Surface polymorphism of silica nanoparticles

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Abstract. A comparative study was performed on the surface properties of silica nanoparticles synthesized by various methods using FTIR, UV-Vis DRS and X-ray diffraction. It is shown that different methods of synthesis affect the surface properties of nanoparticles while maintaining the phase composition of the material. It is also shown that the nanoparticles of each material have unexpected properties. In particular, a significant difference was observed in the concentration of Lewis centres for the samples. This variation in properties indicates the importance of accurately characterizing the surface properties of nanoparticles as they determine the interactions of nanoparticles with other materials.

1. Introduction

Nanoparticles are a special class of materials that are increasingly used in the development of new materials. The fundamental properties of bulk materials have been studied, but the uniqueness of their surface properties still needs further research. Although nanoparticles can have identical chemical and phase compositions, their interaction with different media can vary [1] and is determined by the conditions of the synthesis process [2, 3]. The method and conditions of synthesis determine the interactions of atoms and their associations during the formation of nanoparticles. Formation features can appear during nucleation, during growth of a molecular cluster, or upon the connection of nanoparticles [4].

It is known [2, 5] that a change in the silica synthesis method leads, for example, to a change from densely packed (aerosol) nanoparticles structure to a strip-like one (air gel). However, surface properties, including the content of various functional groups and their heterogeneity, are the most important factors determining the effectiveness of their application [6]. The contradictions in the data on the surface properties of silica and the interpretation of their donor-acceptor properties are also associated with different methods of synthesis. This inconsistency can be associated with the presence of other trace elements, such as aluminium or iron, which are usually concentrated on the surface. This can be determined by the distribution and intensity of the bridging and terminal -OH-groups, as well as other surface components.

Thus, to assess the possible interaction between nanoparticles and their environment, we performed a comparative analysis of the surface properties of nanoparticles synthesized by various methods.

2. Materials and Methods

For the studies, we used nanoparticles of silica produced by (1) liquid-phase synthesis (China), (2) the plasma-chemical method (Plasmotherm, Russia), (3) evaporation by an electron beam [7] and (4) high-temperature flame hydrolysis (Aerosil, Germany). The nanoparticles were of a spherical shape.
and had similar size distributions, and an average size of 25 nm. The size was determined by the optical method on a Shimadzu SALD 7500 device according to the standard method. For control and measurement of particle sizes, photographs taken by an electron microscope JEOL-2010 (Japan) were also used. Both measurements showed identical results.

The X-ray analysis of the structure of samples was carried out in [8, 9] and showed the presence of an identical short-range atomic order with a general X-ray amorphousness of nanoparticles.

The samples were compressed into tablets with a thickness (ratio of the tablet weight to its geometric area) of 15 to 49 mg / cm$^2$. The tablets were placed in a vacuum infrared cuvette and evacuated for 1 hour at a vacuum of $10^{-3}$ Pa. Subsequently, the samples, without contact with the atmosphere, were transferred to the measuring chamber, which made it possible to record spectra at temperatures down to 77 K. Then the basic spectra were recorded at room temperature and then at 77-110 K. The recording of the spectra was carried out on a Shimadzu IRTraser-100 spectrometer in the range of 600-6000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. The spectra were accumulated every 100 scans, which ensured a signal-to-noise ratio of at least 7500. CO adsorption was carried out at doses, which provided a pressure in the cell of 0.1, 0.4, 0.9, 1.4 and 10 Torr at 77 K.

The optical properties of the materials were studied by diffuse reflectance electron spectroscopy (UV-Vis DRS) using a Shimadzu UV-2501 PC spectrophotometer with an ISR-240A diffuse reflectance attachment. The samples were placed in a quartz cell with a sample layer thickness of 2 mm. The spectra were recorded relative to the BaSO$_4$ reflection standard in the range of 190-900 nm (11000-54000 cm$^{-1}$), with a step of 2 nm. Reflection coefficients were converted into absorption coefficients using the Kubelka-Munk function $F(R) = (1-R)^2 / 2R$, where $R$ is the diffuse reflection coefficient, depending on the wavenumber, expressed in cm$^{-1}$. The obtained data were presented in the coordinates of Kubelka-Munk function $F(R)$ vs the wave number.

### 3. Results

#### 3.1 IR spectroscopy

Figure 1 shows the spectra of the CO and OH groups of Sample 1 calcined at 550 °C in vacuum. The spectrum of OH groups exhibits a band at 3745 cm$^{-1}$ related to valent vibrations of SiOH groups. It also shows the absence of a weak broad band at about 3650 cm$^{-1}$ produced by hydrogen-bonded OH groups. Upon CO adsorption, the 3745 cm$^{-1}$ band shifts to the low frequency region down to 3666 cm$^{-1}$. The shift to low frequencies by 79 cm$^{-1}$ is close to that observed for conventional aerosils and silica gels, but it means that the acidity of SiOH groups is lower than that of Sample 2.

