Synthesis of 2-hydroxybenzoic acid from CO_2 and phenol in aqueous heterogeneous photocatalytic systems

Antonino Sclafani, Leonardo Palmisano and Gianluca Farneti

Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, 90128, Palermo, Italy

The photocatalytic reaction occurring in aqueous deaereated suspensions saturated with CO_2 and containing polycrystalline semiconductors, bare or loaded with Pt or Cu, affords 2-hydroxybenzoic acid and catechol as the main products.

Many studies[1–6] have reported the photocatalytic reduction of CO_2 in both gas–solid and liquid–solid heterogeneous systems using mild experimental conditions and in the presence of H_2O. The solids used as photocatalysts were polycrystalline semiconductors, and bare Cu-doped TiO_2 (anatase) proved to be the most suitable.[6] Light organic compounds, such as for instance HCO_2H, MeOH and CH_4, were obtained as the main products and their relative ratios depended on the type of photocatalyst and experimental conditions used.

However, very few studies[7,8] can be found on the insertion of CO_2 in organic aromatic substrates using photochemical methods. The heterogeneous photocatalytic insertion of CO_2 into aromatic molecules, to the best of our knowledge, has not yet been reported.

Here preliminary results are reported on the production of 2-hydroxybenzoic acid (salicylic acid) by the photocatalytic reaction between CO_2 and phenol in aqueous deaerated suspensions containing a polycrystalline semiconductor, bare or loaded with Pt or Cu. Catechol was produced together with 2-hydroxybenzoic acid and its amount depended on the catalyst used.

The experimental runs were performed in a Solarbox manufactured by CO.FO.ME.GRA., Milan, equipped with a 1500 W Xe lamp, simulating the solar spectrum. Pyrex photoreactors (50 ml) containing 25 ml of aqueous phenol (8.2 g l^{-1}) solutions at pH = 5.85 saturated with CO_2 were used for each run. The photon flux provided by the lamp was measured in the locations of the photoreactors by means of the standard potassium ferrioxalate actinometric method which gave 6.6×10^{-7} Einstein s^{-1} with oscillations of only *ca.* 3%. The photocatalyst (2 g l^{-1}) was suspended in the phenol solution and magnetically stirred.

The solids used as photocatalysts were: anatase TiO_2 (Merck), TiO_2 (P25 Degussa), Cu-doped TiO_2 (P25 Degussa), Rutile TiO_2 (Tioxide), WO_3 (Carlo Erba, RPE), Pt-doped WO_3 (Carlo Erba, RPE), ZnO (BDH) and SiO_2 (BDH). The runs lasted 4 h and samples were withdrawn for HPLC analyses. The analyses were carried out after filtration through 0.45 μm cellulose acetate membrane (HA, Millipore) and subsequent centrifugation. One run lasted 8 h (anatase TiO_2 Merck) and it was contemporaneously performed using five identical photoreactors: two of them were used for analyses carried out after 1 and 2 h of illumination, the other three for analyses carried out after 4, 6 and 8 h.

Typically the filtered samples were injected into a chromatograph composed of a Varian model 9010 pump, a Varian 9050 UV–VIS detector and a 10 μm Econosil C18 (Alltech) 250 × 4.6 mm i.d. column. Isocratic elution with methanol–H_3PO_4 0.05 mass% aqueous solution was performed at 1 ml min^{-1}. The products were monitored at $\lambda = 254$ nm.

The results are shown in Table 1. It can be seen that the most significant formation of 2-hydroxybenzoic acid was obtained by using anatase TiO_2 (Merck), while Pt(2 mass%)–WO_3 favoured the formation of catechol TiO_2 (Degussa P25, *ca.* 80% anatase and 20% rutile) was found to be less photoactive than anatase TiO_2 (Merck) which could be due to the higher oxidant properties of TiO_2 (Degussa P25) with respect to TiO_2 (Merck). The high oxidant properties of TiO_2 (Degussa) when used as photocatalyst for degradation reactions of organic molecules carried out in aqueous media are well known. The runs carried out using the other solids showed the formation of significantly smaller amounts of the above compounds. As expected, no 2-hydroxybenzoic acid, only traces of catechol, were found when the insulator oxide SiO_2 was used. Moreover, the poor photoactivity of bare WO_3 should be noted in comparison with the corresponding sample Pt(2 mass%)–WO_3 in the presence of which the biggest production of catechol was observed. The presence of Pt on the surface of WO_3 particles modifies the adsorption of the reagents, but in this case the major role consists in enhancing the lifetime of the photoproduced electron–hole pairs, due to its high work function.[9] The electrons migrate from WO_3 to Pt, giving rise to reduction reactions. The trend of the photoactivity of the samples is not much different if the BET specific surface areas of the powders reported in Table 1 are considered, *i.e.* if the specific photoactivity of the samples is calculated.

