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Structural analysis of amorphous silica prepared by water glass-based precursors and its thermal, spectral characterization

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ABSTRACT

The chemico–physical properties, near infrared and TG-DTA behavior of the non-crystalline silica prepared by water glass with different initial concentrations were systematically investigated. The structural parameters obtained by X-ray diffraction technique showed that the short range order was no more than 5–6 atoms. The variations of calculated co-ordination number and Si–O bond length, which to some extent reflected the structural compactness, explained the variation of the measured oil absorption well.

0. Introduction

Silicon dioxide is widely used in catalysis carrier, polymer, composite material, electronic encapsulation, ceramic, rubber and papermaking, etc, owing to its low density, high purity, high specific surface area, good dispersity, excellent optical, mechanical properties and being able to form hydrogen bonds by its active surface silanol with functional groups in the matrix [1,2]. Especially these days, in areas such as laser technique, electronics, communication [3] and biology [4], silicon dioxide has attracted a lot of interest.

As is known to all, the properties, stability and phase transformation of non-crystalline materials are closely related to the structure. Both X-ray powder diffraction and Extended X-ray Absorption Fine Structure (EXAFS) [5] are effective means to investigate the structure of amorphous materials. They can get similar results. However, the EXAFS method needs synchro-radiation source and complicated computation. It is not used as frequently as X-ray diffraction or neutron diffraction. To the knowledge of the author, some studies on determining the structural parameters of amorphous silica by the method of X-ray diffraction were reported [6,7]. For example, Kanichi Kamiya [8] explained the structure of silica gel by MRO model consisting of the fourfold siloxane ring units. Some researchers [9] simulated the structure of SiO_2 nanoparticles with theoretical calculations like MD (molecular dynamics). However, little attention was paid to the structural studies of silica prepared by water glass-based precursors, especially the relationship between the computational structural characteristics and the experimentally obtained chemico–physical properties.

In this paper, an X-ray structure study based on the RDF and correlation function analysis is applied to silica prepared by water glass-based precursors. Moreover, the calculated results explain well the chemico–physical properties measured experimentally.

1. Experimental section

1.1. The preparation of precipitated silicon dioxide

In the experiment, 17.8% water glass (A.R. Qingdao Haiyang Chemicals Co. Ltd.) was kept at 30–40 °C for 25 min. Then a certain amount of NaCl was added into the solution. While the solution was strongly stirred, 20–30% H_2SO_4 was introduced into the system at the rate of 15–20 drops per min until the pH level reached 11. After that, the system was heated to 80–90 °C. The reaction continued until the pH level reached 8. Standing for 45 min at 90–100 °C the suspension was filtered. The precipitate was washed, dried at 120–150 °C and sifted out. This sample was labeled as a. The other three samples were prepared under the same condition except that the concentrations of the initial water glass were controlled as 20.8%, 23.9% and 26.7%, respectively. They are labeled as b, c and d, respectively.

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1.2. The measurement of chemico–physical properties

Oil absorption is measured according to the reference [10]. Weigh 10–15 g of the test sample and place the weighed test sample on the glass plate. Fill the weighing bottle with DBP (di-n-butyl phthalate), insert a glass tube in it and weigh the bottle. Add the DBP from the bottle drop by drop and after each addition thoroughly mix the DBP and the sample by rubbing with the sharp edged steel spatula. Continue the addition of the DBP until the mixture is just moist enough to cling to one side of the spatula, but does not stick to the glass plate. This is the end point. Weigh the bottle filled with DBP and the glass tube again. Oil absorption can be calculated according to the following equation:

$$\text{Oil absorption} = (B\text{-}C)/A$$

where A is the weight of the test sample; B is the initial weight of the bottle filled with DBP; C is the weight of the bottle filled with DBP after the measurement.

Specific surface area is measured by means of alkaline titration [11]. Weigh accurately 2.5 g of test sample and place the weighed sample in a 400 mL beaker. 250 mL 1 mol/L NaCl solution is introduced into the beaker and mixed evenly with the silica on an electromagnetic stirrer under constant stirring. Use acid or base to regulate the pH level of the suspension to 4. Then, 0.1 mol/L NaOH is titrated into the suspension at the rate of 2–3 drips/s until the pH level reaches 9 and remains unchanged for 5 min after the final addition of the alkali.

Therefore, S=4.816V where S means the specific surface area; V means the volume of the NaOH consumed.

NIR spectrum is recorded on Bruker 22/N equipped with integral sphere by measuring the sample's diffuse reflection. Resolution of the instrument is 4 cm^{-1}.

