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Ageing process of some pyrogenic silica samples exposed to controlled relative humidities
Part I: Kinetic of water sorption and evolution of the surface silanol density

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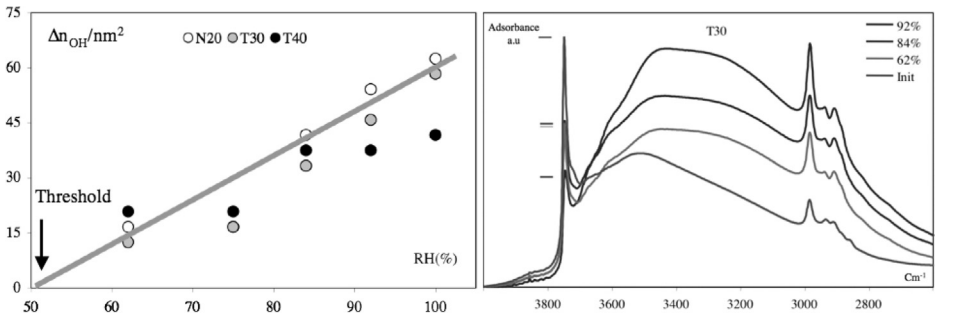
HIGHLIGHTS

- Pyrogenic silicas are, at room temperature, sensitive to RH humidity.
- The surface roughness induces clearly a decrease of the surface reactivity.
- Modification of surface properties of the silicas in a highly humid environment.
- The new silanol groups appears in the vicinity of the pre-existing silanol groups.

GRAPHICAL ABSTRACT



The ageing process of 3 pyrogenic silica samples was studied under various relative humidities (RH). On the left figure, one sees that the ageing process induced an significant inceased of the silanol surface density, whereas Infrared spectroscopy evidences a relative quick increasing of the hydrogen bound silanol groups due to an increase of the local silanol density. These evolutions are explained taking into account a patch like distribution of the silanol groups on the pyrogenic silica surface and the surface morphology: flat or rough.

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In memory to professor J.B. Donnet deceased on November 30th 2014

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ABSTRACT

The kinetic of the ageing process of 3 pyrogenic silica samples, exhibiting increasing surface areas (Wacker N20, T30 and T40), was followed through gravimetric measurements, during about 1000 h at 22.5 °C, under different relative humidities (RH) from 62% up to100%. Silanol chemical titration, and IR spectroscopy were also called on to evidence the change of the surface chemistry induced by the ageing process.

This study evidenced that pyrogenic silicas are, at room temperature, sensitive to RH humidity over a threshold of about 50% of RH. Exposed to high RH, a strong change of the surface functionality occurs bound to an important chemisorption of water. At RH of 100%, the silanol density could increase up to quite 40%. It is more important for low specific area samples than for the higher ones. The limit value of 3.5–3.8 SiOH/nm^2 suggests that no polysilicic layer are formed. Moreover IR spectroscopy indicates that

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Gravimetry
IR spectroscopy

the new silanol groups appear in the vicinity of the pre-existing silanol groups at the border between hydrophilic and hydrophobic domains. It is hence evidenced that the patch like distribution of the silanol groups and the surface morphology, flat or rough play a main role on the ageing process.

1. Introduction

Fumed or pyrogenic silicas were discovered in order to provide an alternative of carbon blacks such as reinforcing fillers for elastomers. Indeed, they have proven to be ideal fillers improving the mechanical properties of silicone rubbers [1]. But they have found other applications as gelification of liquids, conferring them thyxotropic properties for paints and resins but also as flowing agent for powders such as " toner ". Due to their nanoscale size, pyrogenic silicas were recently used for elaboration of the new high performances Vacuum Insulation Panels (VIPs) [2–4], because these finely divided solids exhibit a high porous volume (90%) and pore diameters below 0.1 μm.

These silicas differ mainly from the precipitated silicas by their smaller primary particle size (7–50 nm) and their lower silanol surface density (~2.5 SiOH/nm^2) [1,4]. These superficial silanol groups associated with siloxane bridges govern the reactivity of these materials. It has been shown that the isolated silanol groups are at the origin of the hydrophilic character of silica and that their concentration could change as a function of the temperature and the humidity [1,5–7]. The physical conditions of synthesis of these silicas at high temperature followed by a rapid quenching lead to partially hydrated surfaces, presenting numerous unstable, stressed, siloxane bridges, susceptible to be hydrolysed in the presence of water, leading thus to the formation of new silanol functions at the silica surface. Hence, their properties could be seriously affected when exposed to high atmospheric moisture.

