

Identification of Surface–TiCl_x Groups on Silica by Raman Spectroscopy

Koen Schrijnemakers,* Pegie Cool, and Etienne F. Vansant

University of Antwerp (UIA), Department of Chemistry, Laboratory of Adsorption and Catalysis, Universiteitsplein 1, 2610 Wilrijk, Belgium

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The reaction of TiCl₄ with the surface of silica gel was studied by Raman spectroscopy. New bands were observed which were attributed to low-frequency vibration modes of attached Ti-species. On the basis of band deconvolution and band integration, a model is proposed to determine the relative contribution of the occurring surface reactions. This new method yields results, which are in good agreement with the previously used techniques based on elemental analysis. However, this method provides both qualitative and quantitative information in a single nondestructive experiment.

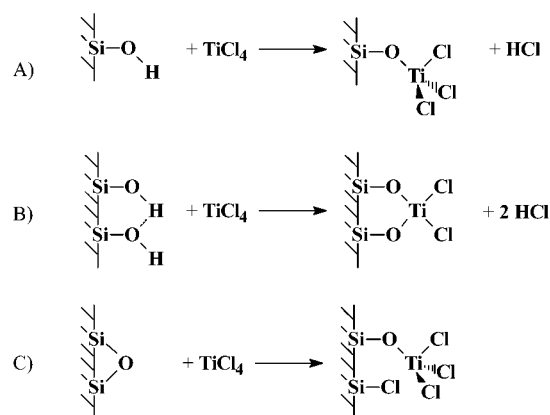
Introduction

TiCl₄ has been used extensively in the past and is still used in the preparation of catalysts by grafting.^{1–7} Generally, the reactions, as depicted in Scheme 1, are considered. TiCl₄ reacts with both isolated and hydrogen-bonded silanol groups on the silica surface leading to the formation of monodentate (reaction A) or bidentate groups (reaction B). The latter species could also be formed by a consecutive reaction in which the attached –TiCl₃ groups react further with neighboring hydroxyl groups. Apart from the reactions with hydroxyl groups, TiCl₄ also reacts with strained siloxane bridges (reaction C).^{8–10} This reaction was questioned by some research groups^{11,12} but was confirmed by us.¹³

The techniques most often used to study this type of reactions are infrared spectroscopy together with elemental analysis. In a few cases Raman spectroscopy and NMR were used. Raman spectroscopy though was used only in a qualitative way,^{14,15} while NMR was used to determine the amount and type of OH groups left after the reaction with TiCl₄.¹² Infrared spectroscopy has the advantage of being highly sensitive. However oxides are strong infrared absorbers, especially in the low frequency region where most of the important vibration modes of the adsorbed species are expected. This means that for transmission spectra a very small amount of sample should be used to avoid saturation of the vibration modes. The commonly used self-supporting disk technique (5–10 mg of SiO₂ per cm²) cannot be used because the disks are opaque to IR radiation below 1300 cm^{–1}. However, Morrow et al.¹⁶ developed the thin film method to avoid saturation in the low wavenumber region. This technique consists of spreading a layer of silica on a transparent window (NaCl, KBr, or CsI) and wiping off the excess so that about 0.1 to 0.2 mg of SiO₂ per cm² remains. This method has been applied successfully to the study of the chemisorption of P(CH₃)₂Cl and TiCl₄ on silica, mostly in a qualitative way.¹⁷ Other techniques such as photoacoustic (PAS) and diffuse reflectance spectroscopy (DRIFT) could also avoid the problem of saturation while at the same time requiring essentially no sample preparation. However, the cutoff is usually situated at higher wavenumbers (around 500 cm^{–1}). Furthermore, in the case of PAS, the signal-to-noise ratio is rather low.

In contrast, oxides are relatively poor Raman scatterers making it possible to study the adsorbed species without

SCHEME 1: Possible Reactions of TiCl₄ with the Silica Surface



interference of the silica support. Moreover, a minimum of sample preparation is required and vibration modes over the entire far and mid infrared region can be detected.

In this paper a method is presented to obtain quantitative information on the occurring surface reactions by deconvolution of the Raman spectra, followed by band integration. This technique has the main advantage of being nondestructive in contrast to the destructive analysis of the Cl and Ti amount. The results obtained with this new method are in good agreement with the method based on the elemental analysis.

