JOURNAL OF Materials CHEMISTRY

Action of silylating agents on a chrysotile surface and subsequent reactions with 2-pyridine and 2-thiophene carbaldehydes

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Received 22nd September 1998, Accepted 11th March 1999

Chrysotile fibres have been modified in two distinct steps: first, the fibers were aminated with silylating agents such as 3-aminopropyltrimethoxysilane or *N*-[3-(trimethoxysilyl)propyl]ethylenediamine to give the products denoted CRI1 and CRI2, respectively. In the second step, these matrices reacted readily with 2-pyridine and 2-thiophene carbaldehydes to form C=N bonds, characteristic of a Schiff base. All immobilized materials were characterized by elemental analysis, IR spectroscopy, thermogravimetry, solid state ^{29}Si NMR, surface area measurements and X-ray diffractometry. Nitrogen elemental analysis indicated the presence of 1.20 and 2.87 mmol g^{-1} of pendant groups on CRI1 and CRI2 surfaces, respectively. The experimental C/N ratios are 3.14, 2.90, 3.14 and 4.49 for modified materials CRI1L^1, CRI1L^2, CRI2L^1 and CRI2L^2, respectively. These results are in agreement with the yields of the successive reaction steps. The original chrysotile structure was maintained for the aminated modified surfaces. The surface area of prepared materials decreased with functionalization to values of <5.0 m^2 g^{-1}. All matrices obtained from reaction with aldehydes showed a C=N band at 1636 cm^{-1}, which is related to Schiff bond formation. Products derived from the reaction with pyridine carbaldehyde showed bands associated with aromatic and aliphatic C–H stretching bands at 3050 and 2930 cm^{-1}, respectively and pairs of bands at 1590, 1570 and 1470, 1436 cm^{-1} are attributed to aromatic ν(C=C). These results indicate that the silylating agents are covalently bonded to the chrysotile surface.

Introduction

Natural chrysotile, also known as white asbestos, is a typical hydrated magnesium silicate, one of a class of compounds which belongs to the serpentine group of minerals. Based on its elemental composition, the empirical formula was established as $Mg_3Si_2O_5(OH)_4$. From the structural point of view, the inorganic constitution can be described as a planar hexagonal network formed by tetrahedral silica (tridimite), which is supported by octahedral layers of magnesium hydroxide, in the well known inorganic brucite like structure. The lattice parameters of the brucite layer are greater than those found for the corresponding tridimite, resulting in an appreciable mismatch between the two layers.[1] This latter arrangement favours the development of a rolled sheet or concentric tube structure, with the tetrahedral silicate anion located inside the fibre layer. Upon leaching successively with acidic solutions, the brucitic layers can be solubilized, leaving under extreme conditions a pure silica framework, as illustrated in Fig. 1.

Asbestos fibres are used as fillers in several industrial fabrications for a variety of materials such as cement, plastics and papers, for adsorption of toxic compounds or as a support for catalysis.[1–4] However, an expansion has been recently to enzyme or microorganism immobilizations.[5–7] Interest in these new materials in many applications by using unprocessed or modified inorganic materials has grown in recent times[8] as illustrated by silica gel, which is used as a support for chemically bonded stationary phases for chromatography,[9] as a support for catalysts and for use in pre-concentration of sorbents.[10,11]

The utility of asbestos fibres in many academic or technological applications has been contested, mainly due to some possible biologically dangerous effects. It has been repeatedly demonstrated that one of the factors responsible for the biological activity of the fibres is its chemical structure, in particular related to the reactivity of the mineral surface.[12–15] Taking into account its development for possible useful applications and to control the biological effects of chrysotile, investigation of the surface reactivity of this mineral has recently received great attention.[12–15]

Asbestos fibres have been chemically modified with various reagents such as $POCl_3$,[16,17] $TiCl_3$,[18] aromatic hydrocarbons[19–21] and organosilanes.[22] However, all these modification processes occurred in a single step. The present report describes chemical modification of chrysotile fibres by two distinct steps, a procedure which has been extensively applied to other surfaces, such as silica gel.[23] In the first stage, the fibres are reacted with aminated organosilanes, and then the anchored pendant species are reacted with the aldehydic function of the desired molecule for anchoring on the surface.

