Structure changes in the sol–gel systems of hydrated oxides†

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Sols of hydrated aluminium oxide, hydrated zirconium oxide and their mixtures were investigated during the xerogel–amorphous-product–crystalline-product transition by SAXS using synchrotron radiation. In the different temperature regions certain changes in structure and morphology were observed. Some correlation between the characteristics of the initial sols and their mixtures (the size and shape of the pores) was observed. In the temperature region 298–1173 K the characteristics of the mixed sol are defined by the characteristics of the initial sols.

1. Introduction

A solid-state reaction, as a rule, occurs *via* the formation of an intermediate state. The chemical stage of the reaction takes place in the reaction zone. To control the reaction it is necessary to know the exact mechanism in the reaction zone.

The hypothesis of the existence of the vacancy structure — an intermediate state which is a distorted crystalline lattice of the initial reagent with vacancies and pores left by removed atoms or molecules of the initial reagent — is a foundation of modern knowledge of the arrangement of the reaction zone. However, the task of investigating a structural rearrangement during a solid-state reaction is very complex (see Garner, 1955; Brown *et al.*, 1980; Prodan, 1976). To simplify the problem we suggested the method of using a model system to simulate solely the new-phase formation stage (see Gaponov *et al.*, 1992). The essence of the simulation method is that in the model system the intermediate-state formation stage is absent, and there is only the stage of rearrangement of the non-crystalline substance (initial product) into the final crystalline product. As a model system we chose the sol–gel process. Fig. 1 outlines the simulation method. The investigation of gelation of the original sol of hydrated zirconium dioxide (HZD), the original sol of hydrated aluminium

oxide (HAO) and binary sols with different component ratios (*n:m* HZD:HAO) showed the presence of 1–2 nm primary particles. Gelation of the binary sols with different component ratios takes place *via* the formation of different secondary particles.

The next step in the investigation of a simplified model system involves the study of the amorphous and crystalline states of the sol–gel system.

2. SAXS experimental details

The SAXS experiments were carried out at BL15A, Photon Factory, National Laboratory for High-Energy Physics, Tsukuba, Japan, and BL5, Siberian Synchrotron Radiation Center, Budker Institute of Nuclear Physics, Novosibirsk, Russia. A focusing optical scheme with a one-dimensional position-sensitive detector was used. The size of a scattering entity and the inter-entity distance that may be defined from the experimental data are limited to a 1–50 nm range.

Original xerosols and the binary xerosol (a mixture with composition ratio 1:1) were prepared during gelation of the original sol of hydrated zirconium dioxide (HZD), the original sol of hydrated aluminium oxide (HAO) and the binary sol (HZD–HAO) at 297 K. High-temperature products were prepared by drying the original and binary xerosols at 723 K and 1173 K. SAXS samples were prepared by fine grinding. Further details of the basic procedure are given by Gaponov *et al.* (1995).

3. Results and discussion

Fig. 2 shows the distance distribution function $p(r)$ for xerosols of HAO (*a*), of HZD (*b*) and of HZD–HAO (*c*) at different temperatures. The plots were calculated from the SAXS data of the corresponding xerosols by calculating the correlation function $\gamma(r)$ (see Feigin & Svergun, 1987). The radius of gyration R_g for each SAXS curve was calculated and is also displayed in the plots.

In the case of fine grinding the monolithic samples of the original xerosols, a strong small-angle scattering is observed (Fig. 3*b*). The samples dried at 298 K were non-crystalline and the samples dried at 723 K were very weakly crystalline. In these cases, the double Bragg reflection is very small and may be neglected. The samples dried at 1173 K were quite crystalline, and for these samples the data interpretation was qualitative. It is clear from the $p(r)$ plots that the maximum size of the scattering
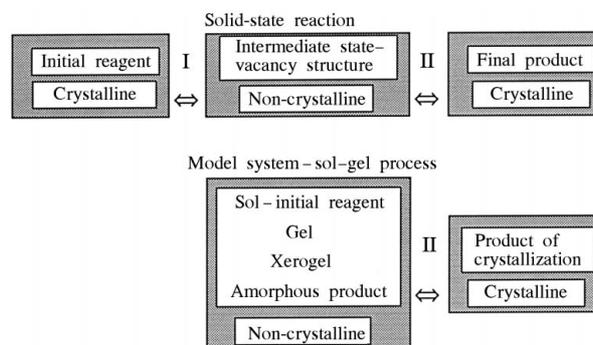

