

Deciphering the silica/silane reaction mechanism for the development of a new generation of low rolling resistance tires

Part 1 – characterization by in situ IR spectroscopy

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By use of suitable organic silanes and controlled mixing conditions, silica/silane systems have proven to be well suited for tire tread formulations with reduced rolling resistance. The bifunctional organosilane is able to react with the silica surface as well as with the polymer. However, silica compounds still present considerable difficulties in processing. The kneader is not only a mixing aggregate but has to fulfill the role of a chemical reactor. It is known from former studies, that the reaction between the silica and the silane is complex. It is up to now not sufficiently understood. Therefore, a better understanding would help many tire producers to control the mixing process more efficiently. Operando IR spectroscopy carried out in-situ during the reaction is the technique of choice to decipher the reaction.

1 Background and introduction: silica as a filler for rubber and its influence on tire properties

There has been an increased use of silica filled rubber treads for tires to give improved rolling resistance and traction. One of the key ways to improve the fuel consumption of a car is to reduce the rolling resistance of its tires. The EU tire labelling came into force in November 2012 and classifies tires due to their rolling resistance, wet traction be-

haviour and noise. In the meantime, similar labels were passed in many other countries (fig. 1) [1–5].


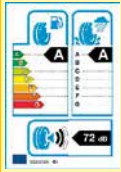




The adjustment of the tire tread properties has the biggest influence on the rolling resistance on a tire, the contribution of this rubber compound has by far the biggest influence (fig. 2) [6]. The rolling resistance of a tire, which is the energy dissipation by deformation and friction, causes 20 % of fuel consumption of passenger cars. Therefore, a

good classification in the tire labelling with regard to the rolling resistance can today be reached by using a modern silica/silane system in the tire tread instead of the former used carbon black according to present knowledge. By use of appropriate organic silanes like Si 69 (bis(3-triethoxysilylpropyl) tetrasulfide, TESPT) and controlling mixing conditions, the silica/silane has proven to be appropriate for tread formulations.

The other important tire property, the wet traction, is positively influenced by the use of the silica/silane system as well (fig. 3). Due to the polar silica surface a breakage of the water film is possible which means that local dry patches are formed creating a higher friction coefficient. Furthermore, the use of highly dispersible silica enables to keep the third important tire property, the abrasion resistance, on the same level as for the former carbon black filled tire tread compounds. Present silica/silane technology has led to the introduction of low rolling resistance tires with improved wet traction behaviour (maintaining the abrasion resistance) [7–9], thus spurring the use of silica and silane throughout the tire industry especially in Europe.

The bifunctional organosilane is able to react with the silica surface as well as with the polymer. One functional group is responsible for the coupling to the hydrophilic silica surface, the other one for the linkage to the hydrophobic polymer matrix. However, silica compounds still present considerable

Fig. 1: Several regional tire regulations with the main focus on fuel efficiency and wet grip (PC: passenger car; LT: light truck; T&B: truck and bus) [1–5]

Region	Japan	EU	Korea	Brazil	China	USA
Tire label						
Valid for	PC summer replacement	All PC, LT, T&B	All PC, LT	All PC, LT, T&B	All PC, LT, T&B	PC replacement
RR & wet grip	January 2010	November 2012	December 2012	October 2016	2016, 2019 mandatory	Under discussion
Min. thresholds	None	RR, wet grip November 2014	RR, wet grip 2013	?	RR, wet grip	None
Treadlife	–	–	–	–	–	Under discussion

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difficulties in processing. The kneader is not only a mixing aggregate but has to fulfill the role of a chemical reactor. The silane has to be chemically bonded to the surface of the silica during the mixing process. Only if this bonding has been carried out properly, a good chemical linkage between hydrophobated silica and polymer can be achieved afterwards during the vulcanization in order to get the balanced tire properties (fig. 4).

