

GRAFTING OF KAOLIN WITH TRIFUNCTIONAL SILANES

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Abstract

Silane-grafted-kaolin was synthesized by using octadecyltrichlorosilane, octyltrichlorosilane and phenyltrichlorosilane. These different silanes used have a prominent effect on the mechanism of the condensation reactions with the clay. The NMR spectroscopy indicated that there are various bonding possibilities of the trichlorosilanes molecules with the kaolin surface. The increase in the relative intensity of Q^3 and the appearance of Q^2 , T^3 , T^2 and T^1 signals clearly indicates the grafting of silane molecules to kaolin surface silanol groups. The same successful graft of silanes was demonstrated by the appearance of characteristic absorption bands in the range of 2800-3000 cm^{-1} in the FTIR spectra, assigned to the C-H stretching and bending vibration.

Keywords: ^{13}C CP/MAS NMR, grafting, ^{29}Si CP/MAS NMR, kaolin.

Résumé

Le greffage du kaolin par des silanes a été synthétisé en utilisant l'octadécyltrichlorosilane, l'octyltrichlorosilane et le phényltrichlorosilane. Ces différents silanes utilisés ont un effet important sur le mécanisme des réactions de condensation avec l'argile. La spectroscopie RMN a indiquée qu'il existe différentes possibilités de liaisons entre les molécules des trichlorosilanes et la surface du kaolin. En effet l'augmentation de l'intensité relative du pic Q^3 et l'apparition de signaux Q^2 , T^3 , T^2 et T^1 indiquent clairement le greffage de molécules de silane sur les groupements silanols situés à la surface du kaolin. La réussite du greffage des silanes a été confirmé par l'apparition de bandes d'absorption en FTIR entre 2800-3000 cm^{-1} caractéristiques des vibrations d'élongations et déformations de la liaison C-H.

Mots clés : ^{13}C CP/MAS RMN, greffage, ^{29}Si CP/MAS RMN, kaolin.

1. INTRODUCTION

In recent years, the chemical modification of silica surface found increasing interest [1],[2]. The covalent grafting of organic units on inorganic surfaces has become a field of great interest for researchers due to its multiple applications such as chromatographic properties of solid supports[3], thin film optics [4] , chemical sensors [5],[6] , microelectronics [7] , supported catalysts[8],[9] and DNA chips[10]. All of them giving great importance nowadays.

Treatments with reactive silanes are among the major methods of modification used to convert silicas into materials carrying covalently

bonded functional groups [11],[12] , then the reaction of trifunctional organosilanes was reported for a large number of inorganic substrates[13],[14].

The presence of silanol groups at the surface onto silica takes a possibility for silanes grafting, the surface properties differ from one silica to another [15],[16]. Grafting of silanes in montmorillonite has been studied and characterized by He and al [17].

This paper reports on the grafting of trichlorosilane onto kaolin surface. The functionalized clay has been characterized with different techniques such as Fourier transform infrared spectroscopy (FTIR), ^{13}C , ^{27}Al and ^{29}Si

nuclear magic resonance spectroscopy and X-ray diffraction.

Many studies have demonstrated that the interaction between hydrophobic molecules and clay surfaces could be greatly enhanced by simple grafting of hydrophobic groups onto the clay surfaces [18],[19]. Then hydrophobic clays also may be used at various industrial applications such as elaboration of ceramic membranes for separation.

2. EXPERIMENTAL

2.1. Materials

Surface modification of kaolin was conducted using octadecyltrichlorosilane [$\text{CH}_3\text{-(CH}_2\text{)}_{17}\text{-SiCl}_3$] (coded as C18), octyltrichlorosilane [$\text{CH}_3\text{-(CH}_2\text{)}_7\text{-SiCl}_3$] (coded as C8) and phenyltrichlorosilane [$\text{C}_6\text{H}_5\text{-SiCl}_3$] (coded as C6), they were purchased from fluka-Germany. Organic solvents used in the present study are: Tetrahydrofuran, methanol they were provided by Merck (Darmstadt, Germany) and carbon tetrachloride supplied by Panreac (Barcelona, Spain). All chemicals were used as received. The clay used in the present study is a kaolin Codex (notes as K-O), it was recommended by the L.P.M Cerina (Laboratoire des Plantes Medicinales, Tunisia). Its chemical composition is given in Table1.

Table 1: chemical composition of kaolin (wt %)

oxides	wt %
SiO ₂	45,39
Al ₂ O ₃	36,39
Fe ₂ O ₃	1,03
TiO ₂	0,49
CaO	0,89
MgO	0,53
K ₂ O	1,03
Na ₂ O	0,1
L,O,I	14,15

2.2. Grafting process

A quantity of 0.5g of kaolin was first dried at 200°C for 3 hours, then introduced into 5 ml of silane, and it was agitated in open air at room temperature. After 24hours 15ml of carbon tetrachloride was added then agitated for 15 min.

