Surface-modification of Silica-particles by nano-scaled Titania-particles via Sol-Gel-Process

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1 INTRODUCTION

Titania based nanoparticles and thin layers are of great interest for a potential application as photocatalyst to clean sewage water from harmful substances. While thin layer TiO₂ catalysts are stable fixed on a substrate material, and thus they are stable against agglomeration, the thin layers have only a small active catalytic surface. In contrast, the electro-statically stabilized nanoparticles, having a diameter < 50 nm, show a very high specific surface area at an acid pH range, but when used in more or less neutral sewage water, these particles have a strong tendency to agglomerate. This is caused by the acting van-der-Waals forces and the reduced electro-static repulsion. Thus, the consequence of it is a very small catalytically active surface of the agglomerates. The effectiveness of the TiO₂ during the cleaning process is insufficient for further industrial application.

To overcome these difficulties, the particle surface and structure have to be modified. For example, it should be possible to coat ultra-fine particulate materials (host particles with a diameter of several hundred nanometers) with much smaller nano-scaled nuclei (guest particles, size < 50 nm). These so-called guest particles are acting as spacers between the ultra-fine materials, adhesion forces are lowering and solid powder handling will be improved.

In the experimental work, ultra-fine silica (Stöber) particles and nano-scaled titania particles are made out of acid and alkaline solution systems. The surface modified ultra-fine SiO₂ particles are built up from the SiO₂ and TiO₂ suspensions simply by mixing. Additionally, another approach for particle coating is possible; the process of nuclei formation of the nano-scaled TiO₂ spacers should occur in the SiO₂ suspension, directly. Thus, the activity of the photocatalytic TiO₂ by a combination of the TiO₂ and SiO₂ particle systems is improved. Well-founded knowledge of the inter-particle interactions, as well as of the stability of both particle systems (TiO₂ and SiO₂) is essential to assure an effective coating-process.

Generally, there are existing different approaches to modify the surface of a host particle. So, the coating process could lead to the formation of (a) a dense, closed TiO₂ layer, (b) a homogeneous layer of mono-disperse TiO₂ particles and (c) a heterogeneous layer of poly-disperse TiO₂ particles around the ultra-fine SiO₂ particle (Fig. 1).

Several procedures have been reported in the literature to modify the ultra-fine SiO₂ particles with nano-scaled TiO₂.
On the one hand, there is the possibility to coat SiO$_2$ particles by using relevant precursors of TiO$_2$ causing a growth process to TiO$_2$ particles or to a TiO$_2$ monolayer on the SiO$_2$ surface, directly. Different processes, e.g. impregnation, precipitation, or sol-gel process, are being applied. Srinivansan and co-workers [1] added 270 nm monodisperse silica particles to a solution of tetra-tert-butyl-orthotitanate in tetrahydrofuran, getting up to a monolayer of TiO$_2$ around SiO$_2$ particles. Hanprasopwattana et al. [2] modified the process using a solution of tetra-n-butyl-orthotitanate in ethanol/water for coating SiO$_2$ with TiO$_2$. Hsu and co-workers [3] used monodisperse SiO$_2$ spheres with different diameters (from 0.40 µm to 1.30 µm), applying as precursor titanyl sulphate in sulphuric acid. In this study, the optimum amount for coating was found as 16 wt% TiO$_2$ related to SiO$_2$ resulting in a most uniform layer (90% by apparent surface coverage). Castillo et al. [4] deposited TiO$_2$ on SiO$_2$ by neutralising an acidic TiCl$_4$ suspension with ammonium hydroxide (16 wt% TiO$_2$/SiO$_2$ leading to 90% apparent surface coverage).

