

# **Characterisation of Some Silica Samples Modified with Aluminium by Inverse Liquid Chromatography using Squalene as Probe - Part IV**

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## **Abstract**

Precipitated silicas modified by aluminium were characterised using inverse liquid chromatography in anhydrous heptane with squalene as probes. Their monolayer capacities of adsorption, Langmuir's and Henry's constants were determined from the desorption isotherms according to frontal analysis. A narrow band consisting of isotherms was observed. The introduction of aluminium has little influence on the monolayer capacity, Langmuir's constants and the Henry constant. Experimental data show that neither the amounts of aluminium on the silica nor the methods of the introduction of aluminium into the silica influence the interactions between the squalene and the silicas.

## **Introduction**

Silica as a filler could strengthen the mechanical properties of the rubbers if people could control properly the interactions between the silica and the elastomer. The optimum interactions between the silica and elastomer require that silica should be dispersed easily into the elastomer matrix and at the same time the silica will have a comparably strong interaction between the elastomer. In order to realise this purpose, people have tried to modify the surface properties of silica. One kind of the method is to reduce the silanol groups by grafting trimethylsilyl groups onto the surface and the modified surfaces have been characterised by inverse gas chromatography [1].

Another kind of method to modify the silica surface is the incorporation of aluminium into silica. Covering silica by a layer alumina has been proved to be able to reduce the silanol groups. [2]. Many literatures have described that the introduction of aluminium on the surface of silica create many high energy sites. The insertion of aluminium will create Lewis acid sites and the strong Bronsted acid sites of  $-\text{Si}(\text{OH})-\text{Al}$  et  $-\text{Si}-\text{Al}(\text{OH})-\text{Si}-$  due to a tetravalent

aluminium atom having an electronic lacuna. [2-11] So the surface properties could be influenced by the ratio of surface density of aluminium to the hydroxyl groups.

There are many methods to introduce aluminium onto the silicas. These methods could be classified by the following categories:

-Decomposition of the mixture of  $\text{SiCl}_4$  and  $\text{AlCl}_3$  in the flame of Hydrogen and oxygen (Industrial Process of Degussa, Germany) in this process, only part of the aluminium occurs on the surface.

-Addition of Aluminate during the precipitation of silica (Process of Rhône Poulenc) [12]. When the silica begins to precipitate from the aqueous solution of sodium silicate, put aluminates into the solution. Most part of the aluminium is located on the very thin layer of the surface.

-Treatment of silica particles by aluminium trichloride in gas phase. Make aluminium trichloride to react with the silica, the state aluminium trichloride is either in liquid phase or in the gas phase. The purpose of this process is to develop catalysts for the isomerisations of alkanes. The type of aluminium on the surface depends on the nature of surface hydroxyl concerned for the fixation of aluminium (in the form of tetragonal or octagonal coordinance).

F.Ozil in his PhD dissertation has studied the precipitated silicas modified with aluminium using inverse gas chromatography. [12] His research shows that the influence of aluminium on the surface properties is complicated. But it is clear that small and polar molecular probes such as  $\text{N}_2$  and  $\text{CO}_2$  could detect the high energy sites created by the aluminium while the big apolar molecular probe such as hexamethyldisiloxane cannot detect the influence of the aluminium.

The purpose of this research is to know the interactions between precipitated silicas modified by aluminium and polybutadiene rubbers. We apply the newly-developed technique-inverse liquid chromatography (ILC) and choose squalene as the rubber model to characterise these silicas modified by different methods.

## **Experimental**

### **Silica samples**

The silica samples used for the study are the experimental samples prepared by the Rhodia Company. Of these samples treated by aluminium, only the silica 1165Mp is applied in the rubber industry as filler and it is represented by the symbol of "I".

The characteristics of these precipitated silicas are listed in Table 1 below.

