

The role of the synthetic procedure on the photoactivity of nanocrystalline TiO₂

S. Ardizzone, C.L. Bianchi, G. Cappelletti, C. Pirola, V. Ragaini

Department of Physical Chemistry and Electrochemistry, University of Milan,
Via Golgi 19, 20133 Milan, Italy, claudia.bianchi@unimi.it

ABSTRACT

The photodegradation, in solution, of 2-chlorophenol (2-CP) used as a model compound, by TiO₂ samples prepared by a multi-step sol-gel procedure is investigated. Photocatalysts with varying surface area and anatase/rutile content are tested and their activity is compared with that of the most commonly studied TiO₂ photocatalyst Degussa P25 as a standard material. The composition of the reacting mixture, in terms of side products, and the total mineralization by TOC is followed throughout the reaction time.

Keywords: TiO₂, 2-Chlorophenol, photodegradation, sol-gel, XPS

1. INTRODUCTION

Because of its stability and nontoxicity TiO₂ has been extensively investigated as an efficient photocatalyst for purifying water and air. The photocatalytic reactions on TiO₂ are initiated by adsorbing UV photons that can excite valence band (VB) electrons to conduction band (CB) in the solid lattice and are completed through the subsequent interfacial electron transfers and thermal reactions occurring on the surface. The photoinduced redox reactions on TiO₂ result in the generation of reactive oxygen species such as OH radicals and superoxides, which are mostly responsible for the strong oxidizing power of TiO₂.

The nanometer scale of the crystals plays a key role in affecting the performance of the material. It is well known that small crystallite size can lead to quantum confinement effects in semiconductors and to a sharp increase in activity when the grain size becomes smaller than the space-charge depth. Consequently a big effort can be seen to prepare photocatalysts consisting of nanometric particles with controlled size/morphology [1,2].

In recent years a great deal of activity was dedicated, by the authors' group, to the study of synthetic routes leading

to nanocrystalline materials with tailored features, mainly in the case of titania. Sol-gel paths, combined with hydrothermal stages performed either in the presence or in the absence of surfactants, have led to nanocrystalline TiO₂ with controlled enrichment in either anatase or rutile [3-5]. There is ample debate in the literature concerning the actual role played by either of the titania polymorphs with respect to the photocatalytic activity of the material[2].

In this work the authors report on the activity of nanocrystalline titania, prepared in the laboratory, with respect to the photodegradation, in solution, of 2-chlorophenol (2-CP) used as a model compound.

2. EXPERIMENTAL

TiO₂ powders were prepared by a previously reported procedure consisting of an initial sol-gel step using titanium propoxide as the Ti source and adopting 50 as the water alkoxide ratio [3]. The dried sol-gel precursors were submitted to calcinations at 300, 450 and 600 °C under an oxygen stream. TiO₂, P25 Degussa was used as the reference photocatalyst. The TiO₂ powders were characterized, by XRPD, N₂ adsorption at subcritical temperatures and XPS. In all runs, an optimal TiO₂ amount (0.1 g l⁻¹) was added directly into the reactor. All the photocatalytic experiments were carried out in a thermostated reactor at 30°C and externally irradiated by a 250 W iron halogenide lamp (Jelosil, model HG 250) placed at a fixed distance from the vessel ensuring a radiation flow on the reactor equal to 2.0x10⁻⁵ einstein s⁻¹. Test samples were analyzed for changes in composition by HPLC (Agilent 1100 Series) at different reaction times and the total mineralization efficiency was followed by TOC (Shimadzu 5000A) throughout the reaction.

3. RESULTS

Fig.1 reports the % degradation of 2-CP as a function of the reaction time. It appears immediately that the present 300 and 400 °C samples show a very fast conversion and that in about 100-150 min the concentration in solution of 2-CP is reduced to zero. The sample calcined at 600°C shows behaviour comparable to the reference P25. It may be relevant to note that, although at short reaction times the degradation by the present 600°C sample is slightly lower than that of P25, at longer reaction times the conversion increases reaching about 90% at 350 min.

sample	S _{B.E.T.} (m ² g ⁻¹)	Phase composition
P25	55	A(85.0%); R (15.0%)
TiO ₂ _300	151	A(60.1%); B (39.9%)
TiO ₂ _450	131	A(65.4%); B (34.6%)
TiO ₂ _600	11	A(18.7%); R (81.3%)

Table 1: Physico-chemical features of the adopted samples

The sequence reported in Fig. 1 seems to suggest that, at short reaction times, the main factor affecting the rate of conversion is the sample surface area (Tab.1). A direct relation between the sample surface area and its photocatalytic efficiency is not a trivial finding. In fact several authors suggest that more efficient charge recombination processes may take place on smaller particles [1], thus reducing the photocatalytic activity of the material. Apparently, in the present case, the occurrence of some degree of aggregation between the crystallites thwarts recombination processes without reducing too much the catalyst surface accessible to the reactants. The conversion sequence reported in Fig.1 suggests further that, at least at short reaction times, the presence of rutile in the phase composition of the TiO₂ photocatalyst is not a primary point imposing the material performance.