This means in the case of TESPT, the triethoxysilyl-group of TESPT reacts with the silanol groups of the silica during the mixing process with release of ethanol. The rubber-reactive tetrasulfide group of the silane reacts with the polymer during vulcanization by forming a rubber-to-filler bond during curing of the rubber compound [10]. It is known from former studies that the reaction

between the silica and the silane is complex [11, 12]. It is up to now not sufficiently understood. Therefore, a better understanding would help many tire producers to control the mixing process more efficiently. But how can this reaction be deciphered?

2 Infrared spectroscopy of silica

Infrared spectroscopy is the technique of choice for studying interaction between molecules and the surface of solids. This spectroscopy of adsorbed species has been well known for more than 50 years [13]. It allows understanding the behaviour of molecules on the surface of solids: how they are transformed, how they interact between themselves and with the surface. Adsorbate to surface interactions can be very complex

and interpretations of the spectra can sometimes be challenging because of the many different surface adsorption sites: electronic vacancies, surface cations, basic and acid sites etc. For such studies, pure silica has always been one of the most studied solids because it only presents one type of adsorption site: the silanol group. These are very weak acidic OH groups on the silicon atom, terminating the surface of the bulk SiO₂ silica.

The mid-infrared spectrum for pure silica thus only displays features arising from the vibrations of the Si-O and O-H bonds. Silica can be considered as the historical case for the infrared study of OH groups on solids. Many review papers have been published on the subject [14, 15] although some issues remain unresolved and some aspects can be very complex. The various SiOH groups can be identified. The amount of SiOH groups in the sample can be determined with faint but very accurate features in the near infrared [16].

In the following, it will be shown how these methods can lead to detailed information on the modifications arising in silica upon the reaction with silanes. Probe molecules, with isotope labelling and exchange, can be used to measure the accessibility index and to understand how the surface modification by silanes can change the way the surface interacts with the environment and for example with the rubber in the tire.

2.1 Experimental: in-situ spectroscopy

Contrarily to what is often used in basic routine IR characterisation, dilution of the

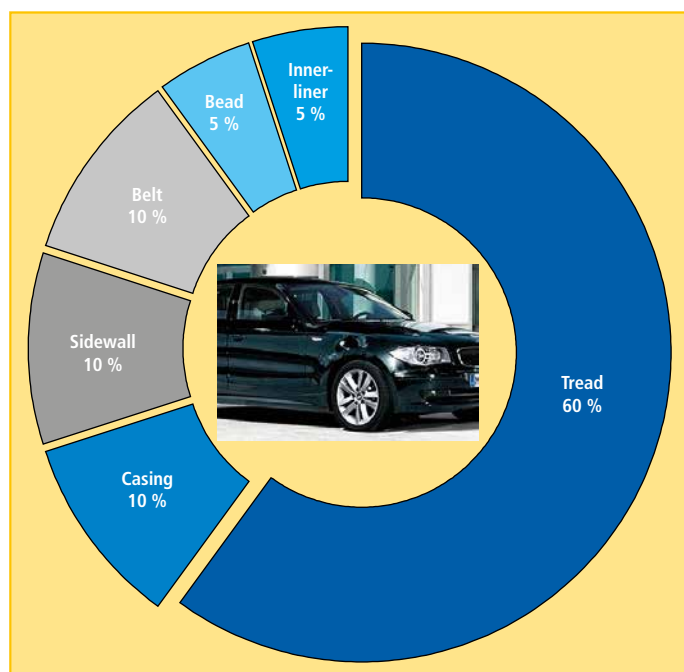


Fig. 3: Possible explanation for the influence of silica filled treads on the wet grip

