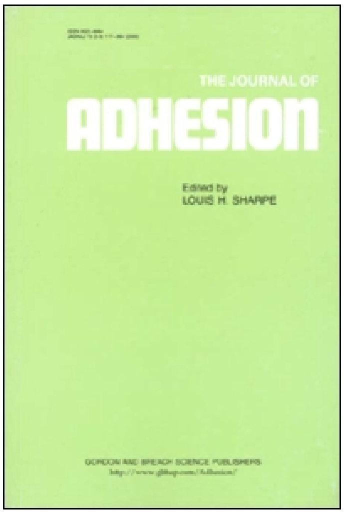

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Comparative Studies on the Adsorption of Trivinylethoxysilane on Oxidized Surfaces of Silicon and Aluminium*

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In situ interactions of trivinylethoxysilane (TVES) with oxidized surfaces of silicon and aluminium was investigated at room temperature by high resolution electron energy loss spectroscopy (HREELS) and reflection-absorption infrared spectroscopy (RAIRS). The molecular interaction was held under vacuum environment. The chemical state of the substrate surfaces was characterized before and after the alkoxysilane interaction by Auger electron spectroscopy (AES), HREELS or RAIRS. Under vacuum conditions, silica surfaces are chemically inactive to the TVES molecules contrarily to oxidized aluminium surfaces where adsorption is realized successfully. Differences among adsorption mechanisms on both substrates are discussed in light of Brønsted acid properties of the oxide surfaces and of the role of physisorbed water.

Keywords: Alumina; silica; alkoxysilane adsorption; HREELS; RAIRS; AES

1. INTRODUCTION

Surface functionalization of solids has found extensive applications [1–5] in recent years and is of prime importance in many fields of

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material science such as adhesion, tribology, organic coatings or corrosion. Organosilanes are often used for this purpose, particularly as adhesion promoters between polymer films and inorganic substrates, as they can establish chemical bonds between the substrate and the organic coating. This can be realized by properly choosing the organometallic functions. Generally chloro- and alkoxy-silanes of the form $R_{(4-n)}$-Si-X_n are chosen, where X is the reactive group towards the surface and R is an organic function. Compatibility for polymer grafting is mainly determined by an appropriate choice of R. In this work, these molecules were used in the interaction with flat surfaces of silica and alumina.

The chemistry of the silicon atom and its compounds were extensively reviewed by Corey and Apeloig [6, 7], where a comparison with the chemistry of carbon compounds is established. In particular, kinetic studies of the hydrolysis and condensation of ethoxy- or chlorosilanes showed the influence of the pH values [8]. As these studies were done in aqueous solutions, it was argued that silane hydrolysis could be base or acid catalyzed. Concerning the base-catalyzed reaction, hydrolysis proceeds by a nucleophilic attack of the hydroxyl in a SN_2 type reaction mechanism. In the case of the acid-catalyzed reaction, the hydrolysis proceeds by a protonation of the leaving group (alkoxy, halogen,...) followed by a nucleophilic attack of the silicon atom by water molecules following the same mechanism. The condensation of silanols follows the same mechanism as the base-catalyzed hydrolysis which was later confirmed [9, 10]. Films of silanes have been used on metal surfaces, and particularly with oxidized aluminium surfaces, as coupling agents and their characterization and structure were largely investigated by Boerio *et al.* [11]. The characterization of molecular adsorbed species has been also performed in numerous studies dealing with the interaction of organosilanes with oxide powders [12–19]. These works clarify the role of physisorbed water and propose clear reaction mechanisms for the adsorption process of silanes on dispersed silica, suggesting the need of water molecules in the vicinity of the interface to promote the grafting of silanes at room temperature. Following this hydrolysis step, the adsorption mechanism implies a further reaction of the previously-formed molecular silanols with the surface hydroxyl entities.

In this work, we ponder the acid-base properties of the solid substrate in light of Brønsted concepts, that is to say by considering protons or hydroxyl group transfer. In the case of oxide surfaces, their reactivity can be approached by Hard and Soft Acid and Base concepts [20, 21]. It was shown that the surface acidity depends, for numerous powdered oxides, on the ratio of the ionic charge to the ionic radius. More recently, theoretical efforts have been undertaken to rationalize acid and base properties of oxide surfaces. Tanabe *et al.* [22] and Noguera *et al.* [23] elaborated electronic structure calculations giving an insight into the adsorption energy of protons and hydroxyls adsorbed on simple oxides. Those trends generally show that the more covalent the oxide is, the more acidic it will be in Brønsted point of view. On the contrary, the more ionic oxide is, the more basic it will be.

