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LETTER

Application of electro-spray ionization mass spectrometry for characterization of titanium polyoxoalkoxides in sol-gel processes

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Sol-gel derived titanium dioxide nanoparticles with controlled size distribution and morphology are of great interest for different applications [1]. Understanding the phenomena occurring during the initial stage of particle growth is especially important, because they determine the properties of the final products (powders, films, gels). The titania sol-gel polymerization follows essentially a different pathway than the relatively well studied silicon based sol-gel process [2]. Generally, in the silicon case, individual monosilicate serves as building units during the process, while in the titania polymerization the role of building blocks can be played by polyoxoalcoxides (titanium oxide clusters) [2–4]. Particularly $Ti_{11}O_{13}(OC_3H_7)_{18}$ was proposed as such a building block in the case of titanium isopropoxide (TTIP) based sol-gel process [3]. A stable solution of these clusters can be obtained by hydrolysis of TTIP under low hydrolysis ratios $H < 1$ (H is the molar ratio of water and alkoxide). It can be analyzed e.g. by O^{17} NMR spectroscopy [4].

In the case of $H > 1.5$ the hydrolysis of TTIP does not result in a stable solution of polyalkoxides: the precipitation of titanium dioxide particles takes place after a so-called induction period. The presence and size evolution of nanoparticles with radius 1.5–6 nanometers during the induction period of the process has been studied by dynamic light scattering (DLS) [5, 6]. However the DLS does not give information about composition of observed nanoparticles. The identification of polyalkoxides directly during the induction period of TTIP based sol-gel process would be of great interest. Electrospray ionization mass spectrometry (ESI-MS) [7] is a valuable tool to such an investigation. It was successfully applied to description of protein compounds [8], and recently was also used to determine the composition of polyaluminium oxyhydroxide clusters [9].

Titanium has 5 isotopes with high natural abundance: ^{46}Ti (8.25%), ^{47}Ti (7.44%), ^{48}Ti (73.72%), ^{49}Ti (5.41%), ^{50}Ti (5.18%). It makes it possible to use the isotope broadening of ESI-MS spectra peaks in order to find the number of titanium atoms in clusters. Afterwards the molecular weight of the clusters can be used to determine the content of other elements (C, O, H).

The theoretical isotope patterns for clusters containing different number of titanium atoms were calculated by using the ‘‘Sheffield ChemPuter Isotope Patterns calculator’’ [10]. The pattern distributions can be well approximated by a Gaussian

$$A \exp\left(-\frac{(M-M_0)^2}{w^2}\right) \quad (1)$$

where A is a constant, M is the mass of a cluster, M_0 is the mass of the most frequent cluster and w is a broadening. The value of w was calculated for the clusters with the number of titanium atoms n from 5 to 15. The dependence of w as a function of n is presented in Fig. 1.

The calibration curve of Fig. 1 can be used to estimate the number of titanium atoms in the cluster.

A usual formula to describe titanium polyalkoxides is $Ti_nO_m(OR)_{4n-2m}$ [3, 4], where R is hydrocarbon group. Taking into account that the surface OR groups can be

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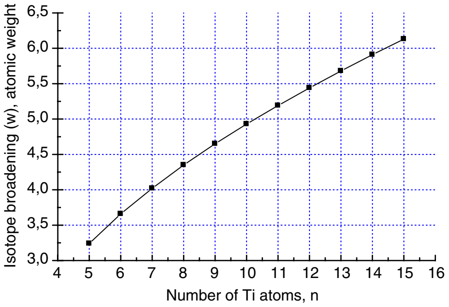