The react product was filtered and washed using different organic solvents which should be used in the following order: carbon

tetrachloride, tetrahydrofuran, methanol, methanol/water (50% methanol volume), methanol and tetrahydrofuran.

The resulting product was placed in a sealed container for characterization; the grafted products prepared from K-O are denoted K-C18, K-C8, and K-C6.

2.3. Characterization

In order to explore the surface reactions, the grafted kaolin was analyzed using the following methods:

Fourier transforms infrared (FTIR) spectra by the KBr method using an IR spectrometer [Perkin-Elmer spectrum BX]. The spectra were collected for each measurement over the spectral range 400-4000 cm^{-1} with a resolution of 4 cm^{-1} .

X-ray powder diffraction (XRD) measurements were performed at room temperature on a Siemens D5000 Diffractometer operating with a copper cathode Cu-K α ($\lambda = 1.5406 \text{ \AA}$).

The grafted kaolin was characterized by high-resolution solid-state NMR using a Bruker WB300 spectrometer operating at a B₀ of 7.01Tesla, corresponding to a tuning frequency of 75.5MHz for ¹³C, 59.6 MHz for ²⁹Si and 78.2 MHz for ²⁷Al.

Samples were spun in zirconia rotors. CP-MAS sequence was used for both nuclei (²⁹Si and ¹³C) with the following parameters:

- For ²⁹Si CP sequence, protons $\pi/2$ pulse length is 2 μs , contact time is 11ms and recycle time is 5 s. For ¹³C CP sequence, protons $\pi/2$ pulse length is 3 μs , contact time is 11ms and repetition time is 5 s.
- The sample spinning frequencies were of 8 kHz.
- All ²⁹Si and ¹³C resonances were referenced to tetramethylsilane (TMS).

Zg-MAS sequence was used for ²⁷Al at speed of 8 kHz with a short pulse of 6 μs and its recycle time was 1s. The chemical shifts were referenced using an aqueous solution of AlCl₃.6H₂O.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the kaolin. It contains kaolinite as the principal mineral. Quartz and illite are minor components in this clay.

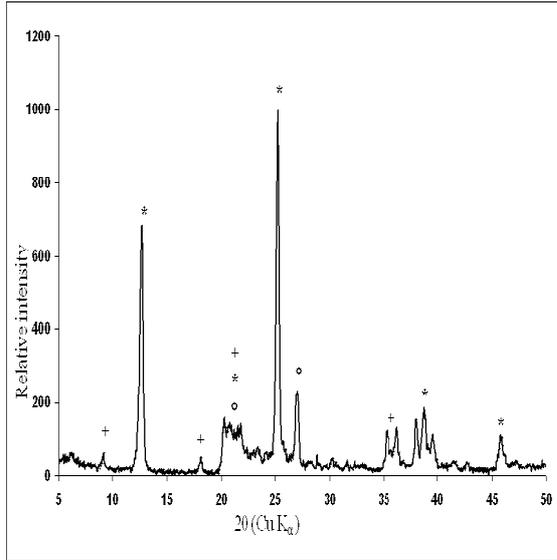


Figure 1. XRD patterns of kaolin (* = kaolinite; ° = Quartz; + = illite).

In order to predict the possible interactions between clay minerals and silanes, it is necessary to take into account the structure and the surface chemistry of kaolin. The main mineral constituent of the kaolin is the kaolinite, this last is a phyllosilicate composed of a silica tetrahedral layer $[\text{Si}_2\text{O}_5]^{2-}$ and an octahedral hydroxide layer $[\text{Al}_2(\text{OH})_4]^{2+}$. At the surface, the structure terminates in either siloxane group ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) with the oxygen atom on the surface, or one of the several forms of silanol groups shown in Fig. 2.

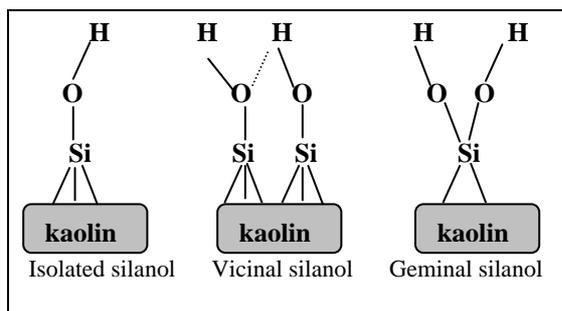


Figure 2. Forms of silanol groups on kaolin surface.

The silanol groups could be isolated (free silanol groups), bridged (vicinal silanol) or geminal. In the literature [20],[21], many studies have shown that hydroxyl groups on the silica surface, resulting from hydrolysis act as active

sites in the grafting reaction between silane and silica.