Flat silica and alumina surfaces, which are studied in this work, seem to be quite appropriate for a comparative study as both present different properties regarding the previously-mentioned parameters. The silicon oxide surface is known to be more covalent and, therefore, more acidic than the alumina surface. The ionicity difference of those oxides is confirmed by the presence of stronger Lewis acid sites on alumina surfaces compared with the silica ones [24]. These differences were also correlated to the oxygen O_{1s} binding energy values measured by XPS [25]. The ionicity variation between those two substrates is expected to influence the reaction mechanism of trivinylethoxysilane (TVES) adsorption, as the nucleophilicity of anionic sites is changed.

HREELS spectra of silica and alumina surfaces are well known from the literature [26–31]. Most of these studies were done using crystalline surfaces; HREELS was then used in the dipole regime where interacting electrons are elastically backscattered in a very narrow lobe around the specular direction. In particular, this scattering mechanism enables the study of surface phonons foreseen by the dielectric theory. In the present case, rough oxidized silica and alumina surfaces are used and electrons are backscattered by short range impact regime in very wide lobes. The impact interaction with the surface entities is mainly realized at typical distances of the order of 1 Å. In these conditions, incident electrons penetrate into the film before being backscattered by a multiple scattering process. Vibrations of oxide bonds and of hydroxyl groups, which are present on the surface, are then excited during this electron impact interaction. Selection rules of the impact regime are less restrictive than the long-range dipole scattering. Infrared and Raman-active modes can be observed. The analyzed region thickness corresponds roughly to the mean escape depth of the interacting electrons in the oxide film; this means a few Ångstroms. Impact regime is also used here to get a better insight into the interfacial chemical bonds after the molecular interaction. For this purpose, a simple *R*-function chosen as the order of magnitude of the analysis depth in impact regime is comparable with the molecular dimensions [32]. Besides, TVES, a monoethoxysilane, was preferred to di- and tri-functionalized molecules to avoid polymerization by lateral condensation. RAIRS and HREELS were chosen to inspect the formation of interfacial bonds, as they are complementary techniques for surface analysis. In fact, RAIRS selection rules have already been observed previously in the interaction of carboxylic acids with identical layers of evaporated aluminum used here [33]. Moreover, the higher resolution of RAIRS is allied to the surface sensitivity of HREELS. Furthermore, this vibrational spectroscopy also allows one to prospect the lower frequency spectral domain of energy losses not available in RAIRS due to the limitations of the infrared source and the detection system.

2. EXPERIMENTAL

2.1. Analytical Techniques

The experimental set-up is composed of two coupled ultra-high-vacuum (UHV) chambers, with a base pressure between 10^{-10} and 10^{-11} Torr, equipped with a sample transfer feedthrough and an introduction chamber. Samples can be transferred between the UHV chambers, positioned in one of the two XYZ manipulators mounted in each chamber of analysis and annealed. One of the chambers is provided with an Auger electron spectrometer cylindrical mirror analyzer CMA (Riber OPC 103), a mass spectrometer (Riber AQ156) for the residual gas analysis and KRS5 infrared transparent windows enabling RAIRS measurements with 85° incidence angle. RAIRS spectra were recorded with a resolution of $4\,\mathrm{cm}^{-1}$ and were obtained by averaging 200 scans. Infrared spectroscopy experiments can be done using a Nicolet

Magna-IR 850 FTIR spectrometer provided with a MCT detector (wide band). The second chamber contains a double-pass, high-resolution electron energy loss spectrometer (Leybold-Heraeus ELS 22). Spectral resolution, given by the FWHM of the elastic peak, is of 3 meV ($\sim 24\,\mathrm{cm}^{-1}$) in straightforward beam and around 10 meV in the electron interaction with the sample surface. HREELS spectra were recorded with 6 eV primary energy and in off-specular geometry where impact processes are important. Current intensity measured across the sample was of the order of 10^{-11} A. Angular analysis of the elastic backscattered beam on the samples shows lobes *circa* 20° (FWHM) wide centered around the specular direction.

