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# Sol–gel reactions of titanium alkoxides and water: influence of pH and alkoxy group on cluster formation and properties of the resulting products

Morten E. Simonsen · Erik G. Søgaaard

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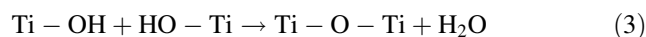
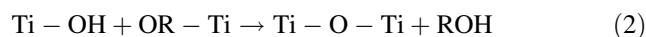
**Abstract** In this work the effect of pH and the titanium precursor on the cluster and particle formation during titanium alkoxide based sol–gel processes was investigated using electrospray ionization mass spectrometry (ESI-MS) and dynamic light scattering (DLS). The influence of pH and the titanium precursor on the particle size, morphology, crystallinity and chemical composition of the resulting particles were investigated using differential scanning calorimetry (DSC), X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FT-IR), BET-adsorption isotherms and high resolution transmission electron microscopy (HR-TEM). ESI-MS investigation of the titanium clusters present during the nucleation and growth period showed that the number of titanium atoms in the clusters varied dependent on the alkoxide used. Moreover, it was found that the titanium clusters formed using titanium tetraethoxide (TTE) were smaller than the clusters formed by titanium tetrakisopropoxide (TTIP) and titanium tetrabutoxide (TTB) under similar conditions. pH was not found to influence the nature of the titanium clusters present in the sol–gel solution. HR-TEM investigation of the  $\text{TiO}_2$  particles prepared at pH 7 and 10 showed that the primary particle size of the particles was around 3 nm. However, it was found that these primary particles aggregated to form larger secondary particles in the size order of 300–500 nm range. At pH 3 the particles grew significantly during the drying process due to destabilization of the colloidal solution leading to the formation of a gel. The highest specific surface area was found for particles synthesized under neutral

or alkaline conditions based on TTIP. XRD analysis of the  $\text{TiO}_2$  particles showed that the particles synthesized at 25 °C were amorphous. First after heating the samples to above 300 °C the formation of anatase were observed.

**Keywords**  $\text{TiO}_2$  · Sol–gel process · ESI-MS · DLS · Particle morphology

## 1 Introduction

Sol–gel derived titanium dioxide nanoparticles with controlled size distribution and morphology are of great interest for many applications. The chemistry of the sol–gel process is mainly based on hydrolysis (Eq. 1) and polycondensation (Eqs. 2, 3) of metal alkoxides leading to the formation of an extended network.



Depending on the chemical conditions under which such compounds are synthesized very different structures can be obtained ranging from colloidal particles to precipitation or gels [1]. The resulting product is strongly affected by the kinetics of hydrolysis and condensation reactions of the alkoxide precursor. Experimental parameters such as the hydrolysis ratio  $n_{\text{H}_2\text{O}}/n_{\text{alkoxide}}$  and the nature of the alkoxy groups (R) are important factors influencing the kinetics of the hydrolysis and condensation reactions [2, 3].

The mechanisms of hydrolysis and polycondensation have been extensively studied in the case of silicon alkoxides, whereas much less data are available for transition-metal oxide precursors [1]. The titania sol–gel process

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follows essentially a different pathway than the silicon based sol–gel process. Generally, it is assumed that individual monosilicates serve as building blocks during the polymerization process [4]. However, in the case of titania, titanium clusters (polyoxoalcoxides) have been suggested to serve as the primary building blocks for particles and gels [5–8]. In particular  $\text{Ti}_{11}\text{O}_{13}(\text{OC}_3\text{H}_7)_{18}$  has been proposed as a building block in titanium isopropoxide (TTIP) based sol–gel processes based on results from  $^{17}\text{O}$  NMR spectroscopy [8, 9]. A stable solution of these clusters can be obtained by hydrolysis of TTIP under low hydrolysis ratios ( $h < 1$ ). However, if  $h > 1.5$  hydrolysis of TTIP does not result in a stable solution of polyalkoxides but results in precipitation of titanium dioxide particles. The precipitation takes place after an induction period in which slow particle growths is observed followed by rapid precipitation. The presence and size evolution of nanoparticles (1.5–6 nm) in the induction period has been studied by dynamic light scattering (DLS) [6, 10, 11]. DLS investigation provides valuable information of the particle size of the titanium clusters present during the induction period and the time scale of the induction period. However, DLS does not provide information about composition of the observed nanoparticles. Identification of the titanium clusters present during the induction period of titanium alkoxide is of great interest, as the nature of these clusters may determine the properties of the final product.

One method which has been used to study the components present during hydrolysis and polycondensation reactions is mass spectrometry. In previous studies, mass spectrometry has been used to study the polycondensation reaction of TEOS [ $\text{Si}(\text{OC}_2\text{H}_5)_4$ ], either in the gas phase via chemical ionization (CI) experiments [12] or in the condensed phase by continuous flow fast atom bombardment (FAB) [13] and electrospray ionization mass spectrometry (ESI-MS) [14]. In the latter investigation it was shown that the polycondensation reaction is initiated by a protonated molecule. Furthermore,  $\text{Si}(\text{OC}_2\text{H}_5)_3^+$  molecule ions were identified although the intensity was considerably lower [14]. ESI-MS has been used to study the polycondensation reactions of  $\text{Ti}(\text{O}-i\text{-C}_3\text{H}_7)_4$  and  $\text{Ti}(\text{O}-n\text{-C}_4\text{H}_9)_4$  [1]. The reported data indicate that ESI-MS can be a valuable tool to obtain information of the polycondensation of alcoxides.

In this work the effect of pH and the titanium precursor on the cluster and particle formation during titanium alkoxide based sol–gel processes was investigated using ESI-MS and DLS. In order to obtain knowledge of the pH and the titanium precursors influence not only on cluster formation but also on the final products, the properties of these products were investigated in greater detail. The resulting products was characterized using differential scanning calorimetry, X-ray diffraction, TEM and BET.

## 2 Materials and methods

The sol–gel process was carried out using titanium tetraisopropoxide (TTIP) (98%, Aldrich), isopropyl alcohol (99.5% anhydrous, Aldrich) and distilled water in a closed vessel under ambient conditions. In a standard experiment a solution of TTIP in isopropyl alcohol (solution A) and a solution of water in isopropyl alcohol (solution B) were prepared. Under intensive stirring the solution B was quickly added to the solution A. The molar concentration of TTIP and the hydrolysis ratio in the final solution was 0.15 M and 2.7, respectively. The pH of the reaction solution was adjusted to pH 3, 7, and 10 using  $\text{HNO}_3$  and  $\text{NH}_3$  by dropwise addition of acid and base and measurement of the pH. Similar reaction solutions were prepared using titanium tetraethoxide (TTE) and titanium tetrabutoxide (TTB). After 48 h of reaction the solutions/suspensions were heated to 105 °C (12 h) in order to evaporate the solvent and obtain the formed  $\text{TiO}_2$  products.

Dynamic light scattering (DLS) was used to study the evolution in particle size during the induction period. The particle size of the clusters/particles in the sol–gel reaction solution was measured using a DLS instrument obtained from Photocor Instruments, Inc. consisting of a photon counting unit (PMT), photocorrelator, and a 633 nm 35 mW laser (JDS Uniphase). This instrument can measure particles in the size range of 3 nm to 5  $\mu\text{m}$ .