• *Reaction chemistry:*

The silane compounds readily react with the surface hydroxyl group of the inorganic support [22]. In the case of trichlorosilanes, due to the highly reactive trichloro-head group ($\text{R}-\text{SiCl}_3$), the reaction takes place at room temperature exposed to free air. According to the literature, the silane molecules are first hydrolyzed by the trace quantities of water present either on the surface of the support or in the solvent followed by formation of a covalent bond with the surface [23]. The reaction rate can be enhanced by the addition of water resulting in the formation of silanol groups of silane.

The reaction mechanisms of trichlorosilanes with the surface hydroxyl groups are shown in Fig. 3.

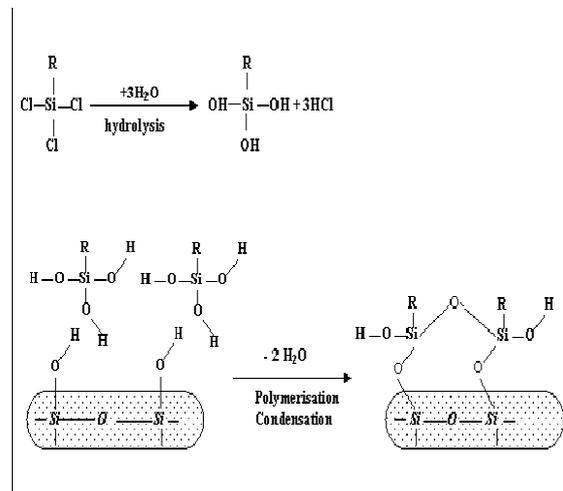


Figure 3. Reaction mechanisms of the trichlorosilane molecules with the surface hydroxyl groups. Other possible structures formed by the trichlorosilane are shown in fig. 6.

The formation of covalent bonds between the silanol groups of kaolin and hydrolyzed trichlorosilanes can be studied by different characterization methods.

^{29}Si CP/MAS NMR spectrum provides supporting evidence for the silylation of silane onto the kaolin surface. ^{29}Si CP/MAS NMR spectrum of K-0 (Fig. 4) displays two signals at -91.52 and -107.56 ppm, corresponding to $\text{Q}^3[\text{Si}(\text{OSi})_3\text{OM}]$ (M stands for Al, Mg, etc.) and $\text{Q}^4[\text{Si}(\text{OSi})_4]$ respectively [24]. The former is characteristic of Si atoms in layered silicates, while the latter relates to Si atoms in quartz, which is an impurity in the kaolin.

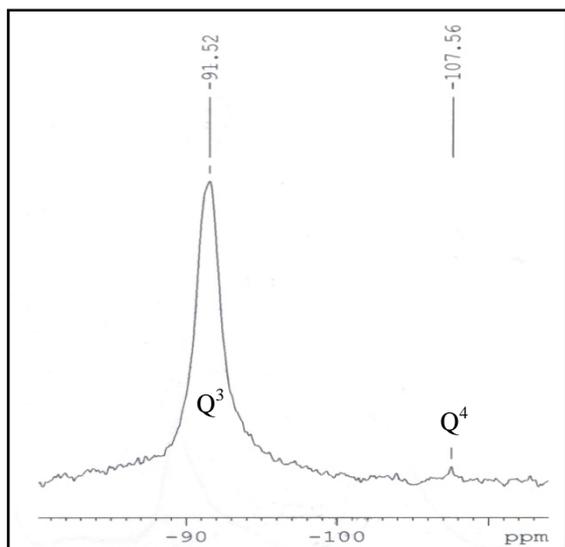


Figure 4. ²⁹Si CP/MAS NMR spectrum of K-0.

After grafting, three additional ²⁹Si signals at -67.72, -58.13 and -47.96 ppm are recorded in the ²⁹Si CP/MAS NMR spectrum of K-C8 (Fig. 5). These signals correspond to the units of T³, T² and T¹ respectively [18]-[25],[26],[27] (Fig.6). This demonstrates the successful grafting of octyltrichlorosilane onto the kaolin surface. We note a signal of Q³ units displaced at -85.33 ppm attributed to isolated silanol groups which are present at the silicate sheet edges probably due to the hydrolysis reaction in the kaolin surface.

