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An improvement of photocatalytic activity of TiO_2 Degussa P25 powder

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ABSTRACT

The photocatalytic activities of Degussa P25 powders annealed at various temperatures in vacuum and air were studied together with investigations of their compositions by XPS, of their crystal structures by XRD and of their specific surface areas by BET. It is shown that the photocatalytic activity of P25 powders was remarkably enhanced after vacuum annealing; the kinetic coefficient can be raised by 75% during annealing at 400 °C. It is obvious that this enhancement is not related to the adhesion ability of the P25 powders.

1. Introduction

It is generally accepted that the theoretical model of photocatalysis on a TiO_2 surface consists of different consecutive steps, where each one is essential for the activity and the efficiency of the photocatalyst [1]. The initial step of the photocatalytic process consists in the generation of electron–hole pairs upon irradiation of the material with photons of energies that are at least equal to those of the band gap values. In the second step, the formed electron–hole pairs can either recombine in the bulk or diffuse to the surface where they can participate in chemical reactions. In this step, the lifetime and the velocity of the electron–hole recombination is crucial. Charge carrier traps are used to promote the trapping of electrons and holes at the surface leading to recombination suppressing and to more efficient charge transfer processes.

The next step is the creation of $H^{\bullet *}$ and $OH^{\bullet *}$ radicals as a result of the electron–hole interaction with water and, finally, a probable multiple step reaction of organic compounds with active radicals. The electron transfer process is more efficient if the species are pre-adsorbed on the surface [2]. However, so far, the influences of the different stages of this model on the final efficiency of the photocatalysts were not well determined.

It should be emphasized that the photocatalytic activity of TiO_2 depends on quite a number of parameters including the crystal structure, the ratio between the anatase and the rutile phases, the particle size, the specific surface area and the mean pore size [3]. In addition, TiO_2 is a material that is very adequate to build tiny structures in all sorts of sizes and shapes [4]. In particular, TiO_2 samples prepared and treated by different methods exhibit a great variety in photocatalytic efficiency even though they have the same crystal form. Beyond this, the kinetic constant of the photocatalytic degradation depends on the conditions of the experiment, namely, whether the heterogeneous catalysis is taking place on the solid/gas surface or on the solid/liquid one.

Using first-principles calculations, the total energies of the stoichiometric TiO_2 surfaces along with the equilibrium shapes (the Wulff construction) of macroscopic rutile TiO_2 crystals have been established [5]. It was shown that the (1 1 0) surface has the lowest surface energy and that (0 0 1) surface has the highest one. The respective calculations of the surface energetics and the shape reconstruction of macroscopic crystals for anatase TiO_2 were also effectuated [6,7]. Anatase (1 0 1) and (1 0 0) surfaces have the lowest energies of 0.44 and 0.53 J/m^2, respectively, and the (1 1 0) surface has the highest energy of 1.09 J/m^2 which are all higher than the rutile (1 1 0) surface energy of 0.31 J/m^2. As a consequence, some of these surfaces can be present in nano-crystalline materials. However, it should be taken into account, for comparison with experimental crystal shapes, that the Wulff construction gives the equilibrium crystal shape of macroscopic crystal and that the

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calculations are strictly valid only at zero temperature. Most of the methods for nanocrystals synthesis do not present equilibrium thermodynamic conditions.

The bulk structures of reduced TiO_{2-x} crystals are quite complex with various types of defects such as oxygen vacancies, Ti^{3+} and Ti^{4+} interstitials and planar defects such as crystallographic shear planes (CSPs). The defect structure varies with oxygen deficiency and the question which type of defect is dominant in which region of oxygen deficiency is still a subject of studies [3].

There is a vast spectroscopic and chemical evidence for the presence of point defects in samples annealed in vacuum that leads to the presence of Ti^{3+} ions. Their concentration is typically reported as being of several percent. The ultraviolet photoemission spectroscopy (UPS) spectra of single-crystal surfaces contain a band gap feature at ~1 eV below the conducting band edge which has been interpreted in terms of occupied Ti 3d states [8].

Various attempts for improving the photocatalytic properties of TiO_2 by annealing the samples in air and/or in vacuum have been made. These attempts were based on different ideas. Some of the obtained results are discussed below. Before, it should be emphasized that TiO_2 nanopowders prepared by different methods can have not only different morphology and different surface chemical composition, but also different crystal compositions. For this reason, all the experimental results can be divided into two classes, namely, into results obtained with powders prepared by different methods [9–13] and into results obtained with P25 powders [14–17]. It should be emphasized that no studies of changes in surface chemical composition along with a thermal treatment were done in all the above mentioned experimental studies. The kind of heterogeneous catalysis used for photolysis experiment is also important.

