Ph.D. thesis

Preparation and Characterization of TiO$_2$ Nanoparticles and TiO$_2$/ Layer Silicate Photocatalyst - Adsorbent Systems

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1. Introduction and objectives

The majority of environmentally harmful toxic compounds are efficiently degradable by conventional chemical and biological methods. Hovewer, there are compounds which are not degradable by these processes. Consequently it is necessary to further improve the already existing efficient and economical water treatment technologies.

Heterogeneous photocatalysis is the one of the most dynamically developing fields of advanced oxidation processes in the past 20 years. Under appropriate conditions semiconductors are efficiently applicable in the degradation processes of organic pollutants. Titanium dioxide – by right of its physical and chemical properties – is the most convenient photocatalyst. The preparation of titanium dioxide with high catalytic activity and suitable properties is still a great challenge. Controlled colloid chemical methods (such as sol-gel technologies) make possible the synthesis of titanium dioxide catalysts with different particle sizes, specific surface areas and crystallinities. Nowadays it has become possible to prepare semiconductor nanoparticles with very small particle size, measuring a few nanometers.

During the water treatment process or technological applications in aqueous medium significant aggregation of the nanoparticles can take place, hence it is practical to fix the titania nanoparticles on the surface of a support or in nanocomposites. The clay minerals with high specific surface area which can be found in the natural environment offer a promising possibility to prepare such nanocomposites.

In case if pollutants cannot be easily removed by simple methods, the concomitant or successive application of adsorption (non-destructive) and oxidative (destructive) techniques may be one of the possible solutions. Hydrophobized clay minerals, which are excellent adsorbents can be combined - under adequate circumstances - with the most efficient titanium dioxide photocatalysts. The suitable adsorbent should not deactivate the photocatalyst and the photocatalyst should not damage the adsorbent under the given conditions.

One of the objectives of my doctoral thesis is the preparation of active anatase nanoparticles with a diameter in the 2-10 nm range. The preparation conditions were optimized in order to obtain large amounts of titanium dioxide with high specific surface area and photocatalytic activity by a simple and fast aqueous synthesis procedure. The size of the primary and secondary (aggregated) particles can be determined by optical characterization of the $TiO_2 \cdot x \, H_2O$ sols. Characterization of the powder samples resulting from the sol-gel process by X-ray diffractometry, nitrogen gas adsorption analysis, transmission electron microscopy and by thermoanalytical measurements was also set as an objective. The possibilities of improving the crystallinity of the titanium dioxide products by additional heat treatment were also investigated.

Titanium(IV) bromide, a new Ti(IV)-precursor compound was applied in polar organic medium – dimethyl sulfoxide – for the synthesis of titanium dioxide nanoparticles. By covering the surface of the produced nanoparticles the extent of their growth was regulated.

A further objective was the development of new techniques for the preparation of TiO_2-montmorillonite nanocomposites. A new type of composite was prepared by preadsorption and subsequent hydrolysis of titanium(IV) alkoxide on sodium montmorillonite in alcoholic medium. Taking into account the material properties of the samples produced, our aim was to find the simplest and most inexpensive heat treatment. This preadsorption method was also tested on hydrophobic clay mineral since it gives an excellent way to stabilize titanium dioxide on a good adsorbent. In order to protect the hydrophobic silicate surface, naturally the hydrothermal heat treatment was chosen.

The parameters of the composite preparation techniques described in the literature were reviewed and some proposals for the improvement of the method were made by more complex investigation of the $TiO_2 \cdot x \ H_2O$ sol. My goal was to produce, by the simplest possible synthesis route, TiO_2-montmorillonite composites already containing the catalytically active phase of titania without a powerful heat treatment. The material properties of the nanocomposites as a function of titania content were studied together with changes in the structure of the produced catalysts caused by calcination.

All these samples were qualified in photocatalytic tests principally by decomposition of salicylic acid, phenol and 2-chlorophenol as model compounds. A wide range of analytical methods were used in order to obtain a better picture of the chemical transformations during decomposition. Observations are made about the relationship between the adsorbed amount of the substrate and the activity of the catalyst used. Microcalorimetry was also performed. The effect of the titanium dioxide content of the nanocomposites and the concentration of the catalyst suspension on the photocatalytic oxidation of phenol was studied. The activities of our samples were compared with that of the well-known and excellent Degussa P25 TiO_2.