2.2. Materials and Sample Preparation

2.2.1. Silicon Samples

Intrinsic silicon wafers (100) from Siltronix were firstly rinsed with carbon tetrachloride (Chromanorm, Prolabo) and then treated by the RCA cleaning method [34]. This treatment consists of two oxidation baths. The sample is introduced firstly in a basic peroxide solution $NH_4OH:H_2O_2:H_2O$ (1 : 1 : 5) at 80°C during 10 minutes, rinsed with deionized water (18.2 MΩ.cm) and then reintroduced in an acidic peroxide solution $HCl:H_2O_2:H_2O$ (1 : 1 : 5) during 10 minutes before being again abundantly rinsed with deionized water. As is shown below, this preparation leads to hydroxylated silica surfaces where hydrocarbon contamination is largely reduced.

2.2.2. Aluminium Samples

Evaporated aluminium layers around 1000 Å thick were deposited on glass. The purity of the aluminium used, which was provided by CECM, was 99.999%. The sample was gently rinsed with alcohol and dried with *U*-quality N_2 before being introduced in the UHV. After introduction in the UHV vessel, the samples were sputtered under an argon ion beam with 500 eV incident energy for periods of 5 minutes. The current measured through the sample was around 50 μA. Substrate surface composition was then analyzed by Auger electron spectroscopy through the whole preparation. AES analysis enables one to control the chemical state of the sample, namely, the presence of carbonaceous contamination (KLL peaks located at 278 eV) and oxide (KLL peaks located at 508 eV). Ion sputtering was stopped when no carbon and no oxygen were detected by AES on the substrate surfaces, only presenting metallic aluminium.

In situ oxidation and hydroxylation of the aluminium surfaces were accomplished by exposing the samples to deionized (18.8 MΩcm) water, introduced in the UHV chamber (10^{-6} Torr) through a capillary tube directed towards the sample surface during 30 minutes. This period of time corresponds to a fully-hydroxylated surface, as is shown by AES and HREELS studies, where spectra reveal no evolution for longer exposure periods [35].

2.3. Molecular Interaction

Trivinylethoxysilane was supplied by ABCR and was used without further purification, after being analyzed by transmission infrared spectroscopy to check product purity. *In situ* molecular interaction with TVES was done at 10^{-6} Torr during 30 minutes. In the case of non-reactive surfaces, molecular exposure was prolonged for more than 48 hours.

3. RESULTS AND DISCUSSION

3.1. Substrate Characterization

3.1.1. Silicon Oxide Surface

In order to characterize the substrate before the molecular exposure, silica surfaces were HREELS analyzed. Figure 1 shows the spectra of a silica surface cleaned with solvents (***a***) and that of a sample submitted to the RCA cleaning procedure (***b***).

The characteristic peaks of silica centered at 425 cm^{-1}, 818 cm^{-1} and 1172 cm^{-1}, respectively, dominate both spectra. These values, clearly shifted upwards from the usual infrared frequencies, are in good agreement with those characteristic of a high coverage oxide layer [26]. Some hydrocarbon contamination is revealed through the peak assigned to aliphatic CH stretching (2875 – 2920 cm^{-1}) and deformation modes (1440 cm^{-1}). The RCA cleaning procedure induces a

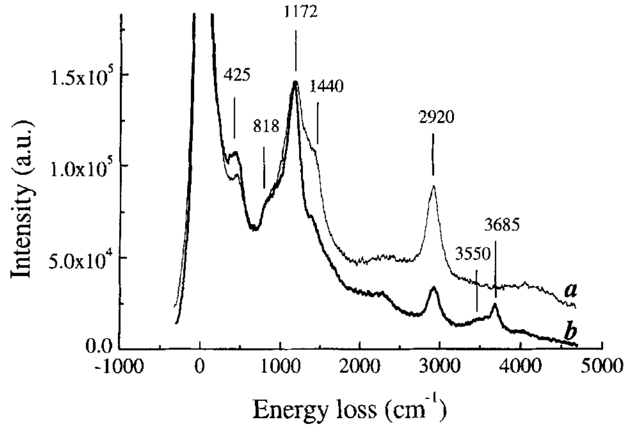

FIGURE 1 HREELS spectra of a silica surface cleaned with solvents (***a***) and a silica surface cleaned with solvents and submitted to the RCA treatment (***b***).

