properties of this nonstoichiometric titania depend on the defect density and the impurity concentration in the crystal [2]. The sol–gel technique is one of the methods for preparing nonstoichiometric titania. A high defect density in the sol–gel titania crystals is produced during the

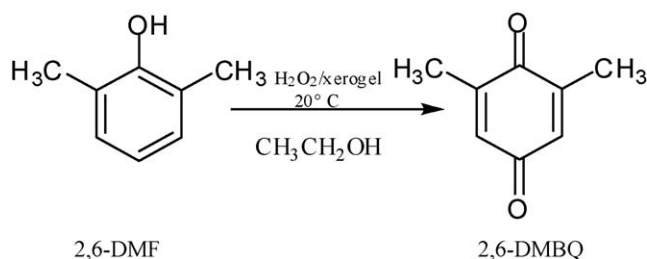
dehydroxylation of the sample. The sol–gel technique can also be used to either incorporate metal atoms into the crystal lattice or to deposit them, as small particles, on the crystal surface.

The physical and chemical features of the material obtained by this method (e.g., particle sizes, surface areas, mechanical properties) can be changed according to the temperature, operating conditions, and the used precursor [3].

On the other hand, the most significant oxide of rare-earth elements in industrial catalysis certainly is CeO₂. It has potential use for the removal of organics from wastewaters (catalytic wet oxidation), as additive for combustion catalysts and in redox reactions [4]. The most important property of CeO₂ is that it can be used as an oxygen reservoir [5].

According to the above-mentioned studies, titania–ceria mixed xerogels were prepared. They were characterized and tested as catalysts in the oxidation of 2,6-dimethylphenol (2,6-DMP) to 2,6-dimethyl-*p*-benzoquinone (2,6-DMBQ) (Scheme 1), using aqueous hydrogen peroxide as oxidant. The 2,3,6-trimethyl-*p*-benzoquinone is an intermediate in the industrial production of Vitamin E

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Scheme 1. Liquid phase oxidation of 2,6-dimethylphenol (2,6-DMP) to 2,6-dimethyl-*p*-benzoquinone (2,6-DMBQ).

[6], and the 2,6-dimethyl-*p*-benzoquinone is a key intermediate for the synthesis of a number of medicines and physiologically active substances. The latter can be used for the synthesis of trimethylbenzoquinone or for the preparation of indophenol [7].

Previously we studied this reaction using aqueous hydrogen peroxide as oxidant at low temperature (20 °C) with catalysts based on heteropolyacids [8]. This work seeks to contribute to the search of new heterogeneous catalysts to carry out the oxidation of organic compounds in an environmentally sustainable way.

2. Experimental

2.1. Materials and synthesis

The material, TiO₂–CeO₂ (90% (w/w) TiO₂ –10% (w/w) CeO₂), was prepared by the sol–gel method using titanium isopropoxide (Aldrich, 97%) and hexahydrated cerium nitrate (Aldrich, 99%) as precursors. Absolute ethanol (Aldrich, 99.8%) was used as solvent for both reactants, with an alkoxide/solvent molar ratio of 1/16 and a 0.2 M concentration for the cerium salt. The mixture was kept refluxing with continuous stirring. The solution pH was fitted to 2 (or 3 or 4) with a HNO₃ (Anedra, 40%) solution 0.01 M. Then, water was added dropwise for 4 h, using a water/alkoxide molar ratio of 8/1.

The selection of reactive amounts and the water addition rate to the mixture were based on the synthesis used by López et al. [9], in order to reach a significant interaction between the involved ions and the hydrolyzed species, for example, –Ti–OH, –Ti–O[–], and –Ti–OR. The reaction mixture was kept refluxing until a yellow gel was formed. The xerogel was obtained by air-drying at 50 °C for 24 h. Finally, it was calcined at two temperatures, 200 and 800 °C for 4 h.

The samples were named Ti9–pH–*T* °C, for the samples with 90% (w/w) TiO₂ –10% (w/w) CeO₂, and according to the preparation pH and drying or calcination temperature. On the other hand, samples without cerium, 100% (w/w) TiO₂, were prepared as reference material, following the same synthesis. They were named Ti10–pH–*T* °C.

2.2. Solids characterizations

2.2.1. X-ray diffraction – XRD

XRD patterns of solid samples were recorded by means of a Philips PW-1732 device with built-in recorder, using the following conditions: Cu K_α radiation ($\lambda = 1.5417 \text{ \AA}$); Ni filter; 20 mA and 40 kV in the high voltage source; scanning angle (2θ) from 20° to 80°, scanning rate 2°(2θ)/min and vertical scale amplitude 2000 counts/s.

