Study of structural short order and surface changes of SiO₂ compounds

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Abstract. In this work dependence between structure, surface and reactivity of SiO₂ is investigated. Different samples are prepared with and without the presence of calcium cations and are characterized by different techniques. The FTIR frequency shifting of the bridging oxygen stretching vibration Si–O–Si and the binding energy shifting of the Si2p and O1s photoelectron peaks have been observed and discussed. Results show the effect of presence of calcium on the structural change, surface and reactivity of SiO₂ aggregate. After reaction, a structural and SiO₂ surface changes occur, as the FTIR spectra illustrate depending on the presence of the calcium cations.

1 Introduction

The compounds based on SiO₂, are of interest in several fields: as strengthening additives in the potter's clay materials, insulator in electronic compounds and in glass industry, concrete, Polymers... [1]. Reactivity of SiO₂ depends on the chemical process that occurs between amorphous or poorly crystallized SiO₂ and the matrix, in turn depends on the surface state of SiO₂ particles [2-4]. SiO₂ surface and short range order is more important in bioactive silica based materials which are characterized by an open structure which enables the accommodation of alkali and alkali-earth cations. The network modifiers such as Ca, K, Na, provoke the disruption of the continuity of starting network due to the breaking of some of the Si–O–Si bonds leading to the formation of non-bridging oxygen groups (Si–O–NBO). This is the key step of the bioactive process, because the concentration of Si–O–NBO groups controls the dissolution rate of the silica through the formation of silanol groups at the glass surface [5].

Detailed knowledge of the atomic structure of Si–O–Si species and the silanols on surface of SiO₂ compounds and the effect of calcium cations on their atomic structure are essential to understand the nature of fluids–silicates interactions and the dehydration processes in the composite materials such as nanocomposites and concrete [6]. The silanol groups (SiOH) are the main surface

reactive sites and their properties (nature, concentration, distribution, accessibility, etc.) will determine the chemical activity of the silica [7]. But there is a strong relationship between reactivity and the structural order of silica compounds [8-9].

The aim of this work is to study the dependence between structure, surface state and reactivity of silica for different heterogeneous SiO₂ compounds with and without the presence of calcium during the reaction.

2 Materials and Experimental

Different type of SiO₂ compounds have been investigated. The materials used in this work are siliceous natural aggregates (called SiO₂-1, SiO₂-2 and SiO₂-3). XRD results show that all compounds are crystalline structure similar to quartz. The results are compared with amorphous α -SiO₂ compound from Alfa Aesar reference.

The experimental protocol was carried out as follows [10]:

The mix of crushed aggregate and calcium oxide Ca(OH)₂ is introduced in the autoclave in an oven at 80°C. After 30 min of preheating, 10 ml KOH solution of 0.79 mol/l are added. The mix is then put in an oven to develop reaction under controlled temperature and reaction time. After reaction time, we put the autoclave in frozen water during 5 min to stop the reaction. The

soluble reaction products are removed by selective acid treatment and filtration. The acid attack is done using 250 ml cold 0.5M HCl solution. The samples are dried by acetone and diethyl ether treatment after the filtration, then kept inside dried atmosphere.

The Transmission Electron Microscope investigations were performed with a FEI Tecnai G2-20 instrument with an accelerating voltage of 200 kV. It is equipped with a filament of lanthanum hexaboride LaB6, a double-tilt holder, an EDS analysis and Gatan digital camera CCD ORIUS.

The XPS measurements were performed using a spectrometer with a monochromatized AlK α X-ray source ($h\nu = 1486.6$ eV). The data were collected on the dried and powdered samples which are pressed onto a substrate and is fixed on a sample holder. The samples are introduced successively in a chamber at a constant pressure ($P = 10^{-3}$ torr) and in an analytical chamber ($P = 10^{-9}$ torr). The ejected electrons photoelectrons whose binding energies are inferior to the X-ray energy are collected according to their kinetic energies into a hemispherical 150 mm mean radius electron analyzer.

FTIR spectra were acquired with a Bruker VERTEX 70 spectrometer in reflection mode. They were recorded by collecting 100 scans at 4cm^{-1} resolution in the range of $400\text{--}5000\text{ cm}^{-1}$.

3 Results and discussion

Figure 1 shows an image of the sample SiO₂-1. Grains of different sizes ranging from ten nanometers to a few micrometers, with angular sides characterizing angles of quartz can be seen. Moreover, other areas of a rather disordered or amorphous appearance are observed. The samples SiO₂-2 and SiO₂-3 are the same appearance except SiO₂-3 which presents more heterogeneous aspect.

Fig. 1. Transmission Electron Microscope image of SiO₂-1 sample.

Analysis of different zones of the samples shows the presence of silicon and oxygen elements as shown in Figure 2. Carbon and copper presence is attributed to the sample holder.