diminishment of the hydrocarbon contamination as can be inferred from the decrease of the intensity of the corresponding peaks. Finally, the RCA treatment also produces hydroxylated surfaces as can also be concluded from the appearance of a characteristic energy loss peak due to OH stretching located at $3685\,cm^{-1}$ with a wide band at lower wavenumber centered at $3550\,cm^{-1}$. The energy losses corresponding to Si—OH stretching modes are also in good agreement with those found in HREELS spectra of hydroxylated silica previously published [27]. The higher frequency component corresponds to free and geminal OH group stretching modes, which are not resolved; the band at lower energy loss is assigned to vicinal OH groups connected to one another by hydrogen bonding [24]. HREELS spectra of silica surfaces annealed under UHV show a modification of the nature and of the surface concentration of hydroxyl groups as was already shown elsewhere [36]. These modifications of the spectra can be explained by a dehydroxylation of the surface through the condensation of vicinal OH groups [24]. Water molecules are then eliminated by the formation of new Si—O—Si bonds.

3.1.2. Aluminium Oxide Surfaces

Figure 2 shows the AES spectra of the aluminium surface as introduced (***a***), after Ar^+ ion beam sputtering (***b***) and exposed to water

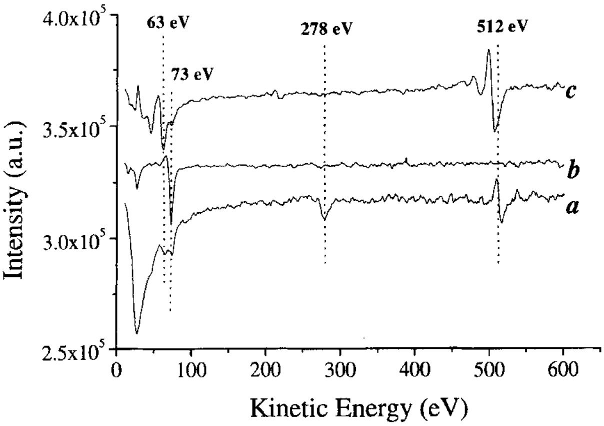

FIGURE 2 Auger spectra of aluminium surfaces: (*a*)–as introduced; (*b*)–after ionic sputtering; (*c*)–after ionic sputtering and water interaction.

after ion beam sputtering (*c*). LVV Auger peaks located at 73 eV and 63 eV are characteristic of aluminium atoms in a metallic and in an oxide environment, respectively. Both peaks exist in spectra of aluminium substrates as introduced in UHV environment. Spectrum (*a*) also shows two peaks at 278 eV and at 508 eV characteristic of carbonaceous contamination and oxygen, respectively, as was referred to above. After Ar^+ ion beam sputtering, spectrum (*b*) reveals the disappearance of the contamination and of the native oxide layer from the surface, as the peaks at 63 eV, 278 eV and 512 eV are absent in (*b*). The characteristic peak of oxygen centered around 508 eV appears and its intensity remains constant, after 30 min of water interaction, attesting to an upper limit of the surface hydroxylation. Concurrently, the characteristic peak of metallic aluminum at 73 eV diminishes dramatically and the intensity of the lower energy peak, at 63 eV, characteristic of aluminium in an oxidized environment, increases. The ratio between these two peaks of aluminium is correlated with the presence of a layer of aluminium oxide about 2 nm thick [35]. At any of these two stages of the surface preparation corresponding to the surface sputtering and to the water exposure, the presence of carbon (278 eV) on the surface was not detected by AES. Rhodin *et al.* [37] have investigated the structural, the electronic and the chemical properties of acid-base sites on alumina thin films as a function of annealing treatments using X-ray and UV photoemission spectroscopy. When done at 300 K, the oxidation process of polycrystalline films by oxygen, or by water, produces an amorphous alumina layer. Following these authors, alumina films prepared at room temperature by exposing aluminium to water in UHV conditions contain *circa* 17% of the surface sites occupied by OH^- groups.