2.2.2. Textural properties

The nitrogen adsorption/desorption isotherms at 77 K on TiO₂–CeO₂ and TiO₂ solids were determined by using Micromeritics ASAP 2020 equipment. The previous degasification was carried out for 700 min at 100 °C and below of 30 $\mu\text{m Hg}$. From these

isotherms it was possible to determine the specific surface area (S_{BET}), the pore volume, and the mean pore diameter of the samples.

2.2.3. Scanning electron microscopy – SEM

The solids were characterized by a Philips 505 scanning electron microscope using an accelerating voltage of 20 eV and a magnification range of 2500–10,000 \times . The samples were metallized with Au.

2.2.4. Transmission electron microscopy – TEM and EDX

In this study a JEOL transmission electron microscope, JEM-2010 model, was used. Above the grid sample holder was placed a film of acetate of cellulose butyrate dissolved in ethyl acetate, and were placed drops of glycerin to form holes. A film of carbon was finally put to increase resistance.

2.2.5. Diffuse reflectance spectroscopy – DRS

The solid samples were studied in the range 200–1100 nm, using a PerkinElmer Lambda 35 UV–vis double beam spectrophotometer, fitted with a diffuse reflectance chamber with an inner surface of BaSO₄. The equipment was used with a scanning rate of 240 nm/min and Spectralon as reference. Samples were compacted in a Teflon sample holder to obtain a sample thickness of 2 mm.

2.2.6. Fourier transform infrared spectroscopy

Thermo Nicolet IR 200 equipment, pellets with BrK, and a measuring range of 400–4000 cm^{–1} were used to obtain the FT-IR spectra of the solid samples.

2.2.7. Catalytic test

The oxidation of 2,6-dimethylphenol was performed under vigorous stirring in a glass reactor at low temperature (20 °C). The reactions were performed by adding 1 ml of H₂O₂ (Analquim, 60% (w/v)) dropwise to a solution of 1 mmol of 2,6-dimethylphenol (Aldrich, 99%), 5 ml of solvent, and 0.1 mmol of catalyst (Xerogel). Acetone (J. T. Baker, 99.7%), ethanol (Soria 96) or a water/ethanol mixture (65% (v/v) water) was used as solvent. The reaction was followed by TLC (thin layer chromatography) at different times. TLC aluminum sheets (silica gel 60 F254, Merck), a commercial standard of 2,6-DMP and 2,6-DMBQ (Aldrich, 99%) and CH₂Cl₂ (Anedra) as solvent were used. The reaction mixture was centrifuged and the catalyst was separated. The solution was diluted with 10 ml of distilled water and extracted with dichloromethane (2 \times 5 ml). The organic extract was dried over anhydrous sodium sulphate and the solvent evaporated by a rotary evaporator. The product obtained (crude product) was analyzed by UV–vis spectroscopy in PerkinElmer Lambda 35. For their analysis the samples were diluted in ethanol (30 ppm).

The reaction product, 2,6-DMBQ, was identified by a MS-GC (Mass Spectrometer (Perkin Elmer Q-Mass 910) coupled to a Gas Chromatograph (Perkin Elmer Autosystem)).

The yield of reaction was calculated as the weight ratio between the obtained amount of 2,6-dimethyl-1,4-benzoquinone (crude product) and the theoretical amount of product that would be formed.

3. Results and discussion

In a previous work [10], several samples of TiO₂–CeO₂ mixed oxides were prepared by the sol–gel method using different pHs, they were dried and calcined at different temperatures. Also samples without Ce were prepared following the same synthesis. The solids obtained were characterized by different techniques.

XRD studies showed for all the samples a similar change of the diffraction patterns as a function of the heating temperature