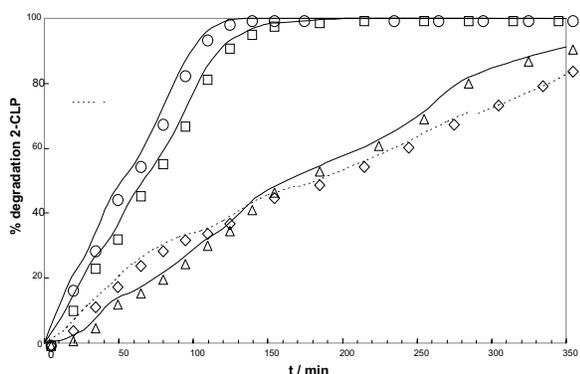


Figure 1: 2-CP degradation: O TiO₂_300; □ TiO₂_450; Δ TiO₂_600; ◇ P25.

Tab.2 reports data concerning the mineralization efficiency (obtained by TOC) compared with the residual organic composition of the mixture determined by HPLC. The mineralization efficiency follows the trend of the 2-CP degradation. Several side products were observed in agreement with literature results. The main side product at the end of the reaction is formaldehyde for all the samples.

sample	ppm C			
	initial	final (HPLC)	final (TOC)	% miner.
P25	76.6	48.6	49.1	36
TiO ₂ _300	74.9	33.0	39.2	49
TiO ₂ _450	70.0	40.0	40.5	43
TiO ₂ _600	69.4	40.6	47.6	31

Table 2: Mineralization efficiency obtained by TOC compared with the residual organic composition of the mixture determined by HPLC .

The XPS region of O 1s was investigated for all samples. The oxygen peak was in any case composite and was fitted by two components the main one at 529. eV due to reticular oxygen and the second one at 531.5 eV due to surface OH groups [7]. Fig.2 shows the trend of the oxygen component atomic ratios for the present samples. It is interesting to observe that the trend of the OH/O_{tot} between the different samples mirrors the trend of the photocatalytic efficiency. The surface density of OH groups seems to be a promoting factor in the photocatalytic efficiency of TiO₂.

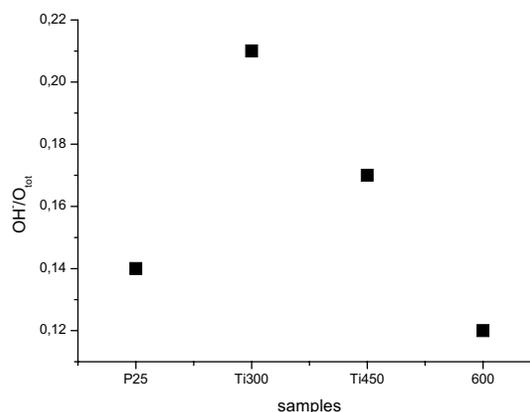


Figure 2: XPS atomic ratios between the O1s peak components

4. CONCLUSIONS

TiO₂ samples obtained by a composite procedure implying a sol-gel stage and calcinations at different temperatures, were used as photocatalysts for the UV degradation of 2-CP. An inverse relation between the pollutant degradation rate and the TiO₂ temperature of calcination was observed. The conversion sequence follows the order of the catalysts surface areas while the presence in the phase composition of the rutile polymorph seems not to be crucial.

The degree of mineralization follows the same sequence of the catalyst performance, the main side product at the end of the reaction time is, in any case, formaldehyde. The surface density of OH groups, determined by XPS, seems to be a promoting factor in the photocatalytic efficiency of the adopted samples.

REFERENCES

- [1] S. Kim, W. Choi, *J. Phys. Chem. B.*, 109 (2005) 5143.
- [2] J. Krysa, M. Keppert, J. Jirkovsky, V. Stengl, J. Subrt, *Mater. Chem. Phys.*, 86 (2004) 333.
- [3] T. Boiadjieva, G. Cappelletti, S. Ardizzone, S. Rondinini, A. Vertova, *Phys. Chem. Chem. Phys.*, 5 (2003) 1689.
- [4] G. Cappelletti, C. Ricci, S. Ardizzone, C. Parola, A. Anedda, *J. Phys. Chem. B.*, 109 (2005) 4448.
- [5] C.L. Bianchi, S. Ardizzone, G. Cappelletti, Dekker *Encyclopedia of Nanoscience and Nanotechnology* in press.
- [6] V. Ragaini, E. Selli, C.L. Bianchi, C. Pirola, *Ultrason. Sonochem.*, 8 (2001) 251.
- [7] G. Cappelletti, C.L. Bianchi, S. Ardizzone, *Appl. Surf. Sci.*, in press