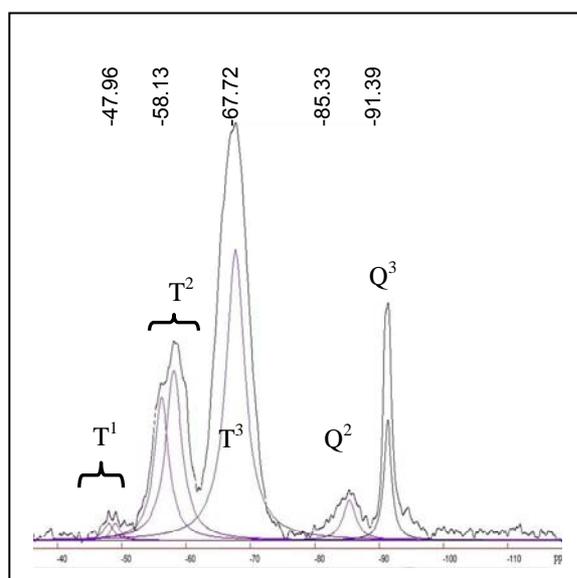


Figure 5. ²⁹Si CP/MAS NMR spectrum of kaolin grafted with octyltrichlorosilane (K-C8).

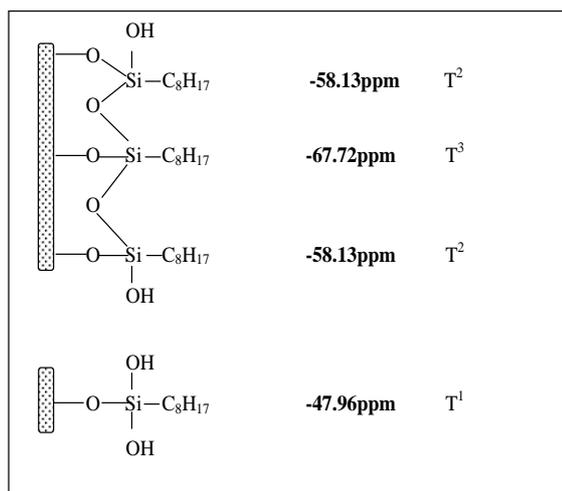


Figure 6. Units of T³; T² and T¹.

We also performed ¹³C NMR measurement on the same kaolin grafted with octyltrichlorosilane (Fig. 7).

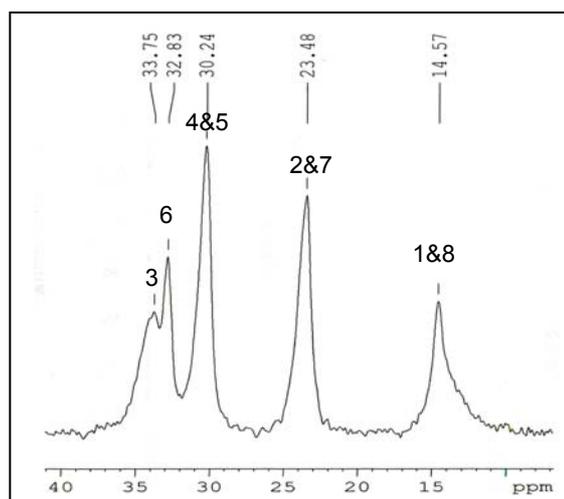


Figure 7. ¹³C MAS NMR spectrum of kaolin grafted with octyltrichlorosilane (K-C8)

The obtained spectrum presents five lines corresponding to the inequivalent carbon sites on the molecule grafted on the kaolin surface. The latter molecule has the following form (Fig. 8):

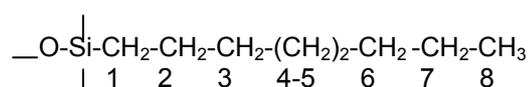


Figure 8. The form of octyltrichlorosilane molecule

According to the literature [28] . we attribute the line at 14.57 ppm to the C_(1&8) carbons and

the line at 23.48 ppm to the $C_{(2&7)}$ ones. The resonance at 30.24 ppm is assigned to the $C_{(4&5)}$ carbons; the line at 32.83 ppm is due to $C_{(6)}$ carbons and the line at 33.75 ppm to $C_{(3)}$ carbons.

The same results were found using octadecyltrichlorosilane as a grafting agent (Fig. 9). But there is no signal of isolated silanol groups in the ^{29}Si CP/MAS NMR spectrum of K-C18. The weaker signal intensity of the Q^3 units suggested that majority of Si (Q^3) have been reacted with the trichlorosilane.

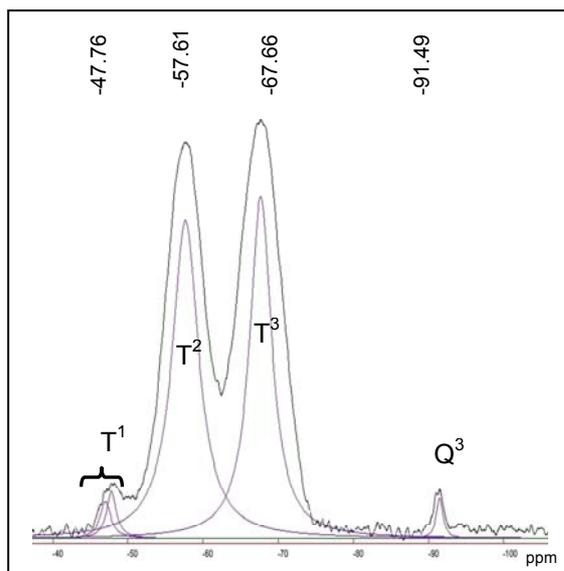


Figure 9. ^{29}Si CP/MAS NMR spectrum of kaolin grafted with octadecyltrichlorosilane (K-C18).