The photocatalytic mineralization of 2-chlorophenol adsorbed on hydrophobic montmorillonite was investigated in suspensions containing adsorbent-TiO_2 physical mixture and hydrophobic nanocomposites. The possibility of reuse was examined by thermoanalytical, X-ray diffraction and adsorption measurements. The applicabilities of hydrophilic and hydrophobic nanocomposites were compared. The examination of the complex applicability of montmorillonite in heterogeneous photocatalytic processes was also set as an aim.

2. Materials and methods

Titanium(IV) ethoxide, titanium(IV) isopropoxide, titanium(IV) chloride and titanium(IV) bromide as titanium(IV) precursor compounds were used in my experiments. The medium of the preparation was high purity water, 2-propanol or dimethyl sulfoxide. Hydrogen chloride, hydrogen fluoride and sodium hydroxide solutions were used to adjust the pH and for the reactions. Sodium citrate and sodium 2-ethylhexanoate were applied as surface modifiers. Bentonite from Mád organophilized with hexadecylpyridinium chloride and Wyoming, Volclay and EXM838 Süd-Chemie sodium montmorillonite were used as clay minerals.

In the photocatalytic test reactions salicylic acid, phenol and 2-chlorophenol model compounds were used. Potassium chloride and sodium fluoride were chosen for adjusting the ionic strength. For the determination of total organic carbon content, potassium hydrogenphtalate as calibration standard and high purity oxygen and argon were used. The reference materials for the photocatalytic tests were Degussa P25 TiO_2 (75 wt % anatase and 25 wt % rutile), Aldrich anatase and Bayertitan anatase.

Absorption spectra of aqueous $TiO_2 \cdot x\ H_2O$ sols were taken and salicylic acid concentrations were determined in an Uvikon 930 and a CHEM2000-UV-VIS (Ocean Optics) spectrophotometer. The fluorescence spectra of the particles prepared in dimethyl sulfoxide were collected by SPEX FluoroMax spectrofluorometer.

Dynamic light scattering experiments were performed using a SEMATech instrument characterizing the average hydrodinamical diameter of the aggregates.

The charge of the particles in aqueous dispersions and their streaming potentials were measured by a Mütek PCD 02 particle charge detector. The composition was determined at the equivalent point of charge neutralization of the sodium montmorillonite and titania dispersions reached upon their heterocoagulation.

The basal distances of the clay minerals and intercalated structures were measured by X-ray diffractometry. Measurements of the powder samples were performed on a Philips diffractometer (PW 1820/1830, CuK-α = 0.1542 nm) in the 1-15° (2Θ) range at room temperature, and the basal distance values of the given clay minerals were calculated from the first Bragg reflections. In the 20-40° (2Θ) range the characteristic reflections of titania crystal phases were analyzed and the average diameters of the particles were obtained by means of the Scherrer equation.

Specific surface area of the samples were determined by a Micromeritics Gemini Type 2375 gas adsorption analyzer. The nitrogen adsorption and desorption isotherms were measured at 77 K.

The titanium dioxide and nanocomposite products prepared were also studied by thermoanalysis using a MOM Derivatograph Q-1500 D instrument. The thermoanalytical measurements were carried out in air atmosphere, in the 25-1000 °C temperature range.

Transmission electron microscopy images were obtained by means of a Philips CM-10 electron microscope, using an accelerating voltage of 100 kV. Particle size distributions and average particle diameters were determined by the UTHSCSA Image Tool program. Titania nanoparticles synthesized in dimethyl sulfoxide medium were studied by high resolution transmission electron microscopy (HR-TEM, JEOL 4000 Ex, 200 kV).

The adsorption of the substrate molecules chosen for the photocatalytic tests was studied by microcalorimetry (Thermal Activity Monitor, TAM 2277).

The determination of the total organic carbon content (TOC) is one of the analytical methods suitable for the characterization of photocatalytic processes. The samples taken from the irradiated suspensions were measured by an Euroglas 1200 instrument.