On the one hand, there is the possibility to coat SiO$_2$ particles by hetero-coagulation. Surface modified ultra-fine SiO$_2$ particles can be built up from SiO$_2$ and TiO$_2$ particles, directly. In general, the electrostatic oppositely surface charged particles are mixed, caused by the repulsively acting electrostatic forces there is an agglomeration process of both particle species. Ryu and coworkers [5] prepared TiO$_2$ coated SiO$_2$ through a sol-gel process. They used nano-scaled TiO$_2$ particles that were redispersed in nitric acid from TiO$_2$ precipitates (conversion of tetra-isopropyl-orthotitanate with water). Monodisperse SiO$_2$ particles (300 nm) were prepared through the procedure originally described by Stöber. The coating process was controlled by the weight ratio of TiO$_2$/SiO$_2$ and the pH of the mixture. Hetero-coagulation is only possible, when both particle species have an opposite electrical charge (zeta-potential). At a pH of 2.0 no hetero-coagulation occurs (both particle species are positively charged), at pH of 3.0 and 6.0 hetero-coagulation is possible, but TiO$_2$ forms agglomerates as a second phase (minimal charge difference), the optimal pH is 4.5 leading to a uniform silica coating with a smooth surface (maximal charge difference).
TiO₂/SiO₂ weight ratio of 5 wt% leads to isolated TiO₂ spots on SiO₂ of 15 wt% to an optimal TiO₂ particle layer, and more than 25 wt% to solid bridges between the particles and agglomeration. A similar approach was done by Hwang and co-workers [6]. SiO₂ (331 nm and 692 nm) and nano-scaled TiO₂ (16.9 nm) particles were used in the hetero-coagulation process. The optimal pH was 3.5, a TiO₂/SiO₂ weight ratio of 15 wt% leads to an apparent surface coverage of 90%. Wilhelm et al. [7] tracked the hetero-coagulation coating process by measuring the change in the zeta-potential during the gradual addition of TiO₂ sol to SiO₂ particles.

2 EXPERIMENTAL

Nano-sized titania particles were prepared by a sol-gel process at a constant temperature of 50 °C by a conversion of tetra-isopropyl-orthotitanate (9.8 g, 0.23 M) as precursor with water in an nitric acid solution (141 mL 0.1 M HNO₃, pH 1.3). This process is characterized by a rapid precipitation of large agglomerates (diameter up to 1000 µm), followed by a slow mechanically and chemically driven particle redispersion. Optimal reaction conditions for this process lead to particles of a size from 7.8 nm (primary particle diameter) up to 30 nm (agglomerate of 40 primary particles) were obtained. At a pH of 1.3, a mean particle diameter of 18.6 nm (volume mean) and 12.0 nm (number mean) is obtained. For a pH > 3.0 particle agglomeration was observed. The redispersion process took place under optimal reaction conditions for 10 hours.

Nano-scaled spherical silica particles (so-called Stöber particles) were synthesized by a sol-gel process with tetra-ethyl-orthosilicate, injected in a water isopropanol mixture under basic pH conditions (between 11.0 and 12.0) and ammonia as catalyst. By using appropriate process parameters, e.g. supersaturation, amount of catalyst, temperature etc., non-porous, monodisperse, spherical Stöber particles with mean diameters of 332 nm, 500 nm, and 800 nm are obtained.

The zeta-potential of the non-modified SiO₂ and TiO₂ particles was measured to determine the isoelectric points (point of zero charge). The IEPs of SiO₂ and TiO₂ are 2.3 and 6.8, respectively. Thus, hetero-coagulation is only possible in this pH range. It has to be kept in mind that TiO₂ is very sensitive to the pH value. A pH value > 3.0 leads to TiO₂ agglomeration (homo-coagulation).

Thus, in the first step of the hetero-coagulation process, TiO₂ sol was added to the acidified SiO₂ suspension. In the second step, the pH of the mixed suspensions was then raised by adding 0.1 M sodium hydroxide solution to induce the interactions between the SiO₂ and TiO₂ spheres. The most important factors that affect the uniformity of coating are the final pH value and the TiO₂/SiO₂ ratio.

3 RESULTS AND DISCUSSION

Figure 2 shows SEM images of TiO₂ coated SiO₂ particles (332 nm) prepared in various molar TiO₂/SiO₂ ratios at pH 3.0 and a temperature of 25 °C.

Fig. 2 SEM images of TiO₂ coated SiO₂ with 2 wt% (left) and 10 wt% TiO₂ (right)
The surfaces of the modified particles are rough and textured, indicating that the SiO$_2$ particle surface was covered by nano-scaled TiO$_2$ particles. While at a TiO$_2$/SiO$_2$ ratio of 2 wt%, single TiO$_2$ spots can be seen. A higher weight ratio of 10% already leads to the formation of solid particle bridges. When the loading of the TiO$_2$ particle is > 16 wt%, a monolayer of the closed hexagonal packing could be possible.

In Figure 3 the change of the zeta-potential of non-coated and coated silica (2 wt%, 10 wt% and 20 wt% TiO$_2$) with the change of the pH value is given. These data give an apparent surface coverage of 10% (2 wt% TiO$_2$), of 34% (10 wt% TiO$_2$), and 53% (20 wt% TiO$_2$), using the isoelectric points of the modified SiO$_2$.

![Figure 3 Change of zeta-potential of coated and non-coated silica particles with the change of pH](image)

**REFERENCE**