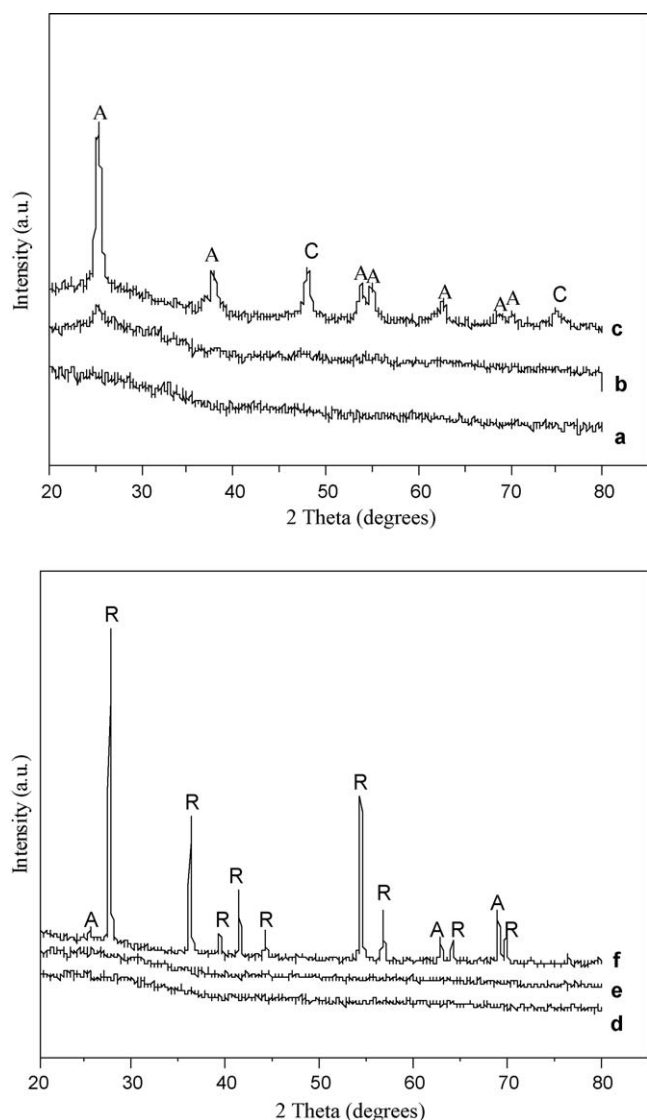


Fig. 1. Powder XRD patterns of samples: (a) Ti9-pH3-50, (b) Ti9-pH3-200, (c) Ti9-pH3-800, (d) Ti10-pH3-50, (e) Ti10-pH3-200 and (f) Ti10-pH3-800. (R) Rutile, (A) Anatase, (C) Cubic CeO₂.

increase. XRD patterns corresponding to the samples Ti9-pH3-*T* °C and Ti10-pH3-*T* °C are shown in Fig. 1. Characteristic patterns of amorphous materials, very wide bands without well-defined diffraction lines, are observed before and after heating at 200 °C (Fig. 1a, b, d, and e). The sample calcined at 800 °C leads to characteristic patterns of crystalline solids showing a series of well-defined peaks.

The presence of anatase phase, as the main species, together with CeO₂ in cubic phase are clearly identified (Fig. 1c) for the Ti9-pH3-800 sample. However, the presence of rutile phase is mainly detected for the Ti10-pH3-800 sample (Fig. 1f).

It is important to emphasize that the presence of Ce stabilizes to the anatase phase of TiO₂, according to ref. [1]. In Fig. 1b (mixed xerogel prepared at pH 3 and calcined at 200 °C) the main peak of anatase begins to be formed, although it is hardly observed. However, the initial formation of anatase is not observed for the Ti9-pH4-200 sample.

The N₂ adsorption-desorption isotherms on mixed oxides are shown in Fig. 2a and b. In Fig. 2a the isotherms for xerogels Ti9-pH3 with different heat treatments are compared. The isotherms of xerogels without Ce (Ti10-pH3-200), and with Ce prepared at

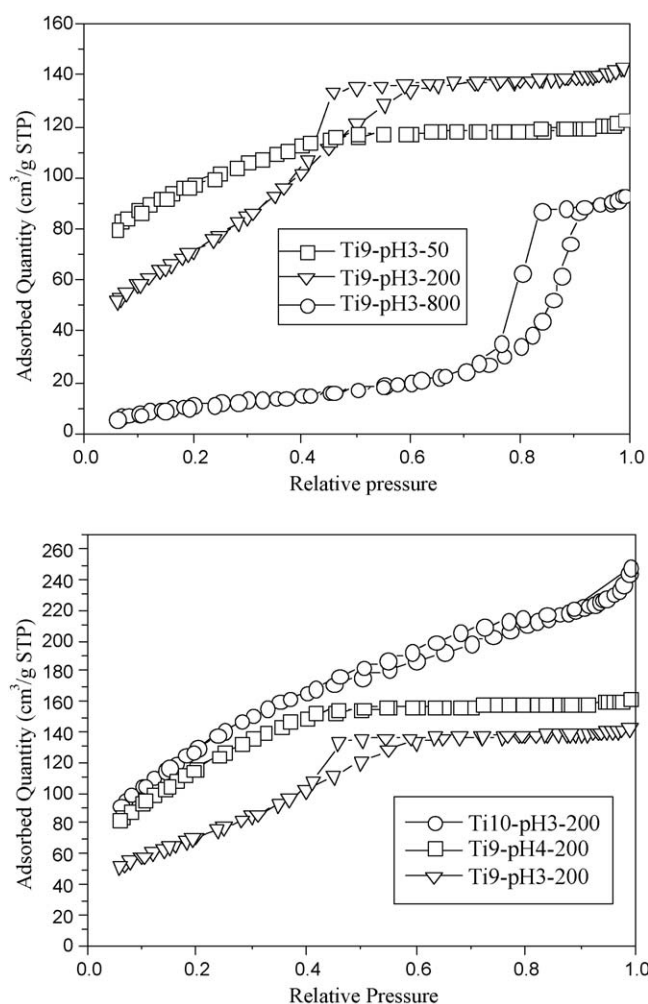


Fig. 2. Nitrogen adsorption-desorption isotherms of samples: (a) Ti9-pH3 dried and calcined and (b) Ti9-pH3, Ti9-pH4 and Ti10-pH3 calcined at 200 °C.

