Shape-selective photocatalytic transformation of phenols in an aqueous medium

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A zeolitic material containing Ti chains activated by light allows a shape-selective transformation of organic compounds; the molecules that can enter into the zeolitic cavities are protected from the light-induced processes, while the other are degraded.

It is well known that light activated processes on TiO$_2$ have applications in several fields such as the removal of water pollutants[1] and organic synthesis.[2,3] When dealing with pollution problems, the complete degradation of the polluting organic molecules is of course the goal. The photoactivity of TiO$_2$ is generally not selective, leading to the complete decomposition of the organic compounds. However, it is intriguing to test the feasibility of selective phototransformation of organic species in an aqueous medium. For this purpose, materials that show shape selectivity properties, such as zeolites, could be used. Among them, ETS-10 (Engelhard Titanosilicate Structure 10)[4] is particularly interesting for photocatalytic applications. In fact, it has two main features: i) it is a semiconductor containing photo-excitable titanium moieties, and ii) its structure is characterized by a three-dimensional set of channels with a free entrance of about 0.8 × 0.5 nm, ref. 5 (Fig. 1). The UV-VIS spectrum of ETS-10 shows two absorption bands at 282 and 214 nm, which have been assigned to ligand-to-metal charge transfer (LMCT) transitions, involving two kinds of oxygen ligands: those which bridge Ti atoms along straight Ti–O–Ti chains (282 nm), and those in the

Si–O–Ti groups (214 nm).[6] The band gap of the –Ti–O–Ti– quantum wire is 4.03 eV[7] and is slightly higher than that of TiO$_2$.[8] A higher energy is then necessary to obtain the production of the active carriers (electrons and holes) and for this reason, in the experiments reported below a 310 nm cut-off filter has been adopted. The irradiation of the single species were carried out on 5 ml of aqueous suspension containing 1×10^{-4} M organic compound and 1 g L^{-1} of catalyst, using a 1500 W Xenon lamp (Solarbox, CO.FO. MEGRA, Milan, Italy) simulating AM1 solar light and equipped with a 310 nm cut-off filter. The irradiance spectrum and the cells have been described elsewhere.[9] The photonic flux entering into the cell is 7.9×10^{-6} einstein min^{-1}. The content of the cell was filtered through a 0.45 μm cellulose acetate filter (Millipore HA) and analyzed by the appropriate analytical technique.

To test the selective photoactivity of ETS-10, molecules of different steric hindrance were investigated: phenol (P), 1,3,5-trihydroxybenzene (3HP) and 2,3-dihydroxynaphthalene (2HPP) have been chosen. A comparison of the relative dimensions of the molecules and of the zeolitic cavities is shown in Fig. 1, while an analysis of the degradation rate ratios is reported in Table 1. In the same Table the results obtained with TiO$_2$ P25 as photocatalyst are reported for comparison. The contribution of direct photolysis is negligible (see Table 1).

An interesting correlation between the size of the molecule and its photodegradability is shown. This is particularly evident comparing P and 2HPP degradation, 2HPP being degraded on ETS-10 with a rate which is 56 times higher than P, and with a degradation efficiency of the same order as TiO$_2$. These results provide, for the first time, evidence of the feasibility of selective photocatalytic degradation in aqueous medium. A study of the intermediates of the degradation of phenol shows that they are the same catechol and quinol on TiO$_2$ and ETS-10. In the case of 3HP and 2HPP, even if the intermediates have not been identified, they show the same chromatographic pattern both on
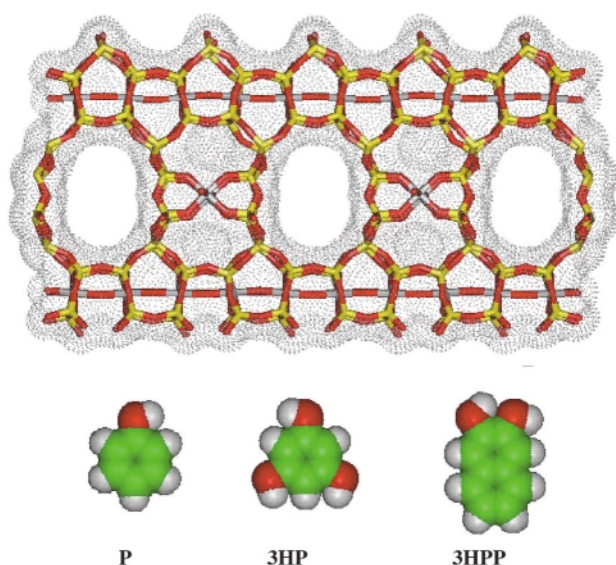

Fig. 1 Structure of zeolite ETS-10 and of the degraded molecules: phenol (P), 1,3,5-trihydroxybenzene (3HP) and 2,3-dihydroxynaphthalene (2HPP). The pointed surface in the zeolite structure evidences the accessible spaces as determined by the Connolly algorithm.[14]

Table 1 Degradation rate of hydroxyaromatic compounds on TiO$_2$ and on zeolite ETS-10. From these experimental data, the process efficiency (rate of degradation/photonic flux incoming into the cell) can be easily calculated;[10] in the case of dihydroxynaphthalene on ETS-10, a process efficiency of 2.8% is obtained. In parentheses are reported the degradation rate ratios (r_x/r_P) obtained comparing the values obtained in each set of experiments with that obtained for P. H-ETS-10 in the acid form was kindly supplied by the Engelhard Corporation (Iselin, NJ, USA); its external surface area is 21 m^2 g^{-1} (T-plot volumetric measurements with N$_2$ made with a Micromeritics apparatus). TiO$_2$ was a commercial Degussa P25 sample (surface area: about 50 m^2 g^{-1})

Rate/10^5 M min^{-1}	TiO$_2$	ETS-10	Direct photolysis
P	2.77 (1)	0.08 (1)	—
3HP	5.74 (2.07)	0.38 (4.75)	—
2HPP	7.90 (2.85)	4.46 (55.7)	0.21

TiO$_2$ and ETS-10. These results indicate that the degradation mechanism is similar and suggests that, like on TiO$_2$, the catalytic active sites of ETS-10 are titanols linked on external surfaces where the –Ti–O–Ti–O–Ti– chains are emerging and the TiO bonds are consequently broken. The bulk Ti atoms of ETS-10 cannot be considered as playing a role in the degradation for two reasons: i) imperfect structures are not directly exposed on the channels walls (see Fig. 1); ii) it has been shown[11,12] that when degradation takes place at centers located in restricted places (like titanols in defects located in zeolitic channels), the intermediate degradation products are able to back react with active species, favoring recombination. It is also to be noted that in the photocatalytic process there is no relation between the absorption on the surface and the rate of disappearance, as shown in the case of phenol (not adsorbed) and catechol (adsorbed).[13]

In view of these results and of the fact that the catalytic centers are located on the surface, it can be concluded that the zeolitic internal cavities offer a protective environment against degradation to those species which, for their small size, easily diffuse inside. This shielding effect against photodegradation is particularly marked for P, which was the smallest molecule investigated, and not present for 2HPP, which is the only studied species whose size surely does not fit the channel size and so it is the most degraded molecule. The ability to diffuse inside the cavities is then the main factor determining the shape selective degradation.

Finally, a further confirmation of the presence of catalytic sites on the external surface is given by the fact that the degradation rate of 2HPP on TiO$_2$ and on ETS-10, which have similar external surface area, is of the same order of magnitude.

Future developments also have to consider the influence of competitive diffusion of the molecules; this probably explains the small differences that can be observed in the rate constant values, compared to the values obtained in the degradation of the single molecules.

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