Based on the structure of chrysotile, the available Mg–OH groups on its surface can interact with the silylating agents 3-aminopropyltrimethoxysilane and *N*-[3-(trimethoxysilyl)propyl]ethylenediamine, similarly as observed for silanol groups disposed on silica gel surfaces, to produce new matrices. In this investigation 2-pyridine or 2-thiophene carbaldehydes reacted directly with the immobilized precursors to produce Schiff bases. These new anchored matrices or their derived forms arising from the reduction of the C=N bonds of the Schiff bases contain basic nitrogen and sulfur centres. A potential applicability can be related to the property of the resulting chelating moieties in extracting cations from aqueous or non-aqueous solutions, as observed for anchored silica gel surfaces.[24]

Experimental

Materials

Chrysotile samples 7ML (fiber length <2.0 mm) were supplied by the SAMA mine, Uruaçu, Goiás, Brazil, and had composition $SiO_2:Al_2O_3:MgO:Fe_2O_3:H_2O$ of 42.5; 1.12; 38.2; 4.05, 14.13 wt%, respectively. The samples were initially degassed at 393 K for 8 h under vacuum. With the exception of ethanol, all other chemical grade reagents were not further purified. The alkoxysilanes 3-aminopropyltrimethoxysilane (Aldrich)

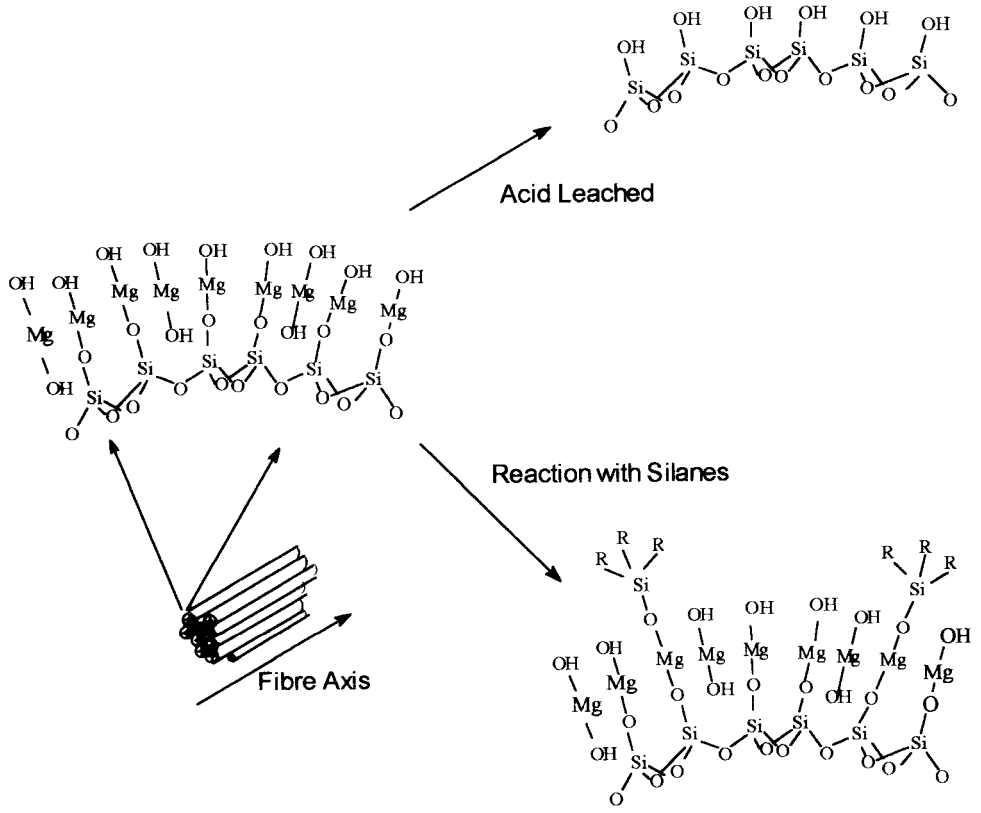

Fig. 1 Crystal structure and morphology of fibrous chrysotile and illustrations of surface modifications.

and *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (Fluka) were used in the anchoring processes. 2-Pyridine carbaldehyde and 2-thiophene carbaldehydes were purified by vacuum distillation.