Samples for the ESI-MS investigation were obtained from the sol–gel reaction solution at different times during the induction period. The samples were diluted 1:100 in the corresponding alcohol (isopropyl alcohol, ethanol, and butanol) in order to avoid clogging of the capillary in the ESI-MS. The ESI-MS spectra were recorded using a LC-MSD-Trap-SL spectrometer from Agilent Technology. The dry temperature was set at 325 °C and the dry gas flow ( $\text{N}_2$ ) was 5 l/min. The capillary exit voltage was 166 V. The solution was injected into the ESI-MS at a flow-rate of 0.3  $\mu\text{l}/\text{min}$ . The ESI-MS spectra of the reaction solutions were recorded in positive scanning mode in the spectral region 50–2,200 m/z.

The specific surface area of the  $\text{TiO}_2$  powder was measured by adsorption of nitrogen using the Brunauer-Emmett-Teller adsorption isotherm (BET). The BET apparatus measures the equilibrium volume of nitrogen physically adsorbed on the  $\text{TiO}_2$  particles at different pressures in vacuum range of 5–250 mmHg. The measurements produce an adsorption isotherm which can be fitted by using the BET isotherm. The BET surface area was measured using a Thermo Quest Sorptomatic 1990 series.

TEM images of the resulting  $\text{TiO}_2$  products were obtained using a Philips CM20 electron microscope.

Reflection X-ray diffraction (XRD) was used to determine the presence of anatase and rutile phases in the resulting  $\text{TiO}_2$  products. The XRD spectra were obtained with Co radiation ( $\lambda = 1.7889 \text{ \AA}$ ) using a Philips X'pert MPD reflection diffractometer.

The Differential scanning calorimetry (DSC) investigation of the different  $\text{TiO}_2$  samples was carried out using a Mettler Toledo DSC822e with a TSO801RO auto sampler. 6.0 mg sample was placed in an aluminum container which was placed in the calorimeter. The heat transfer rate used in the investigation was  $10^\circ\text{C}/\text{min}$  and the applied temperature interval was  $35\text{--}550^\circ\text{C}$ .

Attenuated total reflection (ATR) FT-IR analysis of the resulting  $\text{TiO}_2$  products was made using a Thermo Nicolet Spectrometer, AVATAR 370 FT-IR. The FT-IR spectra's were recorded from  $4,000$  to  $650 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$ .

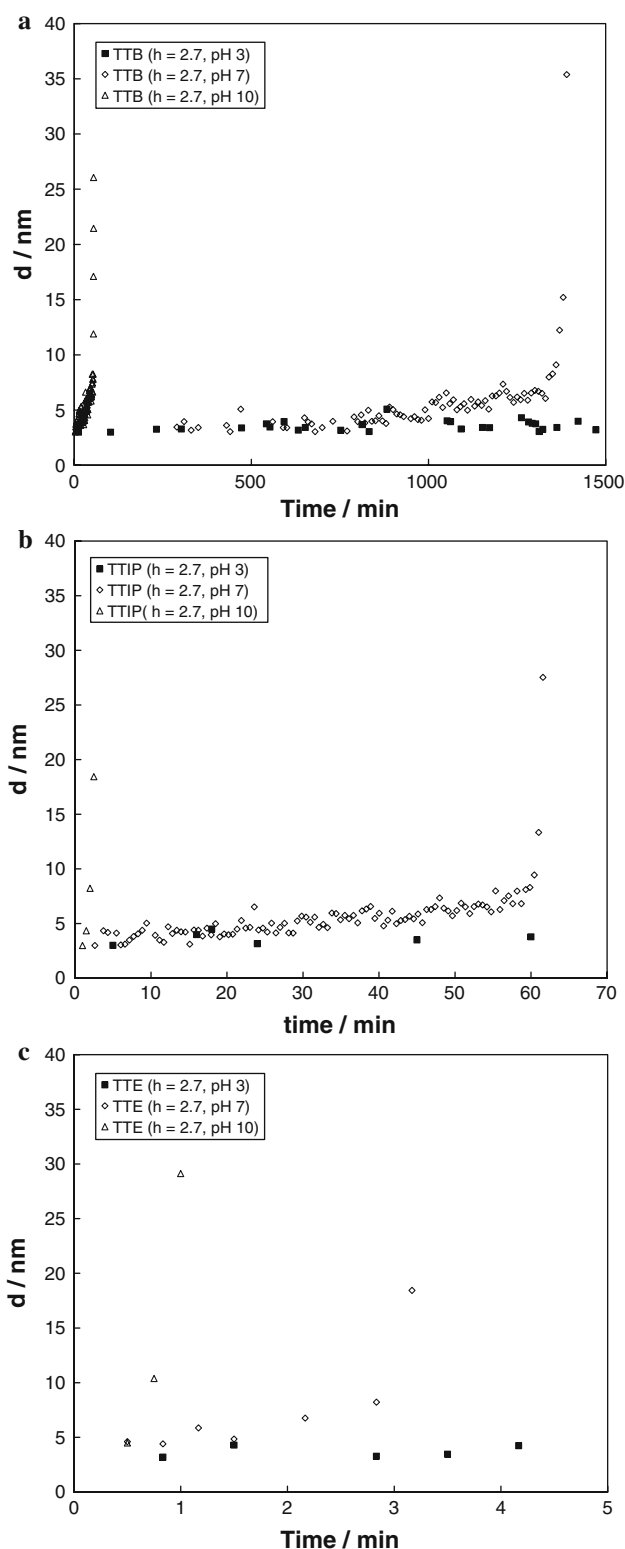
### 3 Result and discussion

#### 3.1 Influence of pH and the alkoxy group on the cluster and particle formation during titanium alkoxide based sol-gel processes

##### 3.1.1 DLS study of the particle formation

From Fig. 1 it is observed that titanium clusters with sizes around 3 nm (diameter) are rapidly formed after mixing of solution A and B. In standard experiments conducted at pH 7 precipitation of  $\text{TiO}_2$  particles takes place after an induction period in which slow particle growths is followed by a rapid precipitation. The growth of the cluster during this induction period is suggested to be due to aggregation of the initially formed Ti clusters as the total mass of the clusters has been found not to change during the induction period [6, 11]. The aggregation is suggested to proceed through hydrolysis and condensation of surface alkoxy groups of the Ti clusters.

Comparison of the results in Fig. 1 shows that the nature of the alkoxy group influenced the length of the induction period. From Fig. 1 it is seen that the reactivity of the alkoxy group are  $\text{OEt} > \text{OPr}^i > \text{OBu}$ . The difference in reactivity of the alkoxides is generally believed to be due to the increasing size of the alkoxy group which causes sterical hindrance during the nucleophilic substitution reaction. Moreover, it is seen from Fig. 1 that pH has an enormous influence on the rate of the particle formation. Independent on the titanium alkoxide (TTIP, TTE, TTB) used in the synthesis the particle formation at pH 3 was found to be very slow. After 48 h the particle size of the particles in solution was found to have diameters around



**Fig. 1** **a** Size evolution of titanium clusters in a solution of TTIP (0.15 M,  $h = 2.7$ ) in isopropanol, **b** TTE (0.15 M,  $h = 2.7$ ) in ethanol, and **c** TTB (0.15 M,  $h = 2.7$ ) in butanol determined by DLS measurements. In the case of experiments conducted at pH 3 the particle size fluctuate around 3–4 nm in size, which is the lower measurable range of the DLS method

3 nm. In comparison synthesis under neutral and alkaline conditions resulted in precipitation of particles after varying induction periods. Under alkaline conditions the induction period was very short. In the case of TTE and TTIP the precipitation of particles occurred after a few minutes. In the case of TTB the induction period was a little longer (50 min). At pH 7 the induction period for particles synthesized from TTE and TTIP was found to be 3 and 60 min respectively. In comparison the induction period for TTB was found to be about 1,300 min.