pH 3 (Ti9-pH3-200) and at pH 4 (Ti9-pH4-200) are shown in Fig. 2b.

The isotherm shape of the Ti9 and Ti10 samples treated at 50 and 200 °C, independently of the pH, corresponds to hysteresis cycles of type H2, characteristic of porous sol-gel materials [11]. However, in some cases the isotherm shape is of this type although the hysteresis cycle can hardly be observed, which may indicate the existence of irregular pores in the solids [12]. On the other hand, the isotherms of all samples calcined at 800 °C are of type II, according to the classification of Brunauer, Deming, Deming and Teller [A. Baiker, 13], corresponding to nonporous solids. The values of specific surface area (S_{BET}), pore volume, and mean pore diameter obtained from the isotherms [14] shown that the temperature variation in the final treatment of the prepared sol-gel samples modified the material textural properties. An increase of calcination temperature to 800 °C led, together with the formation of crystalline phases, to a considerable decrease of S_{BET} and pore volume, and to an increase of the mean pore diameter.

The S_{BET} and pore volume values of xerogel significantly decreased with Ce addition, at around 45% for the samples prepared at pH 3 and calcined at 200 °C (Table 1, entries 1 and 3). However, the mean pore diameter for these samples slightly changed when Ce was added, at around 10%. Also, the S_{BET} of xerogel significantly decreased when preparation pH changes from 4 to 3 (Table 1, entries 1 and 2).

Table 1
Textural properties of the samples prepared by sol–gel method.

Entry	Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (nm)
1	Ti9-pH3-200	264	0.22	3.3
2	Ti9-pH4-200	437	0.25	2.3
3	Ti10-pH3-200	485	0.37	3.0

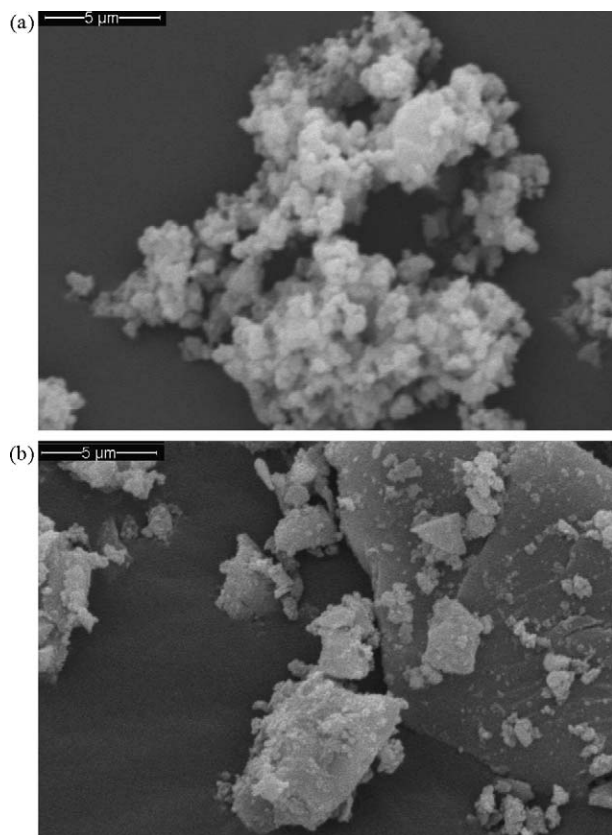


Fig. 3. SEM micrographs of samples (5000 \times): (a) Ti10-pH3-200, (b) Ti9-pH3-200. Effect of cerium addition in xerogels morphology.

The particle morphology of the xerogels treated at different temperatures was studied by SEM. The scanning electron micrographs are presented in Fig. 3. The xerogel of pure TiO_2 (Fig. 3a), Ti10-pH3-200, looked like an open agglomerate of irregular particles with spherical shape. When the particles were calcined at 800 °C, a notable sintering of the particles was observed. This behavior is according to the BET area values mentioned for the calcined solids at the same temperature (Table 1).