Fig. 1 Isotope broadening (w) as a function of number (x) of titanium atoms

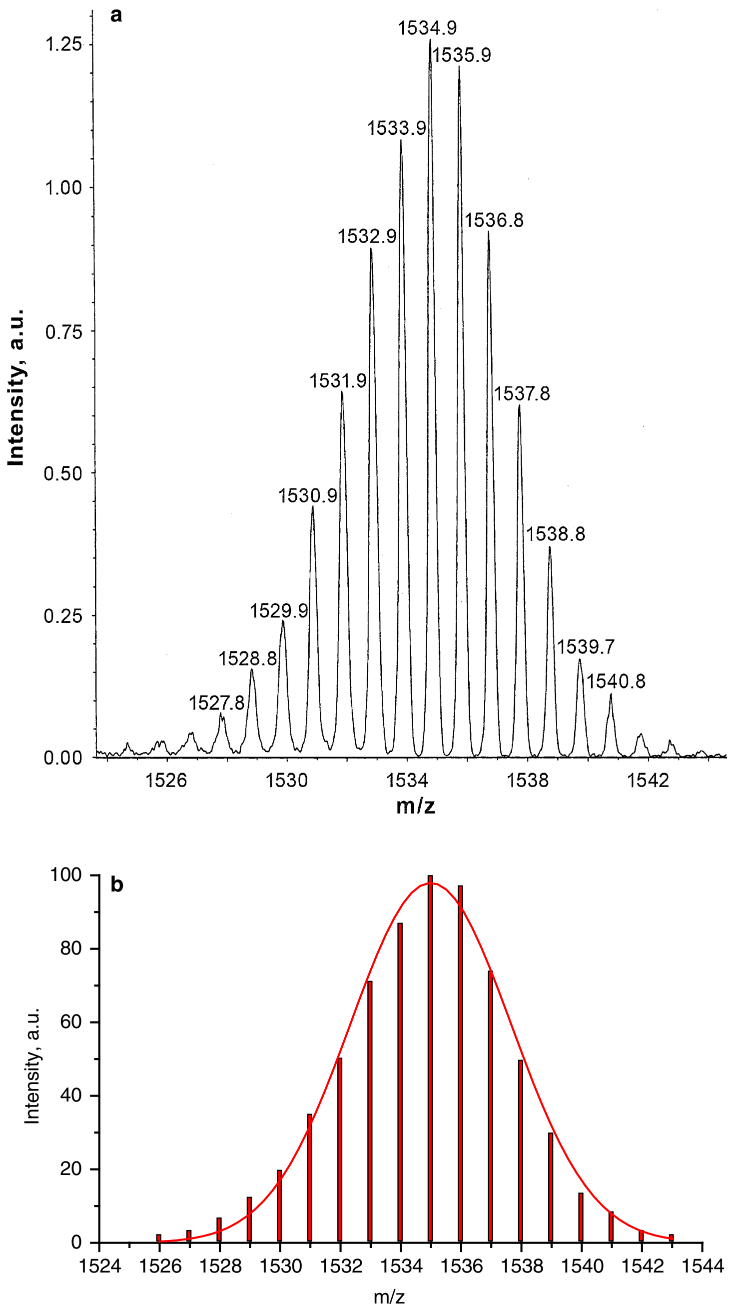
hydrolyzed, the more general formula with 3 parameters can be written:

$$\mathrm{Ti_nO_m(OR)_{4n-2m-k}(OH)_k} \quad (2)$$

Finally the clusters can contain adsorbed water molecules, which gives additional 4th parameter.

In this letter the results of the application of ESI-MS for a TTIP based sol-gel process are reported. The sol-gel process was carried out using TTIP (98+% Acros Organics), isopropanol (99+% Acros Organics, 0.05% maximum water content) and distilled water. A solution of TTIP in

Fig. 2 (**a**) Experimental ESI-MS spectrum. (**b**) Gaussian approximation of the spectrum by formula 1, m = 1535, w = 5.34



isopropanol (solution A) and a solution of water in isopropanol (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. After 30 s the stirring stopped and samples for ESI-MS spectra measurements were performed. Before ESI-MS analysis the samples were diluted 1000 times in isopropanol.

