Preparation, Characterization, and Photoactivity of Polycrystalline Nanostructured TiO2 Catalysts for 4-Nitrophenol Degradation in Aqueous Systems - M. Addamo, V. Augugliaro, A. Di Paola, E. García-López, V. Loddo, G. Marcì (University of Palermo), R. Molinari (University of Calabria), L. Palmisano, and M. Schiavello (University of Palermo)

Heterogeneous photocatalysis over semiconductor oxides has been widely studied since Fujishima and Honda reported the photo-splitting of water on TiO_2 electrodes [1]. Photocatalysis has been found effective for the achievement of the photo-oxidation of many organic pollutants present in liquid effluents [2] or in air as VOC's [3]. TiO_2 is the most used photocatalyst, due to its (photo)stability and low cost [4]. Recently many studies have been reported on preparation and characterisation of various nanostructured semiconductors because it has been found that the nanoparticles exhibit special photochemical characteristics; in particular, the bandgap of the nanoparticles increases with the decrease of the size and other important properties such as optical and physical absorption and luminescence emission undergo drastic changes. TiO_2 nanoparticles have been recently employed in photocatalysis for photodegradation of noxious species in aqueous medium [5], although the existence of stable nanoparticles is known to be not easy, due to their tendency to agglomerate. Even if in most cases the samples used did not consist of discrete nanoparticles but only of nanostructured particles, this kind of photocatalysts are reported to show a high photoactivity compared with that of many commercial samples [6]**.**

In this paper different nanostructured TiO_2 samples were prepared by hydrolysis of $TiCl_4$.

The samples were characterised by X-ray diffractometry, specific surface area determinations, scanning electron microscopy and diffuse reflectance spectroscopy. 4-nitrophenol photodegradation in aqueous medium was employed as a probe reaction to test the photoactivity of the catalysts.

The commercial TiO_2 samples used for the sake of comparison with the home prepared samples were Degussa P25, Merck and Tioxide.

The preparation methods for various nanostructured TiO_2 samples were the following:

hydrolysis of titanium tetrachloride at room temperature for 24 h (molar ratios Ti : water equal to 1 : 60; used volumes (ml) ratios 10 : 100). The resulting clear solution was boiled for 1, 2, 3, 12 and 24 h in order to form a solid.

A dispersion consisting of very small particles was obtained and it was used for the photocatalytic tests. The characterisation of this sample was carried out on the solid obtained by drying the suspension at *ca.* 323 K. The dispersion was also left in suspension for 7, 30, 90 days to observe if ageing phenomena had detrimental effect on the photoactivity of the sample.

SEM observations shows that the bigger particles are the 90 days aged or the samples boiled for 24 hours with sizes of ca. 200 nm, while the sample boiled 3 h shows size of ca. 40 nm.

The higher photoactivity is showed by the samples boiled for 3 h, different times cause a decrease of activity suggesting an optimal boiling time between 2-4 h. The photoactivity of sample aged 7 days showed no difference with the fresh catalyst, but a decreasing photoactivity was observed by increasing times of ageing (30 and 90 days). The photocatalytic activity decreased also by increasing the pH value of the aqueous solution and aggregation of particles was observed in these last cases. The photoactivity of the samples was verified also without any adjustment of pH value (in this case the pH was *ca.* 1).

The obtained TiO_2 appeared very promising by an application point of view because neither separation and washing of the solid nor its calcination were needed to obtain a high active photocatalyst. It is worth reminding indeed that a photoactive anatase phase was obtained only by means of a hydrothermal treatment in very mild experimental conditions. The suspension containing the photocatalyst was stable in acid solution and it was used simply by adding the model pollutant and afterwards transferring the dispersion in the cylindrical batch photoreactor.

The use of such a photocatalyst in a hybrid membrane photocatalytic reactor could be useful because of its very easy "in situ" preparation. Studies are in progress on the behaviour of this submicrometric catalyst in hybrid photoreactors.

References

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