The hydroxylation of aluminium films was followed *in situ* by RAIRS. The hydroxylated samples were then transferred under UHV to the HREELS chamber where they were analyzed. Figure 3 displays the HREELS (***a***) and the RAIRS (***b***) spectra of a hydroxylated aluminium surface. The HREELS spectrum is dominated by a loss of 867 cm^{-1} with a shoulder located at 680 cm^{-1} assigned to subsurface and to top-layer Al—O stretching vibrations [38, 39], respectively. On the other hand, the RAIRS spectrum contains several peaks located at between 650 and 933 cm^{-1} in this same region. We attributed those at 680, 773, 933 and 1070 cm^{-1} to Al—O and Al—OH modes (see Tab. I) [40].

The difference between HREELS and RAIRS spectra can be explained by the different selection rules of each technique. In fact, as was referred to above, HREELS impact mechanisms are dominant, as evidenced by the wide lobes in the intensity angle distributions of the elastically backscattered electrons. In the impact regime, all vibration

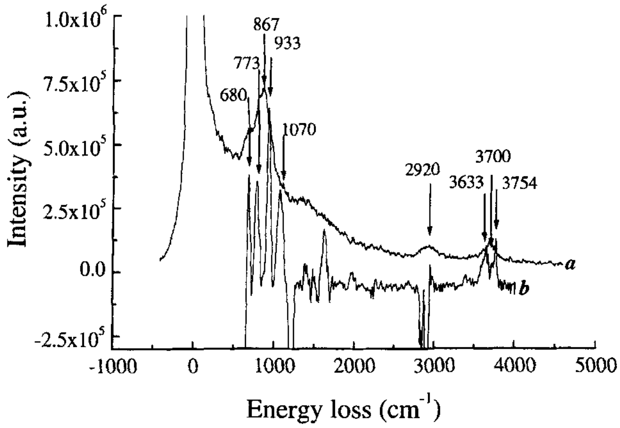

FIGURE 3 Comparison of HREELS (*a*) and RAIRS (*b*) spectra of an hydroxylated aluminium surface.

TABLE I RAIRS and HREELS peak positions and mode assignment for aluminium oxide surfaces

RAIRS wavenumber (cm^{-1})	*HREELS wavenumber* (cm^{-1})	*Assignment*
680 cm^{-1}	680 cm^{-1}	Al—O stretching overlayer oxygen
773 cm^{-1}	–	Al—O stretching
–	867 cm^{-1}	Al—O stretching underlayer oxygen
933 cm^{-1}	–	Al—OH sym. stretching
1070 cm^{-1}	–	
2840 cm^{-1}		C—H sym. stretching
2920 cm^{-1}	2920 cm^{-1}	C—H asym. stretching
3633 cm^{-1}		O—H stretching
	3700 cm^{-1}	O—H stretching
3754 cm^{-1}		O—H stretching

modes present at the surface can be excited by the incident electrons, even Raman-active modes, contrarily to dipole mechanisms where only infrared active modes with dipoles perpendicular to the surface are excited. Therefore, the bands located at 933 cm^{-1} and 1070 cm^{-1} in RAIRS assigned to Al—OH groups and with axes mostly perpendicular to the surface are better observed in RAIRS than in HREELS. Contrarily, the Al—O vibration at 867 cm^{-1} (not necessarily perpendicular to the surface) dominates the HREELS spectrum where the selection rules are not the same. The assignment of these bands is based on the results found in the literature [41]. The presence of the shoulder centered at 1440 cm^{-1} and the bands appearing around 2900 cm^{-1}, evidenced in both spectra of Figure 3, are associated with a slight hydrocarbon contamination on the oxidized aluminum surface. This contamination is not detected by AES, attesting to the higher sensitivity of HREELS, under the impact mechanism, to molecular entities present at the extreme surface of the sample. Around 3700 cm^{-1}, the bands appearing in HREELS and RAIRS spectra are assigned to hydroxyl group stretching modes. These bands correspond to different types of hydroxyls: free and vicinal OH groups [38, 39]. Five different kinds of adsorption sites are cited, depending on the number and on the nature of the neighbor entities. Each of the different OH groups was also identified by the stretching vibration wavenumber. Following the authors cited above, one can conclude that individual OH are excited at wavenumbers higher than 3600 cm^{-1} [38] whereas peaks corresponding to vicinal Al—OH groups are found at lower wavenumbers between 3500 cm^{-1} and 3600 cm^{-1}.