The Euroglas TOC 1200 apparatus is equipped with an optional unit for the determination of halide content, thus the inorganic chloride and the total chlorine contents were measured in the investigated suspensions, solutions and in the separated solid samples.

The concentration profiles of phenol, 2-chlorophenol and their degradation products were monitored by means of HPLC, with a Merck-Hitachi L-4250 UV detector and an L-7100 pump.

In the majority of the experiments a thermostated reactor equipped with an immersion type UV lamp (high-pressure mercury lamp, 150 W) was used. The radiation emitted by the lamp was mainly in the range 240-366 nm. Air or oxygen was bubbled through the stirred suspension (375 mL) in the reactor continuously, ensuring a constant dissolved oxygen concentration. Samples were taken from the irradiated suspension at predetermined intervals and were subjected to analysis. In some experiments a so-called solarbox was used, which is a metal box equipped with three parallel Philips UV tubes (TL K05, λ = 360 nm, I = 33-35 W m^{-2}) at the top inside, below which the irradiated samples can be symmetrically arranged.

3. New scientific results

T.1 *The preparation of titanium dioxide by homogeneous nucleation in 2-propanol-water mixture*

The primary particle diameter of homogeneous $TiO_2 \cdot x\ H_2O$ sol produced by hydrolysis of titanium(IV) isopropoxide and subsequent acidic peptization of the $Ti(OH)_4$ dispersion at 50 °C for 12 h was around 1-2 nm, and the secondary particle diameter (the size of the aggregates) was around 10-20 nm. The majority of the particles was formed in anatase phase (70 wt %) during the heat treatment at 50 °C; the remaining part was amorphous. Depending on the concentration of the $TiO_2 \cdot x\ H_2O$ dispersion and the amount of acid added, only anatase phase or anatase-rutile phase mixture can be synthesized. The important molar ratio determining the crystal phase of the particles and the concentration of the sol is $n_{Ti(OiPr)4} : n_{2-PrOH} : n_{H2O} : n_{HCl}$. The crystallinity of the product was regulated by a hydrothermal sol-gel process (at 100-150 °C): when crystallinity is increased, particle size increases (D = 3-8 nm) and specific surface area decreases.

$Ti(OH)_4$ (or $TiO_2 \cdot 2\ H_2O$) xerogel with very high specific surface area (577 m^2/g) was produced by hydrolysis of titanium(IV) isopropoxide in 2-propanol. At 320-400 °C the xerogel can be fully transformed to anatase titanium dioxide consisting of particles with an average diameter of 12 nm and a specific surface area of 106 m^2/g.

T.2 *The preparation of titanium dioxide by homogeneous nucleation in dimethyl sulfoxide medium*

Stable titanium dioxide sol was prepared in dimethyl sulfoxide by hydrolysis of titanium(IV) chloride and titanium(IV) bromide. In the case of titanium(IV) chloride a very rapid reaction took place after the addition of water. The titanium(IV) chloride and the dimethyl sulfoxide molecules can form $[Ti(Cl)_4(DMSO)]$ and $[Ti(Cl)_4(DMSO)_2]$ complex compounds, which are the precursors of the hydrolysis. The formation of these complexes decreases the reaction rate, thus the growth rate of the particles is diminished, which favours the generation of the ultrasmall nanoparticles. The hydrolysis of titanium(IV) bromide with less ionic (more covalent) character can take place only in the presence of dissolved sodium hydroxide, at a controlled rate. The average particle diameter was determined by X-ray diffractometry and absorption spectrophotometry as 1-2 nm; when measured on HR-TEM micrographs, however, the diameter was around 4-5 nm. The smallest particle size (D = 1-2 nm) was obtained with sodium citrate as organic stabilization agent, measured by HR-TEM; the emission spectra of these particles show very low intensity, also indicating their poor crystallinity. By the evidence of HR-

TEM, the particles prepared at room temperature were already crystallized in the anatase and rutile phases.