These results show that the presence of an acid or base catalyst in the sol–gel solution influences the hydrolysis and condensation rates and particle size of the resulting particles. At pH 3 the hydrolysis reaction is catalyzed by the presence of acidic protons through protonation of the leaving groups (alkoxy group) [4, 15, 16]. However, at the same time protonation of the OH group of the Ti cluster inhibits the nucleophilic attack on Ti in other clusters [15] retarding the condensation reaction. The positive surface charge of the clusters/colloids hinders aggregation due to repulsion forces. Thus, at low pH the slow polycondensation rate results in the formation of a sol. In alkaline conditions besides the shift of the primary nucleophile from water to hydroxide strong nucleophiles are produced via deprotonation of the hydroxo ligands resulting in increased condensation rates. The rapid reaction results in precipitation of  $\text{TiO}_2$  particles.

It is generally known that polymeric clusters and particulate clusters are formed under acidic and basic conditions, respectively [4]. However, differences in the shape and structure of the Ti clusters formed using different titanium precursors at varying pH is difficult to measure using DLS. In DLS the radius of the Ti clusters is determined as a hypothetical hard sphere that diffuses with the same speed as the particle under examination. However, in practice, the Ti clusters in solution may be non-spherical, dynamic (tumbling), and solvated. Thus, the radius calculated from the diffusion properties of the particles is the apparent size of the dynamic hydrated/solvated particle. Also multiple scattering influences the results. However, in this work DLS was principally used to compare the length of the induction time versus pH and titanium precursor.

ESI-MS and HR-TEM was used to investigate the structure and shape of the Ti clusters formed at different pH and titanium precursor during the condensation process and of the final dried products, respectively.

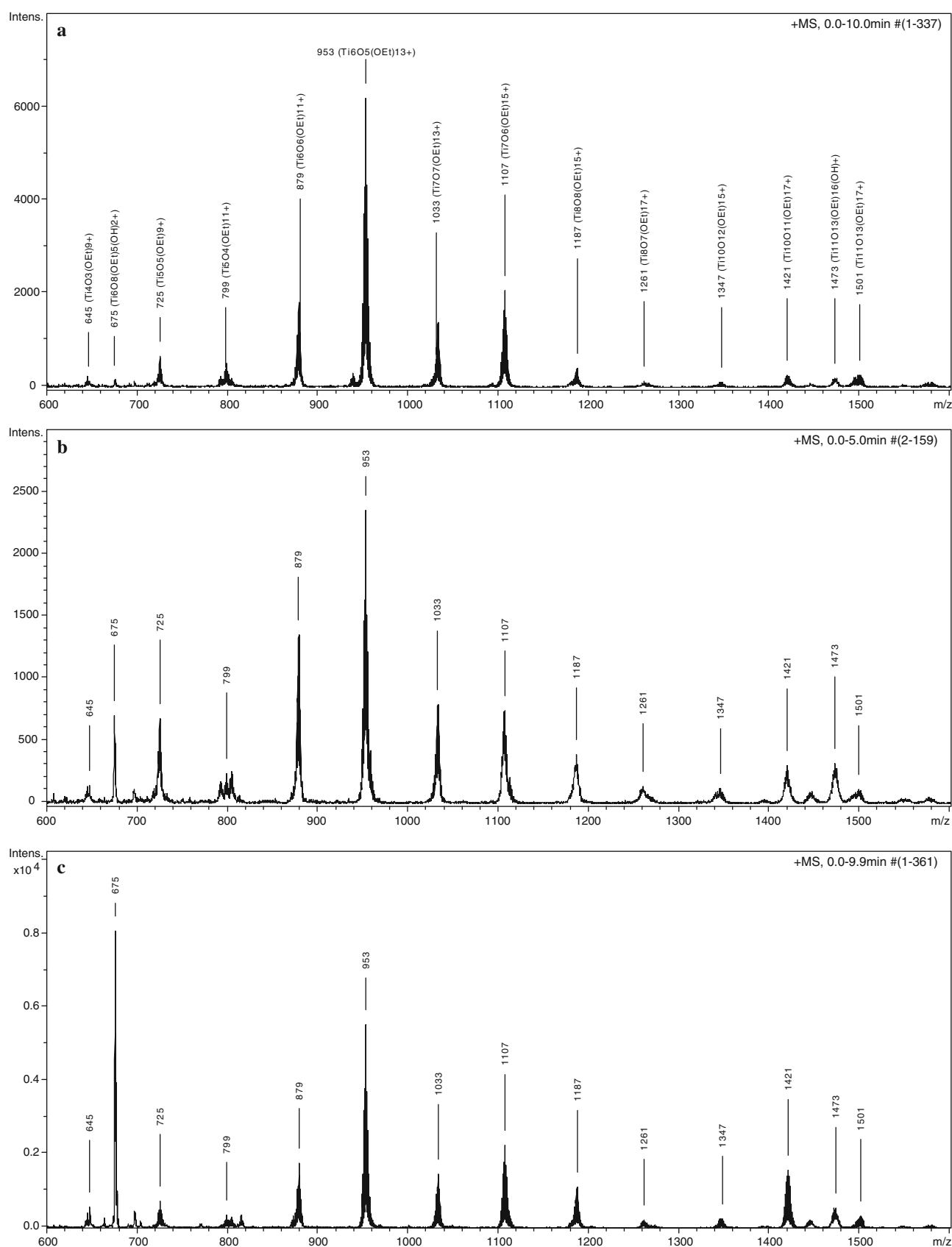
### 3.1.2 ESI-MS study of the influence of pH and titanium precursor on clusters formation

The alkoxy group of the titanium precursor used in the sol–gel synthesis has been reported to influence the morphology (particle size and surface area) and crystallinity of the

