



The mechanism of azo-dyes adsorption on the titanium dioxide surface and their photocatalytic degradation over samples with various anatase/rutile ratios



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ABSTRACT

The joint use of adsorption data, potentiometric titrations, microelectrophoresis, pH change upon adsorption and diffuse reflectance spectroscopy allowed the elucidation of adsorption mechanism for two representative azo-dyes, one acidic (Orange G) and one basic (Yellow 28), on the titanium dioxide (Degussa P25) surface. In both cases the adsorption is realized by chemical bonding with the TiO₂ surface. In the case of Orange G the surface compound is formed through the substitution of positively charged surface hydroxyl groups of TiO₂ by one of the two negative –SO₃[–] groups of the dye. In the case of Yellow 28 the formation of the surface compound probably occurs via the positively charged *N* of the molecule.

The photocatalytic degradation of the above azo-dyes was studied over the titanium dioxide Degussa P25 and a series of samples resulted by calcination of the mother material at various temperatures and times. Although the mother TiO₂ sample (Degussa P25) exhibits the maximum photocatalytic activity per gram, the intrinsic photocatalytic activity is maximized in the samples with A/R ratios 0.8 and 0.5 (for the Orange G and Yellow 28, respectively) in which a relatively large population of heterojunctions between the two TiO₂ phases is obtained indicating the critical role of this parameter. Moreover, the kind of the surface bonds formed seems to influence the kinetics of the photocatalytic reaction though the strong adsorption of both azo-dyes related to the formation of surface compounds seems to favor their photocatalytic degradation.

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1. Introduction

Azo dyes used in the textile dyeing process constitute one of the largest groups of organic compounds that represent an increasing environmental danger because up to 30% of the used dyestuffs remain in the spent dye-bath. The release of those colored waste waters in the environment is a considerable source of non-aesthetic pollution and eutrophication as well as it can originate dangerous byproducts through oxidation, hydrolysis or other chemical reactions taking place in the wastewater phase. Due to the large degree of aromatics present in dye molecules and the stability of modern dyes, the conventional biological methods of treatment are ineffective for discoloration and degradation [1].

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During the last three decades advanced oxidation processes (AOPs), which combine powerful oxidizing agents (catalytic initiators) with UV or near-UV light, have been applied for the removal of resistant organic pollutants and xenobiotics. Among them the photocatalytic oxidation, especially TiO₂ mediated photocatalysis, has been proved to be a promising technology for water treatment in order to destruct a variety of organic and inorganic contaminants [2–5]. TiO₂ is attractive as photocatalyst because of its powerful catalytic activity, high chemical stability and low cost. When TiO₂ absorbs UV light ($\lambda < 385$ nm), electron and hole pairs (e_{CB}^-/h_{VB}^+) are generated respectively in the conduction and valence band. The e_{CB}^- is commonly scavenged by molecular oxygen while h_{VB}^+ can initiate oxidative process at the surface of catalyst. Upon reaction with molecular oxygen, the e_{CB}^- yields superoxide anion radical ($O_2^{\cdot-}$) which can lead to a number of reactive oxygen species (i.e., $\cdot OH$, $O_2^{\cdot-}$, H_2O_2 , 1O_2 , etc.) [6]. In aqueous media, the hole typically reacts with adsorbed H₂O, hydroxide or surface titanol groups (–TiOH) to produce hydroxyl radical ($\cdot OH_{abs}$), a powerful oxidant [7]. The

Table 1

Calcination conditions (temperature (T) and time (t)), composition (% anatase content), textural characteristics (SSA, PV and PD), crystal size of anatase (d_A) and rutile (d_R) as well as values for the energy gap (Eg) of the photocatalysts.

Sample	T (°C)	t (h)	%A	SSA (m ² g ⁻¹)	PV (cm ³ g ⁻¹)	PD (nm)	d_A (nm)	d_R (nm)	Eg (eV)
A/R4.9	250	3	83	50	0.26	57.3	19.1	35.7	3.17
A/R0.8	600	2	46	42	0.17	59.3	24.3	36.7	3.06
A/R0.5	600	7	32	36	0.14	62.9	23.5	36.9	3.04
A/R0.1	700	2	10	22	0.09	61.7	33.7	42.9	3.02
A/R0.02	700	8	2	15	0.06	70.8	52.0	59.1	3.00

reactive oxygen species generated during TiO₂ photocatalysis are responsible for the destruction of problematic pollutants [8].

It is well known that the photocatalytic effectiveness of TiO₂ depends on its crystal phase, particle size, crystallinity, specific surface area and pore structure [9]. TiO₂ consisting of anatase and rutile is usually used as photocatalyst. Anatase generally exhibits much higher activity than rutile. However, the activity of TiO₂ P25 (Degussa), consisting of anatase and rutile (~80/20 w/w), exceeds that of pure anatase in several reactions. Thus, P25 is frequently used as a benchmark for photocatalysts [10].

The enhanced activity of P25 and other anatase and rutile mixtures is generally thought to lie in the interfacial properties between the two polymorphs [11,12] and not due to some cooperative effect of their individual photochemical properties. Chemical contact between particles of these phases has been shown to be necessary to obtain an enhancement from the mixed-phase TiO₂ [13,14].