Table 1 : The principle characteristics of the silicas samples treated by aluminum

silices	$S_{Spe}$ ( $m^2/g$ )	$\tau_{Al}$ (%)	$n_{Al}$ ( $Al/nm^2$ )	$n_{OH}$ ( $OH/nm^2$ )	R(Al/OH)
<i>N20</i>	<i>190</i>	<i>0,0</i>	<i>0,0</i>	<i>1,80</i>	<i>0,0</i>
<b>R</b>	<b>180</b>	<b>0,0</b>	<b>0,0</b>	<b>3,50</b>	<b>0,0</b>
S1	188	0,25	0,37	5,50	0,07
SM2	170	1,18	0,57	4,00	0,14
M2	178	0,81	0,91	4,70	0,19
I*	160	0,30	0,99	6,50	0,15
SM1	184	1,05	1,22	4,20	0,29
S2	152	0,70	1,22	3,40	0,36

- *I* is the silica MP1165 used in the protocol of analysis.

In this table:

- The silica N20, pyrogenic silica, is used as a reference,
- The silica R, prepared without addition of aluminium, is also used as a reference,
- The silica I (MP1165) is the reference for the industrial silica,
- The symbols "S" and "M" are the distribution state of aluminium which is added to the silica either on the surface of the silicas in the process of disintegration or in the mass of the silica in the process of consolidation. For the silicas marked as "SM", the aluminium is added in both processes.
- The specific area ( $S_{Spe}$ ) is measured by nitrogen at 77K,
- The total amounts of aluminium expressed in % are measured by element analysis,
- The surface density of aluminium atom on the surface of silica ( $n_{Al}$ ) is measured by chemisorptions of pivalic acid according to OZIL, 1999.  $n_{Al}$  is expressed in number of Al atoms per square nanometer.
- The surface density of hydroxyl group number on the surface, silanol or aluminol ( $n_{OH}$ ), is determined by etherification by methanol labelled by carbon isotope  $^{13}C$ . The measurement is conducted by  $\beta$  spectroscopy (PAPIRER et coll., 1981, MANSOUR et

coll., 1981 et 1987),

- The ratio of R (Al/OH) is equal to the ratio of the surface density of aluminium to the surface density of hydroxyl group number ( $n_{OH}$ ) on the silica surface expressed in mol./nm<sup>2</sup>.

### Measurement of aluminium atom on the surface

The surface density of aluminium atom on the surface of silica ( $n_{Al}$ ) is measured by chemisorptions of pivalic acid. The samples and the pivalic acid stored in an open capsule are put in desiccators with a valve. Then the desiccators are drawn to vacuum by a vacuum pump and the valve is closed. The desiccators are transferred to an oven and are heated at 100°C for one night so that the surface of the samples is saturated by the vapour of pivalic acid. The samples are cooled down and are extracted by ether in a soxhlet for 6 hours. The samples are dried at 100°C under vacuum for one night. The percentage of carbon fixed on the surface of the sample is measured by element analysis. Admitting that each molecule of pivalic acid corresponds to an aluminium atom, the surface density of aluminium atom on the surface of silica is calculated by Equation [1]:

$$n_{Al} = \frac{t_C \cdot 6023}{60 \cdot S_{spe}} \quad (\text{Equation 1})$$

Where:  $n_{Al}$  is expressed in Al/nm<sup>2</sup>,  $t_C$  is the percentage of carbon measured by element analysis,  $S_{spe}$  is the specific surface area of the silica "60" corresponding to the total value of molecule mass of the five carbon atoms in the pivalic group.

### Analysis of ILC

ILC measurements were performed on a liquid chromatograph fitted with a Gilson pump (Model 302) and a refractive index detector Gilson (Model 133). The ILC protocol was described previously in the first part [13]. The calculation of the isotherms and its main characteristics - monolayer capacity and Langmuir's constant - were performed in the same way using home made software

### Eluent and Probes

Carefully dried and degassed heptane was used as eluent, according to the protocol described in [13]. The column dead volume was determined using cyclohexane as non-

retained molecule, whereas squalene was used to probe the silica surface properties. The both are Aldrich Products of high purity (>99%) and used as such without any further purification.