Instrumentation

X-Ray powder patterns were obtained with nickel-filtered Cu-Kα radiation on a Shimadzu model XD3A diffractometer. IR spectra were obtained in a Perkin-Elmer model 1600 FTIR spectrophotometer, using the KBr pressed pellet technique. Thermal analysis was performed using a DuPont model 1090B thermogravimetric apparatus coupled with a thermobalance 951 heated to 1273 K at a heating rate of 0.16 K s^{-1} in dry nitrogen atmosphere. The samples varied in weight from 15.0 to 30.0 mg. The surface area measurements were made on a Flowsorb II 2300 Micromeritcs instrument and the areas were determined by using the BET equation. Carbon, nitrogen, sulfur and hydrogen contents were determined using a Perkin-Elmer Pe-2400 microelemental analyser. NMR spectra were obtained on AC 300/P Bruker spectrometers at room temperature. The HPDEC technique was employed with a pulse repetition rate of 10 s, splitting rate of 4 kHz, pulse width of 45° and aquisition time of 0.06 s.

Synthesis

Samples of chrysotile were initially washed under a strong water flow on a sieve of 0.0062 mm for 10 min and then the material was dried at 393 K for 12 h. The process of activation was performed by heating the samples at 393 K for 2 days *in vacuo*. In a typical procedure, 5.0 g of activated asbestos was treated with 5.0 cm^3 of 3-aminopropyltrimethoxysilane **1** or *N*-[3-(trimethoxysilyl)propyl]ethylenediamine **2** in xylene. The suspension was refluxed under an atmosphere of nitrogen at 353 K for 7 days with mechanical stirring. After cooling the mixture, the fibres were filtered off, washed with a large volume of ethanol and dried *in vacuo* for 8 h at 353 K, to produce matrices CRI1 or CRI2. The degree of functionalization was determined by the nitrogen content as determined by the Kjeldahl method.

To complete the reaction, in the next stage, samples of the aminated surfaces were suspended in xylene under a gaseous nitrogen atmosphere at 353 K and mechanically stirred and 2-pyridine carbaldehyde (L^1) or 2-thiophene carbaldehyde (L^2) dissolved in xylene was added. These reaction systems were left for another 5 days. The products CRI1L^1, CRI1L^2, CRI2L^1 and CRI2L^2 were filtered, washed with ethanol and dried *in vacuo* for 8 h at 353 K. Some of the products were treated with an aqueous solution of sodium borohydrate for 10 h. The reduced matrices are denoted CRI1L^1 (red), CRI1L^2 (red), CRI2L^1 (red) and CRI2L^2 (red).

Results and discussion

The hydroxyl groups distributed on the surface activated chrysotile are sensitive to chemical interaction with silylating agents, this behaviour resembling that found for silica gel owing to the similarity of both surfaces. The elemental analysis of the modified surfaces presented in Table 1 supports the fact

Table 1 Percentages (%) of hydrogen, carbon, nitrogen and sulfur; expected (calculated) C/N and N/S ratios are also given. Surface area *A* of chrysotile (CRI0) and chemically modified crysotiles CRI*X* (*X*= 1, 2), and the respective aldehydic derivative forms CRI1L^n and CRI2L^n (n=1, 2)

Matrix	H	C	N	S	C/N	N/S	A/m^2 g^{-1}
CRI0							14.2±0.2
CRI1	1.85	5.705	1.68		3.38 (3.0)		4.3±0.5
CRI2	3.93	17.19	8.02		2.14 (2.5)		0.8±0.5
CRI1L^1	1.42	9.48	3.01		3.14 (4.5)		3.6±0.1
CRI1L^2	1.20	8.72	2.73	1.94	2.90 (3.2)	1.00 (1.1)	4.7±0.2
CRI2L^1	4.34	32.13	10.2		3.14 (3.7)		1.7±0.1
CRI2L^2	4.54	29.61	6.6	6.67	4.49 (4.5)	2.00 (2.0)	3.5±0.1

that immobilization was effective. The carbon, hydrogen and nitrogen contents are larger in CRI2 than in CRI1 accord with the organic chain length of the silylating agents. This same behaviour is reflected in the subsequent reactions, where the starting CRI1 surface produced $CRI1L^1$ and $CRI1L^2$, the nitrogen and carbon content of which was increased considerably. In following the same procedure from CRI2 another two surfaces $CRI2L^n$ ($n=1$, 2) were obtained.