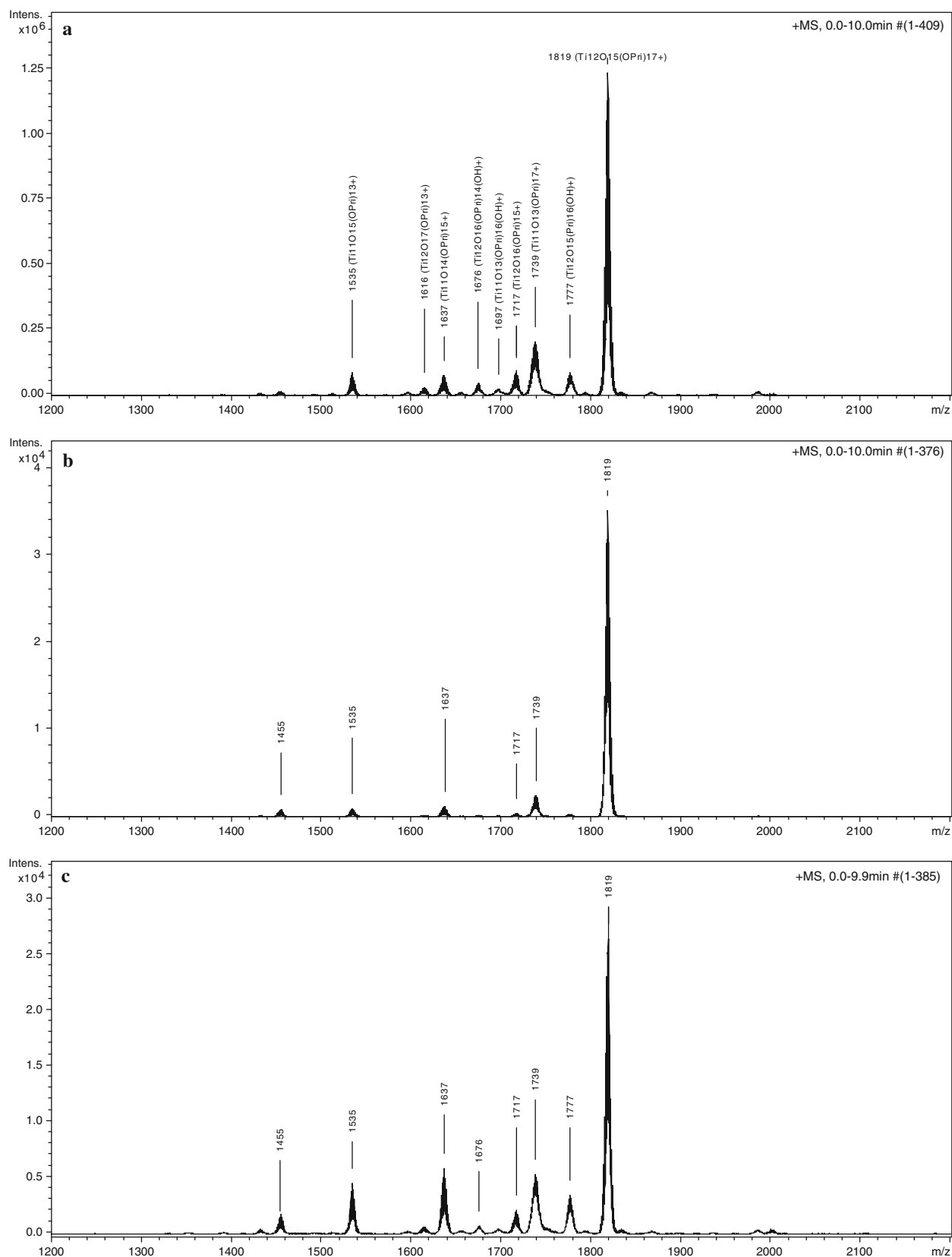
resulting particles [4]. The influence of the titanium precursor has been suggested to be due to differences in the size and structure of the primary building blocks formed during the synthesis [4]. One of the focuses of this work is identification of titanium clusters present in the reaction solutions prepared from different titanium alkoxides and at different pH using ESI-MS. In Figs. 2, 3 and 4 the mass spectra's obtained by injection of the sol–gel solutions based on TTE, TTB, or TTIP at different pH are shown. Analysis of the mass spectra shows that the number of titanium atoms in the titanium clusters observed during synthesis varied dependent on the identity of the used alkoxide. It was found that the titanium clusters identified in a solution of TTE/ethanol/water were smaller (number of Ti atoms 5–9) than the clusters observed in the sol–gel solutions prepared by TTIP (11–12 Ti atoms) and TTB (10–11 Ti atoms) under similar conditions. The most dominant clusters identified during the induction period of TTE based sol–gel processes were  $\text{Ti}_6\text{O}_5(\text{OEt})_{13}^+$ ,  $\text{Ti}_6\text{O}_6(\text{OEt})_{11}^+$ ,  $\text{Ti}_7\text{O}_7(\text{OEt})_{13}^+$ , and  $\text{Ti}_7\text{O}_6(\text{OEt})_{15}^+$ . However, it should be noted that clusters containing 11–13 Ti atoms were observed during optimization in the high  $m/z$  range. This may suggest that titanium clusters containing 6–7 atoms may serve as building blocks during the polymerization process.

The clusters identified at different pH (Fig. 2) were very similar and only a small change in the intensity distributions of the peaks was observed suggesting that the pH does not change the structure of the titanium clusters. The most dominant titanium clusters observed in the reaction solutions prepared from TTE, TTB, and TTIP are listed in Table 1.

The distribution of the peaks in the mass spectra was not found to change significantly during the course of reaction although a decrease in the intensity of the peaks was observed as a function of reaction time. The decrease in the intensity of the peaks may suggest aggregation of the clusters resulting in the formation of clusters larger than 2,200  $m/z$  and therefore undetectable by the ESI-MS method. By using the relation between the particle size and mass reported by Gaun et al. [17] the particle size of the identified titanium clusters can be calculated. From the calculations it was found that the particle size of the most dominant titanium cluster found at 1,819  $m/z$  in the TTIP system is around 1 nm, assuming that the titanium clusters are spherically and has the same density as bulk  $\text{TiO}_2$ . In comparison the particle size of the titanium clusters determined by DLS measurements during the induction period increased from 3 to 7 nm. These results suggest that the titanium clusters observed by ESI-MS are formed rapidly after mixing and that these titanium clusters dependent on the experimental condition aggregate to form larger titanium clusters.