### Preparation of the Column

The columns were made of stainless steel tubing. The tubing was washed with distilled water and acetone and finally dried overnight at 100°C.

The silicas used to fill the column were first pressed under 70 Mpa, in an IR die. The obtained pellets were crushed in a mortar and the obtained powder was sieved between 100µm to 250µm. The column is stainless steel pipe with the inside diameter of 2mm and the length will be between 170mm to 180mm. The weights of the samples will be between 0.36g to 0.39g.

The conditioning of the filled columns was performed by heating them, 4 hours at 160°C under a helium flow rate of 5 ml/min.

Thereafter, the column was cooled down to the room temperature under helium flow and was then connected quickly to the injection valve and to the RI detector inlet. After the stabilisation of the baseline, the experiment could be started.

### Results and Discussions

The adsorption of squalene in the solution of anhydrous heptane has been studied by ILC according to frontal analysis. The isotherms of desorption are shown in Figure 1.

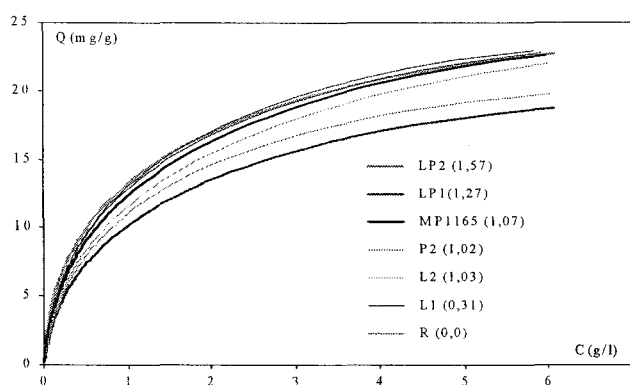


Figure 1. Isotherm of desorption of squalene in anhydrous heptane, measured at 24.8°C for samples of precipitated silicas treated by aluminium. The number in the bracket is the value of aluminium density on the surface by nm<sup>2</sup>

In this figure, the value between the brackets represents the surface density of aluminium on the surface. This figure shows that these isotherms form a very narrow band which

means that the adsorption capacity of these silica is almost the same. Moreover, the shape of these isotherms is very similar.

In order to compare these isotherm more quantitatively, we have calculated the Langmuir's constant ( $L_{\text{Langmuir's}}$ ), the monolayer capacity ( $N_0$ ) of squalene adsorbed on the surface of these silicas and the Henry Constant.

The Langmuir's constant was computed by linearization of the isotherm, according to Equation [2].

$$\frac{C}{Q(c)} = \frac{1}{Q_0 \cdot B} + \frac{C}{Q_0} \quad [\text{equation.2}]$$

Where:  $Q(c)$  is the amount adsorbed at the concentration  $C$  of the probe in the eluent,  $Q_0$  the amount adsorbed at the plateau or the monolayer capacity in mg/g and  $B$  the Langmuir's constant.

The monolayer capacity ( $N_0$ ) of squalene adsorbed on the surface of these silicas was calculated according to Equation 3.

$$N_0 = Q_0 \frac{602.3}{M \cdot S} \quad (\text{Equation 3})$$

Where  $M$  is the molecule mass of squalene and  $S$  is the specific surface area.  $N_0$  is expressed in molecule per  $\text{nm}^2$ .

The Henry constant was determined by the slope of the tangent at the origin point of the isotherm.

We have examined the evolution of these three values in function of the surface density of aluminium ( $n_{\text{Al}}$ ) and in function of the ratio  $R$  ( $\text{Al}/\text{OH}$ ) of aluminium to the hydroxyl groups respectively. The points corresponding to the silica N20 were used as reference.

The evolutions of the monolayer capacity  $N_0$  of squalene, adsorbed on the surface of the silicas, in function with the surface density of aluminium ( $n_{\text{Al}}$ ) and in function with the ratio  $R$  ( $\text{Al}/\text{OH}$ ) of aluminium to the hydroxyl groups were presented in Figure 2 and Figure 3 respectively. In the following figures, the grey band represents the average value of these constants and the height of the band represents the incertitude of the measurements.