T.3 *Heterogeneous nucleation of TiO_2 on hydrophilic and hydrophobic montmorillonite*

3.a TiO_2-montmorillonite nanocomposites were prepared by preadsorption of titanium(IV) isopropoxide and subsequent hydrolysis of alkoxide, and were finally separated and calcined at 400 °C for 4 h (preadsorption method). The specific surface area of the nanocomposites prepared by the preadsorption method was not too high (100-150 m^2/g) and it depended first of all on the TiO_2 content (it increased with increasing semiconductor content). The smaller particles act as pillars in the interlamellar space, whereas the larger particles are located at the external surfaces of the clay mineral lamellae or form only a physical mixture with montmorillonite. The TiO_2-pillar size calculated from basal distance values ($\approx$ 3 nm) and the particle diameter determined from TEM micrographs (3-4 nm) were in some cases in close agreement; at other locations of the samples, however, I also found images of particles free of support and these were considerably larger (D_{TEM} = 10-12 nm).

3.b   The slight intercalation was achieved in the preadsorption process on hydrophobic HDP-montmorillonite dispersed in 2-propanol after hydrolysis of adsorbed titanium(IV) isopropoxide and subsequent hydrothermal heat treatment (at 150 °C for 12 h). The adsorbed molecules were partially hydrolized on the internal surface of montmorillonite, resulting in intercalated nanoparticles. The catalyst-adsorbent hydrophobic nanocomposite (HDPM-T) preserved its adsorption capacity, as confirmed by adsorption measurements.

T.4 *Heterocoagulation of titanium dioxide and montmorillonite*

4.a Nanocomposites containing titanium dioxide can be synthesized by the addition of $TiO_2 \cdot$ x H_2O sols with different pH values (pH = 1 and pH = 4) to aqueous montmorillonite suspensions (heterocoagulation process). These nanocomposites already contains titanium dioxide in anatase phase without any heat treatment (hydrothermal heat treatment or calcination), since crystallization already took place in the sol (50 °C). The novelty of this process is that the heterocoagulation was carried out using titania sol containing anatase nanoparticles with very small primary and secondary particle sizes. The pH values of the titania sols used in the preparation processes published to date were in the range of 0.7-1.8, presuming that pillar formation at higher pH values is prevented by relatively large titanium dioxide aggregates.
4.b The mixing volume ratio of the montmorillonite suspension and the titania sol was systematically varied and TiO_2-montmorillonite nanocomposites

were prepared with 20, 33, 50, 66, 75 wt % TiO_2 content. Although the specific surface area of the samples did not depend on the quality of the montmorillonite applied or the concentration of the TiO_2 sol used, it did depend on the TiO_2 content and the pH of the sol applied. The samples prepared with acidic (pH = 1) titania sol had higher specific surface areas in each case. Increasing the amount of TiO_2 (up to 66 wt %) naturally led to increased specific surface areas up to a maximum of 280 m^2/g, followed by a slight decrease.

4.c   Calcination of the samples at 400 °C increased the size of the particles and decreased their specific surface area; at the same time, however, basal distances did not change in the samples prepared under mild acidic condition (pH = 4). Although pillar size did not change significantly, the size of the particles on the external surfaces was drastically larger. The basal distance values and the particle diameters of the sample containing 50 wt % TiO_2, prepared with acidic sol (pH = 1) and from that calcined sample, were very similar. It follows that this preparation process produces more stable products.

T.5 *The adsorption of salicylic acid and phenol on titanium dioxide*

The adsorption isotherms of salicylic acid were determined on the Degussa P25 titanium dioxide (43 m^2/g), on the $TiO_2/0/AC$-400/4 (106 m^2/g) and on the $TiO_2/0/S2$ (237 m^2/g) catalysts. It is clearly shown that salicylic acid is preferentially adsorbed on titanium dioxide. The adsorbed amounts calculated from the isotherms were 0.059, 0.172 and 0.443 mmol/g, respectively. The adsorbed amount of phenol – due to its very poor adsorption – was not determinable. Adsorption microcalorimetry of phenol on different titanias showed very weak heat effects, only at pH = 7 were any evaluable signs found. The adsorption heat effect of phenol is one order of magnitude smaller than that of salicylic acid.

