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Aging process of some pyrogenic silica samples exposed to controlled relative humidities
Part II: Evolution of their surface properties studied using inverse gas chromatography

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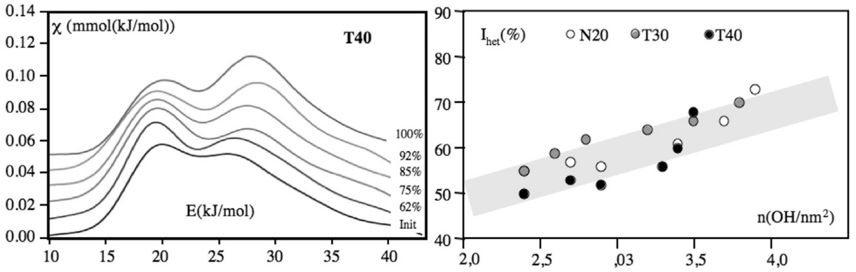
HIGHLIGHTS

- $\gamma_S{}^D$ and nanomorphological index I_M parameters are independent from the RH.
- By IGC-ID: the aging process has a negligible influence on the surface morphology.
- By IGC-FC: the stability of the specific surface area under the aging process.
- The relative intensity of the latter component increases with the silanol density.

GRAPHICAL ABSTRACT



The influence of the aging process under controlled relative humidity of 3 silicas samples was examined. Inverse gas chromatography at infinite dilution using linear alkanes and cyclooctane probes highlights that the aging has no influence the surface morphology. On another hand, IGC at finite concentration, using isopropanol probe, permits to assess the silica surface heterogeneity. The bimodality of the distribution functions testifies of the biphasic character of their surfaces (Left Figure). The heterogeneous character was quantified from the relative intensities (I_{het}) of both components. The rigth Figure shows that surface hydroxylation induces an strong increase of the surface heterogeneity.

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

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ABSTRACT

In the present study, we have examined the influence of the aging process under controlled relative humidity on the surface properties of 3 silicas samples of increasing specific surface area. Both comparison of the specific surface areas, determined using either nitrogen (BET) or cetyltrimethylamonium bromide (CTAB), and the surface nanoroughness indexes, determined by size exclusion inverse gas chromatography, indicates that the ageing process has no significant influence on the surface morphology at the molecular level. On the contrary, IGC at finite concentration using isopropanol as probe evidences clearly an increase of the surface heterogeneity induced by the formation of new silanol groups into the preexisting hydrophilic domains by opening of siloxane bridges by water.

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1. Introduction

Both Fumed and pyrogenic silicas have found many applications in the field of elastomer [1] reinforcement, for paints and resins, as flowing agent for toners, but also for high performances Vacuum Insulation Panels [2–4].

The stability of their surface properties is the most important for these applications. Recently, it was evidenced their surface could be seriously affected when they are exposed to high relative humidity at room temperature. A first study was led by Morel et al. [5,6] and by Balard et al. [7]. Recently a more exhaustive work was led [8], bearing on the kinetic of water sorption on 3 pyrogenic silica samples exhibiting, increasing specific surface areas (Wacker N20, T30 and T40). The aging process, under different relative humidities (RH) varying from 62% up to 100%, was monitored by gravimetric measurements, silanol chemical titration and IR spectroscopy.

This study has evidenced that pyrogenic silicas are sensitive to RH at room temperature over a threshold of about 50% of RH and that the silanol density could increase up to quite 40%, when RH is equal to 100%. The maximal silanol density values around 3,8 SiOH/nm2 is reached at RH equal to 100%. It indicates that no polysilicic layer are formed. The water chemisorption phenomenon is more important for low specific areas than for the higher ones.

On another hand, the observation done by IR spectroscopies indicates that the new silanol groups appear in the vicinity of the pre-existing silanol groups.

It was proposed that these observations could be explained referencing to the model of formation of the primary particles in the flame [9], leading to a strong surface heterogeneity and particularly to a patch like distribution of the silanol groups on the surface.

The aim of the present study is to evidence using mainly inverse gas chromatography at infinite dilution (IGC-ID) et finite concentration (IGC-FC), how the aging phenomena influences the surface properties of pyrogenic silicas.

2. Experimental part

2.1. Material

The main characteristics of the studied silicas -N20, T30 and T40 from Wacker Chemie (Burgausen, Germany)- previously aged [8] during around 1000 h under controlled HR, at room temperature are recalled in the Table 1.