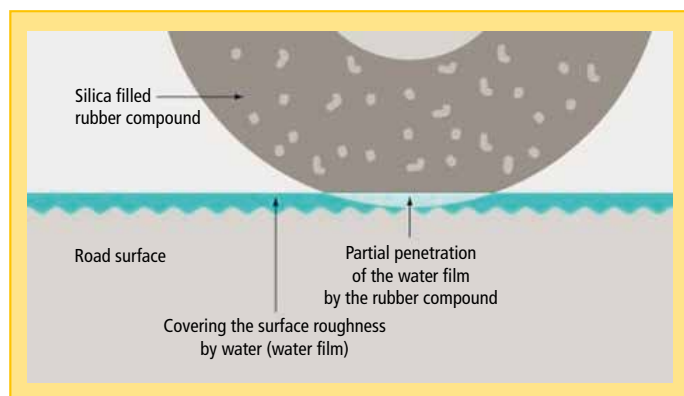
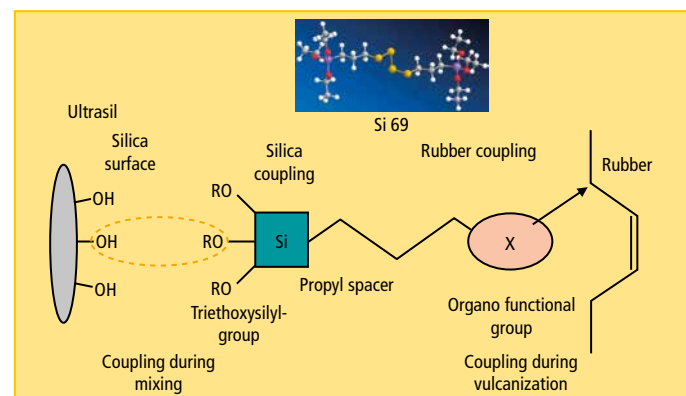


Fig. 2: Contribution of tire components to rolling resistance [6]

Fig. 4: Silica/silane reaction during the mixing process



sample in a solid matrix like KBr is not possible for studying adsorbed species. Indeed, the first necessary step will be the drying of the sample and the removal of any previously adsorbed species, and this means heating the sample (under vacuum). This can only be done on the pure solid, without any possible chemical interference. Moreover, dilution of the sample would decrease the relative amount of silica surface and would decrease the sensitivity of the technique to adsorbed species. The sample (silica powder) must thus be studied as a self supported wafer, which will be as thin as possible to transmit enough infrared light. The typical sample is 10–20 mg, for a 2 cm² wafer. The pressure applied for making the wafer must remain as low as possible in order to keep a good diffusion of gas through the sample and in order not to affect the optical properties of the powder (no aggregation into larger particles). The typical applied pressure is 0,5 t/cm², ca. $5 \cdot 10^7$ Pa. Making the wafer can sometimes be a challenge for some solids, but precipitated silica is usually straightforward.

The characterisation is performed in a homemade in-situ cell, where the self-supporting sample can be heated under vacuum (10^{-6} mbar), and where controlled amounts of gas molecules can be introduced. The wafer can be placed on a quartz sample holder and moved between the oven and the infrared measurement position between the KBr windows (fig. 5).

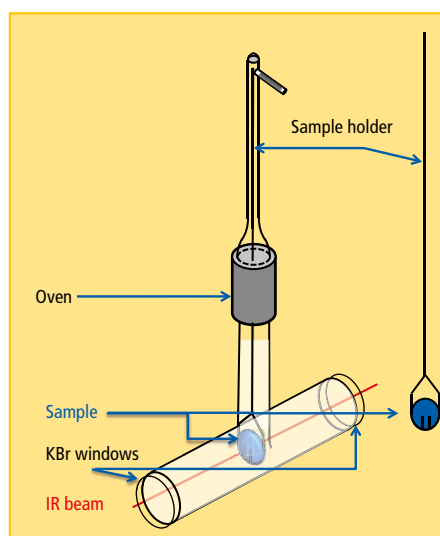
The first step for the observation of the surface of the solid is the cleaning of the surface and the removal of adsorbed water. This is done by gentle thermal treatment (very slow heating up to 500 °C depending on the stability of the solid) under vacuum (10^{-6} mbar). The spectrum of the sample is then controlled to check water or any other adsorbate exclusion.