The same sample has been characterized by ^{13}C MAS NMR (Fig. 10), the obtained spectrum presents three lines at 14.72, 24.50 and 33.32 ppm which we attribute to the $C_{(18&1)}$, $C_{(2&17)}$ and $C_{(3-16)}$ carbons respectively [29].

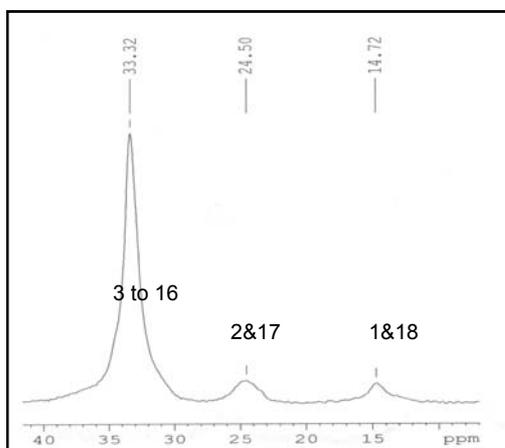


Figure 10. ^{13}C MAS NMR spectrum of kaolin grafted with octadecyltrichlorosilane (K-C18).

The latter molecule has the following form (Fig. 11):

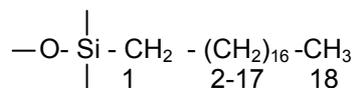


Figure 11. The form of octadecyltrichlorosilane molecule.

Fig. 12 shows ^{29}Si CP/MAS NMR spectrum of kaolin grafted by the phenyltrichlorosilane. Four lines appear at -91.3, -79.44, -70.37, and -62.50 ppm. We attributed these lines respectively to Q^3 , T^3 , T^2 and T^1 . The observed signals for K-C6 in the present case (T^1 , T^2 and T^3) compared to signals recorded in K-C8 and K-C18 evidence that the aromatic silane is more effectively silylated on the kaolin surface. Roshchina et al [30], reported similar results for silanol groups on the silica surface modified with phenyltrichlorosilane accompanied by an additional treatment with N,N-dimethyltrimethylsilylamine made it possible to screen the surface silanol group almost completely.

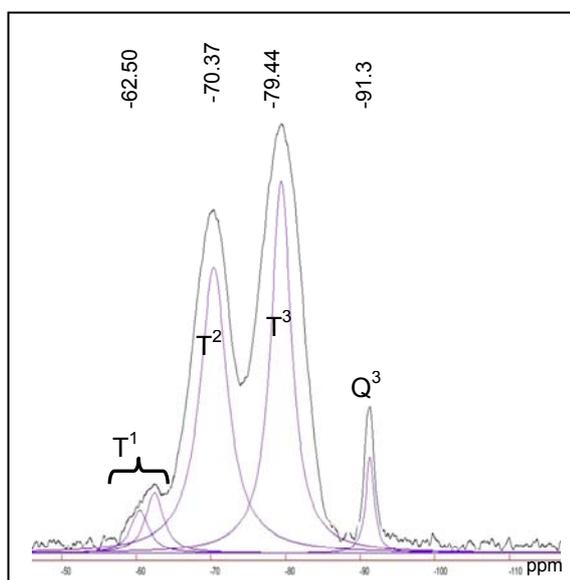


Figure 12. ^{29}Si CP/MAS NMR spectrum of kaolin grafted with phenyltrichlorosilane (K-C6).

We also performed ^{13}C MAS NMR measurement on the same kaolin grafted with phenyltrichlorosilane sample. The obtained spectrum (Fig. 13) presents a group of aromatic

peaks which appears in the range 125-135 ppm. In the silica surface where the phenyl ring is grafted, the following assignments can be made. The signal at 130 ppm corresponds to the carbon atom bonded to the silica; the ortho-carbon atoms are found at 134 ppm and the meta-carbons at 127 ppm; the para-carbon atoms appears as a shoulder at approximately 129 ppm [31]. It demonstrated the successful grafting of phenyltrichlorosilane onto the kaolin surface.

