



## Environmental Green Chemistry Applications of Nanoporous Carbons

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**Abstract** – Influence of surface properties of nanoporous carbons on selectivity during the photooxidation of 4-chlorophenol (4CP) on UV-irradiated TiO<sub>2</sub> is presented. Changes in surface pH of carbons from basic to neutral or acid remarkably increase the production of 4-chlorocatechol (4CT) by a factor of 22 on TiO<sub>2</sub>-AC in comparison of TiO<sub>2</sub> alone. A mechanism of interaction between both solids permits to explain changes in photoactivity and photoselectivity of TiO<sub>2</sub>. Results showed that TiO<sub>2</sub>-AC can be used as an alternative photocatalyst for environmental green chemistry and selective organic synthesis.

An important challenge for industrial organic chemistry is to develop chemical processes for a clean environment. This is the field of green chemistry where TiO<sub>2</sub> is the most efficient photocatalyst in oxidation processes in aqueous phase. However, it has low selectivity and intermediate products are commonly photomineralized. Also, TiO<sub>2</sub> photoactivity is strongly influenced by co-support as activated carbon [1,2]. In this work, the influence of nanoporous carbon's surface pH (pH<sub>PZC</sub>) on selectivity of products formed during the UV photooxidation of 4CP on TiO<sub>2</sub> was studied as a possible strategy for environmental green chemistry.

Photocatalyst was TiO<sub>2</sub> and nanoporous carbons (AC) were prepared from sawdust of *Tabebuia Pentaphyla* wood by pyrolysis [1] under N<sub>2</sub> flow (AC<sub>N<sub>2</sub>-i</sub>, i is temperature) and by chemical activation [2] with H<sub>3</sub>PO<sub>4</sub> solution (AC<sub>H<sub>3</sub>PO<sub>4</sub>-j</sub>, j is concentration). Photocatalytic tests were performed at 25°C with 50mg TiO<sub>2</sub> and 10mg AC under stirring in 25mL of aqueous solution of 4-chlorophenol 0.78x10<sup>-3</sup>mol.L<sup>-1</sup>. A Pyrex batch reactor was used (60mL). Irradiation was provided by a high-pressure Hg lamp. 4CP, hydroquinone (HQ), benzoquinone (BQ) and 4-chlorocatechol (4CT) were analyzed by HPLC.

Table 1 indicates that S<sub>BET</sub> and pH<sub>PZC</sub> influence TiO<sub>2</sub> photoactivity. Photoproducts agree with chlorine substitution by p-hydroxylation yielding HQ and BQ (at equilibrium) and the o-hydroxylation yielding 4CT. Table 1 shows changes in o/p products in 4CP photooxidation. R(o/p) compares maximum 4CT detected against maxima of HQ+BQ. The more acid is pH<sub>PZC</sub> of AC the more higher is R(o/p) with a maxima of 7.45 for TiO<sub>2</sub>-AC<sub>N<sub>2</sub>-450</sub> (pH<sub>PZC</sub> 6.05) in comparison than that on TiO<sub>2</sub> (0.08μmol). A similar trend was detected for F(o/o) that compares 4CT detected on TiO<sub>2</sub>-AC against that on TiO<sub>2</sub> (0.037μmol). A light change in pH<sub>PZC</sub> from 8.9 to 7.9 for AC<sub>N<sub>2</sub>-700</sub> against AC<sub>N<sub>2</sub>-1000</sub>, leads to an increase from 1.60 up to 22.1. Results suggest that pH<sub>PZC</sub> of AC induce important changes in the surface of TiO<sub>2</sub>. From, FTIR, XPS and XANES studies, an interaction mechanism between both solids is proposed. In conclusion, results suggest that AC's pH<sub>PZC</sub> permits to control the selectivity of products formed during 4CP photooxidation and TiO<sub>2</sub>-AC can be used as a highly selective photocatalysts for green chemistry

Table 1. AC properties and kinetic results obtained in 4CP photooxidation

| Photocatalyst   | pH <sub>PZC</sub> | S <sub>BET</sub><br>(m <sup>2</sup> .g <sup>-1</sup> ) | k <sub>app</sub> x10 <sup>-3</sup><br>(min <sup>-1</sup> ) | I <sub>F</sub> | HQ + BQ<br>(μmol) | 4CT<br>(μmol) | R(o/p) | F(o/o) |
|---|-------------------|--|--|----------------|-------------------|---------------|--------|--------|
| TiO <sub>2</sub>  | 6.5               | 50   | 2.02   | 1.00           | 0.476             | 0.037         | 0.08   | 1.00   |
| TiO <sub>2</sub> -AC <sub>N<sub>2</sub>-1000</sub>              | 8.90              | 518  | 4.31   | 2.13           | 0.487             | 0.059         | 0.12   | 1.60   |
| TiO <sub>2</sub> - AC <sub>N<sub>2</sub>-900</sub>              | 8.50              | 590  | 3.37   | 1.67           | 0.300             | 0.068         | 0.23   | 1.84   |
| TiO <sub>2</sub> - AC <sub>N<sub>2</sub>-800</sub>              | 8.00              | 519  | 1.54   | 0.76           | 0.210             | 0.680         | 3.23   | 18.4   |
| TiO <sub>2</sub> - AC <sub>N<sub>2</sub>-700</sub>              | 7.90              | 388  | 1.34   | 0.66           | 0.139             | 0.817         | 5.88   | 22.1   |
| TiO <sub>2</sub> - AC <sub>N<sub>2</sub>-600</sub>              | 7.10              | 360  | 1.07   | 0.53           | 0.135             | 0.805         | 5.96   | 21.8   |
| TiO <sub>2</sub> - AC <sub>N<sub>2</sub>-450</sub>              | 6.05              | 31   | 0.92   | 0.46           | 0.106             | 0.790         | 7.45   | 21.4   |
| TiO <sub>2</sub> - AC <sub>H<sub>3</sub>PO<sub>4</sub>-1</sub>  | 4.70              | 188  | 2.01   | 1.00           | 0.363             | 0.108         | 0.30   | 2.92   |
| TiO <sub>2</sub> - AC <sub>H<sub>3</sub>PO<sub>4</sub>-5</sub>  | 4.00              | 414  | 3.36   | 1.66           | 0.381             | 0.493         | 1.29   | 13.3   |
| TiO <sub>2</sub> - AC <sub>H<sub>3</sub>PO<sub>4</sub>-35</sub> | 3.50              | 1987   | 2.09   | 1.03           | 0.442             | 0.540         | 1.22   | 14.6   |
| TiO <sub>2</sub> - AC <sub>H<sub>3</sub>PO<sub>4</sub>-65</sub> | 3.10              | 1569   | 1.25   | 0.62           | 0.690             | 0.642         | 0.93   | 17.4   |

### References

- [1] T. Cordero, C. Duchamp, J.-M. Chovelon, C. Ferronato, J. Matos, Appl. Catal. B. 73 (2007) 227-235.
- [2] T. Cordero, C. Duchamp, J.-M. Chovelon, C. Ferronato, J. Matos J. Photochem. Photobiol., A., 191 (2007) 122-131.