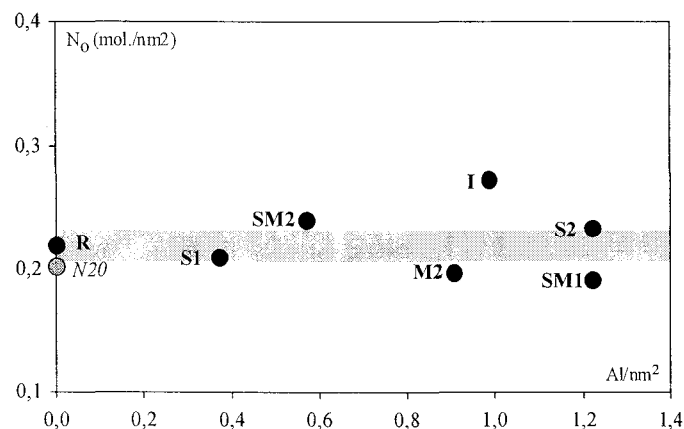


Figure 2. Variation of monolayer capacity of squalene, adsorbed on the surface of silicas, in function with aluminium density on the surface ( $n_{Al}$ ).

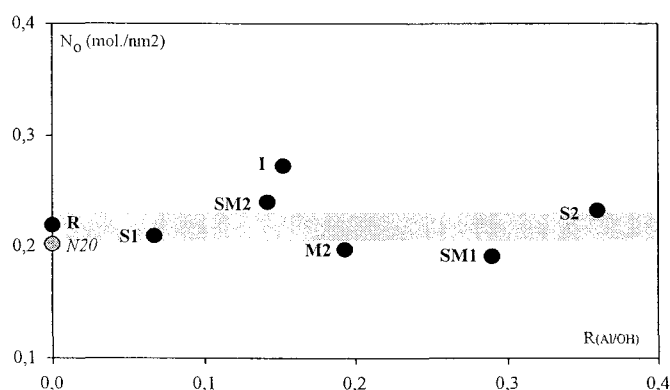


Figure 3. Variation of monolayer capacity of squalene, adsorbed on the surface of silica, in function with the ratio of aluminium atom density to the hydroxyl groups ( $R(Al/OH)$ ).

The experiments proved that no matter what variables are used, either of the surface density of aluminium ( $n_{Al}$ ) or the ratio  $R(Al/OH)$  of aluminium to the hydroxyl groups, the monolayer capacity  $N_0$  is always kept constant. The same results were also observed for the Langmuir's and Henry Constants which are related to the interaction energies between the probe and the samples. Figure 4 and Figure 5 represent the evolution of Langmuir's constant in function with the surface density of aluminium ( $n_{Al}$ ) and the ratio  $R(Al/OH)$  of aluminium to the hydroxyl groups respectively.

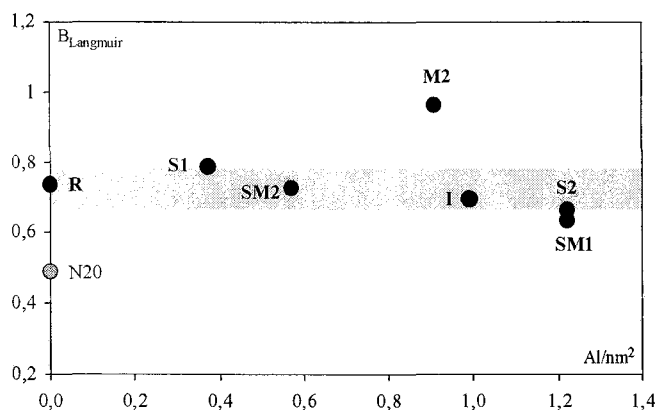


Figure 4. Variation of Langmuir's constant of squalene, adsorbed on the surface of silicas, in function with aluminium surface density ( $n_{Al}$ ).