The results suggest that the photoreactivity is strongly influenced by both the surface physico-chemical and the electronic properties of the catalysts. The adsorption phenomena, indeed, are of primary importance for CO_2 photoactivation and they are related to several factors such as, for instance, the presence of catalytic metals, the surface acid–base properties, the zero charge potential and the surface hydroxylation.

In Fig. 1 the concentrations of 2-hydroxybenzoic acid and catechol *vs.* illumination time are reported when anatase TiO_2 (Merck) is used as photocatalyst.

It can be seen that the production of 2-hydroxybenzoic acid approaches the maximum value asymptotically. This could be

Table 1 Average 2-hydroxybenzoic acid and catechol concentrations per hour and BET specific surface areas (SA) of the photocatalysts used

Catalyst	Surface area/ m^2 g^{-1}	2-Hydroxybenzoic acid/μmol l^{-1} h^{-1}	Catechol/ μmol l^{-1} h^{-1}
Anatase TiO_2 (Merck)	10.5	371.2	44.31
TiO_2 (P25 Degussa)	44	64.2	3.5
Cu (0.1 mass%)–TiO_2 (P25 Degussa)	50	27.9	22.7
Rutile TiO_2 (Tioxide)	20	13.6	8.5
WO_3 (Carlo Erba, RPE)	15.5	18.5	—
Pt (2.0 mass%)–WO_3 (Carlo Erba, RPE)	16.4	117.7	1118.2
ZnO (BDH)	4	9.4	—
SiO_2 (BDH)	n.d.[a]	—	traces

[a] N.d. = not determined.

due to a decrease of CO_2 concentration in the batch discontinuous reacting system and/or to the competition of the photoreaction affording catechol.

By taking into account the experimental results it is evident that CO_2 is reduced by means of a photocatalytic reaction. The reduction process could be given by eqn. (1), where the redox

$$CO_2 + e^- + H_3O^+ \rightarrow \cdot COOH + H_2O \qquad (1)$$

potential, E^0_{redox} is −1.52 V *vs.* SHE.[10] Nevertheless the thermodynamic level of the conduction bands of the semiconductors used is more positive than −1.52 V and, even if the adsorption energy of CO_2[11] and the formation of surface states is considered, the difference between the thermodynamic level of eqn. (1) and the conduction bands of the used semiconductors is too high and, consequently, the above reduction reaction is not likely.

A more likely hypothesis for the reaction mechanism could be given by eqns. (2)–(9).

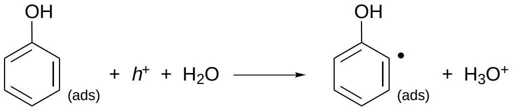
$$TiO_2 + h\nu \longrightarrow TiO_2\,(h_{vb}^+,\ e_{cb}^-) \qquad (2)$$

$$CO_{2\,(gas)} \rightleftharpoons CO_{2\,(sol)} \rightleftharpoons CO_{2\,(ads)} \qquad (3)$$

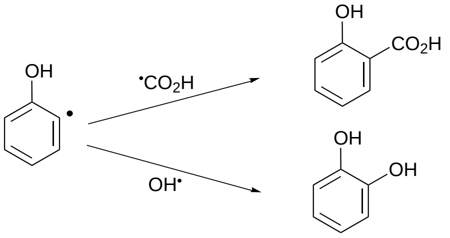
$$CO_{2\,(ads)} + 2e^- + 2H_3O^+ \longrightarrow HCO_2H_{(ads)} + 2H_2O \qquad (4)$$

$$HCO_2H + h^+ + H_2O \longrightarrow {}^{\bullet}CO_2H + H_3O^+ \qquad (5)$$

$$OH^-_{(ads)} + h^+ \qquad OH^{\bullet} \qquad (6)$$



(7)



(8)

$$^{\bullet}CO_2H + OH^{\bullet} \longrightarrow CO_2 + H_2O \qquad (9)$$

The thermodynamic potential of eqn. (4) is in standard conditions equal to −0.11 V *vs.* SHE. This last value is closer to those of the conduction bands of the used semiconductors. Anatase TiO_2, for instance, has the thermodynamic level of the conduction band equal to *ca.* −0.1 V *vs.* SHE,[12] while the conduction band of WO_3 (no variation is induced by the presence of Pt) is equal to 0.26 V *vs.* SHE (−0.059 V for each pH unity).[13]