From the C/N ratios listed in Table 1, the calculated values are in fairly good agreement with the experimental ones, with the highest discrepancy occurring for $CRI1L^1$. In this case, the low value could be attributed to the remaining aminated groups of the CRI1 matrix, which did not react with the carbaldehyde L^1. On the other hand, for both CRI2 surfaces the calculated C/N ratio was in agreement with the participation of all the NH_2 groups of the immobilized silyls to form the Schiff base. Low C/N ratios may be due to the difficulty of the aldehyde to access some of the internal nitrogens of the pendant groups. This type of basic centre distributed on the pendant groups is prone to some steric hindrance and consequently, restrains the effective volume of the aldehyde chain. The obtained N/S ratios for $CRI1L^2$ and $CRI2L^2$ are 1.09 and 2.03, respectively. These values are in agreement that just one nitrogen participating in bonding with the aldehyde group in both cases. The elemental analysis data also suggest that there is 1.20 and 2.87 mmol g^{-1} of nitrogen pendant groups on CRI1 and CRI2, respectively. These values illustrate the effectiveness of the reaction to give CRI2, which covalently bonds twice as many silylating groups as the reaction. The degree of immobilization surpasses that obtained with silica gel,[24,25] which is of the order of 1.0 mmol g^{-1}. These results suggest that chrysotile can potentially be used as a good inorganic support for anchoring processes. The proposed structures for these matrices are illustrated in Fig. 2.

Thermogravimetry of the original chrysotile sample showed a total mass loss of 13.5% whereas the products showed an increase in mass loss of 19.0, 25.5 and 23.0% for CRI1, $CRI1L^1$ and $CRI1L^2$ and 25.5, 40.0 and 39.0% for CRI2, $CRI2L^1$ and $CRI2L^2$, respectively. A complete set of curves are shown in Fig. 3. The increase in mass loss is reflected in the degree of functionalization of these matrices and these values are in agreement with the elemental analysis results.

The derivative thermogravimetric curve (DTG) for crysotile is shown in Fig. 4(a) and the curves for the corresponding modified materials are also shown in Fig. 4(b)–(d). The

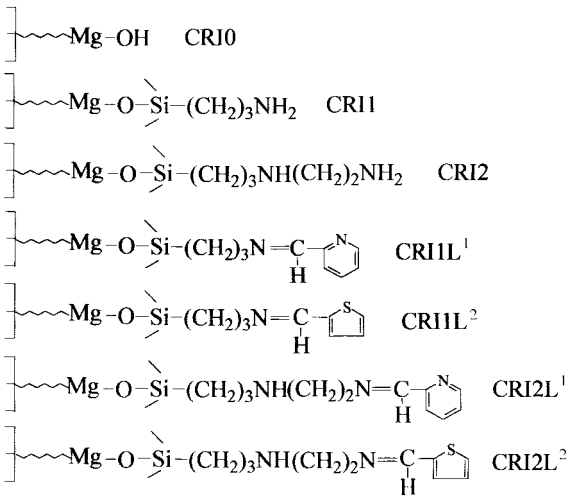

Fig. 2 Representation of chrysotile (a) (CRI0) and immobilized molecules on fibers: (b) aminopropyl (CRI1), (c) propylethylenediamine (CRI2), (d) propyl-2-pyridinaldimine ($CRI1L^1$), (e) propyl-2-thiophenaldimine ($CRI1L^2$), (f) ethylpropylamine-2-pyridinaldimine ($CRI2L^1$), (g) ethylpropylamine-2-thiophenaldimine ($CRI2L^2$).