Another discrepancy between HREELS and RAIRS spectra is the presence of negative peaks located around 1220 cm^{-1} and 2900 cm^{-1}. As the peak at 1220 cm^{-1} is not present in HREELS spectra, we conclude that it is not correlated with a chemical modification of the surface occurring during the hydroxylation process. A quite intense absorption already occurs in the single beam background and the appearance of a peak in the spectrum at the same position should be due to an imperfect baseline correction. The other negative peaks appearing at 2900 cm^{-1} correspond to the disappearance of hydrocarbon contamination during the water interaction.

3.2. Molecular Interaction

3.2.1. Silicon Oxide Surfaces

TVES interaction was accomplished by exposing the hydroxylated silica samples to molecule partial pressures of 10^{-5} Torr during two to ten hours at normal temperature. In all cases, molecular adsorption was not detected after the exposure. HREELS spectra before (***a***) and after (***b***) the TVES molecular interaction are presented in Figure 4.

From the similarities of both spectra of Figure 4, one must conclude that TVES molecules were not adsorbed. In particular, the constant intensity of the stretching peaks of the surface hydroxyl groups around 3700 cm^{-1} before and after the molecular exposure attests that they

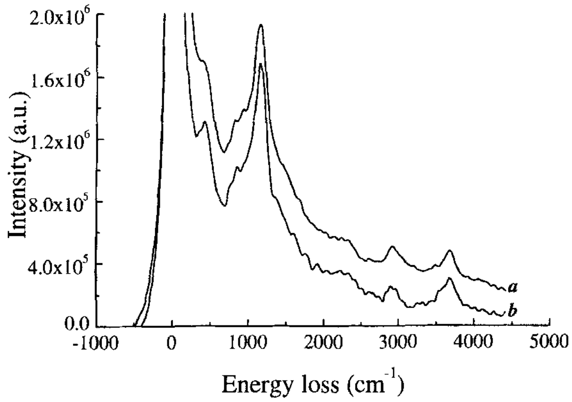

FIGURE 4 HREELS spectra of silica surfaces before (***a***) and after (***b***) TVES interaction.

did not interact with the molecule, contrarily to aluminium oxide as will be shown below.

This result contrasts with those obtained in liquid–solid interaction where alkoxysilanes easily adsorb on silica surfaces [18]. In fact, it is generally admitted that molecular silanols are formed through the reaction of the alkoxysilanes with physisorbed water. Their subsequent adsorption on the solid surface is accomplished through hydrogen bonds of these silanols with surface hydroxyls, followed eventually by dehydratation. This leads to a chemisorption through the formation of siloxane interfacial bonds.

3.2.2. Aluminium Oxide Surfaces

Figure 5 shows HREELS spectra of hydroxylated aluminium surfaces before (***a***) (*cf.* Fig. 3) and after (***b***) TVES interaction.

Notable changes occur after the molecular interaction and specifically:

- a net attenuation of the shoulder at 640 cm^{-1};
- the appearance of an intense contribution centered around 1065 cm^{-1};

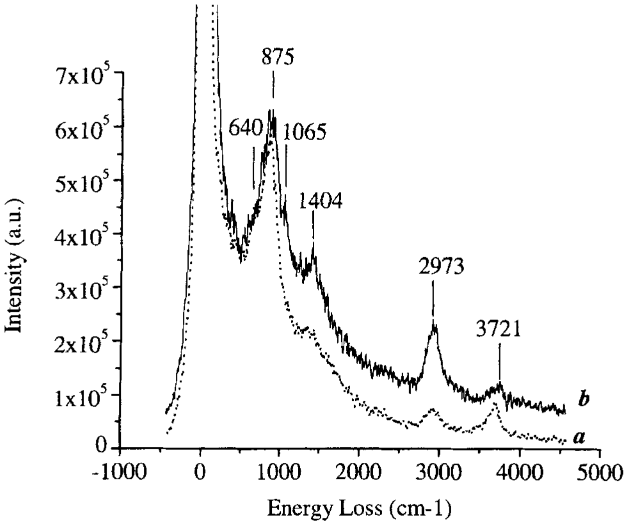

FIGURE 5 HREELS spectra recorded on hydroxylated aluminium surfaces before (***a***) and after (***b***) TVES interaction.