T.6 *Relationship between adsorption properties and photocatalytic degradation rate*

In the case of salicylic acid which can strongly adsorb on titanium dioxide, photodegradation can easily proceed on the surface in direct photooxidation, thus the smaller particle size and the higher specific surface area of the catalyst are beneficial for fast photooxidation. The species most active in direct photooxidation on the surface are chemisorbed salicylic acid molecules, which means that a larger adsorbed amount causes a higher photocatalytic degradation rate. In close agreement with the adsorption and microcalorimetric studies, the initial reaction rates of photodegradation increase in the order of $k_{Bayertitan} < k_{P25} < k_{TiO2/0/AC-400/4}$. In the case of the weakly adsorbable phenol, the photocatalytic activity can be improved by enhancing the crystallinity of the catalyst. The

number of radicals generated can be increased by enhanced crystallinity, thus photooxidation processes can occur with higher probability in the adjacency of TiO_2 surfaces. The hydrothermal crystallization (50-150 °C) of titania produced by the sol-gel process unambiguously increased the catalytic activity of the samples for the photooxidation of phenol, which can be explained by the enhanced crystallinity of the catalysts. It should be emphasized that in the case of heterogeneous photocatalysis it is not necessarily the case that smaller particle sizes and higher specific surface areas always provide higher photocatalytic activities because smaller particle sizes may be associated with higher excitation energies. It can be presumed that the probability of the recombination of the electron-hole pairs generated by irradiation of the semiconductors is high when the crystallinity of the particles is too low.

T.7 *Dependence of the photodegradation rate of salicylic acid and phenol on the composition of TiO_2-montmorillonite catalysts*

The highest rate of salicylic acid degradation was measured in the case of the catalyst with 50 wt % TiO_2 content prepared by heterocoagulation under acidic condition (pH = 1): it exceeded the reaction rate observed on P25 Degussa TiO_2. The amount of salicylic acid degraded per unit time, normalized to titanium dioxide content is significantly higher than that for Degussa P25 TiO_2. Maximum specific decomposition rate was measured at 33 wt % TiO_2 content, indicating that it is at this composition that the surface of TiO_2 particles is most accessible for chemisorption of salicylic acid. Calcination of TiO_2-montmorillonite nanocomposites was not beneficial for the catalytic properties since their structure became more compact, decreasing the active accessible surface area. The mineralization rate of phenol on P25 Degussa TiO_2 was best ($\approx$ 73 %) approached by the nanocomposite containing 66 wt % TiO_2 at the highest catalyst concentration used (0.50 w/v %).

T.8 *Relationship between adsorption and photocatalysis on hydrophobic TiO_2-montmorillonite adsorbent-catalyst systems*

The photodegradation of 2-chlorophenol was measured in direct photolysis, in Degussa P25 TiO_2 photocatalyst suspension, in a suspension containing a physical mixture of HDP-montmorillonite (HDPM) and Degussa P25 TiO_2, in the titania pillared hydrophilic montmorillonite (TPM) suspension and in the hydrophobic nanocomposite (HDPM-T) suspension.

8.a   The hydrophobic HDPM-T system (17 wt % TiO_2, D_{TiO2} = 8 nm) was as good an adsorbent as the physical mixture of HDPM and Degussa P25 TiO_2; however, photocatalytic oxidation of the HDP^+ cation (used to organophilize the adsorbent) by TiO_2 fixed on HDPM proceeded continuously (25 % in 10 h),

since the TiO_2 particles are adjacent to the HDP^+ cations and the alkyl chains are readily available for the photogenerated oxidizing species. The physical mixture is therefore better suited for degradation, because the oxidizing radicals cannot penetrate into the interlamellar space of hydrophobic montmorillonite: they are transformed by reactions before penetration. It was also found that the rate of decrease of total organic carbon content was very similar to the value observed for Degussa P25 TiO_2.

8.b Although the photodegradation rate of 2-chlorophenol was relatively high in the case of hydrophilic TPM system (17 wt % TiO_2), a rather low efficiency of total mineralization was found, because particle size is rather small ($D_{TiO2} =$ 3.4 nm) and thus crystallinity is also low.

4. Publications in connection with the Ph.D. thesis

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