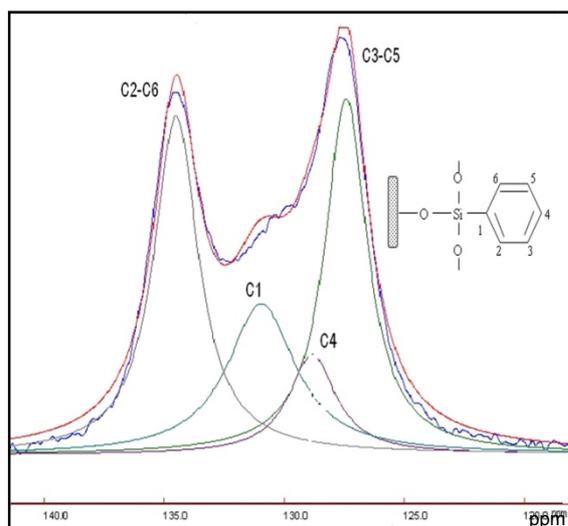


Figure 13. ^{13}C MAS NMR spectrum of kaolin grafted with phenyltrichlorosilane (K-C6).

Fig. 14 shows ^{27}Al MAS NMR spectrum of kaolin before and after grafting with trifunctional silanes, it presents a weaker peak at 68 ppm attributed to tetrahedral Al atoms and another one at -3.5 ppm which can be caused by octahedral Al sites.

This shows that the chemical environment around Al on the surface of kaolin is not altered by the grafting of the silane molecules.

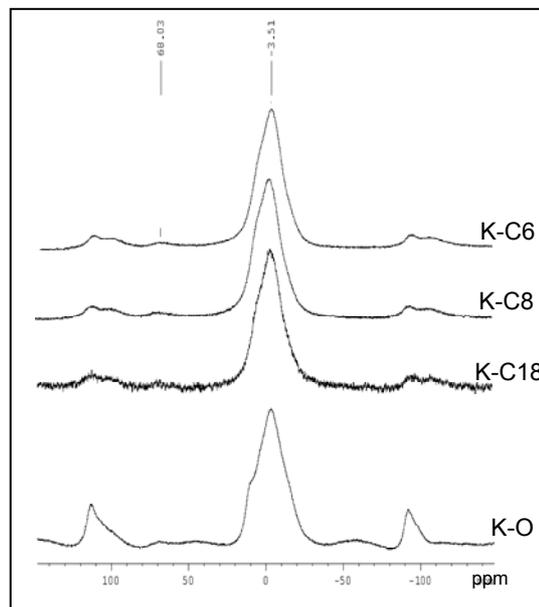


Figure 14. ^{27}Al MAS NMR spectrum of K-O, K-C18, K-C8 and K-C6.

Fig. 15 displayed the FTIR spectra of K-O, K-C18, K-C8, and K-C6, the assignments of FTIR data are represented in Table 2

Table 2: Assignments of FTIR bands for K-O, K-C18, K-C8, and K-C6

Assignment	characteristic wavenumber (cm^{-1})			
	K-O	K-C18	K-C8	K-C6
hydroxyl O-H str	3622,3695	3622,3696	3622,3697	3620,3695
Si-O-Si str	1031, 1106	1030, 1113	1030, 1111	1031, 1110
Al-O str	538	536	537	538
Si-O bend	469	468	467	464
Si-OH str	916	912	913	912
aliphatic C-H str	/	2852, 2921	2856, 2926	/
aromatic C-H str	/	/	/	3050
aliphatic C-H bend	/	1467	1464	/
aromatic C-H bend	/	/	/	1433
C=C aromatic	/	/	/	1569

Fig. 15 shows the FTIR spectrum of the kaolin before and after grafting with the different trichlorosilanes. The bands observed can be allotted in agreement with information available in the literature on silica. After grafting, additional bands are clearly observed in the range of 2800-3000 cm^{-1} , assignable to the C-H stretching vibration. Then at 1460 cm^{-1} , we also note absorption band of C-H bending vibration, these peaks are attributable to $-\text{CH}_3$ or $-\text{CH}_2$ group vibrations. These results show good consistency with the solid-state ^{13}C NMR results and confirm the successful graft of silane onto the kaolin surface. Our results are similar to those of Dai and Huang (1999). At the same time the intensity of the absorption bands of (OH) decreased significantly but still remained, indicating that a limited number of silanol groups were replaced with silane molecules, due to the fairly large surface area of the kaolin.

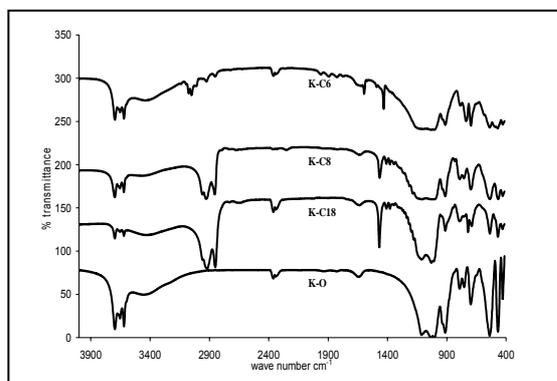


Figure 15 IR spectra of K-O, K-C18, K-C8 and K-C6.