The formation of H_2 as opposed to HCO_2H according to eqn. (4) is thermodynamically less likely because $E_{H+/H2}$ is equal to −0.34 V *vs.* SHE in our experimental conditions (pH = 5.85). In the above mechanism, moreover, the competion among various adsorbed species for the oxidation process is taken into consideration and the occurrence of this competition could explain the different ratios of 2-hydroxybenzoic acid and catechol obtained by using different oxides.

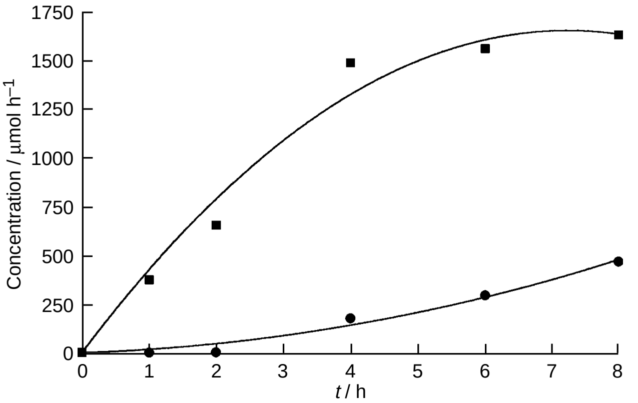


Fig. 1 Concentration *vs.* illumination time of 2-hydroxybenzoic acid (■) and catechol (●) when anatase TiO_2 (Merck) was used

It should be noticed that OH radicals can attack catechol and 2-hydroxybenzoic acid further, giving rise to formation of other oxidation compounds and subsequent opening of the aromatic ring[14,15] and/or to attack methanoic acid with formation of carbon dioxide and water, eqn. (9).

Finally, it is also worth to notice that HPLC analyses indicate the presence of unidentified products and work is in progress to clarify the mechanistic aspects of the photocatalytic reaction.

References

1 M. Halmann, M. Ulmann and B. Aurian-Blajeni, *Sol. Energy*, 1983, **31**, 429.
2 M. Halmann, V. Katzir, E. Borgarello and J. Kiwi, *Sol. Energy Mat.*, 1984, **10**, 85.
3 M. Anpo and K. Chiba, *J. Mol. Catal.*, 1992, **207**, 74.
4 O. Ishitani, C. Inoue, Y. Suzuki and T. Ibusuki, *J. Photochem. Photobiol. A: Chem.*, 1993, **72**, 269.
5 T. Mizuno, H. Tsutsumi, K. Ohta, A. Saji and H. Noda, *Chem. Lett.*, 1994, 1533.
6 H. Yamashita, H. Nishiguchi, N. Kamada, M. Anpo, Y. Teraoka, H. Hatano, S. Ehara, K. Kikui, L. Palmisano, A. Sclafani, M. Schiavello and M. A. Fox, *Res. Chem. Intermedi.*, 1994, **20**, 815 and references cited therein.
7 H. Sugimoto, I. Kawata, H. Taniguchi and Y. Fujiwara, *J. Organomet. Chem.*, 1984, **C44**, 266.
8 H. Tagaya, M. Onuki, M. Karasu and K. Chiba, *Proc. The International Symposium on Chemical Fixation of Carbon Dioxide*, December 2–4, Nagoya, Japan, 1991, B10, p. 195.
9 A. Sclafani, L. Palmisano, G. Marcì and A. M. Venezia, unpublished results.
10 K. W. Frese, Jr., in *Electrochemical and Electrocatalytic Reactions of CO_2*, ed. K. Christ, E. Guard and B. P. Sullivan, Elsevier, Amsterdam, 1993, p. 148.
11 J. Raskó and F. Solymosi, *J. Phys. Chem.*, 1994, **98**, 7147.
12 Y. V. Pleskov, *Solar Energy Conversion*, Springer, Berlin 1990, p. 116.
13 J. Desilvestro and M. Grätzel, *J. Electroanal. Chem.*, 1987, **238**, 129.
14 R. W. Matthews, *J. Phys. Chem.*, 1987, **91**, 3328.
15 S. Tunesi and M. Anderson, *J. Phys. Chem.*, 1991, **95**, 3399.

Received, 13th November 1996; Com. 6/07705F