Fig.2. Energy dispersive spectrum of SiO₂-1

In order to follow the reactivity of each aggregate, we subjected them to reaction according to the procedure described above. Figure 3 shows the results of the mass recovered after the reaction in the absence of calcium. It is observed that the mass recovered after reaction of the amorphous silica is the lowest, which confirms the expected results since it has the most disordered structure and therefore is the most reactive. In fact, the samples can then be classified in order of increasing reactivity, ranging from SiO₂-2, SiO₂-1, SiO₂-3 to a-SiO₂. These results are in good agreement with those obtained by X-ray diffraction [8]. In the presence of calcium, the recovered masses are most important, which shows the reactivity of these compounds decreases in the presence of calcium in agreement with previous study [10].

Fig. 3. Evolution of the mass remaining after reaction without calcium.

In order to follow the evolution of the structure as well as the state of the surface, IR spectra of the different samples are recorded. The SiO₂-1 as an intermediate case is showed as example.

Figure4 shows the FTIR spectra for SiO₂-1 after reaction with and without the presence of calcium compared to SiO₂-1 before reaction as reference. These FTIR spectra present the surface species as indicated in the figure.

Fig.4. FTIR spectra of SiO₂-1 after reaction with the presence and the absence of calcium compared to SiO₂-1 reference before reaction.

The infrared spectra of all samples have a broad band between 1000 cm⁻¹ and 1300 cm⁻¹. This band consists of a strong peak. The mean peak is associated with the stretching vibration of Si-O-Si [11-12]. In addition, different bending vibrations attributed to Si-O-Si [13-15] are indicated in the figure. The bands located at 555 cm⁻¹ and 950 cm⁻¹ are associated with Si-O bending vibrations of no bridging Si-OH bonds and stretching vibration respectively Si [13-15].

In addition, we can notice that the mean band of SiO₂-1 spectra after reaction with and without the presence of calcium is shifted compared to SiO₂-1 before reaction as reference. This pronounced shift may be connected to the structural order change of SiO₂ [13]. Other structural change of Si-O-Si is provided by the band at 800cm⁻¹(Figure5).

Fig.5. FTIR spectra of SiO₂-1 after reaction with the presence and the absence of calcium compared to SiO₂-1 reference before reaction.

Furthermore, it can be seen that SiO₂-1 after reaction in the presence of calcium has a more intense peak associated to Si-OH groups and located at 950 cm⁻¹ compared to SiO₂-1 before reaction as reference and after reaction without calcium. The peak height from silanols groups increases in SiO₂-1 with presence of calcium in comparison of SiO₂-1 reference and SiO₂-1 without the presence of calcium. This result shows that the surface state of SiO₂-1 with the presence of calcium is different compared to SiO₂-1 reference and SiO₂-1 without the presence of calcium.

The XPS spectra were carried out to characterize the surface compositions of samples. Figure 6 presents O1s and Si2pXPS spectra of SiO₂-1 after reaction with the presence and the absence of calcium compared to SiO₂-1 reference before reaction. Major elements detected are silicon and oxygen for all the samples.

Samples exhibit a clear binding energy difference between the Si2p and O1s lines. In addition, the relative intensities of the Si2p peak and of the O1s peak vary from one sample to another; i.e., the samples do not display the same Si/O atomic ratio. These features evidence that the chemical environment of silicon and oxygen is significantly affected by the presence of calcium more than the SiO₂-1 sample with absence of calcium.

It is important to notice that the results represent typically the surface difference between the different samples confirming the changes and the results obtained with FTIR as explained before.

Fig.6. XPS spectra of SiO₂-1 after reaction with the presence and the absence of calcium compared to SiO₂-1 reference before reaction, (a) O1s, (b) Si2p

The O1s photoelectron spectra for the samples are shown in Fig. 6a. The O1s signal is expressed by a symmetric function and it shifts towards lower energies with the presence of calcium. A similar behavior has been observed for the Si2p photoelectron peak, but shifts towards higher energies as shown in Fig. 6b typically with the presence of calcium.

Crystallized SiO₂ samples are formed by an ordered network with perfect SiO₄ tetrahedral connected to the adjacent tetrahedral by bridging oxygen atoms to form a three-dimensional connected network. Consequently, the contribution of Si-OH infrared band is negligible as shown in Figure 4. The presence of calcium with SiO₂ during the reaction changes the degree of connectivity in the silicon-oxygen disordered network. In fact, the short range structural modifications occur as can be successfully detected by FTIR and XPS spectra.

In fact, the pronounced shift of the position of the peak and the increase of silanols surface species with the presence of calcium show a simultaneous modification of the structure and the surface of the starting aggregate after reaction. These results are interesting in a future study concerning the improvement of the interface properties of some composites materials with the presence of different silica compounds.

4 Conclusion

Dependence between structure, surface and reactivity of SiO₂ is investigated. Different SiO₂ samples with and without the presence of calcium cations are prepared and characterized by different techniques. Based on FTIR and XPS spectroscopy, frequency shifting of the bridging oxygen stretching vibration Si-O-Si and the binding energy shifting of the Si2p and O1s photoelectron peaks have been observed and discussed. Results show the effect of presence of calcium on the structural change, surface and reactivity of SiO₂ aggregate. After reaction, a structural order and SiO₂ surface changes occur, as the FTIR spectra illustrate depending on the presence of the calcium cations. TGA/TD and NMR experiments are planned in order to obtain more details about the silanols behavior.

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