The SEM micrographs of TiO_2 – CeO_2 mixed xerogels (Ti9-pH3-200) show a heterogeneous morphology; particle agglomerates, similar to those previously described, separated by larger irregular particles were observed (Fig. 3b).

In Fig. 4, series of TEM micrographs of mixed xerogel samples are presented. In all them particle agglomerates are observed. For Ti9-pH4-200, a particle size of 9–11 nm was estimated. When the solid calcination temperature was 800 °C, it is possible to prove a particle size increase up to 13–17 nm, and crystal formation. In the latter case, perceptible signs of the crystallographic planes corresponding to (1 0 1) for TiO_2 anatase phase, and to (2 2 0) for CeO_2 [15] were observed. This analysis agrees with the obtained XRD results.

On the other hand, the sol–gel materials were characterized by diffuse reflectance spectroscopy. Pure TiO_2 samples (white solid)

DRS spectra present a band between 250 and 350 nm. A band shifting to the visible, between 250 and 600 nm, is observed when cerium was added (yellow solid). According to ref. [16], a band in the range between 200 and 240 nm is due to the charge transfer of the isolated sites of tetrahedral titanium between the O^{2-} and central atoms of Ti (IV), while for octahedral Ti the band appears around 260–330 nm. Then in all the samples it is possible to observe Ti (IV) in octahedral coordination.

The FT-IR spectra of the mixed and pure xerogels, calcined at 200 °C, are shown in Fig. 5. It is possible to distinguish wide absorption bands at 3421 cm^{-1} for all the samples, corresponding to the elongation mode of the –OH group, which is ascribed to the presence of occluded water and surface titanol groups (Ti–OH) with hydrogen bridges. The presence of an intense peak at 1633 cm^{-1} corresponds to stretching of the hydroxyl groups present [17]. The band around 600 cm^{-1} appears due to the Ti–O–Ti vibration bond, which results from the condensation reactions [18]. This band is very wide and intense for the pure Ti sample, but it is modified for Ti/Ce mixed oxides, which indicates the presence of Ti–O–Ce bonds in the mixed xerogels.

Also, it is possible to see contamination by nitrate, an intense peak at 1385 cm^{-1} for the sample dried at 50 °C, which disappears after heating at 800 °C (Fig. 6). The main absorption peak of TiO_2 is ascribed to the Ti–O bond that appears at 500 – 510 cm^{-1} and corresponds to the anatase phase [19]. This is observed for Ti9-pH3-800 (Fig. 6) in accordance with XRD results.

Previous experiences were carried out using the prepared xerogels as catalysts in the 2,6-DMP oxidation to 2,6-DMBQ with hydrogen peroxide as oxidant and acetone as solvent. They allowed us to conclude that the catalysts prepared at pH 3 and 4 and calcined at 200 °C are the most catalytically active [10]. This result is a consequence of their low crystallinity and high specific surface area, as XRD and S_{BET} values demonstrated.

Therefore, the xerogels Ti9-pH4-200 and Ti9-pH3-200 were used as catalysts in the above-mentioned reaction, using in this case ethanol instead of acetone, because that solvent is more environmentally benign. Also the catalyst without Ce, Ti10-pH3-200, was tested.

The catalytic activity results of the 2,6-DMP to 2,6-DMBQ oxidation reaction are shown in Table 2. Experiences without catalyst were carried out in both reaction solvents. In these cases, the conversion of 2,6-dimethylphenol after 6 h of reaction, followed by TLC, was not observed (Table 2, entry 1). Also, conversion to 2,6-DMBQ was not obtained when the reaction was carried out without H_2O_2 but in the presence of catalyst (Table 2, entry 2).

When Ti9-pH4-200 was used as catalyst, total conversion of 2,6-dimethylphenol, 100% conversion of 2,6-DMP to 2,6-DMBQ according to the TLC following was observed after 6 h of reaction (Table 2, entry 3). From the crude product, yellow crystals with needle shape, a 96% yield in the respective quinone was estimated (Table 2, entry 3). The UV–vis spectrum of the crude product resulting from this reaction showed the presence of 2,6-DMBQ, because this product has its absorption maximum at 253 nm, and 2,6-DMP at 205 nm with a shoulder at 215 nm, and another band at 272 nm (Fig. 7). This result was corroborated by MS–GC.

On the other hand, the same experience was carried out but the catalyst was taken out of the reaction system after 2 h. This reaction solution was analyzed by TLC after 4 h, and 2,6-DMBQ was not observed. This result proves that the catalyst was not leaching during the reaction.