Experimental Section

Silica gel (Kieselgel 60 from Merck, $S_{\text{BET}} = 351 \text{ m}^2/\text{g}$, average pore radius $\cong 4 \text{ nm}$) was used as the substrate. It was pretreated at different temperatures (200–700 °C) at ambient pressure prior to the reaction with TiCl₄, to dehydrate and to dehydroxylate the silica surface. After heat treatment the silica was quickly transferred to the sample holder in a N₂ purged glovebox to prevent rehydration. The sample holder was then attached to a flowreactor as described in a previous publication.¹⁸

TiCl₄ (Fluka, >99%) was purified and degassed by several freeze–thaw cycles. The reaction was carried out in vacuum at room temperature. After the reaction, the sample was further evacuated to remove excess TiCl₄ and possible reaction products.

Chlorine was determined argentometrically while titanium was determined spectrophotometrically after quantitative release of the titanium species from the surface by sulfuric acid.

* Corresponding author. E-mail: koen.schrijnemakers@ua.ac.be.

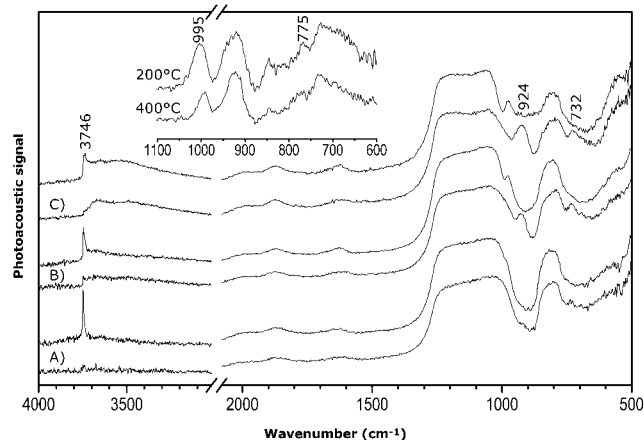


Figure 1. Infrared spectra of silica gel pretreated at different temperatures before and after reaction with TiCl_4 , (A) 700 °C, (B) 400 °C, and (C) 200 °C. The inset shows the difference spectra between the modified and nonmodified silicas pretreated at 200 °C and 400 °C.

IR spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer equipped with a photoacoustic detector. The PA detector is a prototype of the MTEC-100 cell, constructed by J. F. McClelland. The photoacoustic cell was flushed with zeolite-dried helium and the mirror velocity set to 0.16 cm/s.

Raman spectra were recorded on a Nexus 670 bench equipped with a Raman module using a Ge detector. Samples were measured in a 180° scattering configuration using a Nd:YAG laser. Five thousand scans were averaged for each spectrum. When samples were measured again, no significant changes were observed in the spectra, indicating that the TiCl_x species did not decompose in the laser beam under the present conditions. The samples were transferred from the sample holder to a quartz Raman sample cell in a N_2 purged glovebox and sealed in a flame to prevent hydrolysis of the samples during the measurements.

Results and Discussion

When the reaction temperature is kept low (<200 °C), no reaction of HCl , liberated during the reaction of TiCl_4 , with the surface silanol groups occurs. Therefore the Cl/Ti ratio, determined by the elemental analysis, provides a measure of the contributions of the different surface reactions. The contribution of the siloxane reaction can be detected only at high pretreatment temperatures of the silica (≥ 700 °C).¹³ In this case the contribution is still low (9%). At lower pretreatment temperatures, siloxane reaction does not occur and the Cl/Ti ratio yields an easy indication of the amount of mono and bifunctional reaction by the relation:

$$\text{mono} = \text{Cl}_{\text{Ti}} - 2 \quad (\text{A})$$

where mono is the fraction of monofunctional reaction and $\text{di} = 1 - \text{mono}$.

Qualitative Description. Figure 1 represents the infrared spectra (FTIR-PAS) of silica gel pretreated at different temperatures before and after reaction with TiCl_4 at room temperature. For pretreatment temperatures exceeding 500 °C a total disappearance of the silanol band at 3746 cm^{-1} is observed after reaction. New bands are observed at 924 cm^{-1} and at 732 cm^{-1} . The difference spectra reveal two more bands, one around 995 cm^{-1} and one around 775 cm^{-1} . The bands at 924 and 995 cm^{-1} can be assigned to the $\nu(\text{Si}-\text{O})$ of either mono- or bidentate

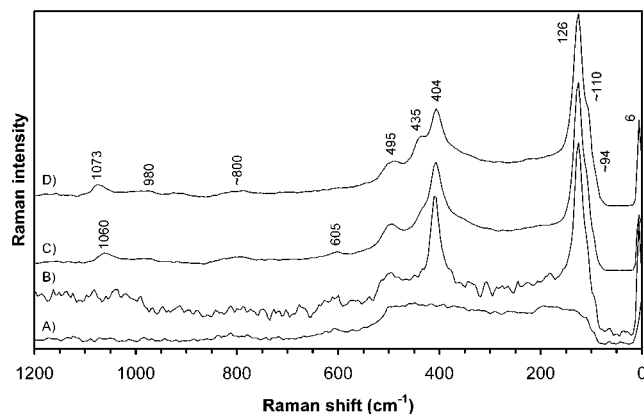


Figure 2. Raman spectra of silica gel pretreated at 500 °C (A) and silica gel pretreated at different temperatures after reaction with TiCl_4 , (B) 700 °C, (C) 400 °C, and (D) 200 °C.

