

## Oxidation of 2,6-Dimethylphenol to 2,6-Dimethyl-1,4-Benzoquinone with Hydrogen Peroxide Catalyzed by TiO<sub>2</sub>-CeO<sub>2</sub> Mixed Xerogels

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Titania (TiO<sub>2</sub>) 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<sup>+</sup>, or when the titanium valence is reduced from 4<sup>+</sup> to 3<sup>+</sup>. The chemical and electronic properties of this nonstoichiometric titania depend on the defect density and the impurity concentration in the crystal [2]. The nonstoichiometric titania, in our case, was prepared by sol-gel technique.

The most important property of CeO<sub>2</sub> is that it can be used as an oxygen reservoir, which stores and releases oxygen via the redox shift between Ce<sup>4+</sup> and Ce<sup>3+</sup> under oxidizing and reducing conditions, respectively [3].

According to the above-mentioned studies titania-ceria mixed xerogels were prepared in a previous paper [4]. 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. This quinone is a key intermediate for the synthesis of a number of medicines and physiologically active substances; it can be used for the synthesis of trimethylbenzoquinone or for the preparation of indophenol [5].

On the other hand, previously we studied this reaction using aqueous hydrogen peroxide as oxidant at low temperature (20 °C) with catalysts based on heteropolyacids [6].

With the objective to enlarge the studies carried out about this oxidation reaction, in this work titania-ceria mixed xerogels are used as heterogeneous catalysts and mixed ethanol-water as solvent giving a possible mechanism of reaction.

### Materials and Methods

The catalysts, TiO<sub>2</sub>-CeO<sub>2</sub> (90% (w/w) TiO<sub>2</sub> -10% (w/w) CeO<sub>2</sub>), were prepared by the sol-gel method using titanium isopropoxide and hexahydrated cerium nitrate as precursors (4). The Ti9-pH3-200 and Ti9-pH4-200 samples, in according to the pH and calcination temperature of synthesis, were used in this work. Their characterization and the details of catalytic test were shown in the previous work (4).

The liquid phase oxidation of 2,6-DMP (Scheme 1) was followed by TLC (thin layer chromatography). One unidentified product (red) was studied using different techniques. Melting point of the compound was determined in a sealed capillary tube in a Büchi equipment and is uncorrected. <sup>13</sup>C-NMR and <sup>1</sup>H-NMR (CDCl<sub>3</sub>) spectra were recorded on Bruker 200 MHz spectrometer, at room temperature, using TMS as internal standard. Low-resolution mass spectra were recorded on a Perkin Elmer GC-MS model (Q-MASS 910). UV-visible spectra

were recorded on a Perkin Elmer spectrophotometer (Lambda 35).

To provide evidence of a radical mechanism, the oxidation was performed with the addition of a radical scavenger (*t*-butanol) and without this compound. The reaction conditions were: 0,0764 gr. of catalysts, 0,1230 gr. of 2,6 DMP, 5 ml of *t*-butanol and 1 ml of H<sub>2</sub>O<sub>2</sub>. The reaction was followed by TLC. 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 x 5 ml). The organic extract was dried over anhydrous sodium sulphate and the solvent evaporated by a rotary evaporator.

### Results and Discussion

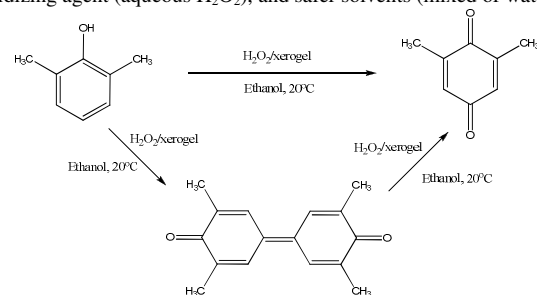
The red product was identified as **3,3',5,5'-tetramethyl-4,4'-diphenquinone**. Their characteristics are: dark red crystals; mp: 205-208 °C (lit. [7] mp 207-210 °C); <sup>1</sup>H- NMR δ/ppm (200 MHz, CDCl<sub>3</sub>, TMS): 2.16 (s, 12H), 7.72 (s, 4H); <sup>13</sup>C-NMR δ/ppm (50 MHz, CDCl<sub>3</sub>, TMS) 17.17, 129.66, 138.98; MS (EI), 70 eV, m/z (rel. intensity): 242 [M<sup>+</sup>] (100), 240 [M] (20), 212 (8), 165 (7), 121 (13), 43 (27); UV-Vis (CHCl<sub>3</sub>) λ<sub>max</sub>/nm: 422.

The 2,6-DMBQ selectivity decreased as % water increased in the solvent mixture.

The oxidation was much suppressed by the addition of a radical scavenger shown that the reaction includes a radical path.

### Significance

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, low temperature (20 °C), cleaner oxidizing agent (aqueous H<sub>2</sub>O<sub>2</sub>), and safer solvents (mixed of water/ethanol).



Scheme 1. Liquid phase oxidation of 2,6-DMP to 2,6-DMBQ

### References

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