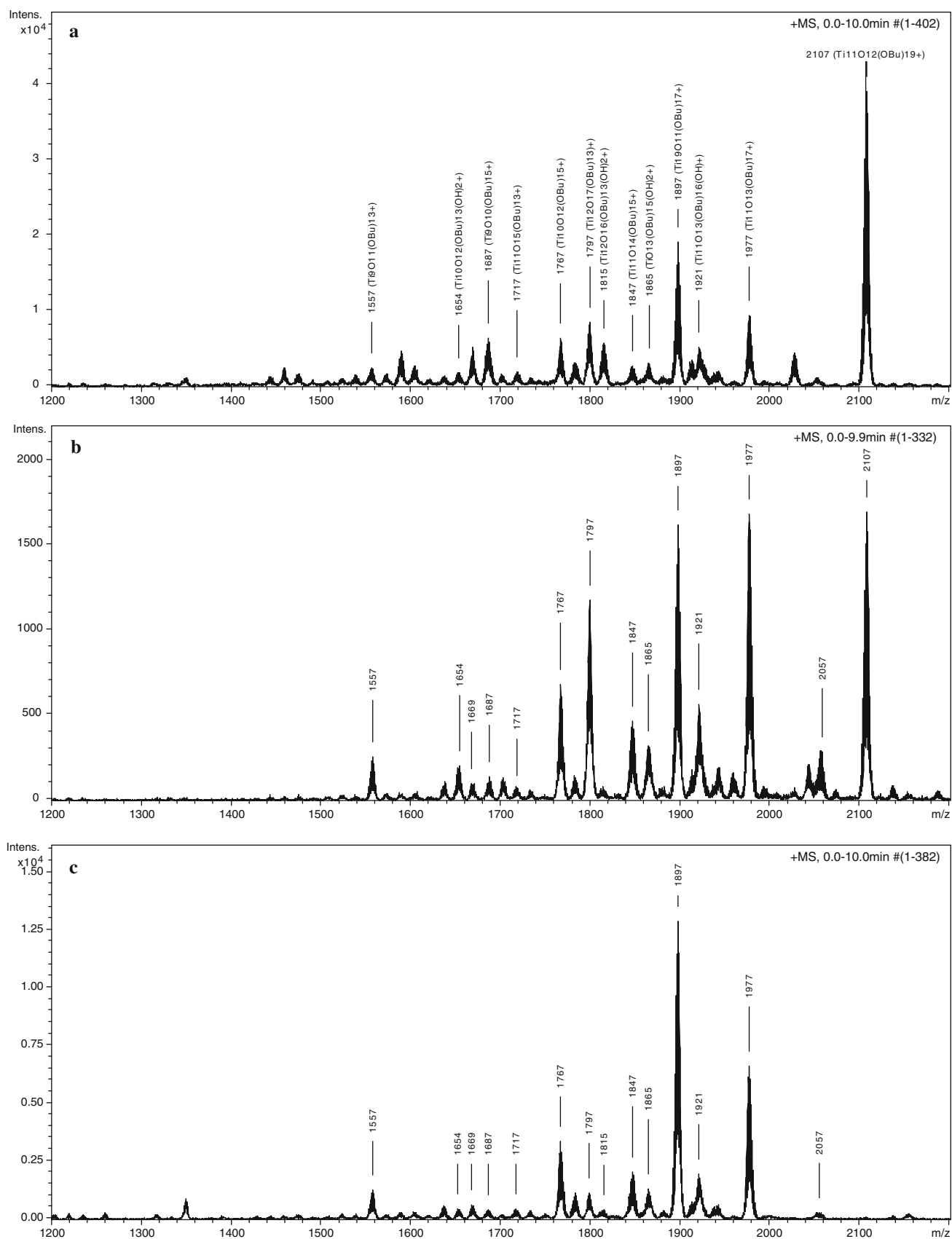


**Fig. 2** ESI-MS spectra of the sol-gel reaction solution prepared from TTE at **a** pH 3, **b** pH 7, and **c** pH 10



**Fig. 3** ESI-MS spectra of the sol-gel reaction solution prepared from TTIP at **a** pH 3, **b** pH 7, and **c** pH 10





**Fig. 4** ESI-MS spectra of the sol-gel reaction solution prepared from TTB at **a** pH 3, **b** pH 7, and **c** pH 10

**Table 1** Identified titanium clusters in sol–gel solutions prepared from TTE, TTB, and TTIP

Alkoxide	Compound	m/z
TTE	Ti <sub>6</sub> O <sub>8</sub> (OEt) <sub>5</sub> (OH) <sub>2</sub> <sup>+</sup>	675
	Ti <sub>6</sub> O <sub>6</sub> (OEt) <sub>11</sub> <sup>+</sup>	879
	Ti <sub>6</sub> O <sub>5</sub> (OEt) <sub>13</sub> <sup>+</sup>	953
	Ti <sub>7</sub> O <sub>7</sub> (OEt) <sub>13</sub> <sup>+</sup>	1,033
	Ti <sub>7</sub> O <sub>6</sub> (OEt) <sub>15</sub> <sup>+</sup>	1,107
TTB	Ti <sub>10</sub> O <sub>12</sub> (OBu) <sub>15</sub> <sup>+</sup>	1,767
	Ti <sub>12</sub> O <sub>17</sub> (OBu) <sub>13</sub> <sup>+</sup>	1,798
	Ti <sub>10</sub> O <sub>11</sub> (OBu) <sub>17</sub> <sup>+</sup>	1,897
	Ti <sub>11</sub> O <sub>13</sub> (OBu) <sub>17</sub> <sup>+</sup>	1,977
	Ti <sub>11</sub> O <sub>12</sub> (OBu) <sub>19</sub> <sup>+</sup>	2,107
TTIP	Ti <sub>11</sub> O <sub>15</sub> (OPr) <sub>13</sub> <sup>+</sup>	1,535
	Ti <sub>11</sub> O <sub>14</sub> (OPr) <sub>15</sub> <sup>+</sup>	1,637
	*Ti <sub>11</sub> O <sub>13</sub> (OPr) <sub>17</sub> <sup>+</sup>	1,739
	Ti <sub>12</sub> O <sub>15</sub> (OPr) <sub>16</sub> (OH) <sup>+</sup>	1,777
	Ti <sub>12</sub> O <sub>15</sub> (OPr) <sub>17</sub> <sup>+</sup>	1,819

\* Previously observed in <sup>17</sup>O NMR investigations of similar systems [8, 9]

### 3.2 Influence of pH and titanium precursor on the particle properties of the resulting products

#### 3.2.1 Particle size and morphology

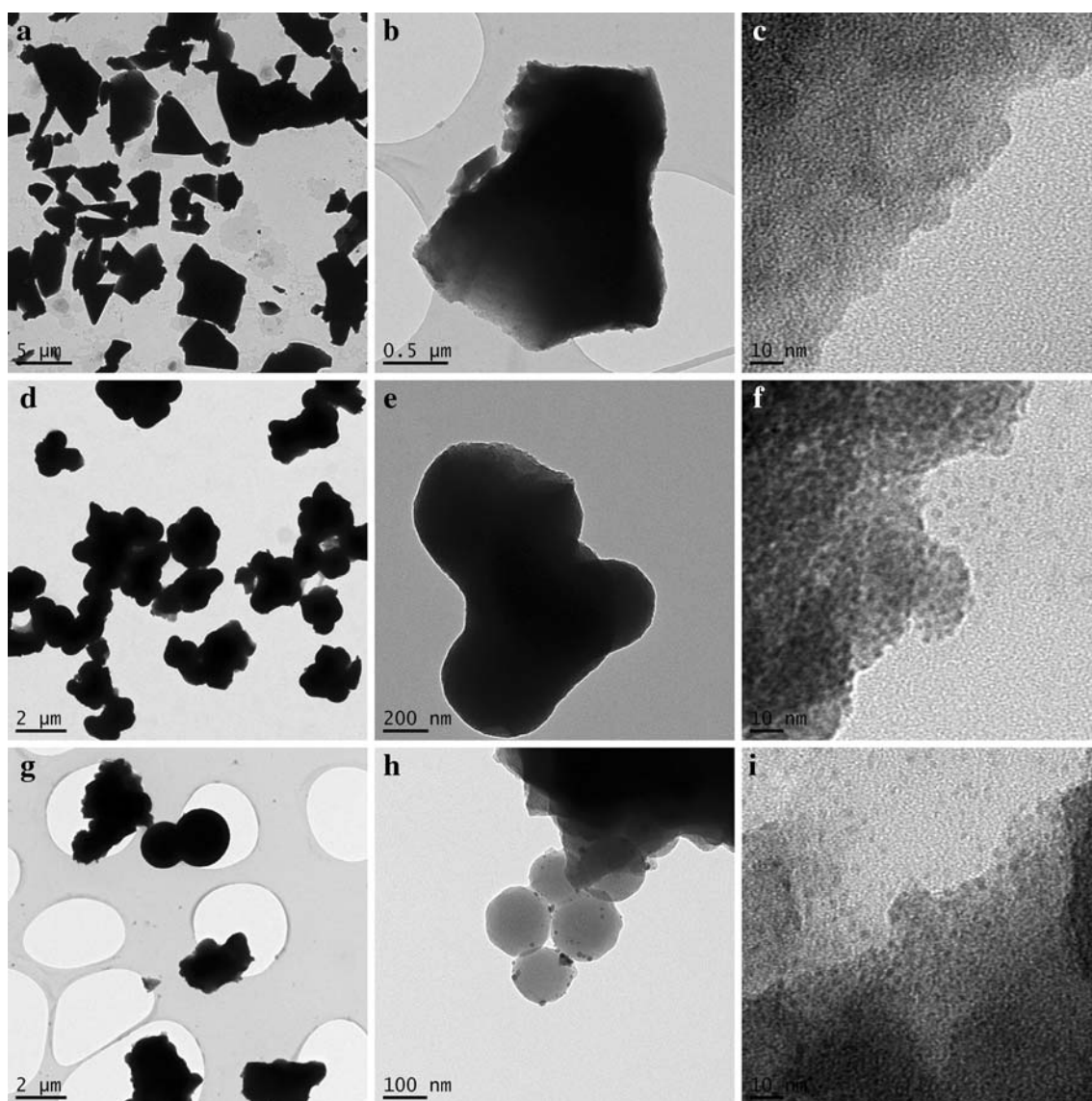
In the present work the effects of the pH and the titanium precursor on the morphology and crystal structure of the resulting products was investigated. From DLS measurements it was found that the pH of the solution had a huge effect on the rate of formation of particles. In Table 2 the particle size of the TiO<sub>2</sub> particles in suspension after 48 h is shown. Under acidic conditions the particle size of the TiO<sub>2</sub> particles was found to be around 3 nm independent