The XRD methods were employed to study kaolinite order that provides an approximation of the real structure. kaolinite order is influenced by many factors such as stacking layer disorder, cation distribution disorder, non-plane layer structure etc.

The XRD patterns of the kaolin before and after grafting are shown in Fig. 16. This analysis indicates that after the grafting reaction we note a decrease of the (001) and (002) reflections of the K-O corresponding to the kaolinite; it gives good explanation, indicating that most of silane molecules have been grafted onto kaolin surface. This conclusion supports our proposal about the grafting of organic molecules onto kaolin surface based on the NMR and IR spectra.

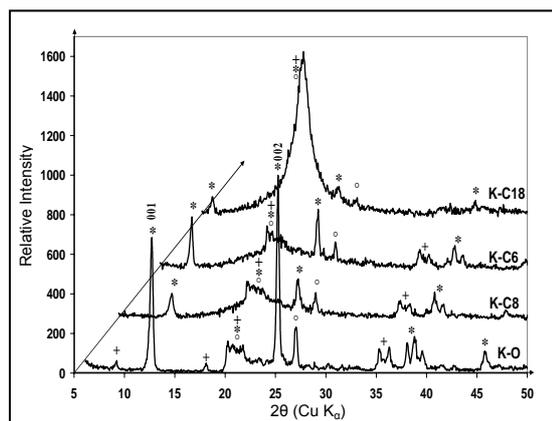


Figure 16. XRD patterns of the kaolin before and after grafting (* = kaolinite; ° = Quartz; + = illite).

4. CONCLUSION

In summary, our present study demonstrates that the grafting of trifunctional silanes on kaolin surface was realized successfully. We report on high-resolution CP/MAS solid-state NMR experiments that were used to investigate the grafting reaction, the different arrangement of silane molecules in the kaolin surface results in the various T^n and Q^n units. This was confirmed by IR analysis showing appearance of new peaks in the range of 2800-3000 cm^{-1} that correspond to $-\text{CH}$ asymmetric and symmetric stretching indicating the presence of the silane on the kaolin surface.

REFERENCES

- [1] O.Y. kwon, K.W. Park, The Preparation of Flaky Layered Carbon by Using Layered Silicate Template, Bull. Korean chem. Soc.vol. 24, (2003), p. 1561.
- [2] P.H. Thiesen, K. Beneke, G.J. Jagaly, Silylation of a crystalline silicic acid: an MAS NMR and porosity study, chem. Mater.vol. 12, (2002), p. 3010.
- [3] J.J. Pesek, Proceedings of the Symposium on chemically Modified oxide surface, ed. D.E. Leyden, W.T. Collins (Eds), Gordon & Breach, New York 1990.
- [4] C. Bubeck, A. Laschewsky, D. Lupo, D. Neher, P. Ottenbreit, W. Paulus, W. Prass, H.

