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ORIGINAL CONTRIBUTION

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Preparation of spherical, mixed SiO_2/TiO_2 particles by the sol technique

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Abstract Preparation of silica, titania and mixed silica/titania particles has been studied. The region for formation of monodisperse SiO_2 particles in the phase diagram tetraethyl orthosilicate (TEOS)-ethanol-H_2O was studied as a function of NH_3 concentration at room temperature. Titania particles could be prepared at lowered temperatures and concentration of ammonia up to 0.01 M. The size of SiO_2 particles was 0.03–1 μm whereas TiO_2 particles were size range 0.5–0.8 μm. Mixed SiO_2/TiO_2 particles were prepared from prehydrolyzed TEOS/EtOH solutions by adding tetraethyl orthotitanate (TEOT). This was accomplished at 3 °C and slightly alkaline solutions. The final particle size of the mixed particles was about 0.3 μm.

Key words Silica – titania – mixed silica/titania particles – preparation – sol technique

Introduction

Stöber et al. [1] were the first to introduce a method for preparation of monodisperse silica particles from aqueous alcohol solutions of silicon alkoxides containing ammonia. After this pioneering work a lot of studies have been performed in this area [2–11]. Three reactions are generally used to describe the hydrolysis and condensation of metal alkoxides [12, 13]:

Hydrolysis:

$$\equiv M\text{–}OR + H_2O \Leftrightarrow \equiv M\text{–}OH + ROH \tag{1}$$

Alcohol condensation:

$$\equiv M\text{–}OH + \equiv M\text{–}OR \Leftrightarrow \equiv M\text{–}O\text{–}M \equiv + ROH \tag{2}$$

Water condensation:

$$\equiv M\text{–}OH + \equiv M\text{–}OH \Leftrightarrow \equiv M\text{–}O\text{–}M \equiv + H_2O \tag{3}$$

If two metallic compounds are involved, heterocondensation is possible [12].

$$\equiv M^{I}\text{–}OH + \equiv M^{II}\text{–}OR \Leftrightarrow \equiv M^{I}\text{–}O\text{–}M^{II} \equiv + ROH \tag{4}$$

where M is a metallic compound, normally Si or Ti, and R is an alkyl group, C_xH_{2x+1}, in most cases $-C_2H_5$ or $-CH_3$.

The reactions are highly pH dependent. At low pHs a three-dimensional gel network is formed, and at high pHs discrete particles [5]. In the following we will only discuss the formation of particles.

The most common mechanism for the formation of uniform particles has been proposed by LaMer and Dinegar [14, 15]. According to these authors an increasing supersaturation of the hydrous oxide due to a change in temperature or pH takes place until a critical concentration is reached. At this critical concentration a rapid self-nucleation stage will occur. This period should be short in order to obtain uniform particles. The precipitation reduces the supersaturation below a concentration where further nucleation is unlikely. The particle growth is governed by diffusion of monomers to the nuclei. This model has been claimed to be an oversimplification of the real mechanisms. Zukoski et al. [16–19] have proposed the growth mechanism in which the particle size is controlled by aggregation of subparticles in size of a few nanometers. In their studies the electron micrographs show the coexistence of large spheres and a large number of small aggregating particles [16], and they assumed that some step in the condensation pathway is rate determining. In contrast to this Matsoukas and Gulari [20–22] and van Blandeeren [23] concluded that the growth process is limited by the production of hydrolyzed monomers. Matsoukas and Gulari [20–22] suggested the particle nucleation to be a result of the reaction between two hydrolyzed monomers and the balance between monomer addition and nucleation determines the polydispersity and the final size.

Bailey et al. [24] have studied the mechanism of the silica particle growth by cryo-TEM measurements. They found that the dense particles seen upon drying are artifacts of the dried specimen preparation. The first dense particles appear, at the earliest, after 24 min reaction and these solutions may also contain low density particles. This indicates that the particles are in different stages in their growth. The authors could not find dense particles with sizes of 2–12 nm in the solution and concluded that the mechanism for stable particle formation could not be aggregation of particles in this size range. The authors proposed the following growth mechanism for silica particles. The alkoxide monomers undergo polymerization to form expanded polymeric species in solution and these molecules continue to grow by addition of monomers. Simultaneously they are also cross-linking internally by intramolecular reactions leading to their densification. The clusters continue to grow until they are no longer soluble, at which point they collapse. Once collapsed, hydrolysis and condensation continue, binding the particles together.

Stöber [1] found that the size of the silica particles obtained from the tetraethyl orthosilicate-ethanol-water mixtures varied from 50 nm to 1 μm. Bogush et al. [10] found that the largest average particle diameter with a narrow distribution is about 700 nm. The particle size was found to be dependent on the silicon alkoxide and alcohol used. Particles prepared in methanol solution were the smallest. The particle size increases with the chain length of both the alcohol and the alkoxide [1].