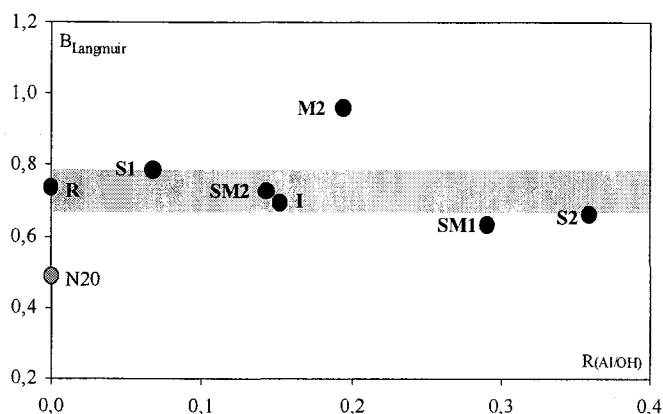


Figure 5. Variation of Langmuir's constant of squalene, adsorbed on the surfaces of silicas, in function with the ratio of aluminium atom surface density to the hydroxyl groups ( $R (Al/OH)$ ).

Except for sample M2, all other points stay in the same band, which proved that the surface properties of these precipitated silica are independent of the two factors: aluminium atom and hydroxyl groups on the surfaces. The following two figures Figure 6 and figure 7, which represent the evolution of Henry constant in function with the surface density of aluminium ( $n_{Al}$ ) and the ratio  $R (Al/OH)$  of aluminium to the hydroxyl groups respectively, confirmed again this independence.

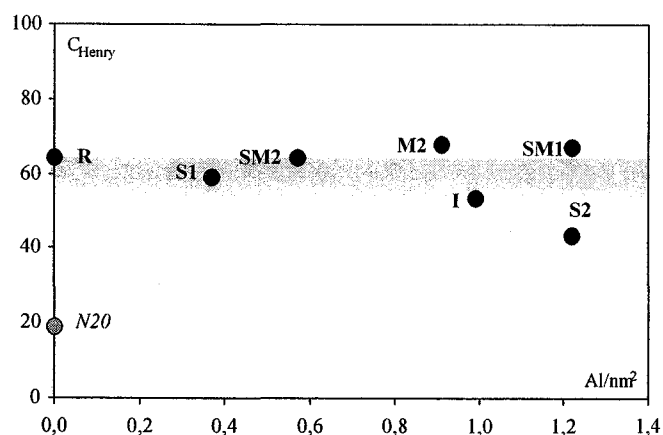


Figure 6. Variation of Henry constant of squalene, adsorbed on the surfaces of silicas, in function with the aluminium surface density ( $n_{Al}$ ).

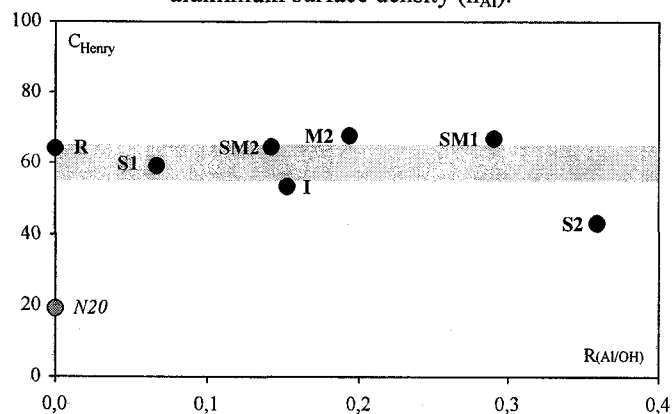


Figure 7. Variation of Henry constant of squalene, adsorbed on the surfaces of silicas, in function with the ratio of aluminium atom surface density to the hydroxyl groups ( $R (Al/OH)$ ).