- Ringsdorf, G. Wegner, Amphiphilic Dyes for Nonlinear Optics: Dependence of Second Harmonic Generation on Functional Group Substitution, *Adv. Mater.*vol. 3, (1991), p. 54.
- [5] I. Willner, E. Katz, Integration of layered redox-proteins and conductive supports for bioelectronic applications, *Angew. Chem., Int. Ed.*vol. 39, (2000), pp.1180–1218.
- [6] P. Cléchet, N. Jaffrezic-Renault, C. Martelet, Sensitization of dielectric surfaces by chemical grafting. Application to ISFETs and ENFETs, *Chemical Sensor Technology*, ed. S. Yamauchi, Kodansha. Tokyo.vol. 4, (1992), pp.205–225.
- [7] N.L. Jeon, P.G. Clem, D.A. Payne, R.G. Nuzzo, A Monolayer-Based Lift-Off Process for Patterning Chemical Vapor Deposition Copper Thin Films, *Langmuir*.vol.12,(1996),p. 5350.
- [8] M.A. Harmer, Q. Sun, M.J. Michalczyk , Z.J. Yang, Unique silane modified perfluorosulfonic acids as versatile reagents for new solid acid catalysts,*Chem. Commun* (1997),p. 1803.
- [9] A. Cauvel, G. Renard, D. Brunel, Monoglyceride Synthesis by Heterogeneous Catalysis Using MCM-41 Type Silicas Functionalized with Amino Groups, *J. Org. Chem.*vol. 62,(1997),p 749.
- [10] S.L. Beaucage, Strategies in the preparation of DNA oligonucleotide arrays for diagnostic applications, *C. Med, Chem.*vol. 8, (2001), pp.1213–1244.
- [11] K.K.Unger, Porous Silica, Its Properties and Use as Support in Column Liquid Chromatography, *Journal of Chromatography Library*, Elsevier, Amsterdam. Vol.16, 1977.
- [12] A. Vidal, E. Papirer, A.P. Legrand, *The Surface Properties of Silicas*, Wiley. New York. 1999.
- [13] A. Ulman, Formation and Structure of Self-Assembled Monolayers ,*Chem. Rev.* Vol.96, (1996),p. 1533.
- [14] R. Maoz, J. Sagiv, On the formation and structure of self-assembling monolayers I. A comparative ATR-wettability study of Langmuir-Blodgett and adsorbed films on flat substrates and glass microbeads, *J. Colloid Interface Sci.*vol. 100, (1984),p. 465.
- [15] R.K. Iler, *the Chemistry of Silica*, Wiley. New York. 1979.
- [16] A.P. Legrand, *the Surface Properties of Silicas*, Wiley. Chichester. 1998.
- [17] H. He, J. Duchet, J. Galy , J.F. Gerard, Grafting of Swelling Clay Materials with 3-aminopropyltriethoxysilane ,*J. Colloid Interface Sci.* Vol.288, (2005),pp. 171-176.
- [18] N.N. Herrera, J.M. Letoffe, J.L. Putaux, L. David, E. Bourgeat-Lami, Aqueous dispersions of silane-functionalized laponite clay platelets: A first step toward the elaboration of water-based polymer/clay nanocomposites, *Langmuir*.vol. 20, (2004), pp.1564-1571.
- [19] M. Park, I.K. Shim, E.Y. Jung, J.H. Choy, Modification of external surface of laponite by silane grafting, *J. Phys. Chem. Solids*.vol. 65, (2004), p. 499.
- [20] K.C. Vrancken, L.D. Coster, P.V.D. Voort, P.J. Grobet , E.F. Vansant, The role of silanols in the modification of silica gel with aminosilanes, *J. Colloid Interface Sci.*vol. 170, (1995), p. 71.
- [21] J. Duchet, J.F. Gerard, J.P. Chapel , B. Chabert, Grafting of alkylchlorosilanes onto silica from solution for adhesion enhancement, *J. Adhesion Sci. Technol.*vol.14,(2000),p. 691.
- [22] C.J. Kluth, M.M .Sung, R. Maboudian, Thermal Behavior of Alkylsiloxane Self-Assembled Monolayers on the Oxidized Si(100) Surface *Langmuir*.vol.13, (1997),p. 3775-3780.
- [23] P. Silberzan, L. Leger, D. Ausserre, J.J. Benattar, Silanation of silica surfaces. A new method of constructing pure or mixed monolayers *Langmuir*.vol.7, (1991), p.1647-1651.
- [24] H.P. He, J.G. Guo, X.D. Xie, H.F. Lin, L.Y. Li, *Clay. Clay Miner.*vol. 37, (2002),p. 323.
- [25] K. Isoda , K. Kuroda, Interlamellar Grafting of γ -Methacryloxypropylsilyl Groups on Magadiite and Copolymerization with Methyl Methacrylate, *Chem. Mater.*vol. 12, (2000), pp.1702-1707.
- [26] K.C. Vrancken, L.D. Coster, P.V.D. Voort, P.J. Grobet, E.F. Vansant, The role of silanols in the modification of silica gel with aminosilanes, *J. Colloid Interface Sci.* Vol.170, (1995),pp.71-77.
- [27] S.Ek, E.I. Iiskola, L. Niinistö, A ¹³C and ²⁹Si CP/MAS NMR study of bi- and trifunctional γ -aminopropylalkoxysilanes deposited onto

porous silica in the gas phase, *J. Phys. Chem. B*.vol. 108, (2004), p. 454.

[28] H. A. M. Verhulst, L. J. M. van de Ven, J. W. de Haan, H. A. Claessens, F. Eisenbeiss, C. A. Cramers, Patching in reversed-phase high-performance liquid chromatographic materials studied by solid-state NMR spectrometry, *J. Chromatography A*.vol. 687, (1994), pp. 213–221.

[29] K. Saleh, M. Lazghab, P. Guigon, Chemical hydrophobisation of silica-based porous particles with n-Octadecyltrichlorosilane (ODTCS) by a solventless process in a fluidised-bed reactor, *Powder Technology*.vol. 190, (2009), pp. 192–199.

[30] T.M. Roshchina, N.K. Shoniya, L.E. Kitaev, K.B. Gurevich, A.A. Kazmina, A Study of Silica with Grafted Phenyl Groups by the IR Spectroscopy, Adsorption, and Chromatographic Methods, *J. Phys. Chem., Engl Trans*.vol. 74, (2000), p. 2026.

[31] R.K. Harris, J.J. Jones, S. Ng, ²⁹Si and ¹³C NMR Studies of organosilicon chemistry. IX. Silatrane, *J. Magn. Resonance*, vol. 30, (1978), pp. 521-535.