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Structural characterisation of binary SiO₂/TiO₂ nanoparticle aerogels by X-ray scattering

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Abstract. The effect of SiO₂ to TiO₂ aerogels content on their local structure is evidenced from X-ray scattering measurements. TiO₂-SiO₂ aerogels were prepared by sol-gel method followed by supercritical drying with liquid CO₂ and heat treatment. The local structure of TiO₂-SiO₂ system was investigated by analysing the atomic pair distribution function PDF, $G(r)$, obtained from X ray scattering data. The modified coordination radius values obtained for the first coordination spheres by addition of SiO₂ denotes a diminution of the atom packing in this system. The PDF of the 300⁰C heat treated TiO₂ aerogel sample shows well-defined features allowing an unambiguous structure search and refinement. In particular, the first peak in the PDF of the precursor phase is quite narrow and centered at about 1.9 Å, which is the Ti-O distance in Ti-O₆ octahedra. This observation shows that well-defined Ti-O₆ octahedra are already formed during the homogeneous precipitation stage of the chemical process. Inspecting the data from the analysis of the atomic pair distribution function $G(r)$ one remarks the occurrence of Si-O pair as a first coordination formation at a distance of 1.49 Å and the interatomic distances at 2.18 Å for the first Si-Si and 3.58 Å for the second Si-Si bond.

1. Introduction

Silica-titania materials TiO₂-SiO₂ aerogels have received significant attention as high performance photocatalysts because of their larger specific surface area and higher porosity. These porous solids combine the mechanical properties of silica with the chemical properties of titania. Anderson and Bart [1] have demonstrated that a mixed oxide of TiO₂ and SiO₂ produced by a sol-gel method was a more efficient photocatalysts for the photodecomposition of rhodamine-6G than TiO₂ alone. The increase in efficiency was attributed to the presence of SiO₂ as adsorbent, which enhances the concentration of the organic material near to the TiO₂ sites. The heat treatment temperature influences the structure of the TiO₂-SiO₂ aerogels and also their photoactivity. In this work, we prepared TiO₂-SiO₂ aerogels with different contents of Ti and Si, which are subsequently heat treated at different temperatures. We studied the local structure particularities of the prepared TiO₂-SiO₂ aerogels by means of an X-ray scattering experiment. Along with the neutron scattering the X-ray scattering from disordered materials is largely used to investigate their local structure [2, 3]. The non-crystalline state of a compound can occur in a large structural variety depending on the preparation conditions. This is due

to the fact that during the sample preparation the “freezing” process of the atoms arrangement has an important effect on the atom bonds and atom relaxation energy barriers. The XRD pattern for the TiO₂-SiO₂ aerogels, however, is very diffuse in nature and could not be analyzed in the traditional way. That is why the local structure investigation was considered in terms of the atomic pair distribution function (PDF) analysis, an approach that has recently proven to be very successful in structure studies of heavily disordered oxide materials [4].

2. Experimental

In order to study the influence of Si content and thermal treatment temperature on the properties, SiO₂-TiO₂ aerogels with different TiO₂ content were synthesized by sol-gel method followed by low temperature supercritical drying and different temperatures thermal treatment [5].

The sols were prepared from Ti(IV) isopropoxide (Merck), tetramethoxysilane (Merck), anhydrous ethanol (Fluka), water and nitric acid reagent (Aldrich). The molar ratio of reactants was: [Ti/Si]:[H₂O] = 1:3.5, [Ti/Si]:[C₂H₅OH] = 1:23.33, [Ti/Si]:[HNO₃] = 1:0.08.

The as prepared gels were kept for 4 weeks in closed vessels and then were dried using supercritical CO₂ in a SAMDRI – 790 A (Tousimis) critical point dryer. Annealing, at 300°C, 600°C and 700°C for 2 h was performed to obtain crystalline phases of TiO₂ and to remove residues of organic substances [5].

The X-ray diffraction patterns were obtained using a standard BRUKER D8 Advance X-ray diffractometer, working at 40 kV and 40 mA. The Cu K α radiation was monochromatized with a germanium monochromator placed in the incident X-ray beam. The data of the X-ray diffraction patterns were collected in a step-scanning mode with $\Delta 2\theta = 0.02^\circ$ steps.

The specific surface area of the as prepared samples was determined using Brunauer-Emmett-Teller (BET) method, in a partial pressure range of $0.05 < P/P_0 < 0.3$. Krypton adsorption was carried out at 77 K. Before each measurement, the samples were heat-cleaned at 333 K for 2 h.

In table 1 are presented the Ti composition and the BET specific surface area of the TiO₂-SiO₂ aerogels.

Table 1. The Ti molar percentage content of the TiO₂-SiO₂ aerogels and the specific surface area of the TiO₂-SiO₂ aerogels.