on the titanium precursor used. However, drying of the sol (heat treatment at 105 °C for 12 h) lead to gelation due to destabilization of the sols by evaporation of the alcohol. Apparently, during this drying process the small particles cannot withstand gel formation probably due to their huge vulnerable surface area and the high temperature resulting in a high level of Brownian motions and increased reaction velocity. During the original condensation process the small particles were protected by protons charging the surface. After drying yellowish transparent gels were obtained. The color is believed to be a result of the presence of alkoxy groups captured inside the gel. These gels were grinded into a fine powder which was used for further analysis. HR-TEM analysis of the resulting TiO<sub>2</sub> powders also supported the pronounced model that the particles synthesized at pH 3 grow significantly during the drying process leading to the formation of a gel. In Fig. 5a–c representative TEM images of the gels obtained at pH 3 are shown. From the TEM analysis of the obtained gels (Fig. 5c) it is not possible to observe or identify individual titanium clusters serving as building blocks. In comparison synthesis under neutral and alkaline conditions resulted in precipitation of TiO<sub>2</sub> particles. From the DLS results shown in Table 2 it is found that the TTE generally lead to the formation of larger particles or aggregates in solution compared to TTIP and TTB. This may be due to the higher reactivity of the ethoxy group compared to the isopropoxy and butoxy groups probably due to less sterical hindrance from the ethoxy group in both the primary nucleophilic reaction and the polymerization process compared to the larger alkoxy groups. TEM investigation of the particles synthesized under neutral and alkaline conditions (Fig. 5f, i) shows that the particles are formed from clusters around 3 nm. These results suggest that the TiO<sub>2</sub> particles are formed from aggregation of the titanium clusters

**Table 2** Particles properties of the TiO<sub>2</sub> particles synthesized using different titanium precursors at different pH

	BET SSA	TEM Particle size of dried TiO <sub>2</sub> particles	DLS Particle size of TiO <sub>2</sub> particles in suspension (nm)
TTIP			
pH 3	6 m <sup>2</sup> /g (non porous)	>2 μm	3 ± 1
pH 7	130 m <sup>2</sup> /g (micro porous)	0.5–1 μm (3)	282 ± 10
pH 10	196 m <sup>2</sup> /g (micro porous)	0.5–1 μm (3)	1,080 ± 30
TTE			
pH 3	0.789 m <sup>2</sup> /g (non porous)	>2 μm	3 ± 1
pH 7	100 m <sup>2</sup> /g (micro porous)	0.5–1 μm (3)	808 ± 15
pH 10	153 m <sup>2</sup> /g (micro porous)	0.5–1 μm (3)	2,380 ± 80
TTB			
pH 3	0.99 m <sup>2</sup> /g (non porous)	>2 μm	3 ± 1
pH 7	24 m <sup>2</sup> /g (micro porous)	1–2 μm (3)	362 ± 20
pH 10	31 m <sup>2</sup> /g (micro porous)	1–2 μm (3)	1,054 ± 25

The number in the parenthesis indicate the cluster size in nm determined by HR-TEM



**Fig. 5** **a–c** Representative TEM images of the particle morphology of the  $\text{TiO}_2$  gel obtained at pH 3. **d–f** Representative TEM images of the particle morphology of the  $\text{TiO}_2$  particles synthesized at pH 7.

**g–i** Representative TEM images of the particle morphology of the  $\text{TiO}_2$  particles synthesized at 10

observed initially after mixing of the reaction solution. The size of these aggregates is in the size order of 100–400 nm (Fig. 5e, h). Moreover, further aggregation of these aggregates occurs resulting in the structures shown in Fig. 5d, g.

BET investigation of the  $\text{TiO}_2$  powders showed that particles prepared from TTIP have the largest surface area, followed by the particles prepared from TTE. The surface area of the  $\text{TiO}_2$  particles prepared from TTB was found to be considerable lower compared to the two others (Table 2). Moreover, it was found that the pH of the sol-gel solution has a crucial influence on the specific surface area of the resulting particles. The highest specific surface area was found for particles synthesized under alkaline

conditions independent on the titanium alkoxide used. Relatively high specific surface areas (24–130  $\text{m}^2/\text{g}$ ) were also found for the particles synthesized at pH 7. However, under acidic conditions the surface area was found to be very low (<6  $\text{m}^2/\text{g}$ ). Analysis of the BET adsorption isotherms of the  $\text{TiO}_2$  gel/powder obtained under acidic conditions showed that the particles were non porous. In comparison the  $\text{TiO}_2$  particles synthesized under neutral and alkaline conditions were found to be microporous with a pore diameter around 1 to 2 nm correlating with the TEM analysis. These findings suggest that fast precipitation (DLS experiments) lead to porous particles and slow particle formation resulting in non-porous particles/gels. The rate of particle formation was in the present work found to

be influenced by both the pH and the nature of the alkoxy group of the titanium precursor.