Probe molecules (silanes for example) can be introduced into the cell: their spectrum can be measured in the gas phase and after adsorption on the surface of silica. Observation of the whole of the mid infrared range gives information on the modification of the surface and of the surface molecule, and on any chemical modification.

2.1.1 Quantitative IR measurements

Since the spectrum is measured through the wafer (fig. 6), the light is either transmitted (I_t) or absorbed by the sample (reflected light I_r is kept to a minimum and is neglected). The ratio of the collected light to the incident light (intensity collected through the sample divided by the intensity without the solid sample) is the transmittance, and the logarithm of its inverse is absorbance, which

Fig. 5: In-situ cell used for the characterisation of silica



is proportional to the amount of light-absorbing molecules in the infrared beam. When spectra are plotted in absorbance values, the integrated intensity of the infrared band is proportional to the concentration of the molecule under study, with a proportional factor ϵ which is the molar absorbance coefficient for the given species at this wavelength. Experimentally, the experiments were always reproduced several times and checked that the results were within 3 % reproducibility.

Fig. 6: Scheme of the transmission of light through a solid sample. $I_{o\lambda}$ is the incident light at wavelength λ , $I_{t\lambda}$ is the transmitted light at wavelength λ , and $I_{r\lambda}$ is the reflected light at wavelength λ . T is transmittance, R is reflection and A is absorbance.

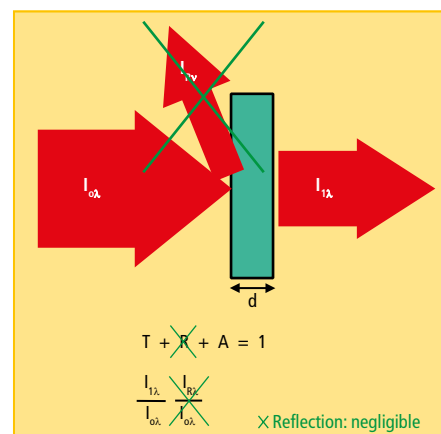
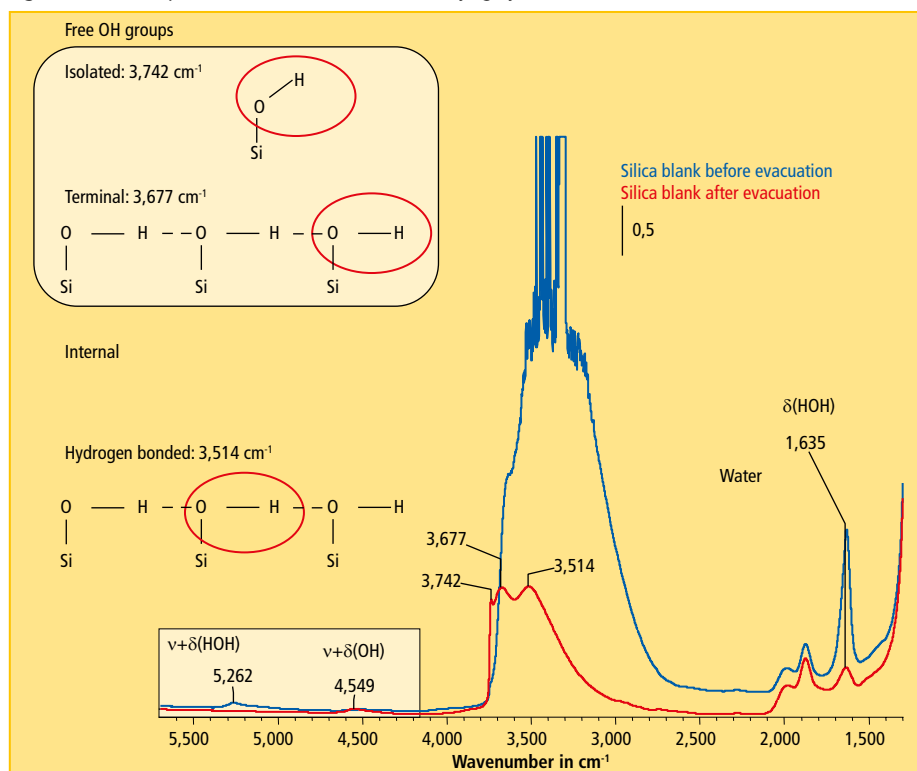