species, while the bands at 732 and 775 cm^{-1} are attributed to $\nu(\text{Ti}-\text{O})$ of the grafted species.¹⁰

In Figure 2 Raman spectra are shown of silica gel reacted with TiCl_4 . Bands around 430, 490, 605, 800, and 980 cm^{-1} are attributed to Raman modes of the silica support.^{19,20} After reaction with silica gel pretreated at 700 °C, new bands are observed in the mid-IR region at 404 and 495 cm^{-1} . For pretreatment temperatures below 700 °C other bands are observed, situated at 435 cm^{-1} and around 1070 cm^{-1} . In the low frequency region, a very strong band at 126 cm^{-1} , two shoulders at 110 and 94 cm^{-1} , and finally a band at 6 cm^{-1} are observed independent of the pretreatment temperature. Both shoulders as well as the band at 6 cm^{-1} have never been observed before. Based on the literature, the strong band at 404 cm^{-1} is assigned to the symmetric $\nu_s(\text{TiCl})$ of a $-\text{TiCl}_3$ group^{14,15} while the band at 435 cm^{-1} is assigned to a similar vibration in $=\text{TiCl}_2$.¹⁵ From the spectra it is therefore clear that at 700 °C no bidentate species are present since no band is observed at a frequency of 435 cm^{-1} , which is expected for bidentate groups. The antisymmetric TiCl_x modes are usually weak in Raman, and are expected around 500 cm^{-1} ,¹⁵ as well as the $\nu_s(\text{Si}-\text{O}-\text{Ti})$.¹⁴ The bands around 1070 cm^{-1} are assigned to silica vibrations perturbed by the presence of Ti ¹⁹ indicating the chemical bonding between TiCl_4 and the silica surface. The low-frequency band at 126 cm^{-1} can be attributed to deformation modes $\delta(\text{Cl}-\text{Ti}-\text{Cl})$ of both $-\text{TiCl}_3$ and $=\text{TiCl}_2$ groups.¹⁴

Tetrahedral TiCl_4 has four distinct vibrational modes and all of them are Raman active. Substitution of one of the chlorine atoms for a surface oxygen atom lowers the local symmetry to C_{3v} , further substitution leads to a local symmetry of C_{2v} , leading to 6 and 9 Raman active vibrational modes, respectively. In addition to the 6 bands for a $-\text{TiCl}_3$ group other vibration modes are expected due to the $\text{Si}-\text{O}-\text{Ti}$ structure, such as a symmetric and antisymmetric $\nu(\text{Si}-\text{O}-\text{Ti})$ vibration and four low-frequency modes such as a TiCl_3 torsion, an in-plane $\text{Si}-\text{O}-\text{Ti}$ bend, an out-of-plane $\equiv\text{Si}-\text{O}-\text{TiCl}_3$ twist, and a $\equiv\text{SiO}-\text{TiCl}_3$ rock.¹⁴ This leads to a total of 12 expected vibration modes. For $=\text{TiCl}_2$ low-frequency TiCl_2 wag, scissor, twist, and rocking modes are expected among many other. A maximum of 15 Raman active vibrations can be expected for the bidentate groups. Since both shoulders (110 and 94 cm^{-1}) and the band at 6 cm^{-1} are also present in the spectrum of the silica pretreated at 700 °C, these bands must be assigned to vibration modes of the $-\text{TiCl}_3$ group. Torsion vibrations are known to have very low frequencies so that the band at 6 cm^{-1} was attributed to the torsion of the heavy $-\text{TiCl}_3$ group.

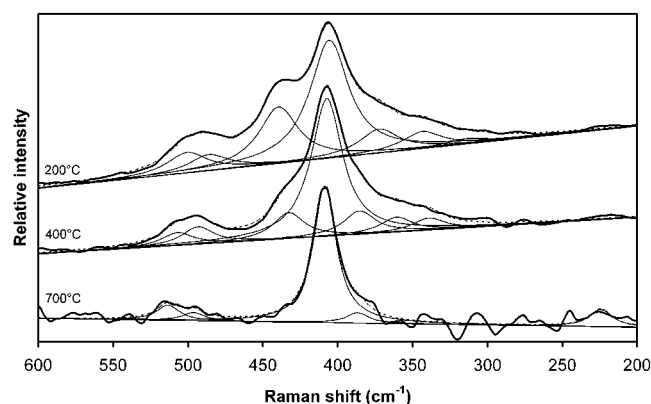


Figure 3. Deconvolution of the Raman spectra shown in Figure 2 in the region 200–600 cm^{-1} .