Generally, the SiO_2 particle size is found to increase with increasing concentrations of water and ammonia up to about 7 and 2M, respectively. In excess of these concentrations the particle size is decreasing [1, 3, 10, 12, 13]. The final particle size is usually reached within 3–10 h [2, 3] and the average particle size tends to decrease and standard deviation increases when the concentration of tetraethyl orthosilicate is increased. Tan et al. [25] studied the effect of temperature on the size of the silica particles. They found that a decrease in temperature gave larger monodisperse particles with a size of 2 μm. According to Bogush et al. [4] an addition of an electrolyte will increase the final particle size. Lindberg et al. [26] mapped the regions of existence of monodisperse particles in ternary diagrams of TEOS-water-C_2H_5OH for different ammonia concentrations.

The preparation of monodisperse TiO_2 particles follows the same hydrolysis/condensation route as for SiO_2 particles. In comparison with TEOS tetraethyl orthotitanate undergoes a fast hydrolysis already at room temperature. Matijevic et al. [27] prepared TiO_2 particles by aging an acidic solution of $TiCl_4$ which contained Na_2SO_4 at an elevated temperature. The particles obtained were spherical and they were of a narrow size distribution. The size of the particles increased with increasing ageing time and sulphate to titanium ratio. Visca et al. [28] obtained spherical TiO_2 particles by hydrolysis of aerosols consisting of liquid tetraethyl orthotitanate. The droplets were brought in contact with water vapor to start the hydrolysis. The size of the particles was varied by changing the flow rate of the carrier gas and the temperature. High-purity, uniform TiO_2 particles can be synthesized from titanium isopropoxide in a dilute alcohol solution [11]. The average particle size was varied by changing the concentration of the reagents.

Although the preparation of monodisperse SiO_2 and TiO_2 particles has been extensively reported in literature, only few attempts to prepare mixed SiO_2/TiO_2 particles exist. In one case mixed silica/titania particles was obtained by hydrolysis of aerosols containing tetraethyl orthotitanate and silica chloride [29]. The vapor of $SiCl_4$ was adsorbed into droplets of the alkoxide and the composite aerosol was hydrolyzed with water vapor. The particle size could be controlled by changing the temperature and the flow rate of the carrier gas.

Hsu et al. [30] found that monodisperse silica particles prepared from alkoxides could be coated with titania. The optical properties of the spheres were investigated as a function of particle diameter, the thickness of the titania shell and calcination temperature. It was found that the optimum opacity was obtained with particles of ≈ 1 μm coated with 40 wt% titania. These particles are comparable with commercial TiO_2.

In this study we have investigated the possibilities to prepare monodisperse, mixed SiO_2/TiO_2 particles. To start with, we undertook a study of the parameters influencing the formation of SiO_2 particles. This was necessary since TEOS and TEOT have very different hydrolysis rates.

In our preparation of silica particles, the influence of ammonia, water and tetraethyl orthosilicate concentrations on the particle size, monodispersity and aggregation of particles was mapped. Also addition of electrolyte and replacing ethanol with propanol, iso-propanol or butanol and their mixtures with ethanol were studied.

When pure titania particles were prepared ammonia and water concentrations and temperature were the parameters in this study.

In the preparation of silica/titania particles the influence of water concentration in the prehydrolysis and TEOS to TEOT mole ratio on the particle size and monodispersity was investigated.

Experimental

Materials

The tetraethyl orthosilicate (> 98%) (TEOS) and the tetraethyl orthotitanate (97%) (TEOT) were both from Fluka. The dehydrated ethanol and the iso-propanol were from A/S Vinmonopolet. The propanol (p.a.) was from Fluka and the butanol (p.a.) was from Riedel-de Haën. The ammonia (25%) and the electrolytes, NaCl (p.a.), $NaNO_3$ (p.a.) and Na_2SO_4, (p.a.) were from Merck. All chemicals were used without further purification. The water was distilled and ion exchanged (Serlapur pro 90 CN, < 0.1 μS/cm).

Preparation

SiO_2 particles

Alcohol, water and ammonia were weighed into glass vials with screw caps and mixed by shaking. TEOS was added and the mixing was started immediately. The samples were mixed for 8 h in an ultrasonic bath. Electrolytes were added as aqueous solutions before addition of ammonia. The experiments were performed at room temperature (22 °C).