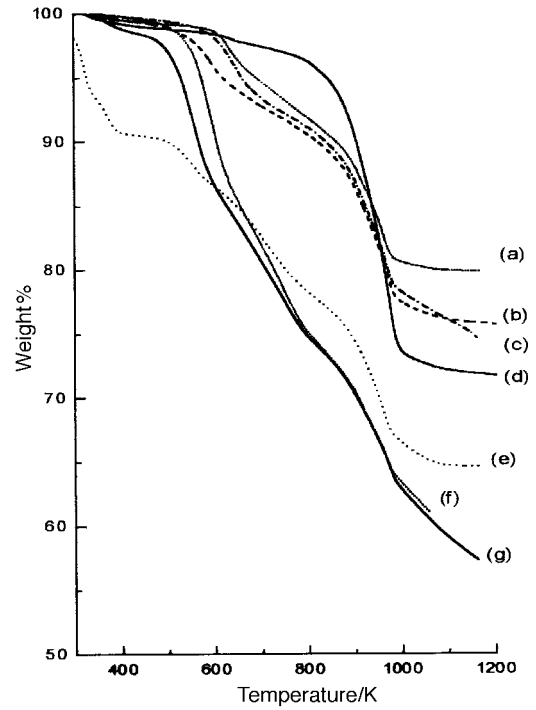

Fig. 3 Thermogravimetric curves of (a) CRI0, (b) CRI1, (c) $CRI1L^1$, (d) $CRI1L^2$, (e) CRI2, (f) $CRI2L^2$ and (g) $CRI2L^1$.

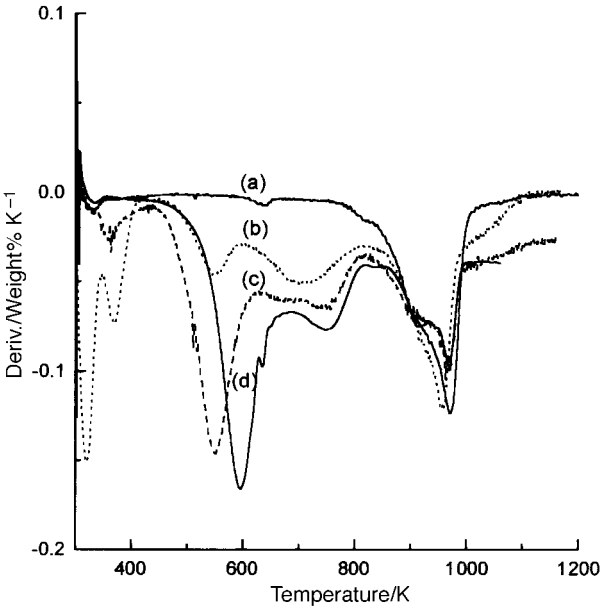

Fig. 4 DTG curves of (a) CRI0, (b) CRI2, (c) $CRI2L^1$ and (d) $CRI2L^2$.

thermal decomposition of chrysotile [Fig. 4(a)] from room temperature to 523 K is associated with the loss of adsorbed water.[26–29] The hydroxy groups bonded to magnesium, corresponding to the brucite-like structure, started to release water near 673 K. However, the dehydroxylation of the remaining Mg–OH groups continues up to 873 K, showing a maximum at 973 K, with a total mass loss of 13.0%. The final anhydrous product resulting from this decomposition is amorphous. This residue underwent two distinct processes at 1083 K: (i) crystallization resulting from an exothermic transformation to give the forsterite structure and (ii) formation of amorphous silica. An enstatite like structure is formed above 1273 K.[26–29]

The derivative curves for the CRI1 and CRI2 matrices showed two main peaks at 320 and 373 K, which are associated to the release of different water molecules bonded to the

immobilized compounds. CRI2, CRI2L[1] and CRI2L[2] showed two peaks with maxima between 400 and 800 K, as shown in Fig. 4(b)–(d), which can be attributed to the loss of the organic fraction bonded to the matrices. For CRI1 two peaks were observed with maxima at 630 and 826 K. However, CRI1L[1] and CRI1L[2] showed peaks related to decomposition at temperatures 50 K higher than the first peak for CRI2L^n ($n=1$ and 2). These data indicated that the thermal degradation of the matrix CRI2 and its corresponding derivatives may involve more complex reactions, however, those processes occur more readily and commence at lower temperature.

X-Ray diffractograms showed that chrysotile presents an interlamellar distance of 743 pm, as illustrated in Fig. 5 and 6. This original distance increased by *ca.* 30 pm after immobilization, however, the crystallinity of all products suggested that ordered structures were maintained.

One important contribution to the understanding of the distribution of the groups on a surface comes from the ^{29}Si solid state NMR spectra as shown in Fig. 7. The spectrum of the original chrysotile showed a peak at δ −92.8, which is attributed to isolated silanol groups that are present in the internal tridimite layer.[30] The reaction of chrysotile with alkoxysilanes led to the appearance of peaks, depending on the manner in which alkoxysilanes can be bonded, *i.e.* mono-, bi- or tri-dentate forms on the surface.[31–33] In principle, these species are expected to have chemical shifts between δ −49.8 to −50.5, −57 to −58 and −65 to −67, respectively. The collected data corroborated with the fact that silicon is bonded to the surface in bi- or tri-dentate forms, while no evidence of the monodentate form was observed. On the other hand, peaks related to silanol groups continued to be observed. Taking into account the intensity of these peaks, for spectra obtained under identical conditions, there is some indication that the amounts of the original silanol groups are larger than those resulting from the hydrolysis of the alkoxide groups, which originate from the silylating agent. Defined side bands are identified at δ −24.74 and −160.9.