The necessity for “anatase–rutile” contact draws from their relative band edge positions. Because the band gaps of the two polymorphs are slightly different (3.0 eV for rutile and 3.2 eV for anatase), there exists the possibility for formation of a heterojunction between the two in which electron transfer can occur [15–17]. In this sense, “anatase–rutile” interfaces can potentially facilitate charge separation. Many groups have proposed that after Fermi level alignment, the conduction band edge of rutile should be lower than that of anatase, resulting in favorable conditions for electron transfer from anatase to rutile [17].

Studies on the anatase to rutile ratio and its influence on photocatalytic activity of TiO₂ for the photodegradation of organic compounds are not scarce in the literature [18–23]. On the other hand, the photocatalytic activity of titanium dioxide is expected to depend also on the mode of adsorption of reactants on its surface. Thus, the knowledge of the mechanism of adsorption of the various reactants on the surface of titanium dioxide would be extremely useful for understanding its photocatalytic behavior. However, studies concerning this issue are rather scarce in the literature [24–30]. On the other hand, the progresses pointed out concerning the elucidation of the deposition modes of various ionic species at interfaces of “oxidic carries/aqueous solutions” including titanium dioxide [31–36] and the mapping obtained for the surface sites developed on the surface of titanium dioxide P25 in contact with aqueous solutions [37], allow us to approach the aforementioned issue in a molecular level.

In a recent work we have investigated the effect of calcination temperature and time on the structural and textural changes of commercial TiO₂ P25 sample. We have found that a fine control of anatase to rutile ratio (A/R) in this material and thus of the energy-gap and the population of heterojunctions may be obtained by proper adjustment of the calcination temperature and time [38].

The purpose of the present work is twofold: (i) the elucidation of the mechanism of adsorption of two representative azo-dyes, one acidic (Orange G) and one basic (Yellow 28), on the titanium dioxide (Degussa P25) surface, (ii) the study of the influence of the anatase to rutile ratio, obtained by the proper adjustment of the calcination parameters of TiO₂ P25, and the concomitant regulation

of the population of heterojunctions between these phases on the photocatalytic degradation of the aforementioned azo-dyes.

2. Experimental

2.1. Photocatalysts preparation

TiO₂ P25 (Degussa) has been used as starting material and its A/R ratio was changed by air calcination at various temperatures up to 700 °C for various time intervals. The calcined samples, denoted as A/R x , where x indicates the value of the A/R ratio and the corresponding calcination conditions are compiled in Table 1.

2.2. Photocatalysts characterization

X-ray diffraction patterns (recorded in a Bruker D8 Advance diffractometer using CuK α = 1.5418 Å filtered by Ni) were used for the determination of the aforementioned ratio and the sizes of anatase and rutile crystals. The step size and the time per step were respectively fixed at 0.02° and 0.5 s in the range of 20° ≤ 2 θ ≤ 80°. The percentage of anatase and rutile in the studied samples was calculated using their most intensive peaks and their sensitivity factors balanced towards corundum. The mean crystallite size was estimated using the Scherrer's equation. The textural characteristics (specific surface area – SSA, pore volume – PV and mean pore diameter – PD) of the calcined samples were determined by N₂ physisorption measurements using a Micromeritics Tristar 3000 apparatus. The band gap values (Eg) of the samples were determined by UV–vis diffuse reflectance spectroscopy (DRS) using a Varian Cary 3 instrument equipped with suitable integration sphere. Properly modified diffuse reflectance spectra ($[F(R_{\infty})/h\nu]^{1/2}$ vs. $h\nu$) were used. The intercepts from the extrapolation of the linear part of these spectra provided the Eg values [39]. The point of zero charge of TiO₂ P25 was determined by potentiometric mass titrations (PMT) [40] in the presence and absence of the two azo-dyes in the electrolyte solutions. The isoelectric points of TiO₂ P25 were also determined by micro-electrophoresis using Zetasizer Nano series ZS Malvern instrument in the presence and absence of the two azo-dyes. Adsorption edges of the two azo-dyes on TiO₂ P25 were recorded in the pH range of 2.5–9.0.

2.3. Photocatalysts evaluation

The photocatalytic behavior of the calcined samples was determined at room temperature in a 600 ml semi-batch photoreactor (Heraeus) fed with 15 ml/min air. The reaction mixture, containing 0.3 g of photocatalyst and 400 ml of aqueous solution of azo-dye (0.1 g/l), was remained under stirring for 0.5 h in dark in order adsorption equilibrium to be achieved. Then, it was irradiated using an immersion low pressure Hg lamp (TQ 150) being in a glass cooling jacket filled with re-circulated deionized water. In this way the UV irradiation in wavelengths lower than 300 nm was cut off (see the spectrum of irradiation coming in the reaction suspension in Fig. S₁). The reaction progress was monitored by spectroscopic analysis of filtered (Millipore cellulose filters 0.22 μ m) samples withdrawn

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