TiO_2 particles

Ethanol and water were weighed into glass vials with screw caps. Different amounts of TEOT as an alcohol solution was added to the samples. The samples were mixed by shaking. The effect of ammonia concentration was investigated. Two different ammonia concentrations were chosen, 0.007 M and 0.07 M. These samples were cooled to 3 and − 18 °C before addition of TEOT.

SiO_2/TiO_2 particles

TEOS was prehydrolyzed with different amounts of water for 5h at 50 °C [13] with an ammonia concentration of 0.01 M before addition of TEOT and water/ammonia. The chosen water to TEOS mole ratio (R) in the prehydrolysis were 1, 1.5, 2, 3 and 4. Water/ammonia was added as ice (water to (TEOS + TEOT) mole ratio $\approx 40 - 50$) to achieve a complete condensation. The concentration of ammonia in the water was 4.75 M.

Characterization

Electron microscopy

A scanning electron microscope, JEOL JSM-6400, was used to examine the particles. Samples were made by placing a drop of the solution on an alumina specimen plate. The solvent was allowed to evaporate at room temperature.

SiO_2 particles were coated by a mixture of gold and platinum (Polaron equipment limited SEM coating unit ES100, 20mA, 2.5 min, Ar gas atmosphere). Particle sizes were estimated from SEM pictures and monodispersity or polydispersity was judged by comparison of different samples.

X-Ray analysis

A Tracor x-ray micro analysis system (EDS-system, series II) was used to analyse the composition of the particles. The system is energy dispersive.

Results and discussion

SiO_2 particles

Figures 1 and 2 display the influence of different ratios of water, ethanol and TEOS on the size, monodispersity and aggregation of the silica particles. The particle size in ethanol solution was in the range 30–1000 nm and the monodisperse particles were between 70 and 640 nm. The particle size increases with increasing amount of water up to 9 M in ethanol. This is somewhat higher than earlier reported [1, 3]. Stöber et al. [1] found no effect of TEOS concentration on the final particle size. Contrary to this, Bogush et al. [3] reported increasing particle size with increasing TEOS concentration, while van Helden [2] found decreasing particle size. Our results are in good agreement with those of Bogush et al. [3].

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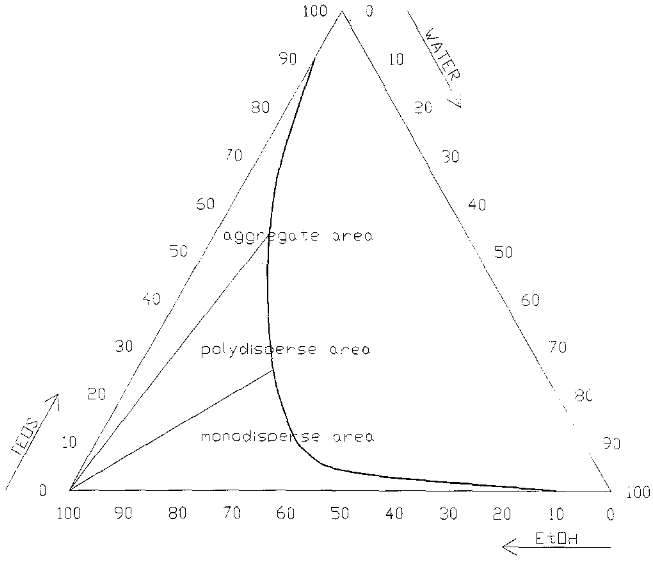
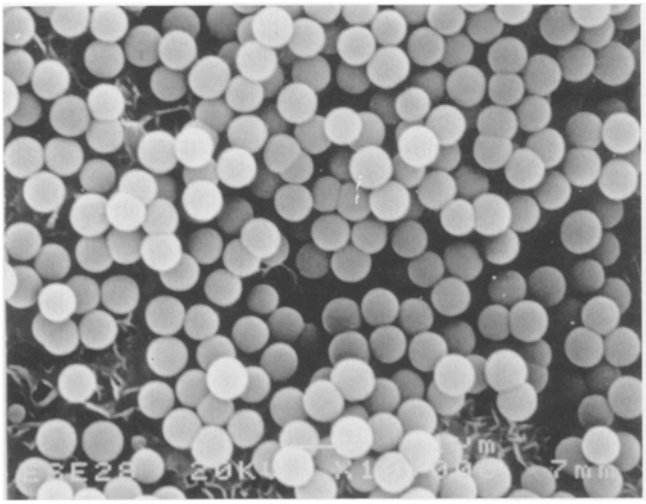