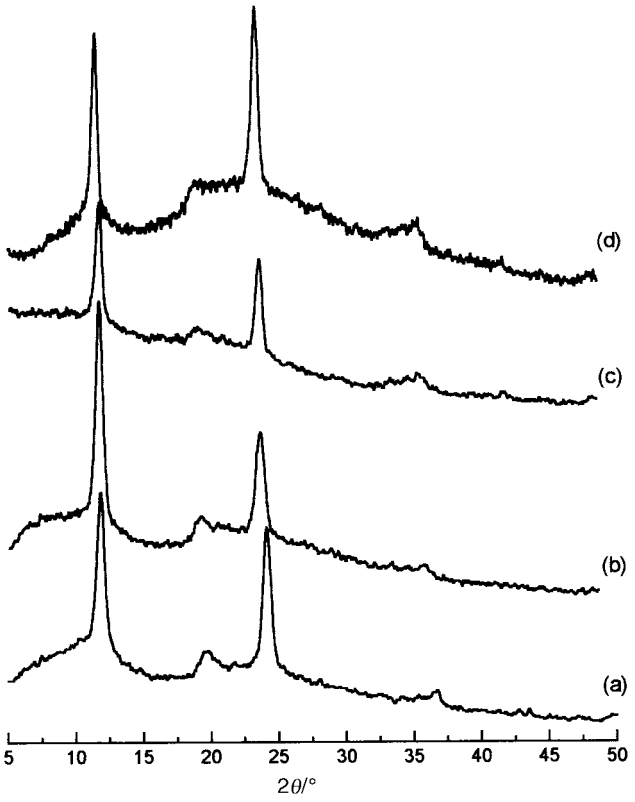

Fig. 5 XRD patterns of (a) CRI0, (b) CRI1, (c) CRI1L[1] and (d) CRI1L[2].

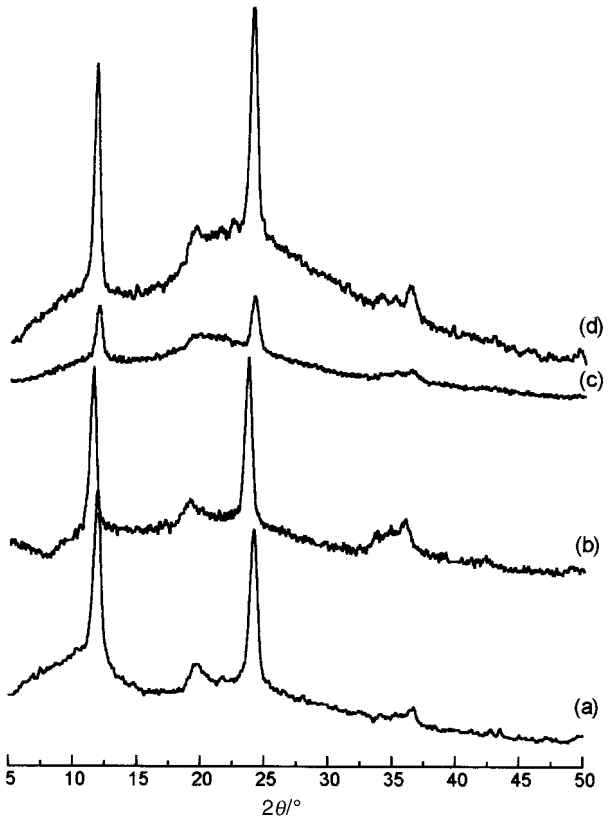

Fig. 6 XRD patterns of (a) CRI0, (b) CRI2, (c) CRI2L[1] and (d) CRI2L[2].