Only few studies were led on the ageing of silica in presence of water. They concern mainly silica gels, which are highly hydroxylated silica and are therefore relatively instable due to the silanol condensation reaction that could take place, at first, during synthesis [8], but also during the drying step and storage [9]. To our knowledge no studies were published on the ageing of precipitated or pyrogenic silicas in presence of moisture, if we except the recent work of Morel [10] who have led a study of the influence of the relative humidity (RH) but also of the specific surface area and the synthesis process, on the ageing process of 2 pyrogenic silicas HDK T30 (Wacker) and A200 (Evonik), and one precipitated Sipernat 500 (Evonik). They have monitored the evolution of the specific surface area and surface hydroxylation with ageing time, but only the results concerning the T30 sample were published in the literature [11].

More recently Donnet et al. [12] have led a comparative study of the ageing of two synthetic pyrogenic silicas, in presence of a water containing atmosphere, two pyrogenic silicas, having respectively a specific surface area of around 200 m^2/g (N20) and 300 m^2/g (T30) were aged under a relative humidity (RH) of 94% at 25 °C. The evolution of their surface properties was followed by gravimetry and immersion microcalorimetry. The ageing phenomenon, under a RH of 94%, induces an important water intake of 25% for the N20 sample and 38% for the T30 one, but the water sorption kinetic is quite identical. The chemisorbed water amount due to the ageing process was also assessed. On the contrary, the two silicas behave very differently when measuring the heats of immersion of the dried or water precovered aged samples in water. This difference was related to their surface morphology, N20 being flat at a molecular level whereas T30 exhibits a rough surface.

Table 1
Values of the RH used for the aging experiments at 22.5 °C.

solutions	A	B	HR (%)
NH_4NO_3	3.54	853	62
NaCl	69.20	25	75
KCl	49.38	159	84
KNO_3	43.22	225	92
Pure water	–	–	100

Wexter's equation: RH(%) = A.Exp(B/T) where T is the absolute temperature (K).

In view of these previous studies, it was interesting to examine the behaviors of silica samples toward RH, having high specific surface area (200, 300 and 400 m^2/g) and increasing surface roughness in order to evidence the influence of these parameters. Several investigative techniques, gravimetry, IR spectroscopy and chemical titration were used to monitor the effect of ageing on the surface properties of these silica samples.

2. Experimental part

2.1. Preparation of the silica pellets and ageing device

The 3 studied samples are N20, T30 and T40 pyrogenic silicas from Wacker Chemie (Burghausen, Germany). They were received directly from the factory in thigh plastic bottle which were carefully kept closed, between each pickup, in dry and tempered place. From industrial experience, it is well known that their characteristics evolve during the first week following the reactor output and remain stable thereafter in current European atmospheric conditions (20 °C and 50% RH).

Because pyrogenic silica are very fluffy solids, the powder was poured into a cast and was now "hand pressed". Pellets having a 20 mm diameter and a thickness of about 3 mm were obtained. Their apparent density was close to 240 g/l against 40 g/l for the initial uncompressed powder. Such silica pellets look like white big drug pellets as it is shown schematically in Fig. 1-right, but they remain mechanically brittle. Compression of silica facilitates the manipulation of the samples and prevents the loss of material due to the fluffy character of the raw silicas.

Then the samples were aged in a thermostated box at 22.5 °C ± 0.2 °C, described on Fig. 1. The saturated salt solution and around 5 g of the silica pellets were placed into two different vessels of 80 mm in diameter and then introduced in a convenient plastic box fitted with a tight cover. So it was possible to led simultaneous experiments with different samples and at different RH values.

For controlling the relative humidity, five saturated salt solutions and pure water were used giving the following controlled RH, calculated using the Wexter's equation, except for pure water. These data are reported in Table 1.

In order to follow the ageing process, the vessel containing the silica pellet was regularly extracted from the tight box, covered with a glass plate and quickly weighted. Before starting the ageing experiment, the silica samples were dried in presence of phosphorus pentoxide, until a constant weight was reached. Then, the convenient saturated solution was introduced in the box and the silica pellets were regularly weighted, at least one time per week,