Figure 1
Scheme of the solid-state reaction and sol–gel process: I, formation of the intermediate product; II, formation of the final crystalline product. Stage II occurs both in solid-state reactions and in the sol–gel process.
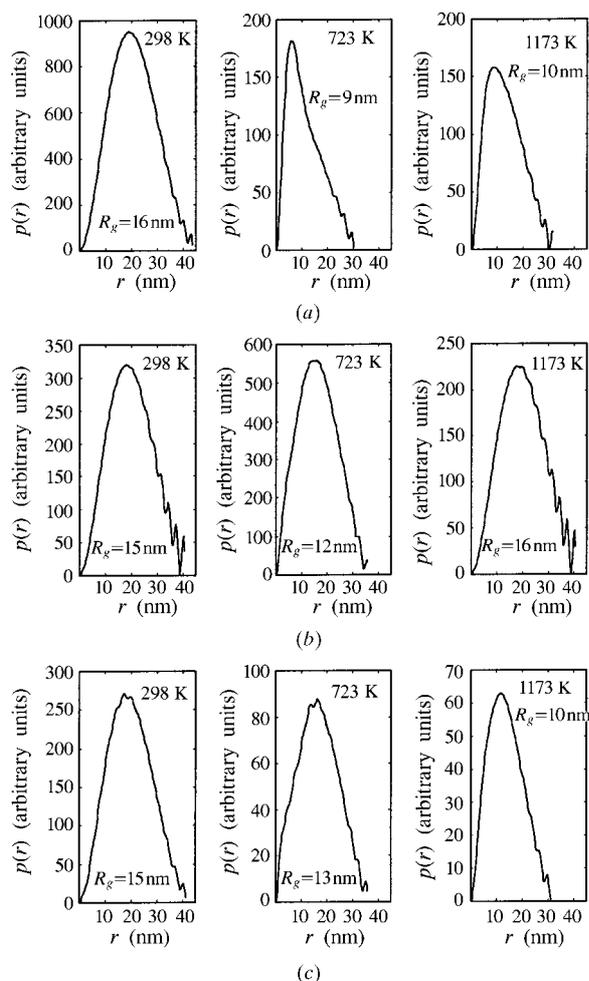
Figure 2
Plots of the distance distribution function $p(r)$ of each of the systems investigated (at different temperatures): (a) xerosol of HAO; (b) xerosol of HZD; (c) xerosol of HZD–HAO.

Figure 3
The SAXS curves for the xerosol of HAO: (a) monolithic sample; (b) fine-ground sample.

HAO (at a temperature of 723 K) allows one to conclude that there are pores with sizes 30–35 nm and, possibly, 10–15 nm.

Comparison of the $p(r)$ curves of the original xerosols and binary xerosols shows the correlation between the size and shape of the pores in the original sols and the size and shape of those in the binary sols. The size and shape of the pores of the binary xerosol of HZD–HAO (at 723 K) and of the original xerosol of HZD (at 723 K) are the same. The size and shape of the pores of the binary xerosol of HZD–HAO (at 1173 K) and of the original xerosol of HAO (at 1173 K) are the same. The size and shape of the pores of the binary xerosols at the different temperatures are defined by the structure and properties of the different original xerosols.

4. Conclusions

During the fine grinding of the original xerosols of HAO, HZD and binary xerosol of HZD–HAO the process of pore formation takes place. The pores are spherical with a size of about 40 nm. The subsequent drying of the xerosols at 723 K causes a decrease of the pore size to 10–30 nm with a change in the pore shape.

The size and shape of the pores of the binary xerosol of HZD–HAO at the different temperatures correlates with the size and shape of the pores of the different original xerosols. At 723 K, the process of pore formation in the binary xerosol of HZD–HAO is defined by the structure and properties of the xerosol of HZD. At 1173 K, the process of pore formation in the binary xerosol of HZD–HAO is defined by the structure and properties of the xerosol of HAO.

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objects is about 30–45 nm. Such scattering objects were not observed in the monolithic samples of the original xerosols (these contained uniform particles of about 1–2 nm, Fig. 3a) (see Gaponov *et al.*, 1995). Consequently, one may conclude that the process of formation of the pores or, possibly, vacancy and/or defect clusters, takes place during the fine grinding. During gelation a large quantity of solvent is removed from the sample. As a result, a large decrease in the sample volume occurs. In this case we observed practically no cracks in the sample, from which it may be concluded that inner microtensions are occurring. Relaxation of such microtensions during fine grinding possibly takes place *via* pore formation and the rearrangement and grouping of the vacancies and defects.

The analysis of the $p(r)$ plots leads to the conclusion that there is a temperature-dependence of the size and shape of the pores. The xerosol samples dried at 293 K have spherical pores with a size of about 40–45 nm. The xerosol samples dried at 723 K have pores with a size of about 30–35 nm. The analysis of the $p(r)$ curve of the xerosol of HAO (at a temperature of 723 K) leads to the conclusion that the pores have extended parallelepiped (or cylinder) shapes with dimensions of $10 \times 10 \times 30$ nm. The an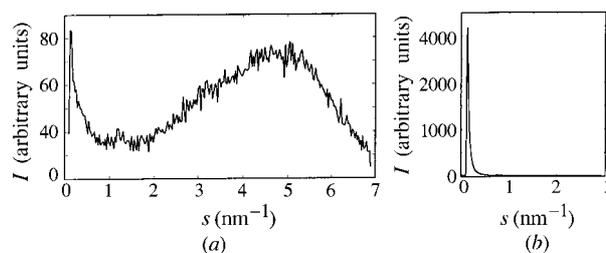alysis of the $p(r)$ curves of the xerosol of HZD and of HZD–