- an intensity increase of CH peaks centered at 1404 and 2960 cm^{-1};
- an intensity decrease in the low-frequency part of the OH peak.

All these changes can be interpreted as a signature of the adsorption of TVES molecules with the hydroxylated alumina surface. In actuality, the surface interaction must involve the on-top Al—O sites of the oxide surface, as the feature located at 640 cm^{-1} decreases in intensity. On the other hand, the appearance of peaks located around 1065, 1404 and 2970 cm^{-1} confirms the presence of TVES hydrocarbon groups on the surface. Finally, the intensity decrease of the feature at 3700 cm^{-1} after the molecule exposure shows that a part of the surface hydroxyls disappeared during the interaction. The perturbation of the surface hydroxyl groups can be a sign of their involvement in the reaction. A detail of the HREELS spectra of Figure 5, in the OH stretching spectral domain, is presented on Figure 6.

The comparison of spectra recorded before (*a*) and after (*b*) TVES interaction confirms that a part of hydroxyl groups disappears from the surface after the molecular interaction. One can also clearly distinguish that the strongest intensity decrease is located towards the wavenumber where free hydroxyl group modes are assigned. This fact translates into a preferential consumption of individual OH groups and their

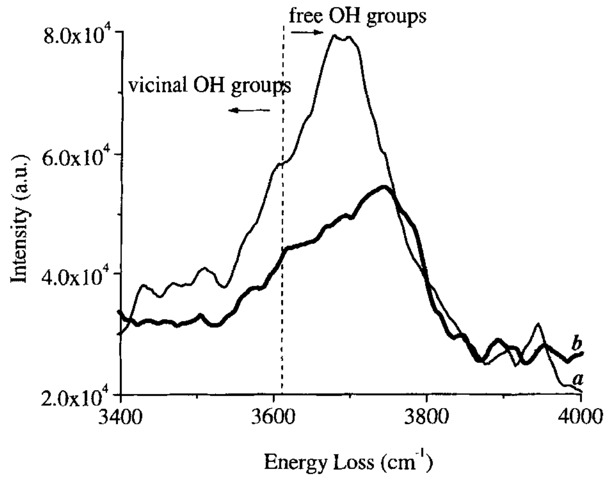

FIGURE 6 HREELS spectra of an aluminium surface before (*a*) and after (*b*) TVES interaction in the spectral domain of the stretching modes of hydroxyl groups.

involvement in the reaction. This conclusion fits well with the study on the interaction of ethoxysilanes with low coverage OH alumina recently published by Yates *et al.* [13].

Comparing with the results presented above for silica surfaces, one should conclude that the probability of the reaction to occur is higher when a TVES molecule meets free OH groups with a stronger Brønsted basic character.

Although the changes observed in HREELS spectra lead to the recognition of a chemisorption of TVES on aluminium oxide, one can have more detailed information about the adsorbed species (see Fig. 7).

Figure 7 compares HREELS and RAIRS spectra of the hydroxylated aluminium surface after TVES interaction. As one can remark, both spectra attest to the disappearance of hydroxyl groups, connected with the presence of the negative peak at 3738 cm^{-1}, and associated with the emergence characteristic peaks of the vinyl group at 3054, 3016, 2942, 1410, 1065 and 938 cm^{-1}. This correlation confirms the adsorption of the TVES molecule on the aluminium surface with the involvement of the overlayer oxygen sites in the reaction. During the molecular grafting, negative peaks respectively located at 2920 and