Fig. 7: Infrared spectrum of silica before and after drying by evacuation.



2.1.2 Infrared features of silica: OH groups

The infrared spectrum of silica is shown in **figure 7**. The main features after removal of water are the bands due to the solid itself below $2,000\text{ cm}^{-1}$, and the vibration bands from the OH groups above $3,000\text{ cm}^{-1}$ (silanol groups). Free OH groups lead to a band at ca. $3,745\text{ cm}^{-1}$, hydrogen bonded silanols produce a broad band around $3,515\text{ cm}^{-1}$, and the band around $3,675\text{ cm}^{-1}$ is due to "internal" silanols, not really hydrogen bonded but located inside the solid and not on the external surface. These internal silanols are thus not accessible to molecules adsorbed on the solid, as will be seen later. The two very weak but clear bands above $4,500\text{ cm}^{-1}$ are combination bands from the OH fundamental vibrations, and will be very useful for quantifying the OH groups on the surface.

2.1.3 Measuring and identifying the OH groups involved in the reaction

To follow the surface reactions and the modifications of silica, it is of prime importance to determine the number of surface OH groups modified during the silica/silane process. Quantification of OH groups is however often very difficult with infrared spectroscopy, because of the hydrogen bonding and the overlap of the bands. Hydrogen bonding dramatically affects the quantitative response of infrared spectroscopy: vibrating bonds engaged in hydrogen bonding

lead to a huge and non-linear increase of their intensity, and no quantitative estimation is possible. This problem was solved by simultaneous measurement of the weight of the wafer and of the infrared intensities [16]. During the removal of the OH groups on the surface of silica (by intensive heating under vacuum), the number of surface OH removed was compared to the various band intensities, and the intensity of the band at $4,549\text{ cm}^{-1}$ was shown to be linearly varying with the amount of silanols in the sample, whereas the band at $5,262\text{ cm}^{-1}$ was found as a very good measurement of the amount of water in the sample (**fig. 8**).

Not all OH groups on the surface are involved in the reaction with silane molecules. One of the main reasons for that might be the accessibility of these silanols to incoming molecules [17]. A method was devised to determine the relative amount of silanol groups in the sample that were accessible to incoming molecules. After complete deuteration, the silica samples were brought into contact with alcohols of varying size to perform a back exchange of the OD into OH groups. Accessibility was thus measured for each of the alcohols as the number of OH groups recovered versus the total number of OH groups in the sample. A scale was obtained for each of the samples, giving accessibility vs size of the probe molecule (alcohol). Accessibility was then checked before and after reaction with silane molecules in order to assess the extent and quality of the coupling reaction.

Hydrophilicity is also a way of assessing the extent and quality of the coupling reaction, which is sometimes referred to as hydrophobation of silica. However, measuring the amount of water on a sample is a difficult problem for infrared spectroscopy. Introduction of controlled amounts of water into in-situ glass cells is nearly impossible, and the resulting infrared bands are perturbed by hydrogen bonding and often overlap those of the solid [18]. This problem was solved recently by using the near-IR band at ca. $5,260\text{ cm}^{-1}$ [19].

Interesting relationships were found between the amount of surface water and the number of OH groups on silica:

- The number of free OH groups on dry silica is proportional to the BET surface measured by nitrogen adsorption.
- Except on porous silicas, the water content in untreated (hydrated) silica is proportional to the number of Si-OH groups.