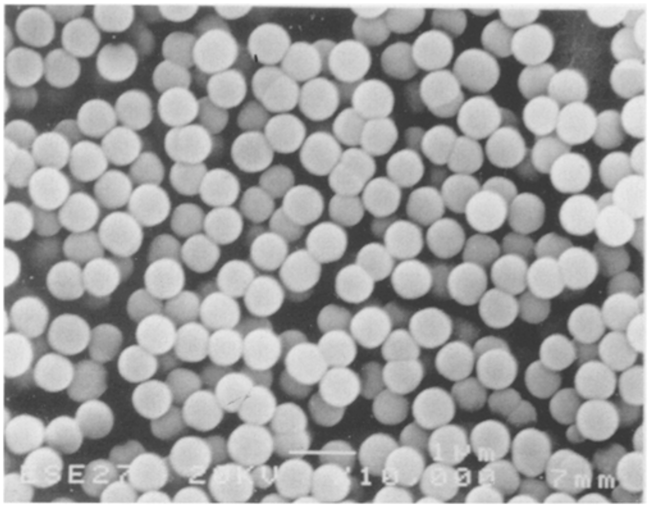
Fig. 1 Phase diagram TEOS-$H_2O(NH_3)$-EtOH. $[NH_3] = 0.8$ M. The micsibility line has been estimated from [12]. Lines dividing the phase diagram to different parts are drawn arbitrarily according to the nature of the particles obtained from different samples

From Fig. 3 it can be seen that the optimum particle size is achieved with an ammonia concentration of about 1 M which is the half of the earlier reported value [1, 3]. For maximum particle size the water to TEOS mole ratio (R) should be about 50. Several authors [3–5, 10] have reported a maximum particle size at a ratio of 40. The

Fig. 2 Scanning electron micrographs (SEM) of SiO_2 particles obtained from a) 0.20 M TEOS, 9.1 M water and 0.8 M NH_3 in ethanol. b) 0.60 M TEOS, 11.2 M water and 0.8 M NH_3 in ethanol. c) 1.00 M TEOS, 6.9 M water and 0.8 M NH_3 in ethanol. d) 1.80 M TEOS, 5.0 M water and 0.8 M NH_3 in ethanol



a)



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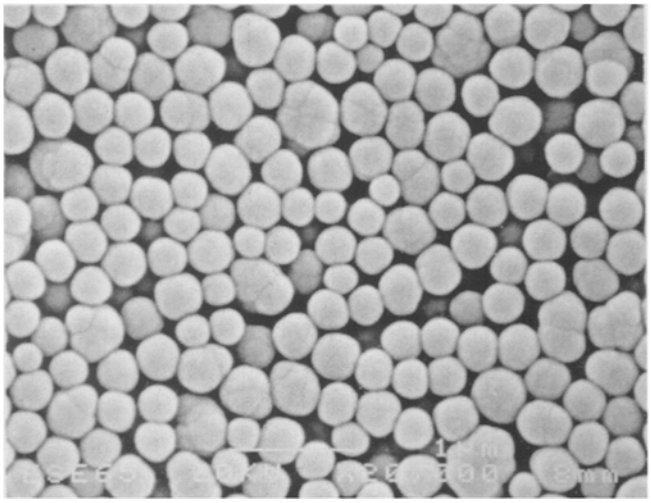

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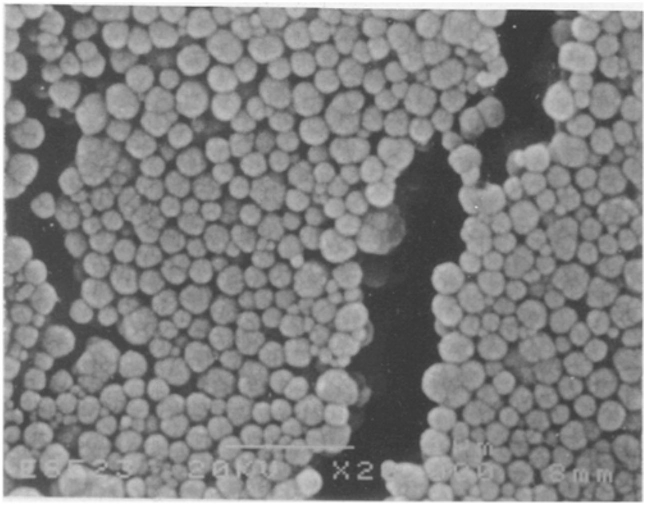