### 3.2.2 Crystallinity

XRD analysis of the TiO<sub>2</sub> powders showed that the particles synthesized at 25 °C were amorphous. After heating the samples to 300 °C formation of the crystalline structure anatase were observed. Generally, it may be argued that TiO<sub>2</sub> particles synthesized from TTIP crystallize easiest as the anatase peak of these particles has the highest intensity (Table 3). As the temperature was increased to 450 °C an increase in intensity of the anatase peak was observed for all the TiO<sub>2</sub> powders. At 600 °C all the TiO<sub>2</sub> powders were found to have approx. the same amount of anatase (similar intensity). In addition, some of the powders were found to contain small amounts of rutile. The crystal size determined from the broadening of the peak using Scherrers formula showed that the crystal size increased with increasing temperature. At 600 °C the size of the anatase crystals were found to be very similar. These results may indicate that the particles obtained after heat treatment at 600 °C are very similar and that the difference arising from the surface area and particle size at 25 °C may have despaired due to a collapse of the porous structure by grain growth.

### 3.2.3 Chemical composition

DSC spectra of the TiO<sub>2</sub> powders are shown in Fig. 6. The small endothermic peak at 30 to 150 °C can be ascribed to desorption of physical adsorbed water and hydroxyl groups. The exothermic peak region from 200 to 400 °C can be ascribed to removal of carbon originating from the alkoxy groups [18–20]. The variation in the area of the

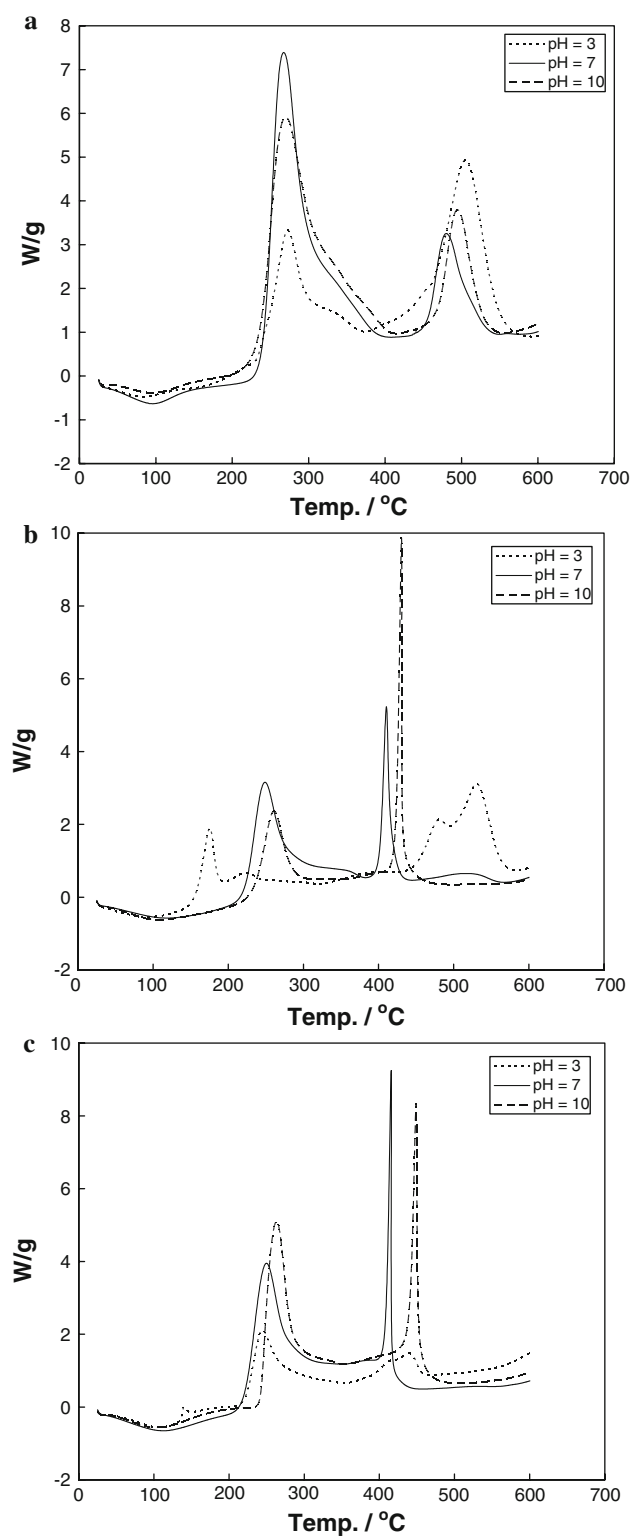
exothermic peak observed at different pH independent on the titanium precursor used suggests that the particles synthesized at pH 3 contained lower amount of residual carbon. However, further analysis of the TiO<sub>2</sub> powder obtained at pH 3 have indicated that all the carbon present in the TiO<sub>2</sub> powder was not removed at temperatures up to 400 °C as these TiO<sub>2</sub> particles were more compact (BET results). It is believed that some residual carbon was trapped inside the particles and that heating of the particles at temperatures up to 400 °C only removed surface carbon resulting in the formation of a TiO<sub>2</sub> shell encapsulating the remaining carbon. This carbon was then removed during the crystallization process explaining the double peak in the DSC spectra observed for the TiO<sub>2</sub> particles synthesized at pH 3 above 400 °C. Thus, comparison between the amounts of residual carbon in the TiO<sub>2</sub> particles synthesized at different pH is difficult. The difference in the amount of residual carbon observed for particles synthesized using different titanium precursors can partly be explained by the number of carbon atoms in the different alkoxy groups. The exothermic peak in the region from 400–550 °C can generally be assigned to crystallization of the amorphous TiO<sub>2</sub> particles. From the obtained DSC spectra it is seen that the formation of anatase occur over a temperature interval dependent on the particle morphology. High surface area and porous particles → narrow crystallization temperature interval and dense particles → broad temperature interval.

An additional experiment was performed for TTIP with a large excess of water ( $h = 25$ ). The results of this experiment showed that at pH 3 a gel was immediately obtained without drying. However, in this case no double peak was observed in the DSC spectra near the crystallization temperature of anatase as in the experiments with