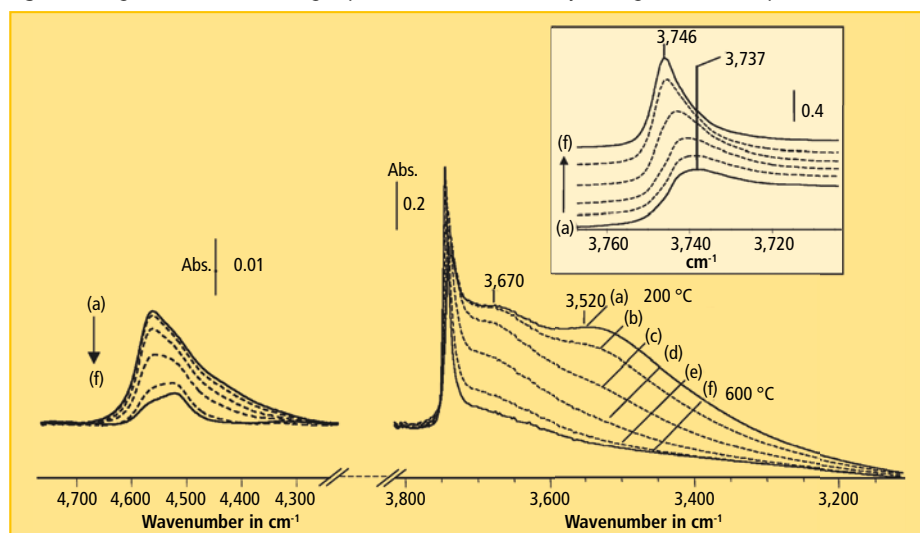
The coupling reaction, grafting silanes on the surface of silica, leads to an efficient hydrophobation of the solid and decreases the interaction of silica with water.

3 Understanding the coupling reaction with Operando IR spectroscopy

Infrared spectroscopy also allows the observation of the surface chemistry during the chemical reaction. This in-situ study inside a working reactor is called operando spectroscopy. It needs a specially designed reactor with windows letting the infrared light through the reaction chamber, but otherwise similar to any chemical reactor.

In the typical setting, reactants are sent as vapours with a carrier gas inside a heated stainless steel tube containing the solid as a very thin bed (self supporting wafer), through which the infrared beam is let by KBr, CaF_2 or ZnSe windows (**fig. 9**). The gases after the reaction are analysed with the usual on-line analysis techniques such as mass spectroscopy, gas chromatography or IR gas analysis.

Fig. 8: Progressive removal of OH groups on the surface of silica by heating to $600\text{ }^\circ\text{C}$ (adapted from [17])



All the individual steps of the surface reaction can be followed. The first important step is the adsorption of the reactants on the solid, with the increasing concentration of silanes on the silica. The adsorbed species will then react with the surface: some species disappear (physisorbed silanes and some surface OH groups) and new species are detected on the surface (surface grafted silanes). Some surface intermediates are sometimes detected (mostly in some other systems like heterogeneous catalysis). The reaction products go back to the gas phase and are collected at the exit port of the reactor.

Understanding the reaction means relating the amount of reaction products formed over time with the amount of reacting species on the surface. The power of operando spectroscopy is the ability to verify a proposed reaction mechanism by assessing the corresponding kinetic laws between surface species and reaction products. This is of course only possible and relevant when the reactor is under real working conditions (**fig. 10**). Infrared spectroscopy then becomes a key tool for understanding surface reactions.

The real time analysis of the coupling reaction was performed at 110–120 °C, in a flow of nitrogen as a carrier gas (**fig. 11**). The initial physisorption of silanes on the surface was shown by the coming of a large and broad band at 3,384 cm^{-1} , indicating the new hydrogen bonding. New bands for C–H bonds appeared progressively, while some ethanol was detected in the exit port. This indicated the slow hydrolysis of surface silanes by the OH groups.