Sample	Sample type	Ti [%mol]	S _{BET} [m ² /g]
A300	TiO ₂ aerogel Heat treated for 2 h at 300°C	100%	56
A600	TiO ₂ aerogel Heat treated for 2 h at 600°C	75%	52
A700	TiO ₂ aerogel Heat treated for 2 h at 700°C	75%	44

3. Results and discussion

Titania, TiO₂, is used in a number of important technological applications such as functional ceramics, reinforced polymers, pigments, photocatalysts, gas sensors, solar energy conversion [6, 7]. It occurs in three crystalline polymorphs: rutile, anatase, and brookite. All are built of Ti-O₆ octahedra; the way the octahedra couple to each other into a 3D network is slightly different in the different polymorphs. Bulk rutile is the most thermodynamically stable polymorph of titania, and an irreversible phase transition from brookite to anatase and then to rutile usually occurs with increasing temperature. The thermodynamic stability of titania polymorphs, however, also depends on the crystallite size, and because most applications require fine titania powders, it is actually the anatase polymorph that is most frequently used. Anatase, however, exhibits a relatively large band gap (~ 3.2 eV), which is unfavorable to some applications such as photocatalysis. This has inspired an intensive search for fine crystallite titania powders with a narrower band gap. The titania powders were found to exhibit

photocatalytic activity in the sequence of pure brookite > mixture of rutile and brookite/anatase > pure rutile [8].

The local structure of TiO₂-SiO₂ system was investigated by analyzing the atomic pair distribution function PDF, G(r), obtained from X ray scattering data using a PEDX program [9].

The frequently used pair distribution function PDF, is defined as:

$$G(r) = 4\pi r [\rho(r) - \rho_0] \quad (1)$$

where $\rho(r)$ and ρ_0 are the local and average atomic number densities, respectively, and r is the radial distance [9]. As defined, the PDF G(r) is a one-dimensional function that oscillates around zero and shows positive peaks at distances separating pairs of atoms, *i.e.* where the local atomic density exceeds the average one. The atomic pair distribution function G(r) shows maxima and their position, width and area are determined by the distribution of atom pairs in the structural disordered sample (figure 3).

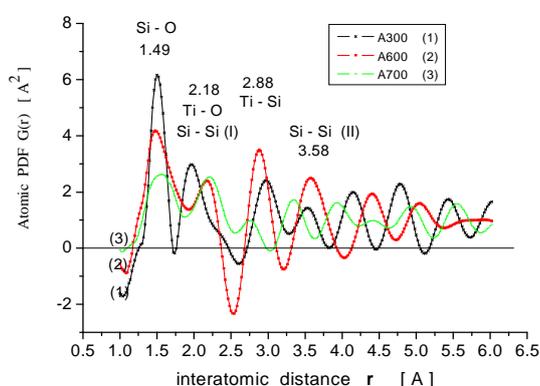


Figure 1. The atomic pair distribution function G(r) for TiO₂-SiO₂ aerogels; A300, A600 and A700 samples.

The real space distance corresponding to the maxima determined from the data obtained in this study may be compared with results reported for other similar systems [8, 10] and allow to identify the atom pairs orderly disposed in the investigated TiO₂-SiO₂ system. They are summarised in table 1.

Table 1. The atom pairs orderly disposed in the vitreous system, identified from the analysis of atomic pair distribution function G(r).

Coordination sphere	Atom pairs	Interatomic distance [Å]
I	Si - O	1.49
	Ti - O	1.96
II	Ti - O	2.18
	Si - Si	2.18
III	Ti - Si	2.88
IV	Si - Si	3.58
	Si - Si	3.58

Inspecting the data obtained for the A300 sample from the analysis of the atomic pair distribution function G(r) one remarks the occurrence of Si - O pair as a first coordination formation at a distance of 1.49 Å. The interatomic distances at 2.18 Å for the first Si---Si and 3.58 Å for the second Si---Si bond agree well with data on bond lengths in the current literature [11].

The PDF of the A300 sample shows well-defined features at about 1.96 Å, which is the Ti---O bond distance in Ti-O₆ octahedra. A distortion of the Ti-O₆ octahedra was observed in the A600 and

A700 samples indicated by the rise of the Ti---O bond distance to 2.18 Å. This observation shows that well-defined Ti-O₆ octahedra are already formed during the homogeneous precipitation stage of the chemical process employed by Yin *et al* [12] It prompted us to narrow the search for the precursor phase structure to models built of Ti-O₆ octahedra [8]. A well-defined feature at 2.88 Å that appears in the PDF function of the TiO₂-SiO₂ aerogel samples indicates the formation of a Ti---Si bond in the system. This bond distance gets shorter in the A700 sample. The new TiO₂-SiO₂ system formed after heat treatment at 700°C has the lowest photocatalytic activity [5].

4. Conclusion

In this work, we prepared TiO₂-SiO₂ aerogels with different contents of Si, which are subsequently heat treated at different temperatures. The morpho-structure of the as obtained silica-titania aerogels was studied by X-ray diffraction and specific surface area measurements.

X-ray scattering results indicate changes induced in the local structure of TiO₂ aerogels containing SiO₂. Total X-ray scattering and atomic pair distribution function PDF data analysis can be successfully employed to determine the atomic scale local structure of heavily disordered oxides. The disordered phase is found to be built of nanosize layers/fragments of Ti-O₆ octahedra arranged according the coupling scheme found in lepidocrocite. The well-defined Ti-O₆ octahedra are already formed during the homogeneous precipitation stage.

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