![Figure 1. The IR spectra of CO adsorbed on Sample 1. 1- calcined sample (the thickness 16.3 mg / cm$^2$), 2-6 – the spectra taken after CO adsorption at pressures of 0.1; 0.4; 0.9; 1.4 and 10 torr.](image1)

![Figure 2. The IR spectra of CO adsorbed on Sample 1. 1- calcined sample (the thickness 22.8 mg / cm$^2$), 2-6 – the spectra taken after CO adsorption at pressures of 0.1; 0.4; 0.9; 1.4 and 10 torr.](image2)
The same complexes are characterized by the CO band at 2156 cm\(^{-1}\). The 2138 cm\(^{-1}\) band has been produced by physically adsorbed CO. For Sample 1, upon adsorption of the first CO doses, bands of CO valent vibrations at 2170 cm\(^{-1}\) also appear. Bands in this range are specific to CO complexes with strong Bronsted acid sites. Curve 2 (upper part of the figure) clearly shows that CO adsorption shows two bands of hydrogen-bonded OH groups - 3565 and 3645 cm\(^{-1}\), which have the shift of 180 and 100 cm\(^{-1}\), respectively. Along with the appearance of the CO band at 2170 cm\(^{-1}\), this can be interpreted as the introduction of small alumina clusters into the silica surface. The number of such clusters (based on the intensity of the 2170 cm\(^{-1}\) band) can be estimated as 45 µmol / g (0.1 wt\%).

Figure 2 shows the spectra of CO and OH groups of Sample 2 calcined in vacuum at 550 °C. The spectrum of OH groups has a band at 3744 cm\(^{-1}\), valent vibrations of SiOH groups and a weak broad band at about 3650 cm\(^{-1}\) of hydrogen-bonded OH groups. Upon CO adsorption, the 3744 band shifts to the low-frequency region by 87 cm\(^{-1}\) to 3657 cm\(^{-1}\). The same complexes are characterized by a CO band at 2156 cm\(^{-1}\), which is also typical for aerosils and silica gels. The 2138 cm\(^{-1}\) band has been related to the physically adsorbed CO.

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Figure 3 shows a wide band at 927 cm\(^{-1}\) at room temperature, which belongs to strained Si-O-Si bridge bonds. As the temperature decreased, this band split up into two components 902 and 956 cm\(^{-1}\). During the decrease in temperature from 110 to 77 K (not measured), the splitting of the band increased.

![Figure 3](image1)

**Figure 3.** The IR spectra of Sample 1 (thickness 16.3 mg / cm\(^{2}\)) recorded in the region of absorption bands of strained bridges at different temperatures.

Subsequent heating leads to the restoration of the broad band at 927 cm\(^{-1}\). Apparently, the presence of alumina clusters leads to the existence of other types of strained bridges. At room temperature, it can be Si-O-Si-O-Al formed due to the kinematic bond of fragments, or Si-O-Al with a common silicon atom; they make a wide band. At low temperatures, due to the general decrease in vibrational energy, the kinematic connection is weakened. Therefore, a high-frequency component at 956 cm\(^{-1}\) related to the Si-O-Si fragment and a low-frequency component of the weaker Si-O-Al bridge bonds are created. In figure 4, in the region of 800–1000 cm\(^{-1}\), we observe a broad band at 930 cm\(^{-1}\), which is caused by strained Si-O-Si bridge bonds. One should point out that an increase in the band’s intensity with a decrease in temperature down to the liquid nitrogen one occurred. These effects have not been previously described.

![Figure 4](image2)

**Figure 4.** The IR spectra of Sample 2 (thickness 22.8 mg / cm\(^{2}\)) recorded in the region of absorption bands of strained bridges at different temperatures.

Samples 3 and 4 show a different structure of bending vibrations. The bands in the region of 1090-1300 cm\(^{-1}\) belong to the antisymmetric valent vibrations of SiO\(_4\) tetrahedra, and the band at 450 cm\(^{-1}\) belong to the symmetric vibration of the same fragment. The 810 cm\(^{-1}\) band is related to the bending vibrations of Si-O-Si. In addition, for Samples 3 and 4, bands at 886 and 946 cm\(^{-1}\) were found. They can correspond to bending vibrations of Si-OH or vibrations of strained bridge bonds of Si-O-Sifragments, the structure of which can be represented by the diagram [Si-O-Si].

In figure 5 the spectra show bands at 1626 and about 3400 cm\(^{-1}\), ascribed to adsorbed water, band 1868 caused by vibrational overtones of SiO\(_4\) and Si-O-Si. Bands in the 2147-2261 cm\(^{-1}\) region, close
in position to the valent vibrations of silicon hydrides, were found only for Samples 3 and 4. A high water content is distinguished only for Sample 3. Sample 4 is characterized by the maximum number of SiOH groups, the band at 3746 cm\(^{-1}\). Moreover, in contrast to Sample 3, the content of molecular water in this sample is insignificant; it turned out to be hydrophobic, despite the high concentration of silanol groups.