After the reaction, the surface was flushed and cleaned with pure carrier gas, to see what remained on the surface. The global amount of Si–OH (silanols) had decreased by 25 %, while some of the CH bands remained. The amount of ethanol formed and detected was in agreement with the amount of Si–OH removed, which evidenced the slow coupling of silanes with the surface of silica. **Figure 12** shows intensity changes over reaction time for the main infrared bands on the solid. Not all of the silanols were affected the same way

during the reaction. The internal OH groups are not accessible at all, and it was shown that they could not even be touched by water. Of course, these internal silanols were not affected by the coupling reaction. Only the isolated free silanols on the external surface were involved in the reaction. They were initially perturbed by the silanes coming to the surface (hydrogen bonding), and in a second step were progressively removed while alkane chains were chemically grafted on silica.

Some of the silanes also contain SH (thiol) groups, and the corresponding very weak band was also detected around 2,580 cm^{-1} , in quantities that agreed with the extent of grafting determined by the formation of ethanol.

The extent and quality of the surface modification was tested in the reactor by subjecting the hydrophobized silica samples to thermal treatment after the coupling reaction. Physisorbed silanes were easily removed at 120 °C, while at the same time the infrared feature for the hydrogen bonded Si–OH disappeared. The system then remained the same up to 300 °C, indicating that coupled silane (chemisorbed by covalent bonding) were stable up to 300 °C. The amount of missing Si–OH from the initial silica was measured to determine the number of grafting points and the type of coupling (mono-/bi-dentate), in agreement with the approximate quantification of surface silane by the CH bands. This allowed the determination of the coupling efficiency. At temperatures higher than 300 °C, the degradation of the

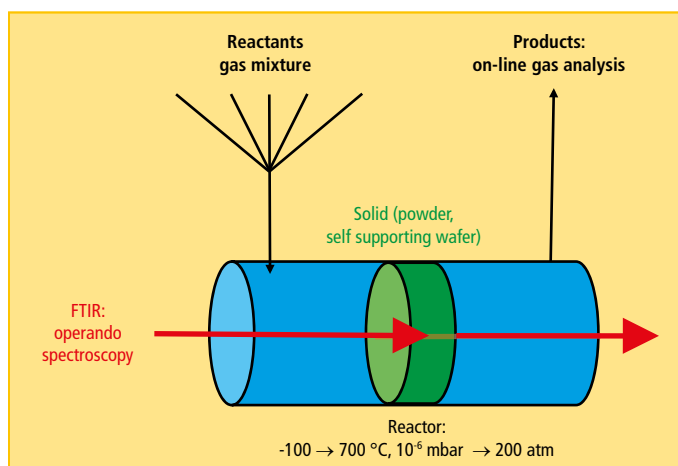
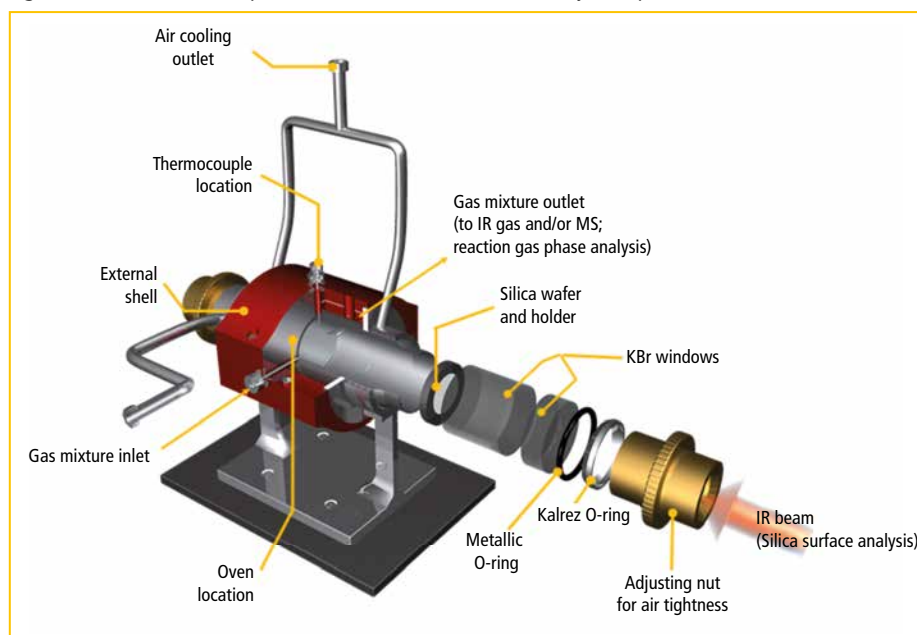