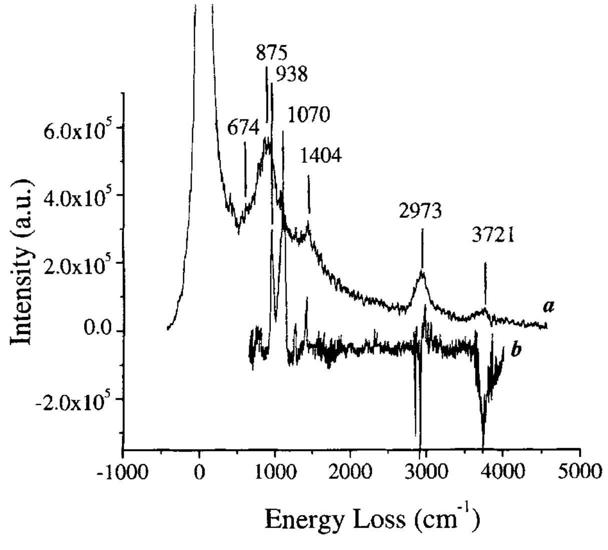

FIGURE 7 Comparison of HREELS (*a*) and RAIRS (*b*) spectra of an hydroxylated aluminium surface after the TVES interaction.

2858 cm^{-1} appear, attesting again to an aliphatic hydrocarbon decontamination of the surface. A consumption of hydroxyl groups is also observed using RAIRS. The negative peak located at 3721 cm^{-1} is mostly high frequency shifted, agreeing well with the HREELS results and those of Yates referred to above [13].

4. CONCLUSIONS

In situ interaction of trivinylethoxysilane (TVES) with oxidized surfaces of silicon and aluminium was investigated at room temperature by high resolution electron energy loss spectroscopy (HREELS) and reflection-absorption infrared spectroscopy (RAIRS). The main conclusions of this comparative study are presented in Schema I.

The inability of silica to react with TVES is explained by the Brønsted acidity of the Si—OH groups present on the surface. In fact, theoretical studies show that the hydroxylated silica surfaces have a Brønsted acidic character, as the adsorption energy of protons (4.8 eV) is much weaker than that of hydroxyl ions (10.3 eV) [25]. As the OH$^-$ ions are strongly bonded to the surface, they are not able to participate in the primary nucleophilic attack of the molecular silicon atom in the silane hydrolysis mechanism, hindering the formation of trivinylsilanol. Notwithstanding, in the case of liquid–solid interaction [36]

Gas-solid interaction TVES/Silicon oxide (Brønsted acid surface)

$(CH_2{=}CH)_3SiOCH_2CH_3 + OH/SiO_2/Si \rightarrow$ *reaction does not occur*

Liquid-solid interaction TVES/Silicon oxide (Brønsted acid surface)

$(CH_2{=}CH)_3SiOCH_2CH_3 + H_2O \rightarrow (CH_2{=}CH)_3SiOH + CH_3CH_2OH$

$(CH_2{=}CH)_3SiOH + OH/SiO_2/Si \rightarrow (CH_2{=}CH)_3SiOSiO_2/Si + H_2O$

Gas-solid interaction TVES/Aluminium oxide (Brønsted basic surface)

$(CH_2{=}CH)_3SiOCH_2CH_3 + OH/Al_2O_3/Al \rightarrow (CH_2{=}CH)_3SiOH + CH_3CH_2OAl_2O_3/Al$

$(CH_2{=}CH)_3SiOH + OH/Al_2O_3/Al \rightarrow (CH_2{=}CH)_3SiOAl_2O_3/Al + H_2O$

SCHEMA I

alkoxy or halogen groups react with the physisorbed water, present on the silica surface, and form intermediary silanols, which easily bind to the surface silanols through hydrogen bonds.

Contrarily to silicon oxide surfaces, the aluminium oxide surfaces contain hydroxyl groups with a marked Brønsted basic character, enabling the formation of the intermediary silanols. These OH groups are able to bind to the surface hydroxyls, as was shown above.

From this work, we deduced that on basic oxide substrates like aluminium oxide, physisorbed water is not necessary to promote the grafting of the silane molecule as is the case for acidic substrates like silicon oxide.

The consumption of surface hydroxyls was here characterized by two different vibrational spectroscopies: RAIRS and HREELS. Both techniques show the disappearance of individual OH groups at 3725 cm^{-1}. Concerning the reaction mechanism, our results suggest that OH surface groups acts as nucleophilic agents in the primary step of the reaction, which agrees with usual mechanisms proposed in the literature for the hydrolysis of ethoxysilanes.

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