When the catalyst prepared at lower pH than the above-mentioned one was used, sample Ti9-pH3-200, yield decrease to 87% and an increase of reaction time to 7 h were observed (Table 2, entry 6). This result could be due to this catalyst presented lower specific surface area (Table 1, entries 1 and 2) and greater solid crystallinity than the Ti9-pH4-200 catalyst as it was above-

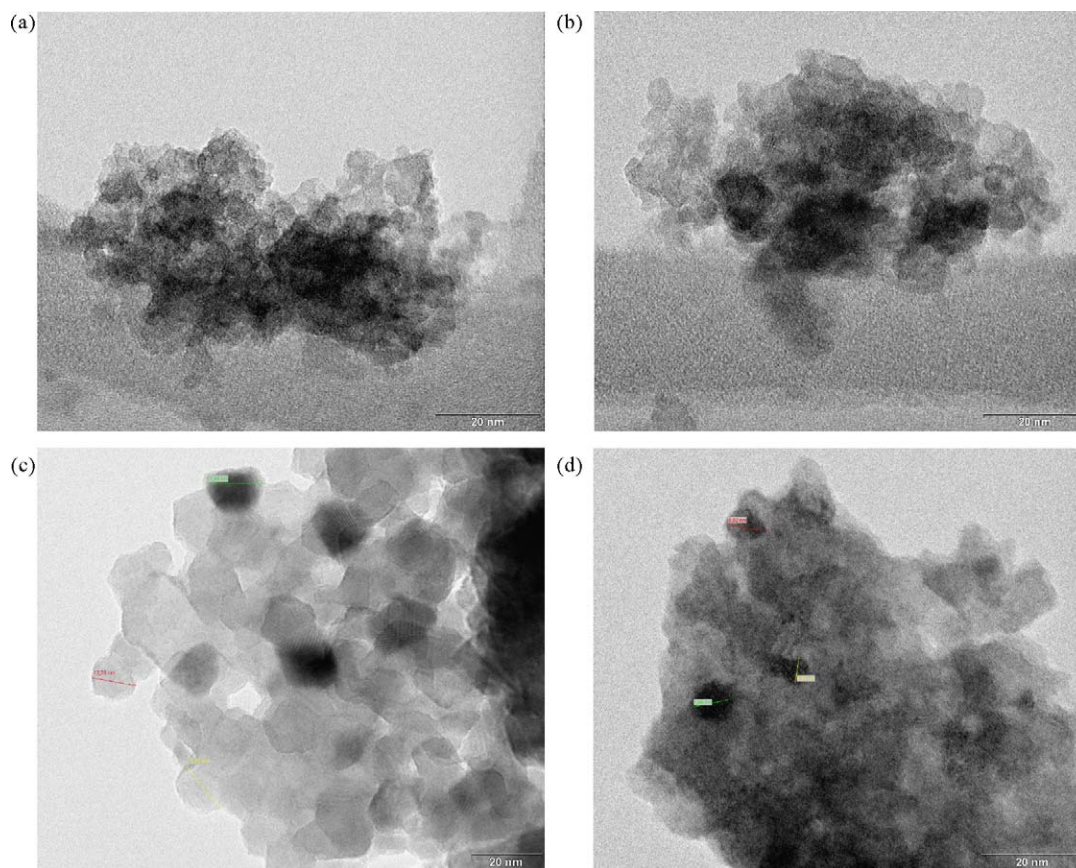


Fig. 4. TEM micrographs of prepared xerogels: (a) Ti9-pH3-50, (b) Ti9-pH3-200, (c) Ti9-pH3-800 and (d) Ti9-pH4-200. Effect of temperature during the heat treatment.

mentioned. Due to both facts, the Ce dispersion decrease and also decrease the oxygen capacity storage, and therefore the catalytic activity in the oxidation of 2,6-DMP to 2,6-DMBQ is lower [5]. The reactions using the catalysts prepared at pH 3 (Ti9-pH3-200) and pH 4 (Ti9-pH3-200) were again carried out with the catalyst recovered after its first use. Only a light yield decrease, lower than 2%, was observed (Table 2, entries 4 and 7). With respect to the analyses of the remaining crude products by UV-vis and MS-GC (Table 2, entries 4, 6 and 7), they also mainly showed the presence of 2,6-DMBQ.

On the other hand, when the reaction was carried out with the catalyst without Ce, prepared at pH 3 and calcined at 200 °C (Ti10-pH3-200), a decrease to 49% of the 2,6-DMBQ yield was observed (Table 2, entries 7 and 8). The positive effect of cerium on catalytic activity is observed. As above-mentioned, the CeO₂ can be used as an oxygen reservoir, which stores or releases oxygen via the redox shift between Ce⁴⁺ and Ce³⁺ under oxidizing or reducing conditions, respectively [5].