Fig. 9: Concept of the operando setup.

Fig. 10: Reactor cell for IR operando studies at the Laboratoire Catalyse et Spectrochimie, Caen



silane took place, and some of the free Si-OH were recovered (but not all of them).

4 Conclusion

Infrared spectroscopy was used to study the surface of silica samples for their use as rubber filler in the tire industry. Various important parameters were determined, such as the water content, the amount and distribution of OH groups on the surface, and the accessibility of the OH groups to incoming molecules. The reaction of the surface of silica with organic silanes for preparing hydrophobized silicas was studied by operando infrared spectroscopy. Variations in the silica/silane pair allowed exploring the various parameters of the reaction. The hydrophobation was measured, as well as

coupling efficiency, in many different series of silicas and silanes. The influence of surface roughness was evaluated, as well as the concentration of OH groups and of the method for the preparation of silica. In the silanes, the functional groups and the structure of the Si-OR moiety was changed, and the coupling conditions were evaluated. These methods allow a better understanding of the hydrophobation reaction, and its fine tuning for the optimisation of the silica-filled rubber.

5 References

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Fig. 11: Changes in the IR spectrum during the reaction of silanes with silica.

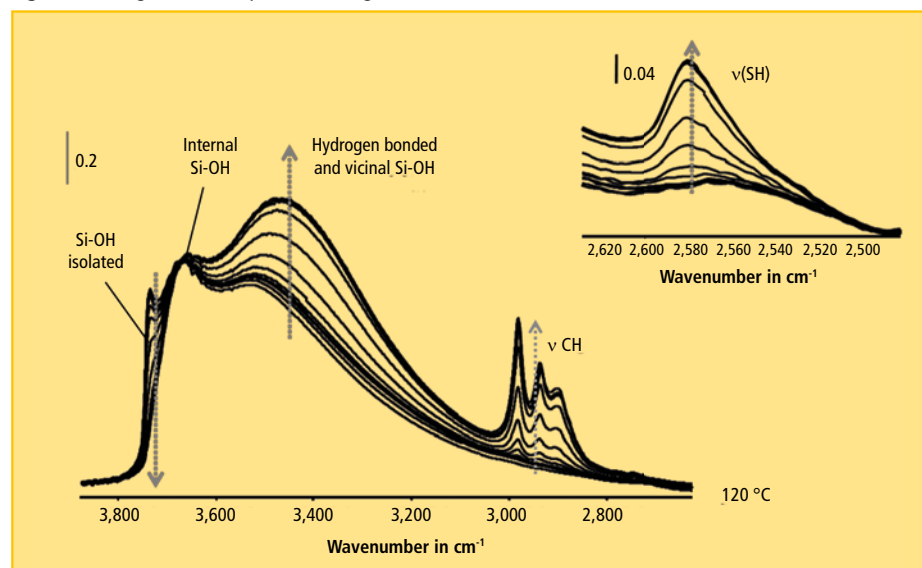


Fig. 12: Intensity changes over reaction time for the main infrared bands on the solid