The existence of anomalies in temperature dependence of dielectric constant in anatase thin films was experimentally established in [18]. These anomalies can be easily created by annealing in vacuum and be suppressed in low pressure of oxygen and, therefore, they are supposed to be connected with oxygen vacancies. It means that electronic charge distributions in the region around vacancies are not symmetrical so that additional dipole moments are present [18], which can favourably influence the electron–hole separation. This mechanism was not considered neither by theory nor in experiments. Therefore, the essential new feature in the present paper is the aim to create oxygen vacancies by annealing in vacuum and to compare the results with annealing in air. Since, the presence of various species adsorbed on the TiO_2 surface influences the photocatalytic activity and changes in the surface chemical composition during temperature treatment XPS measurements were performed. In addition, based on the fact that the phases of anatase and rutile of P25 contain separated nanocrystals and that a direct electron transport between rutile and anatase through the common boundary does not exist, it is possible to estimate changes in the photocatalytic activity of anatase phase, separately.

2. Materials and methods

2.1. Sample preparation

Samples were prepared using the Degussa P25 powder with a grain size of about 20 nm. One series of the samples was annealed in vacuum ($\sim 2.5 \times 10^{-5}$ mbar) at temperatures between 20 and 750 °C for 4 h. During annealing the samples were placed in titanium foil crucibles within a stainless steel furnace with a copper cylinder for temperature homogenization. As heaters, two halogen lamps (1 kW) were used. Another series of samples were prepared by annealing in air at the same temperatures for 4 h.

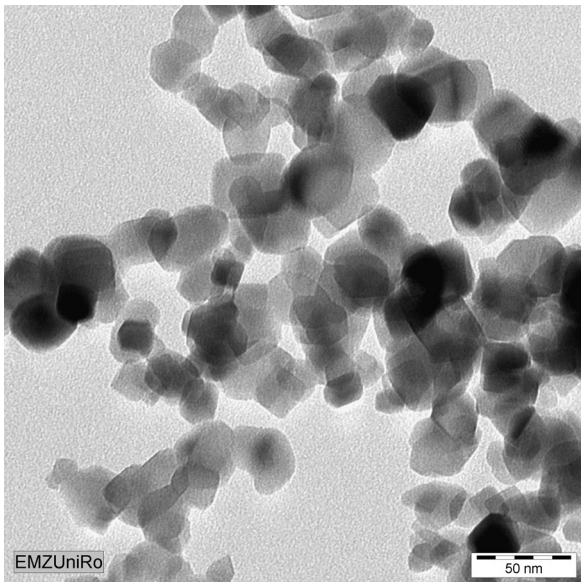

Fig. 1. TEM image of the Degussa P25 powder sample annealed at 200 °C, during 4 h.

In Fig. 1, a typical transmission electron microscopy (TEM) image of the sample annealed in vacuum at 200 °C is shown, evidencing that the grain sizes remained after annealing.

2.2. Phase control measurements

The crystal structure of the samples was studied using a high-resolution PANalytical x'PertPRO XRD instrument with Cu Kα radiation (λ = 1.54184 Å) in θ–2θ configuration. The anatase/rutile ratio in the samples was determined using Rietveld refinement procedure provided by FullProf program [19,20] as well as commercial PANalytical x'PertPRO software. For typical XRD pattern 2θ interval was 10–100° with the step $\Delta\theta = 0.008°$, the results of Rietveld refinement are shown in Fig. 2. The typical parameters of the refinement were $R_P \approx 5.4$, $R_{WP} \approx 7.81$, GOF–index ≤ 1.7.

2.3. XPS composition control

The TiO_2 samples were analyzed by X-ray photoelectron spectroscopy (XPS) using XSAM800 (KRATOS) X-ray spectrometer operated in the fixed analyser transmission (FAT) mode. An Al Kα (1486.7 eV) X-ray source was used. The analyser was operated at 20 eV pass energy both for detailed and survey spectra. All the binding energies were referenced to the C 1s peak at 285.0 eV, assigned to carbon singly bound to carbon and hydrogen. For quantification purposes, the following sensitivity factors were used: Ti 2p – 1.8, O 1s – 0.66 and C 1s – 0.25. Other details on data acquisition and treatment were as published elsewhere [21]. Some studies dedicated to the determination of the relation between Ti^{3+}/Ti^{4+} states for the samples annealed *in situ* in ultrahigh vacuum (10^{-9} mbar) were done using XPS setup with a PHI 5600ci spectrometer at the Leibniz Institut für Werkstoffkunde, Dresden. A monochromated Al Kα (1486.7 eV) X-ray source is used. The analyser operated at 5.85 eV pass energy for detailed spectra using a 0.05 eV step width. Calculation of the Ti^{3+}/Ti^{4+} concentration is based on the area ratio of these two titanium species in the $Ti2p_{3/2}$-peak.

2.4. Effective surface area measurement

To determine the specific surface area and the pore size distribution, a Micromeritics ASAP 2020–Physisorption Analyzer was