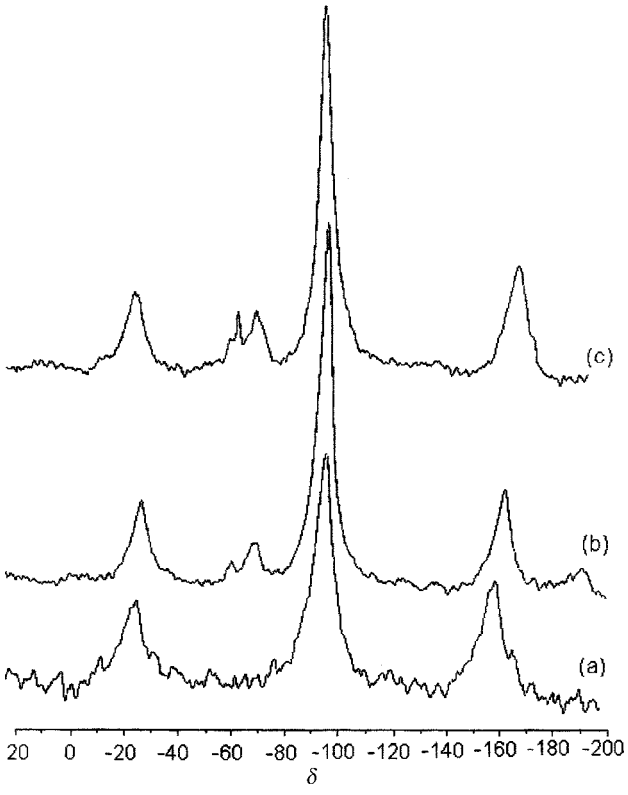

Fig. 7 ^{29}Si NMR spectra of (a) CRI0, (b) CRI2 and (c) CRI1.

IR spectra are shown in Fig. 8 and 9. The IR spectrum of chrysotile presents bands at 3690 and 3650 cm^{-1}, which are attributed to Mg–OH, stretching frequencies. The former is due to free hydroxy groups and the latter is related to hydroxy groups located inside of the structure.[26,34–37] The molar ratio

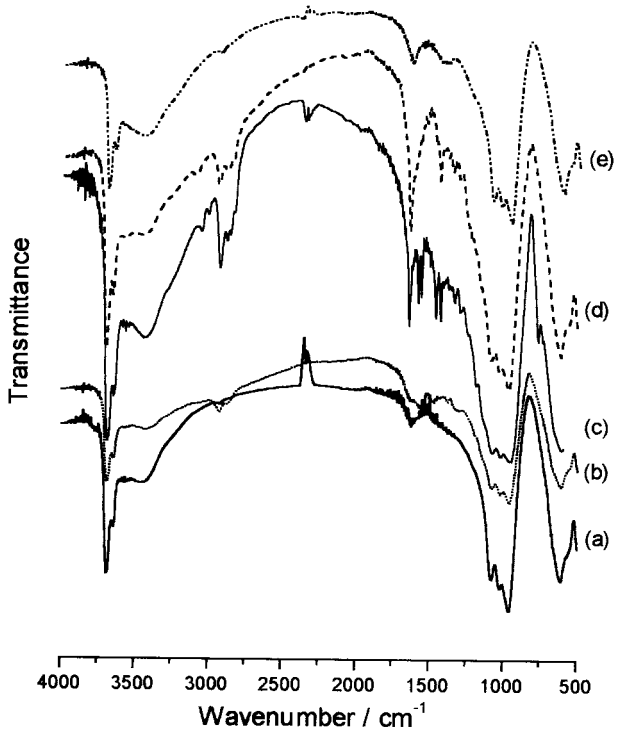

Fig. 8 IR spectra of (a) CRI0, (b) CRI1, (c) CRI1L[1], (d) CRI1L[2] and (e) CRI1L[2] (red).