Quantitative Description. To gain quantitative information from the Raman spectra (Figure 2), the spectra have to be deconvoluted. Especially the bands at 404 and 435 cm^{-1} are of interest because the latter band becomes more and more pronounced with decreasing pretreatment temperature. On the basis of elemental analysis it was found that at lower pretreatment temperatures more bidentate groups were formed,¹³ which would lead to an intensification of the $\nu(\text{TiCl})$ of the corresponding group. Furthermore, it was thought that band integration of the deconvoluted spectra could provide us with the relative contribution of the two occurring reactions.

Since the pure silica did show a background spectrum it had to be subtracted first. The results of the deconvolution are shown in Figure 3. Apart from the bands at 404 and 435 cm^{-1} two bands were found around 495 cm^{-1} , one around 490 cm^{-1} and one around 505 cm^{-1} . As already mentioned above, two vibration modes are expected here. As the wavenumber of the antisymmetric Ti–Cl stretching mode is not expected to change considerably for the series TiCl_x (with $1 \leq x \leq 4$),¹⁷ this band is expected at 505 cm^{-1} . We can therefore attribute the band around 505 cm^{-1} to $\nu_{\text{as}}(\text{TiCl}_x)$. The band around 490 cm^{-1} can then be assigned to $\nu_s(\text{Si–O–Ti})$. At the low-frequency side of the $\nu_s(-\text{TiCl}_3)$ mode more bands are situated as seen in Figure 3. As already mentioned before, many bands are expected upon chemisorption. It is therefore logical to attribute these bands to other vibration modes of both $-\text{TiCl}_3$ and $=\text{TiCl}_2$ groups.

Band integration was carried out to obtain quantitative information. Based on the amount of Ti–Cl bonds per attached Ti group it was assumed that the area of the $\nu_s(-\text{TiCl}_3)$ band was in correlation with 3 times the amount of $-\text{TiCl}_3$ groups while the area of the $\nu_s(=\text{TiCl}_2)$ band was in correlation with 2 times the amount of $=\text{TiCl}_2$ groups. This being accepted, the intensity ratio of the band at 404 cm^{-1} to the band at 435 cm^{-1} can be translated into a ratio of the number of mono- to bidentate groups and the contribution of the monofunctional reaction can be calculated. The contribution of the monofunctional reaction calculated from elemental analysis as well as from the new method based on band deconvolution and integration is presented in Table 1.

It is clear from this table that at higher pretreatment temperatures TiCl_4 reacts progressively more via a monofunctional reaction and that the obtained results are in good agreement with the results obtained by elemental analysis. It should be pointed out that when the Cl/Ti ratio cannot be used to obtain information on the reaction mechanism, such as in the case of a reaction with HCl or a direct chlorination of the silica surface at high reaction temperatures, the method based on Raman spectroscopy still gives good contributions of the occurring

TABLE 1: Relative Contribution of Mono Functional Reaction Based on Elemental Analysis and Raman Deconvolution as a Function of the Silica Pretreatment Temperature

pretreatment temperature/ $^{\circ}\text{C}$	intensity ratio ^a	% mono (deconvolution)	% mono (elem. analysis)
200	2.1 ± 0.2	58 ± 5	51 ± 2
400	5.3 ± 0.3	78 ± 5	85 ± 4
700	∞	100 ± 4	99 ± 6

^a The intensity ratio is defined as the ratio of the integration value of the band at 404 cm^{-1} to the band at 435 cm^{-1} .

surface reactions since the method is not based on the total concentration of Cl and Ti but on Raman bands of the species caused by the actual reactions. As the reaction of TiCl_4 with other pure silica materials such as mesoporous molecular sieves MCM-41, MCM-48, HMS, etc., are similar to the reactions on silica gel, the method described herein will also be applicable to these materials.

Conclusions

The Raman spectroscopic study of the reaction of TiCl_4 with the silica surface leads to the detection of previously undiscovered vibration modes of attached species. Moreover, quantitative information on the relative contribution of the occurring reactions can be obtained from the same experiment by deconvolution and band integration. The results were in good agreement with those obtained by elemental analysis.

The technique is nondestructive, requires essentially no sample preparation and permits the analysis of the highly hydrophilic $-\text{TiCl}_x$ species.

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