**Table 3** XRD analysis of the prepared TiO<sub>2</sub> particles at different temperatures

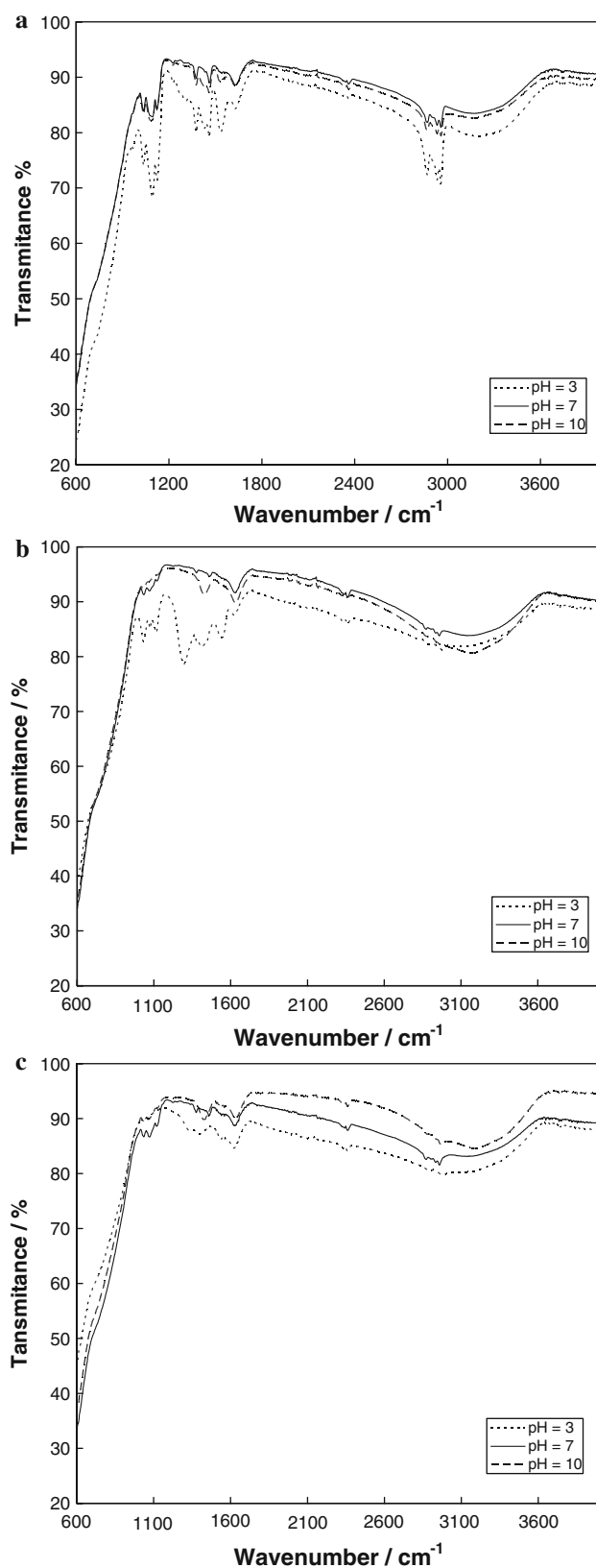
	25 °C	150 °C	300 °C	450 °C	600 °C
<b>TTE</b>					
pH 3	–	–	A [4.3] (129)	A [8.5] (995)	A [23.5] (3048)
pH 7	–	–	A [16.4] (508)	A [16.6] (2273)	A [24.8] (3599)
pH 10	–	–	–	A [14.7] (1803)	A [23.2] (3389) R [35.8] (66)
<b>TTIP</b>					
pH 3	–	–	A [11.7] (1125)	A [13.6] (1757)	A [25.7] (3264)
pH 7	–	–	A [12.4] (176)	A [14.1] (1949)	A [22.9] (3558) R [31.8] (54)
pH 10	–	–	A [11.0] (845)	A [13.0] (1751)	A [21.2] (3066)
<b>TTB</b>					
pH 3*	–	–	A [4.9] (118)	A [6.7] (194)	A [24.1] (953)
pH 7	–	–	A [8.5] (426)	A [10.8] (1424)	A [25.7] (3545)
pH 10	–	–	A (100)	A [10.1] (1120)	A [22.6] (3028) R [36.8] (50)

\* Lower amount of material in the sample holder. The number in the square brackets denotes the crystal size of anatase (A) and rutile (R). The numbers in the parenthesis denote the intensity of the anatase and rutile peaks



**Fig. 6** DSC spectra of the resulting  $\text{TiO}_2$  powders prepared from **a** TTE, **b** TTIP, and **c** TTB at different pH

$h = 2.7$ . Thus, the residual carbon was not trapped in the  $\text{TiO}_2$  matrix and as a result of this the crystallization temperature for the anatase phase was 150 °C lower.



**Fig. 7** ATR FT-IR spectra of the resulting  $\text{TiO}_2$  powders prepared from **a** TTE, **b** TTIP, and **c** TTB at different pH



Moreover attenuated total reflection FT-IR was used to study the amount of residual carbon present in the  $\text{TiO}_2$  particles after synthesis. From the FT-IR spectra in Fig. 7 it is seen that the  $\text{TiO}_2$  particles synthesized under acidic conditions in every case independent on the alkoxide used has the highest absorption at the bands located between 1,045 and 1,114  $\text{cm}^{-1}$  which is assigned to Ti–O–C groups [21, 22]. Moreover, high absorption was observed at the bands located at 1,388 and 1,489  $\text{cm}^{-1}$  assigned to  $\text{CH}_2$  bending and at 1,411 and 1,443  $\text{cm}^{-1}$  assigned to  $\text{CH}_3$  bending [21]. The band found at 2,958  $\text{cm}^{-1}$  is assigned to the asymmetric stretching of the  $\text{CH}_3$  group and the bands at 2,923 and 2,853  $\text{cm}^{-1}$  are assigned to the asymmetric and symmetric stretching of the  $\text{CH}_2$  group. Moreover, the absorption band at 1,620  $\text{cm}^{-1}$  is assigned to O–H stretching. From the identified absorptions bands it is clear that the  $\text{TiO}_2$  particles obtained at pH 3 contained the most residual carbon originating from unreacted alkoxy groups. Comparing the reactivity of the different alkoxy groups suggest that the butoxy group is the least active due to the highest absorption at the Ti–O–C band indicating that higher amounts of butoxy groups remain after reaction. This correlates with the observed slow particle formation in the DLS study. Also the BET measurements showed decreased surface area in case of butoxide as alkoxy group and also from DSC-results it was observed that a larger amount of carbon remained. In general, a higher amount of carbon remaining in the gel or powder results in lower surface area and porosity. Therefore, using TTIP at pH 7 or higher is the best choice for the production of  $\text{TiO}_2$  if high surface area and porosity are important as when  $\text{TiO}_2$  is used for photocatalysis.

#### 4 Conclusions

ESI-MS investigation of the titanium clusters present during the nucleation and growth period showed that the number of titanium atoms in the clusters varied dependent on the alkoxide used. It was found that the titanium clusters formed using TTE were smaller than the clusters formed using TTIP and TTB under similar conditions. pH was not found to influence the nature of the titanium clusters.

The influence of pH on the particle properties showed that the small 3 nm particles synthesized at pH 3 grow significantly during the drying process due to destabilization of the colloidal solution leading to the formation of a gel confirmed by help of HR-TEM.

HR-TEM investigation of the  $\text{TiO}_2$  particles prepared at pH 7 and 10 showed that the primary particle size of the particles was around 3 nm. However, it was found that these primary particles aggregated during the induction

period to form larger secondary particles in the size order of 300–500 nm range.

BET investigation of the resulting  $\text{TiO}_2$  powders showed that particles prepared from TTIP had the largest surface area, followed by the particles prepared from TTE. The surface area of the  $\text{TiO}_2$  particles prepared from TTB was found to be considerable lower. The highest specific surface area could be found for particles synthesized under alkaline conditions independent of the titanium alkoxide used due to the porosity of the secondary particles confirmed by TEM analysis. Under acidic conditions the surface area was found to be very low. The surface area was in general highest with lowest amount of carbon remaining in the  $\text{TiO}_2$  matrix.

XRD analysis of the  $\text{TiO}_2$  particles showed that the particles synthesized at 25 °C were amorphous. First after heating the samples to 300 °C the formation of anatase were observed. FT-IR analysis of the  $\text{TiO}_2$  showed that the  $\text{TiO}_2$  particles obtained at pH 3 contained the most residual carbon originating from unreacted alkoxy groups. Moreover, comparison of the reactivity of the different alkoxy groups suggests that the butoxy is the least reactive in the primary hydrolysis and polymerization processes.

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