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SAXS- and ASAXS-investigation of TiO_2 - SiO_2 gels

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Gels in the system SiO_2 - TiO_2 were prepared by hydrolytic polycondensation of the corresponding alkoxides by use of acetyl acetone as an additive in order to reduce the rate of hydrolysis of the Ti-alkoxide as well as by use of pre hydrolysis of the slower reacting Si-alkoxide and storage before mixing with the Ti-alkoxide. All investigated gels are characterized by very small particles varying in Guinier radius in the range between 0.8 nm and 1.0 nm. These particles aggregate to form fractal clusters with a fractal dimension of nearly 2.0. Anomalous SAXS at the Ti-K-edge gives information about the behaviour of the TiO_2 in the process of gelation. The resonant part of the scattering curve of the samples characterized by a high content of acetyl acetone shows that the TiO_2 component is equally distributed in the system and does not take part in the formation of fractal cluster.

Introduction

One method to manufacture solids or thin films out of a "molecular construction set" is the catalytic hydrolysis and polycondensation of tetra-alkoxides in alcoholic environment. By choosing the chemical conditions it is possible to control the reaction kinetics of structure formation and, thus, the properties of the gels produced. The hydrolysis and polycondensation of the corresponding metal-ethoxides differ drastically from each other. It is necessary to harmonize this process to get an homogenous gel or a stabilised sol.

There are several possibilities for preparing homogeneous TiO_2 - SiO_2 -gels:

- a) Increase of the reaction rate of the Si-alkoxide in relation to Ti-alkoxide
- b) Pre hydrolysis of the slower reacting Si-alkoxide
- c) Use of double alkoxides
- d) Decrease of the reaction rate of the Ti-alkoxide by use of hydrolysis controlled chemical additives (HCCA).

In the following Small Angle X-ray Scattering (SAXS) and Anomalous SAXS are used to investigate the structure forming in the system: SiO_2 TiO_2 .

Experimental

In a first series we take 0.3 mol TEOS, 0.7 mol TEOTi , 10 mol H_2O , the catalyst (0.2 mol HCl) and the solvent (0.5 mol $\text{C}_2\text{H}_5\text{OH}$) in this fixed ratio and vary only the quantity of acetyl acetone (HCCA) in the range from 0.03 to 0.6 mol. A second series with a two step process was carried out.

The ageing time of the Si-ethoxide sol was varied before the Ti-ethoxide was added to the solution (0.4 mol TEOS, 0.6 mol TEOTi, 8 mol H₂O, 35 mol C₂H₅OH).

The SAXS-measurements were performed with a slit collimation (Kratky Kompact Kamera) and position sensitive detector (Braun OED-50 M).

ASAXS measurements were carried out at the SAXS-beamline A1 at the HASYLAB [1].

Results

In Figure 1 representative scattering curves of the first series are shown. The results are summarized in table 1. All gels are characterized by very small primary particles varying in Guinier radius in the range between 0.8 and 1.0 nm.

Figure 1 SAXS curves of the gel of series 1 with 0.15, 0.12, 0.09 and 0.06 mol acetyl acetone (T11..T14)

These particles aggregate to form fractal cluster of fractal dimension d_f . The addition of acetyl acetone has a minor influence on the gel structure for acetyl acetone contents up to 0.15 mol. The aim of our chemical procedure was to reach a nearly homogenous distribution of the two components on the molecular level. However, in two-component systems there is no possibility to distinguish between the particular components by means of normal SAXS-experiments. Anomalous SAXS at the Ti-K-edge should give information about the behaviour of the TiO₂ in the process of gelation.

The measured intensity $S_m(s, \lambda)$ (s -amount of the scattering vector, λ -wavelength) consists of the non-resonant part $S_O(s)$, the cross-term $S_{OR}(s)$, the resonant part $S_R(s)$ and the fluorescence Flu according to [2] with :

$$S_m(s, \lambda) = S_O(s) + 2 \cdot f(\lambda) \cdot S_{OR}(s) + (f^2(\lambda) + f''^2(\lambda)) \cdot S_R(s) + f_l(\lambda) \cdot Flu \quad (1)$$

The dispersion term f and the absorption term f'' of the correction are calculated from the energy dependent absorption curve of the sample.

Sample	CLUSTER	PRIMARY PARTICLES
HCCA [mol]	d_f	R_G [nm]
0.15	2.20	1.03
0.12	2.08	0.98
0.09	1.96	0.92
0.06	2.05	0.88
0.03	2.05	0.82

Table 1: R_G - Guinier radius; d_f - fractal dimension

By making ASAXS-measurements at more than three energies near the absorption edge the partial scattering parts of equation (1) can be extracted.

We measured our samples at 6 or more different energies. That is why the equation system is over determined. It was solved by least square method.

Figure 2: Scattering curve of sample with 0.15 mol acetyl acetone measured in the energy range between 4890 and 4990 keV.

Figure 3: Scattering terms obtained by dispersion analysis of the curves of figure 2.

1- non resonant term; 2-cross term; 3-resonant term; 4- fluorescence term

Figure 4: Scattering curves of the sample with 0.6mol acetyl acetone

Figure 5: Result of the dispersion analysis of the curves of figure 4

Figure 2 shows the scattering curves at energies between 4890 and 4990 keV of the sample with 0.15 mol acetyl acetone. The samples with less than 0.15 mol acetyl acetone look like this example. The scattering curves measured at higher energies are shifted nearly parallel to the curve with the lowest energy. That means the resonant part and the cross term of the scattering curve which are involved only at higher energies have the same pattern than the non resonant part. The solution of the equation system represented in figure 3 shows the same result. That means SiO_2 and TiO_2 take part in the aggregation process with equal rights.

With the increase of the content of acetyl acetone the relation between the aggregation probability of SiO_2 and TiO_2 change clearly. The energy dependent scattering curves of the sample with 0.6 mol acetyl acetone are shown in figure 4. In this case the solution of the equation system (figure 5) clears up the roll of the titanium. The resonant part and the cross term of the scattering curve do not own particle scattering. It is evident that TiO_2 molecules are

equally distributed in the gel structure of the SiO_2 aggregats. They do not take part on the aggregation process.

Figure 6: Scattering curves of the sample with pre hydrolysis process.

Figure 7: Result of the dispersion analysis of the curves of figure 6

The sample with the pre hydrolysis of the slower reacting Si-alkoxide shows a different scattering behaviour seen in figure 6. Only the dispersion analysis (figure 7) permits an interpretation of experimental results. The resonant term of the scattering curve shows only for s -values smaller than 0.8nm^{-1} a particle scattering. That means that TiO_2 participates in formation and aggregation of the fractal clusters. But the later addition of the Ti-ethoxides prevents the formation of TiO_2 primary particles. The TiO_2 monomers take directly place in the aggregation of the available SiO_2 - clusters.

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