The ESI-MS spectra were registered with an interval of 10 min during the induction period (which was about 30 min). The LC-MSD-Trap-SL spectrometer was used with a drying temperature of 325°C and a capillary exit voltage of 164 V. A spectral region 1000–2000 m/z with z positive was investigated. Maximum intensity peak with m/z = 1535 was present on all spectra. The spectrum in the region 1524–1542 m/z is presented in Fig. 2a.

The fact that the distance between the fine structure lines is 1 m/z indicated that clusters had a unit positive charge ($z = +1$). The intensity of the peak did not change significantly with time. The Gaussian approximation (1) of the experimental spectrum (Fig. 2b) gave the broadening $w = 5.34$, which corresponded to 11 titanium atoms. Fixing $n = 11$ and varying m and k in formula (2), as well as a number of water molecules, permitted us to find the following system, which can correspond to the observed spectrum: $Ti_{11}O_{13}(OR)_{10}(OH)_8 + 4H_2O + H^+$ ($R = C_2H_7$), with a mean cluster mass $M_c = 1535$ and a unit positive charge.

After the calculation of the number of carbon atoms, the consistence of the isotope broadening with the composition of the resulting system must be checked again, because of the presence of isotope ^{13}C, which can also contribute to the broadening of the ESI-MS spectra. However this contribution was not significant in our case. Theoretical calculation of the isotope broadening of this system, taking into account ^{13}C atoms, gave the value of $w = 5.42$, which is still in a good agreement with the experimental value.

The analyses of the ESI-MS spectra seems to confirm the hypothesis that clusters containing 11 titanium atoms serve as building bricks during induction period of TTIP based sol-gel process. The constant intensity of the peak corresponding to these clusters suggests that the aggregation mechanism is a reasonable explanation of nanoparticle growth during the induction period of the process [11]. If fact, if the process consisted of a transformation of smaller clusters into bigger ones, the former would be consumed in the course of the induction period. In the contrary, aggregated particles containing Ti_{11}-polyalkoxides as elementary units can disaggregate during ESI-MS analysis and their number can therefore remain constant.

The explanation of the details of cluster composition is not obvious. Namely, it is not clear why the stable form of this cluster has just 8 hydrolyzed alkoxy groups and 4 adsorbed water molecules. It is worth noticing that in spite of the extremely mild character of spray preparation and ionization, surface of the clusters can be changed (e.g. hydrolyzed) during this process, so that the observed structure of the cluster can be slightly different to that in the solution. However we believe that the number of titanium atoms in a cluster cannot be changed during the ESI-MS analysis and a reliable value is obtained in such an experiment.

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References

1. Yoda S, Suh DJ, Sato T (2001) J Sol-Gel Sci Tech 22:75
2. Brinker CJ, Scherer GW (1990) Sol-gel science, the physics and chemistry of sol-gel processing. Academic Press, San Diego
3. Day VW, Eberspacher TA, Klemperer WG, Park CW (1993) J Am Chem Soc 115:8469
4. Blanchard J (1997) PhD Thesis, Université Pierre et Marie Curie, June 1997
5. Soloviev A, Ivanov D, Tufeu R, Kanaev AV (2001) J Mater Sci Lett 20:905
6. Soloviev A, Tufue R, Sanchez C, Kanaev AV (2001) J Phys Chem B 105:4175
7. In: Cole RB (ed) Electrospray ionization mass spectrometry: fundamentals, instrumentation, and applications. John Wiley and Sons, 1997
8. Boysen RI, Heatn MTV (2000) J.Biochem.Biophys.Methods 45:157
9. Søgaard EG (2002) In: Hahn HH, Hoffmann E, Ødegaard H (eds) Chemical water and wastewater treatment VII: proceedings of the 10th Gothenburg Symposium. June 17–19, 2002, Gothenburg, Sweden, p 3
10. http://www.shef.ac.uk/chemistry/chemputer/isotopes.html
11. Soloviev A, Jensen H, Søgaard EG (2003) J Mater Sci 38:3315