The use of an ethanol–water mixture as solvent in the reaction was studied in order to make the reaction more environmentally

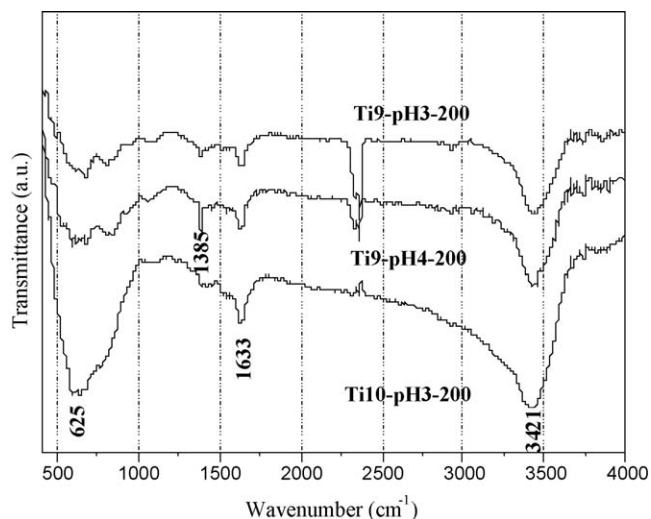


Fig. 5. FT-IR spectra of calcined xerogels at 200 °C.

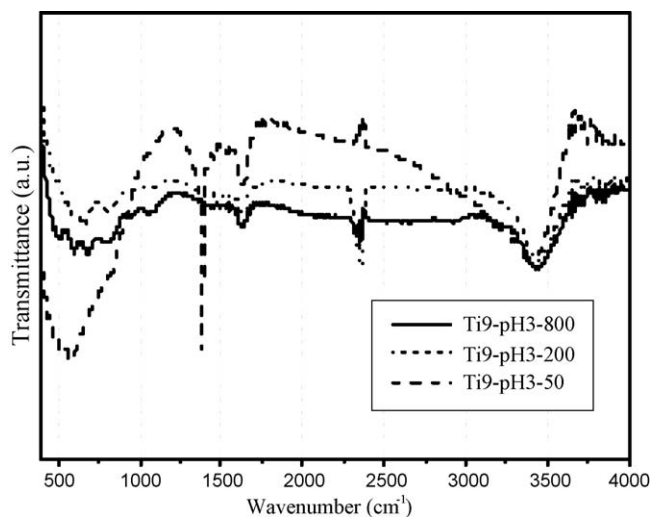


Fig. 6. FT-IR spectra of Ti9-pH3-T xerogels. Effect of temperature.

Table 2
2,6-dimethylphenol oxidation with H₂O₂ catalyzed by Ti/Ce sol–gel mixed oxides.

Entry	Catalyst	Reaction time (h)	2,6-DMP conversion (%) (TLC)	2,6-DMBQ yield (%)
1	–	7	0	–
2 ^a	Ti9-pH4-200	7	Traces	–
3	Ti9-pH4-200	6	100	96
4	Ti9-pH4-200 re-used	6	100	95
5 ^b	Ti9-pH4-200	4	100	70
6	Ti9-pH3-200	7	100	87
7	Ti9-pH3-200 re-used	7	100	85
8	Ti10-pH3-200	4	100	49

Reaction conditions: 1 mmol 2,6-DMP, 5 ml ethanol–water (96:4% (v/v)), 0.1 mmol catalyst, 1 ml H₂O₂, 20 °C.

^a Without H₂O₂.

^b Solvent: ethanol–water (35:65% (v/v)).

Table 3
By-product characterization.

Characterization techniques	Results
m.p. (lit. mp. [20] 207–210 °C)	205–208 °C
¹ H NMR (200 MHz, CDCl ₃ , TMS)	X/ppm 2.16 (s, 12H), 7.72 (s, 4H)
¹³ C NMR (50 MHz, CDCl ₃ , TMS)	X/ppm 17.17, 129.66, 138.98
MS (EI), 70 eV, m/z	(Relative intensity): 242 [M+2] (100), 240 [M] (20), 212 (8), 165 (7), 121 (13), 43 (27)
UV–vis (CHCl ₃)	λ _{max} /nm: 422
IR (KBr, cm ⁻¹)	1590 (vs)

friendly. Then, solubility tests of 2,6-DMP in ethanol–water mixtures were performed, and the limit solubility value was found in a 35% (v/v) ethanol solution. The activity of the Ti9-pH4-200 catalyst in the studied reaction using this solution as solvent was determined. Total conversion of the initial reactant, after 4 h of reaction at 20 °C, with 70% yield in 2,6-DMBQ, was observed (Table 2, entry 5). Under these conditions a red by-product, insoluble in the reaction solution, was formed. This by-product was isolated and characterized (Table 3). It was possible to identify it as 2,6-DMBQ dimmer (3,3',5,5'-tetramethyl-4,4'-diphenoquinone).