All the thermodynamic experiments are performed on a shimadzu DT-30 thermal analyzer under the protection of nitrogen gas flow. The heating rate is 10 K/min.

Step-scan powder X-ray diffraction patterns are obtained at room temperature by a Philips diffractometer model X Pert MPD using CuK_α radiation equipped with diffracted-beam Soller slits and a graphite-diffracted beam monochromator. PC-APD 4.0 software is used to separate $K_{\alpha 2}$ from $K_{\alpha 1}$. Sample offered by NIST is used to determine the instrumental broadening line profile $g(x)$.

The scanning region is divided into three sections according to the diffraction intensity. Small divergence slit 0.5° and step size 0.1° are used in low diffractive angle 20–75° where non-crystalline peak appears and relatively large divergence slit 3° and step size 0.6° are applied in smooth attenuation area from 75 to 150°. A constant medium width receiving slit is applied in the measurement. Measuring is kept for 30 s at each step in order to reach 10^4 counts. The scanning regions with different divergence slits overlap 2–3° so as to normalize the diffraction intensity by calculating the coefficient between different divergence slits.

1.3. Theories

The measured intensity $I_M(2\theta)$ must be corrected for air scattering, sample absorption, polarization, background scattering. The contribution of the Compton scattering to the experimental data is removed after carrying out a normalization with respect to the sum of the theoretical coherent and incoherent scattering intensities. After the conversion of 2θ according to the relationship $s=4\pi\sin(\theta)/\lambda$, $I_M(2\theta)$ is reduced to $I(s)$. Structural parameters are then calculated according to the following 3 equations [12].

$$\mathrm{RDF}(r) = 4\pi r^2\rho(r) = 4\pi r^2\rho_a + \frac{2r}{\pi}\int_0^\infty s[I(s)\text{-}1]\sin(sr)\,ds \quad (1)$$

$$G(r) = \frac{2}{\pi}\int_0^\infty s[I(s)\text{-}1]\sin(sr)\,ds \quad (2)$$

$$g(r) = 1 + \frac{G(r)}{4\pi r\rho_a} \quad (3)$$

In these equations, RDF(r) is radial distribution function; $g(r)$ represents pair distribution function; $G(r)$ means reduced radial distribution function; ρ_a is the average atomic density calculated by bulk substance density.

Here we can see that the Fourier transform of the intensity data yields the radial distribution function. The RDF gives the distribution of the interatomic distances in the sample. The first peak represents the nearest neighboring atomic distance; the area of the peak is related to the number of such distances in the sample. The peak width illustrates the variation of this distance due to the distribution of equilibrium distances and thermal motion. The second peak represents the second nearest neighboring atomic distance.

The nearest mean atomic distance, the co-ordination number and the size of orderly domain [12], the most important parameter characteristics of the structure of amorphous materials, are calculated from radial distribution function (RDF), $g(r)$ and $G(r)$.

2. Results and discussion

2.1. Determination of chemico–physical properties and thermal analysis

The oil absorption of amorphous silica increases from 2.13 to 2.30 mL/g with the increase of water glass concentration from 17.8 to 20.8%. But with the further increase of water glass concentration it plumps quickly. Fig. 1 shows the correlation between particle size (on the left), specific surface area (on the right) and the water glass concentration. From Fig. 1 we can see that they vary in opposite ways. Generally speaking, specific surface area is not necessarily opposite to the particle size as it includes both the outer surface area and the inner surface area of complicated tunnels and holes. But here, the value of specific surface area measured by the method of alkali titration really means the area of outer surface. The value of particle size measured by laser scattering reflects the diameter of particle

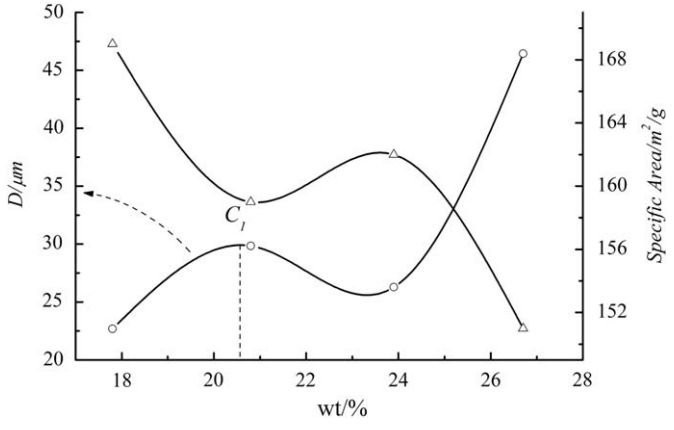

Fig. 1. The relation of concentration (wt%) of water glass vs. specific surface area and particle size.