## Conclusion

This purpose of study is to examine if there any influence on the interactions between the elastomer chains and the silica surfaces by introduction of aluminium onto the precipitated silica samples during its production processes. To realize this purpose, we have resorted to inverse liquid chromatography (ILC) of frontal analysis using squalene as probe, model of polyisoprene chain and heptane as effluent.

All the parameters of the isotherms of the desorption of squalene, the monolayer capacity  $N_0$ , Langmuir's constant ( $L_{\text{Langmuir's}}$ ) and the Henry Constant ( $C_{\text{Henry}}$ ), demonstrated that the adsorption of squalene by these precipitated silicas treated by the aluminium is influenced:

- Neither the surface density of aluminium, even though it varied in a very large range from 0 to 1, 22 Al/mn<sup>2</sup>.
- Nor by the method of the introduction of the aluminium. No matter in what process aluminium is introduced into the silica- introduction of aluminium into the mass of the silica at the end of the consolidation process symbol led as silica "M", onto the surface of the silica in the process of disintegration symbol led as silica "S" or in both process symbol led as "SM".

The interaction of elastomers-silica is thus not necessarily the predominant parameters. However, it should be considered that the when silica is applied as filler of the rubber, the organosilanes or coupling agents are always present. The formulations of theses materials are listed below, which connect the elastomers to the surface of silica by intermediate covalent liaisons.



It is reasonable to think that the presence of aluminium could influence the interactions between the silica surface and the coupling agents.

The independence of the surface properties on the aluminium is maybe caused by the surface morphology. The aluminium could be situated in some positions where the large squalene chain cannot approach due to the space hindrances.

Thus it would be interesting to study the morphology of the silica surface and the distribution of aluminium on it.

## Reference

1. H. Balard, E. Papirer et al., Trimethylchlorosilane Modified Silica Surface :Characterization by Inverse Gas Chromatography Using PDMS Oligomers as Probes, *Composite Interface*, Vol.6, No. 1, (1999) 19-25.
2. W. Lutz et al., Hydrothermally Resistant High-Silica Y Zeolites Stabilized by Covering with Non-Framework Aluminium Species, *Microspores Materials* 12(1997)131-139.
3. M.J. Meziani, J. Zajac et al., *Langmuir* 13(1997) 5409.
4. M.J. Meziani and H. Benalla, Liquid Phase Microcalorimetry Applied to Evaluation Surface Polarity of MCM-41 Type Aluminosilicates, *Thermochimica Acta* 372(2001)103-107.
5. V. La Parola et al., Effects of the Al/Si Ratio on Surface and Structural Properties of Sol-Gel Prepared Aluminosilicates, *Journal of Solid State Chemistry* 174(203)482-488.
6. Hanna Harelind Ingelsten et al., The Influence of Surface Acidity on NO<sub>2</sub> Reduction by Propane under Lean Conditions, *Journal of Molecular Catalysis A: Chemical* xxx(2003)xxx-xxx.
7. J.M. Parera, N.S. Figoli, *J. Catal.* 14(1969)303.
8. M.V. Landau et al., Mesoporous Alumina Catalytic Material Prepared by Grafting Wide Pore MCM-41 with an aluminium Multilayer, *Microporous and Mesoporous Materials* 49(2001)65-9.
9. B. Chiche et al., Butene Oligomerization over mesoporous MTS-Type Aluminosilicates, *Journal of Molecular Catalysis A: Chemical* 134(1998)145-157.
10. M.L. Ocelli et al., Effects of the Nature of the Aluminium Resource on the Acidic Properties of Some the Mesostructured Materials, *Microporous and Mesoporous Materials* 26(1998)193-213.
11. G.K. Chuah et al., Surface Properties of Mesoporous Catalytic Supports, *Applied Surface Science* 169-170(2001)253-258.
12. F. Ozil, Ph.D. Dissertation.
13. J.B. Donnet, Z.T. Zhang, J.F. Pilard, J.C. Brosse and H. Balard, *Kautschuck Gummi und Kunststoffe* (in press).