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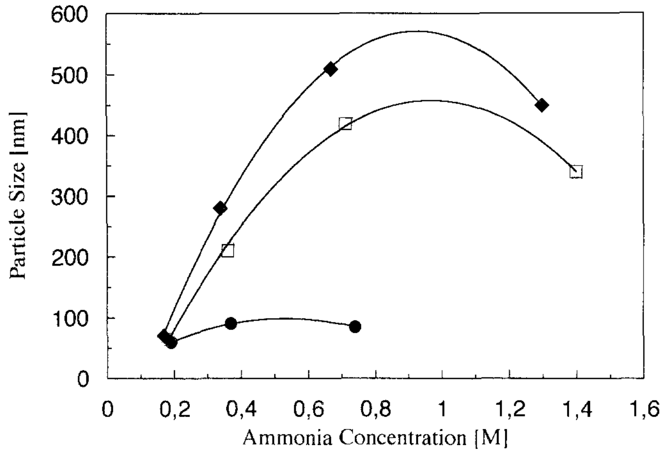


Fig. 3 The particle size as a function of ammonia concentration. • [TEOS] = 0.18 M and $R = 11.6$; □ [TEOS] = 0.17 M and $R = 23.1$; ◆ [TEOS] = 0.16 M and $R = 40.8$

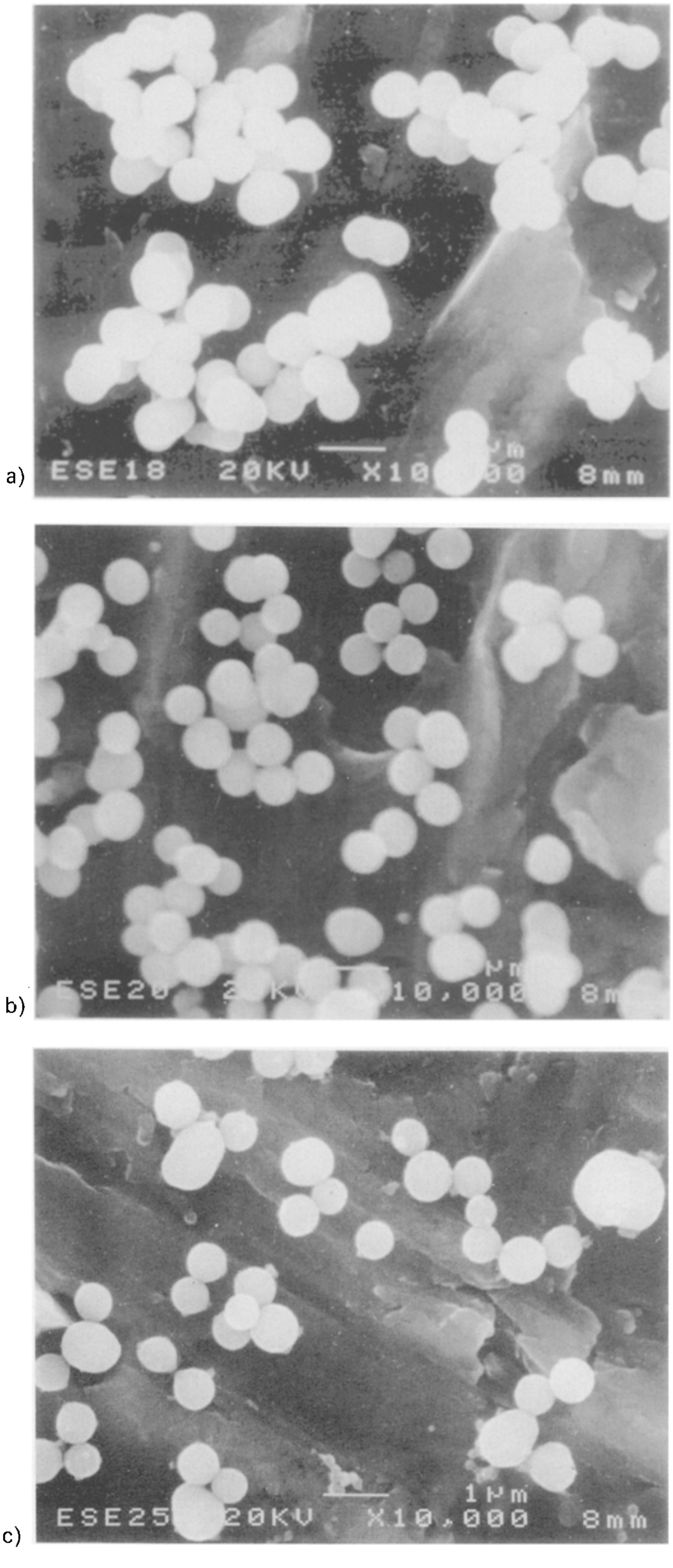
polydispersity of the particles increases as the concentration of TEOS increases and the water concentration decreases. According to van Helden et al. [2] the particles become more irregular and the size distribution wider as the TEOS concentration exceeds 0.2M. The crucial parameters in preparing silica particles seem to be the water and ammonia concentrations.