It is important to underline that this by-product was observed in very few amounts when ethanol 96% (v/v) was used as solvent. This result was observed by TLC of the reaction mixture and by UV–vis of the crude product.

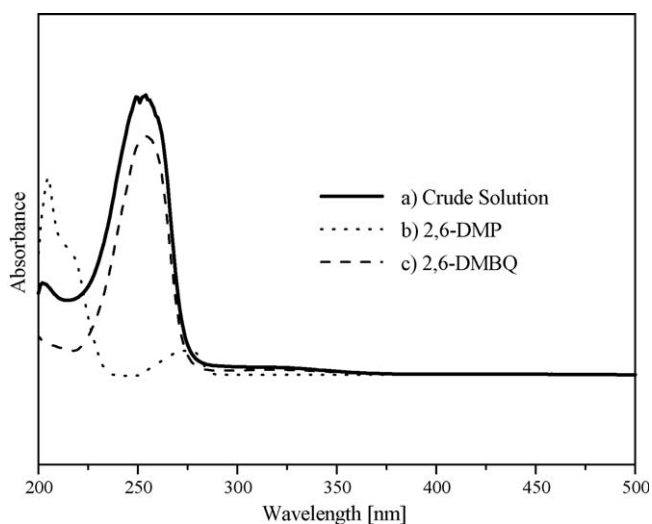


Fig. 7. UV–vis spectra of: (a) crude solution of studied reaction using Ti9-pH4-200 as catalyst, (b) 2,6-DMP and (c) 2,6-DMBQ commercial samples.

On the other hand, the 3,3',5,5'-tetramethyl-4,4'-diphenoquinone was oxidized to 2,6-DMBQ using ethanol–water (96:4% (v/v)), Ti9-pH4-200 as catalyst, and H₂O₂ as oxidant.

Then, it is possible to conclude that when a greater percentage of water is used in the reaction solvent, the selectivity to 2,6-DMBQ is lower, however the catalytic activity increases (Table 2, entries 3 and 5). This is probably due to the greater insolubility of 3,3',5,5'-tetramethyl-4,4'-diphenoquinone in a more polar solvent. Therefore, it is necessary to reach an agreement between the use of water in the reaction solvent and the yield to 2,6-DMBQ obtained.

4. Conclusions

Titania–ceria mixed xerogels were prepared with a 10% (w/w) CeO₂ content at different pH values, and a sample without cerium, 100% (w/w) TiO₂, was also prepared so as to keep it as reference material. The cerium addition led to morphological heterogeneity in the xerogel, and also led to a decrease of the S_{BET} and pore volume in the case of gels calcined at 200 °C. For the catalysts calcined at 800 °C, when Ce was added, their textural parameters considerably increased. The morphological and textural changes observed correlated with the changes in xerogel crystallinity, with amorphous structure those calcined at 200 °C, and with crystalline structure those calcined at 800 °C.

The xerogels were tested as catalysts in the liquid phase oxidation of 2,6-dimethylphenol at 20 °C, using ethanol as solvent and aqueous hydrogen peroxide as a clean oxidizing agent. The 2,6-dimethylphenol conversion was of 100% in 6 h, and the 2,6-dimethyl-*p*-benzoquinone achieved was of 85–96% using the mixed xerogels as catalysts. However, this yield was of 49% when the catalyst of titania without cerium was used.

The activity of the Ti9-pH4-200 catalyst in the studied reaction using an ethanol–water mixture (35:65% (v/v)) as solvent was determined. Total conversion of the initial reactant, after 4 h of reaction at 20 °C, with 70% yield in 2,6-DMBQ, was observed. Under these conditions a red by-product, insoluble in the reaction solution, was formed. This by-product was isolated and characterized and it was identified as 2,6-DMBQ dimmer (3,3',5,5'-tetramethyl-4,4'-diphenoquinone). This by-product was observed in very small amounts when ethanol (96% (v/v)) was used as solvent. Therefore, it is necessary to reach a trade off between the use of water in the reaction solvent and the yield to 2,6-DMBQ obtained.

On the other hand, the 3,3',5,5'-tetramethyl-4,4'-diphenoquinone was oxidized to 2,6-DMBQ using ethanol–water (96:4% (v/v)), Ti9-pH4-200 as catalyst, and H₂O₂ as oxidant. These results enabled us to propose a reaction mechanism.

The obtained results are very useful since the quinones are products of interest in the fine chemicals industry, as key intermediates for the synthesis of a number of biologically active compounds. On the other hand, this study has contributed to the search for heterogeneous catalysts to carry out the oxidation of organic compounds at low temperature, with cleaner oxidizing agent and safer solvents.

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