The IR spectra of adsorbed CO on Samples 3 and 4 are shown in figures 6 to 9. The figures also show the concentrations of different types of OH groups and small amounts of concentrations of Lewis acid sites. It can be seen from the figures that both samples have a similar concentration of OH groups. Bands were found at 3750, 3690, and 3580 cm\(^{-1}\). The first band belongs to isolated terminal SiOH groups, and the second and third bands to weak and strong hydrogen-bonded groups. During the adsorption of CO, interaction takes place only with the first band groups, which shifts to the low frequency region by 83 cm\(^{-1}\). This is slightly less than the shift for the SiOH bands of the aerosil groups. From the CO spectra recorded at a pressure of 10 Torr, it is possible to conclude that the surfaces of Samples 3 and 4 are almost equivalent. The samples are distinguished only at lower pressures (figures 6 and 8). For Sample 4, there is a small content of Lewis centres characterized by a band at 2200 cm\(^{-1}\) (centres of medium strength). This may indicate a metal impurity, possibly aluminium; the total content of such impurities is estimated at 20-30 ppm. An analysis of the UV-Vis DRS spectra (figure 10) shows that the spectra of all samples are divided into two parts: intense absorption in the visible region of the spectrum up to 25,000 cm\(^{-1}\) and relatively strong absorption in the region above 30,000 cm\(^{-1}\).

**Figure 5.** The IR spectra of diffuse reflectance of Samples 3 and 4 in the region above 1500 cm\(^{-1}\).

**Figure 6.** The IR spectra of adsorbed CO on Sample 3 at different portions of adsorption - 1 CO - 0.1 Torr, 4 CO - 0.4 Torr, 9 CO - 0.9 Torr.

**Figure 7.** The IR spectra of OH groups of Sample 3 before (ini) and difference of spectra after adsorption at 10 Torr CO.

### 3.2 UV-Vis DR spectroscopy

Absorption in the visible region of the UV-Vis DRS spectrum is usually caused by the d-d-transitions of various impure d elements of 3-5 periods [10]. The intensity of absorption may depend on several factors. First, it depends on the amount of impure cations of d elements in any matrix, including the matrix containing oxygen. Second, various distortions of the octahedron or tetrahedron around the
central cation of the d element increase the absorption intensity, since changes in the cation-anion distance in the first coordination sphere are observed when the influence of the ligands of the second and subsequent spheres on the central cation is considered. Third, the absorption intensity is inversely related to the size of the absorbing particles, i.e. the smaller the particle size, the more the light is scattered from them and appears in the absorption spectrum [11].

Figure 8. The IR spectra of adsorbed CO on Sample 4 at different portions of adsorption - 1 CO - 0.1 Torr, 4 CO - 0.4 Torr, 9 CO - 0.9 Torr.

Based on these findings, we can conclude that all the samples contain at least two particle bands: small (about 5 nm) and large (up to 25 nm). In this case, the samples have the next particle size: 1 > 3 > 4 > 2, consequently, an increase in intensity is observed: 1 < 3 < 4 < 2. Thus, more absorption due to scattering is observed for Sample 2, which indicates that its particles are smaller than all the other samples. The smallest absorption occurs for Sample 1, which has the largest particles among the samples studied.

Usually, absorption is observed in the UV region of the UV-Vis DRS spectra, which is caused by the manifestation of ligand - metal charge-transfer bands (L – M PCR), which have a high intensity [10]. Also in the UV region of the UV-Vis DRS spectrum for massive, for example, oxygen-containing or other systems, as well as well-conducting systems, the fundamental absorption edge (FAE) is manifested, which corresponds to the bandgap (Eg) of semiconductors and dielectrics [12]. It is also known [13] that for many years the size of the oxide particles has been characterized by the FAE value. Moreover, it is known that the larger particles make the large red shift and decrease the Eg value [11, 14, 15].

Based on the analysis of absorption in the UV region of the UV-Vis DRS spectra, it can be concluded that the samples in the UV region are divided into two groups: Sample 1 and three other samples (Curves 2-4). The FAE value for Sample 1 is 4.4 eV, and for the other three, it is very close to 3.9 eV. A higher FAE value indicates a small size of large particles in Sample 1 compared to other samples. However, for the other three samples having close FAE values, there is a variation in the absorption intensity, which may indicate a variation in the texture of the particles themselves and the presence of pores in these particles (free volume and looseness of these particles). Moreover, for Sample 2, all these characteristics should be higher, i.e. its particles should be fluffier and should repel each other more strongly; therefore, the free volume between the particles becomes larger, which leads to an increase in the absorption intensity in the UV region of the UV-Vis DRS spectrum, owing to an increase in the distance between individual atoms.

Figure 9. The IR spectra of OH groups of Sample 4 before (ini) and difference of spectra after adsorption at 10 Torr CO.
Conclusion

Thus, it has been shown that different conditions for the synthesis of silica nanoparticles form a surface cover with different types and concentrations of OH groups, Lewis acid sites, strained siloxane bridge bands and other characteristic elements. Specific differences in the UV-Vis DRS spectra due to the inclusion of Fe$^{2+}$ Oh cations were also noted. The possibility of varying the effect of nanoparticles on the material containing them, depending on the surface properties of the particles, has been demonstrated.

It is noted that the size distribution can have a different shape (for example, two peaks) under different synthesis conditions, which cannot be determined by the nitrogen absorption method.

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Figure 10. UV-Vis DRS spectra of the silica samples.