When iso-propanol, propanol or butanol or their mixtures with ethanol were used as reaction media, the particle size increased slightly but the polydispersity and aggregation increased. The particle size was in most cases $< 1 \mu m$. Addition of electrolytes ($1 \cdot 10^{-3}$ M) resulted in a slight increase in particle size, but now the particles tended to aggregate. We could not observe any differences between the electrolytes NaCl, $NaNO_3$ and Na_2SO_4.

TiO_2 particles

In samples without ammonia the particles grew in size and aggregated less with decreasing water concentration. Using a constant water to TEOT mole ratio, addition of ammonia increased the hydrolysis rate but no condensation took place and consequently no particles were formed. Decreasing the amount of water from ≈ 20 to ≈ 5 molecules per TEOT resulted in small aggregates of particles with $[NH_3] = 0.007$ M. Lowering the temperature of the samples to 3 ° and − 18 °C before addition of TEOT gave rise to particles at $[NH_3] = 0.007$ M and aggregates at $[NH_3] = 0.07$ M, Fig. 4. By lowering the temperature, the hydrolysis rate decreased so much that TiO_2 particles could be formed even at enhanced ammonia concentrations. The particle size was in the range 300–600 nm.

Fig. 4 Scanning electron micrographs (SEM) of TiO_2 particles obtained from a) [TEOT] = 0.07 M; $R = 8.0$; and $T = 22$ °C; b) [TEOT] = 0.07 M; $R = 6.3$; $[NH_3] = 0.007$ M and $T = 3$ °C; c) [TEOT] = 0.07 M; $R = 6.1$; $[NH_3] = 0.007$ M and $T = -18$ °C



These values can be compared to sizes found by various methods earlier.

Barringer et al. [11] investigated solutions with concentrations in the range 0.1–0.2 M TEOT and 0.3–1.5 M water. The water to alkoxide mole ratio was higher than 3. They found that the particle size was in the range 300–600 nm. By aging $TiCl_4$ in HCl containing Na_2SO_4 Matijevic et al. [27] found that the particle size increased with an increasing aging time. Particles sizes in the range 1–3.5 μm were obtained. By the aerosol method [28] TiO_2 particles in the size range 60–600 μm are obtained.

SiO_2/TiO_2 particles

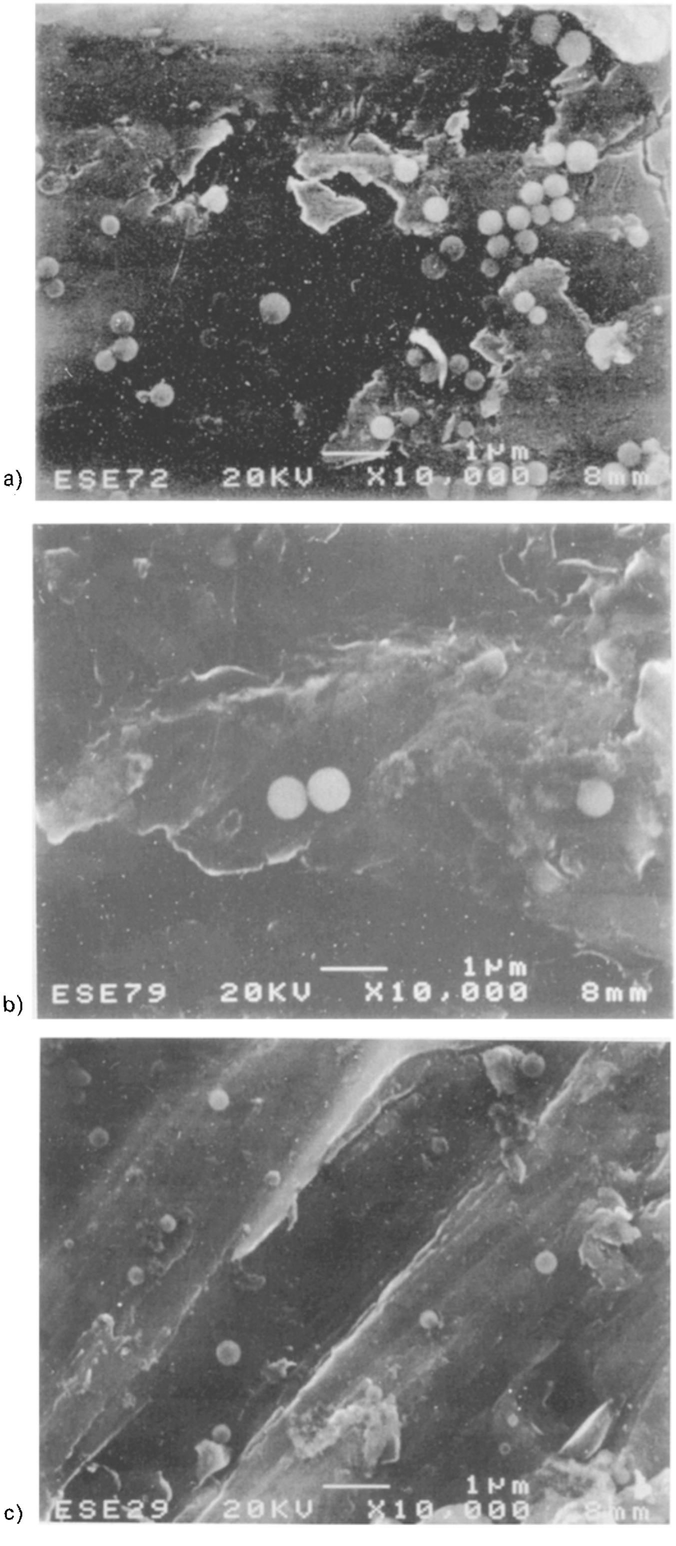
Due to the different hydrolysis rates of TEOS and TEOT, TEOS has to be prehydrolyzed with water at an enhanced pH and temperature before addition of TEOT [30]. Three different molar ratios between TEOS and TEOT were chosen, approximately 1/1, 5/1 and 10/1. At the lowest ratio no particles were formed, although the tests were repeated for different water contents, i.e. up to $R = 4$, where R is the molar ratio between water and TEOS. Instead some aggregated clusters were formed, consisting of equal amounts of silica and titania. Obviously this reaction cannot be controlled to give uniform particles.