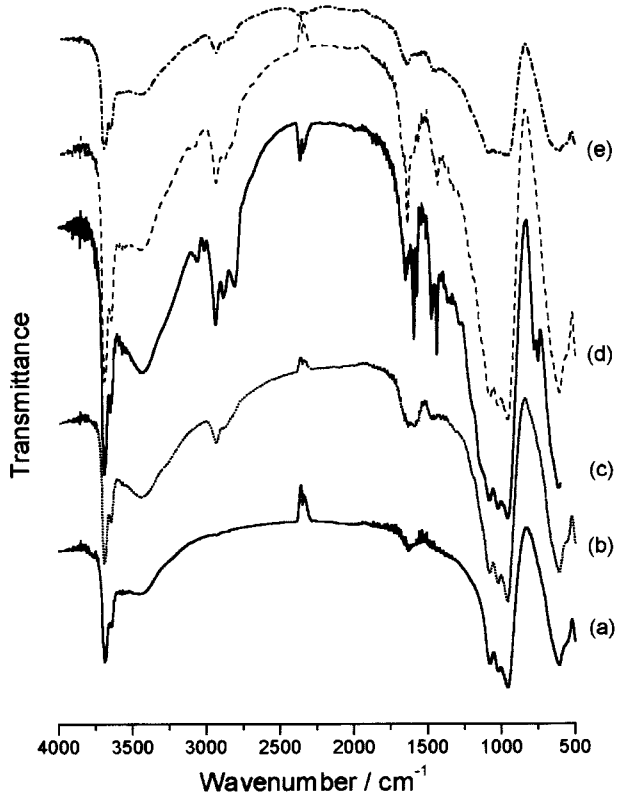

Fig. 9 IR spectra of (a) CRI0, (b) CRI2, (c) CRI2L[1], (d) CRI2L[2] and (e) CRI2L[2] (red).

between internal and external OH groups was established as 3:1, but the internal ones may undergo condensation on heating,[26] causing a disappearance at temperatures above 833 K. Such groups are at low concentration and not very accessible to interaction with external reagents. A set of three other important bands appear 1075, 1015 and 950 cm^{-1}, which are attributed to Si–O–Si vibration modes. For the matrices CRI1 and CRI2, new bands occur at 2930 cm^{-1}, attributed to the aliphatic C–H stretching frequency mode. Again, in these spectra the same set of three bands associated with the Si–O–Si group appear but with different intensities. However the reaction with 2-pyridine carbaldehyde led to a change in spectra. Thus, the IR spectra of the products CRI1L[1] and CRI2L[1] showed bands associated to aromatic and aliphatic C–H stretching bands at 3050 and 2930 cm^{-1}, respectively. The pairs of bands at 1590 and 1570; and 1470 and 1436 cm^{-1} are attributed to aromatic C=C stretching band frequencies expected to appear between 1600 and 1475 cm^{-1}, however, the conjugation effect of the ring with the C=N double bond leads to shifts of these bands to lower frequencies.[38,39] The sharp middle band at 1650 cm^{-1} is attributed to the C=N vibration mode and the low intensity band at 766 cm^{-1} is another indication of the presence of the pyridinic ring. Both matrices CRI1L[2] and CRI2L[2] showed a C=N band at 1636 cm^{-1} related to Schiff bond formation.

The expected absorption of the C=C group of the ring and the C–H stretching frequency for C=CH were not observed, owing to the low concentration of these groups in the thiophene ring. The absorption related to the C–S–C group is absent from the IR spectra, owing to symmetry considerations.[38,39] After reducing the Schiff bases by chemical treatment with sodium borohydrate, the spectra showed the absence of C=N bands (Fig. 8 and 9).

The collected results of surface areas of these matrices show a decrease in values after functionalization. The original area of chrysotile (14.2 ± 0.2 m^2 g^{-1}) decreased drastically with surface modification, as indicated in Table 1. This series of values is also a confirmation of the high efficiency on functionalization. The same behaviour was also observed in other surface modifications with silylating agents, where the reduction in area is attributed to the presence of pendant groups that hinder the access of the nitrogen to the surface during measurements.[40] This fact can be explained by considering the obstructing effect of the anchored groups, following a degree of surface coverage.

Conclusion

The differences in the spectroscopic determinations of pure chrysotile and functionalized chrysotile clearly demonstrate that the matrix products have organo derivatives strongly attached to the inorganic backbone and not merely physically adsorbed to the fibres. All observations indicated that the silylating agents are covalently bonded to the surface. The sequence of reactions with the aldehydes was shown to be very effective, as indicated by Schiff base formation and then further reduction.

The two step reaction sequence opens a route for immobilizing desired molecules on the chrysotile surface. This procedure could be useful to produce new materials with diverse properties of the original inorganic support, and basic centres attached through chemical reactions can be also explored, for example, in chelating cations from aqueous and non-aqueous solutions.

The authors are indebted to FAPESP for financial support and to CNPq and CAPES-PICD for fellowships.

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Paper 8/07383J