It appears clearly that their silanol densities increase notably with the RH values.

Table 1
Characteristics of studied samples: specific surface area (S_{N2}) of initial samples and silanol surface densities (n (OH/nm^2)) of initial and aged silica samples.

	RH%	0	62	75	84	92	100
	S_{N2} (m^2/g)	n (OH/nm^2)					
N20	195	2.4	2.7	2.9	3.4	3.7	3.9
T30	288	2.4	2.6	2.8	3.2	3.5	3.8
T40	380	2.4	2.7	2.9	3.3	3.4	3.5

2.2. IGC experiments

2.2.1. Preparation of the silica columns

In order to fill the columns having a good chromatographic efficiency, aged silica particles of 400 μm in mean diameter were placed into a round bottom sieve, of 100 μm meshes, in which 3 glass balls of 2 cm in diameter were placed as grinding bodies. A vibrator was used for performing the grinding process as described previously [8]. Glass columns, 4 mm of internal diameter, and 75 mm long were retained so that we can easily control the filling of the column. The powder was slowly poured into the column, which was slightly vibrated. The column was then connected to the chromatograph using Teflon "Swagelock" leak-tight gas seal rings. So efficient columns containing about 70 mg of silica and having very reasonable pressure drop, lower than 0.3 bar, under a carrier gas flow rate (helium) around 20 cm^3/min were prepared. They were conditioned during one night at 120 °C under a helium flow rate of about 10 ml/min.

A chromatograph fitted with two FID detectors was used. The acquisition of the signal was done using a IOTECH A/D converting device connected through USB cable to a PC computer. Display and record of the chromatographic signal were realised using a software developed under DASYLab® soft.

Linear alkanes and cyclooctane were used as probes for IGC-ID experiments, whereas isopropanol was selected for IGC-FC analysis. They are solvents having a degree of purity higher than 99%.

2.3. IGC-ID theoretical aspects

Two IGC-ID parameters were acquired. The dispersive component of the surface energy ($\gamma_S{}^D$) and the indexes of nanomorphology (I_M). The dispersive component was determined according the Doris and Gray approach [10] by injecting a set of linear alkanes in the column filled with silica samples of interest. The dispersive component of the surface energy ($\gamma_S{}^D$), which is directly related to the surface polarisability, can be readily calculated according to the Eq. (1).

$$\gamma_s^d = \frac{(\delta\Delta G_a^{CH_2})}{4Na_{CH_2}^2\gamma_{CH_2}} \tag{1}$$

where: $\delta\Delta G_a{}^{CH_2}$ is the increment of free energy per methylene groups, N is Avogadro's number, a_{CH2} is the area covered by one methylene group (0.06 nm^2), and γ_{CH2} is the surface energy of pure methylene group surface, i.e., polyethylene, $\gamma_{CH_2} = 35.6 + 0.058\,(293 - T)$, in mJ/m^2.

The indexes of nano-morphology were obtained from the retention times of branched or cyclic alkanes, comparing with those of linear alkane probes.

When stereochemistry hinders branched or cyclic isomers from entering the structures in which linear alkanes could absorb, much lower retention times are measured for non-linear isomers. It corresponds to a decrement of adsorption free energy. The indexes of surface nano-morphology (I_M) [11] were computed according to the Eq. (2):

$$I_M(X_t) = 1 - \exp\left(\frac{\delta\Delta G_a^M}{RT}\right) \tag{2}$$

where: $\delta\Delta G_a{}^M$ is the decrement of free energy of he cyclic probe, $X(t)$ is the topological index of the probe [12].

When $I_M(X_t)$ is equal to 0, the solid surface could be considered as flat at the molecular level. As the surface roughness increases, $I_M(X_t)$ decreases readily down to a value of 0.1 e.g., for some solids like talcs [13], which exhibit slot like sites of adsorption on their lateral surfaces.

2.4. IGC-FC theoretical aspects

The isotherm of desorption was computed from IGC-FC chromatograms of isopropanol used as probe because of its ability to exchange strong interactions with the silanol groups through hydrogen bounds.

The "elution characteristic point method" (ECP) was used allowing the acquisition of the desorption isotherm from a unique chromatographic peak. The first derivative of the adsorption isotherm can be readily calculated starting from the retention times