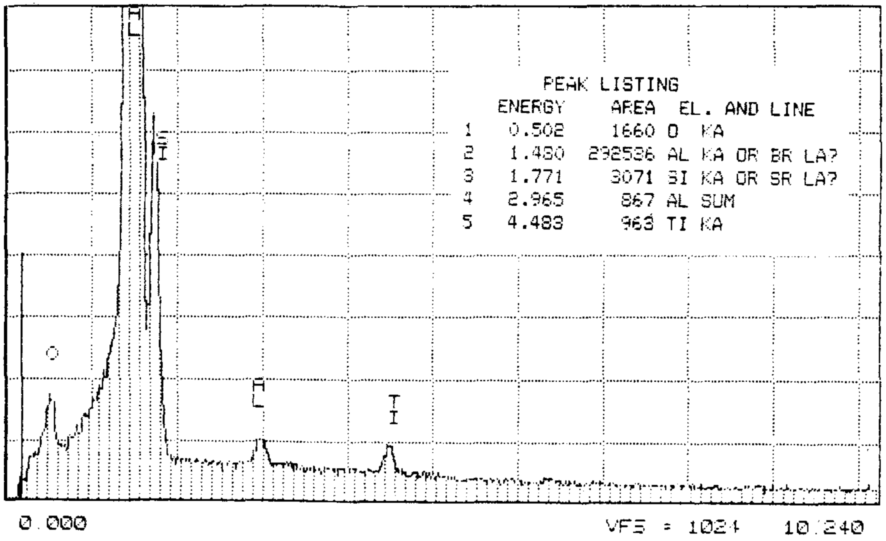
For the two other ratios between TEOS and TEOT particles were formed when $1 \leq R \leq 2$, Fig. 5.

The composition of the particles varied with the amount of water in the prehydrolysis. Low water contents ($R = 1$ and 1.5) gave rise to particles consisting of both silica and titania, Fig. 6. The ratio of [Si]/[Ti] is at these conditions approximately 3. It is not possible by this x-ray method to determine whether the Ti compound is located on the surface or homogeneously distributed through the particle. Visca et al. [28] found by atomic absorption using ICP emission spectroscopy a molar ratio of [Si]/[Ti] = 3 in particles prepared by the aerosol method. ESCA investigations indicated an enrichment in Ti at the surface of the particles. The analysis shows that the particles consist of a mixture of SiO_2 and TiO_2 and that they are inhomogeneous. Higher amounts of water ($R = 2$) resulted in particles with silica as the main component, in many cases the only component. The size of these particles were in the range 300–600 nm.

At the highest TEOS to TEOT mole ratio ($\approx 10/1$) the fraction of silica in the particle was increasing with increasing water concentration in the prehydrolysis, Table 1. With a water addition giving $R \leq 2$ it can be assumed that all the water molecules are consumed by the hydrolysis. When $R > 2$, some free water may still be in the solution after the prehydrolysis stage has been finished.

Fig. 5 Scanning electron micrographs (SEM) of SiO_2/TiO_2 particles obtained from a) Prehydrolysis conditions: $R = 1$; TEOS/TEOT = 8.6 and $[NH_3] = 0.01$ M; b) Prehydrolysis conditions: $R = 1.5$; TEOS/TEOT = 3.1 and $[NH_3] = 0.01$ M; c) Prehydrolysis conditions: $R = 2$; TEOS/TEOT = 8.9 and $[NH_3] = 0.01$ M





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PEAK LISTING
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2   1.480  292536 AL KA OR BR LA?
3   1.771    3071 SI KA OR SR LA?
4   2.965     867 AL SUM
5   4.483     963 TI KA
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Fig. 6 X-ray diffraction analysis of mixed particles. TEOS/TEOT = 8.6; $R = 1$ and $[NH_3] = 0.01$ M

Table 1 Composition of the particles. TEOS to TEOT mole ratio in the solution is $\approx 1/10$

R	Si/Ti
1	3
1.5	7
2	∞*

* Only SiO_2 was detected.

The formation of SiO_2 particles is dependent on both ammonia concentration (pH) and water to TEOS mole ratio. Recent investigations by Lindberg [31] showed that no SiO_2 particles were formed within 24 h at pH = 10.5 and for a value of R as high as 20. For the conditions above with pH = 9.5 and $R \leq 4$ it is then obvious that the level of condensation should be low and no detectable SiO_2 particles are formed.

Yoldas [14] argued that addition of TEOT to partially hydrolyzed TEOS solutions would cause a heterocondensation ($\equiv$ Si–O–Ti $\equiv$), Eq. (4), because this reaction is faster than the homocondensation of the silicates, Eqs. (2) and (3).

Since $Ti(OR)_4$ is known to catalyze silanol condensation [32], Basil et al. [33, 34] tested Yoldas hypothesis by observing the effect of addition of TEOT on silanol concentrations in partially hydrolyzed solutions of TEOS. They found that the addition of TEOT had no effect upon concentration of unreacted TEOS, i.e. it did not promote hydrolysis. On the other hand, 62% of the silanol groups were removed by a minor addition of TEOT. With an addition of 0.1 equivalent, no silanol groups were detected. The loss of the silanol groups is followed by a production of condensed silicon ethoxides with a higher molecular weight. They concluded that TEOT primarily catalyzes the silanol condensation. When added to a partially hydrolyzed solution, TEOT could only be incorporated in oligomers. There was no sign of reaction between singly hydrolyzed silicate monomers and TEOT, forming $\equiv$ Si–O–Ti $\equiv$.

Based on above mentioned findings and our data, possible reaction paths for preparation of mixed SiO_2/TiO_2 particles would hence be

Hydrolysis:

$$Si(OEt)_4 \rightarrow Si(OH)_x(OEt)_{4-x} \tag{5}$$

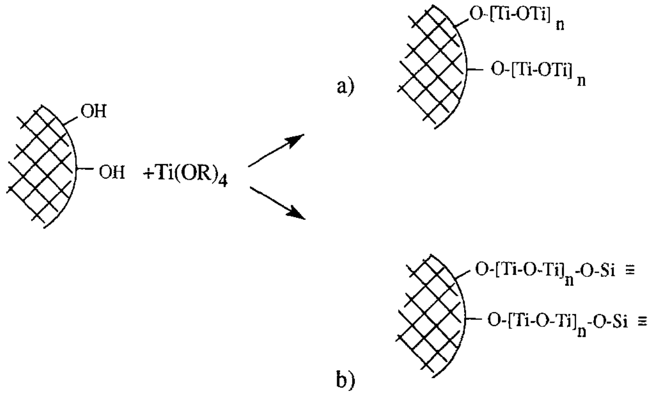
TEOT catalyzed condensation:

$$Si(OH)_x \xrightarrow{TEOT} Si\text{-}(OSi)_y(OH)_{x-y} \tag{6}$$

Final particle formation:

$$[Si\text{-}(OSi)_y(OH)_{x-y}]_n + TEOT \rightarrow [Si\text{-}(OSi)_y(OTi)_z(OH)_{x-y-z}]_n . \tag{7}$$

Alternatively reaction (7) could be visualized as



For the final particle with a size of $\approx 0.3\ \mu m$ reaction (7) should represent a termination generating a SiO_2/TiO_2 particle with excess surface Ti. This is also found experimentally by Balboa et al. [29] who from ESCA measurements determined a surface ratio of $[Ti]/[Si] = 33$. In reactions 7 a and b above the surface coupled titanate chains cannot exist as independent chains, but they must at some point undergo a cross-linking reaction giving rise to an amorphous particle with excess surface Ti.

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