Functionalization of Porous Clay Heterostructures with Silane Coupling Agents

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The goal of this paper was to study the modification of porous clay heterostructures (PCHs) with various silane coupling agents. Two commercial coupling agents (3-aminopropyl-triethoxysilane (APTES) and 3-glycidoxypropyl-trimethoxysilane (GPTMS)) with different functional groups (amine and epoxy groups) were used as modifying agents for the PCHs functionalization. The functionalization of PCH with APTES and GPTMS was evaluated by Fourier transform infrared (FTIR) spectrometry, thermogravimetric analysis (TGA), X-Ray Diffractions (XRD) and BET Analysis. FTIR spectra of modified PCHs confirmed the presence of characteristic peaks of silane coupling agents. TGA results highlighted an increase of weight loss for the modified PCHs that was assigned to the degradation of silane coupling agents (APTES and GPTMS) attached to the PCHs. The XRD results showed that the structure of modified PCHs was influenced by the type of the silane coupling agent. The functionalization of PCHs with silane coupling agents was also confirmed by BET analysis. Textural parameters (specific surface area (S_{BET}), total pore volume (V_t)) suggested that the modified PCHs exhibit lower values of S_{BET} and a significant decrease of total pore volume than unmodified PCHs.

Keywords: Porous clay heterostructures (PCH), 3-aminopropyl-triethoxysilane (APTES), 3-glycidoxypropyl-trimethoxysilane (GPTMS), functionalization

Porous clay heterostructures (PCHs) are innovative materials that combine microporosity and mesoporosity [1]. The versatile properties such as high textural properties (surface area, total volume pore, pore size distribution), high thermal stability and adsorption capacity and surface acidity of PCHs recommend these materials in a wide range of applications such as: carriers, adsorbents, catalysts, decontamination agents and encapsulation agents [2-6].

The treatment of inorganic materials with organic silane coupling agents is an attractive strategy used to enhance some properties like drug encapsulation efficiency, stability of immobilized enzymes, adsorption capacity, catalytic activity, physical and chemical properties. These modified materials can be used in many fields such as: wastewater purification, catalysis, encapsulation of various therapeutic agents and enzyme immobilization [7-12]. For example, modified MSN with APTES exhibited a high drug encapsulation efficiency, controlled drug delivery profile and an enhanced uptake ability for cancer cells [16]. Modified montmorillonite (MMT) with APTES presented an improve adsorption capacity, and therefore may be considered a potential material for treating wastewater [15]. Modified halloysite (HNT) showed an improved capacity for enzyme immobilization and controlled release and modified SBA-15 presented enhanced catalytic properties [7].

Organic modification of mesoporous materials can be accomplished by two methods: (1) co-condensation strategy that consists in co-condensation of the siloxane and silane coupling agent. (2) post-synthesis modification method that involves the modification of inorganic material surface by the reaction of the free silanols and organosilane agents. This method presented many advantages for the modified materials, such as: higher hydrothermal stability, functional groups can be chosen depending on the application [7, 12, 13].

The aim of this paper was to prepare and characterize PCHs modified with different silane coupling agents (3-aminopropyltriethoxysilane **(APTES)** and 3-glycidoxypropyl-trimethoxysilane (**GPTMS**)). The proposed strategy can be included in the class of post-synthesis modification method. The modification of PCHs was investigated using different characterization methods such as: FTIR Spectrometry, X-Ray diffraction (XRD), Thermogravimetric Analysis (TGA) and BET Analysis.

Experimental part

Materials and methods

A natural montmorillonite (Nanofil 116 (MMT-Na)) with a cationic exchange capacity (CEC) of 116 mEq/100 g clay was supplied from Southern Clay Products. Hexadecyltrimethylammonium bromide (**HDTMA**), tetraethyl orthosilicate (**TEOS**), dodecylamine (**DDA**), 3-aminopropyl-triethoxysilane (**APTES**), 3-glycidoxypropyl-trimethoxysilane (**GPTMS**) were supplied from Sigma-Aldrich and used as received. The chemical structures of the raw materials are shown in figure 1.

Synthesis of PCH

The PCH was synthesized using a similar protocol presented in our previous paper [4]. The preparation of PCH involves three main steps: **(A)** Modification of MMT with HDTMA; **(B)** Generation of nanosilica between layers of modified MMT (MMT-HDTMA); **(C)** Removing of the organic fraction by thermal treatment.

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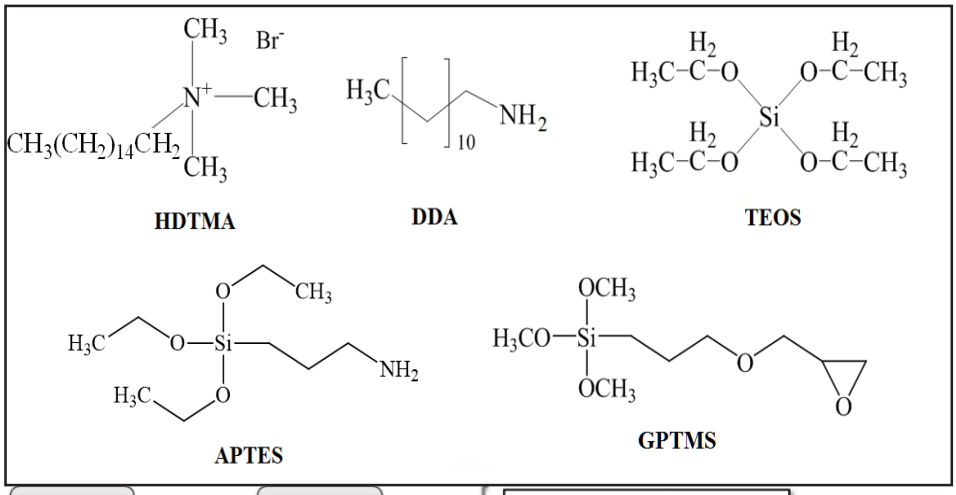
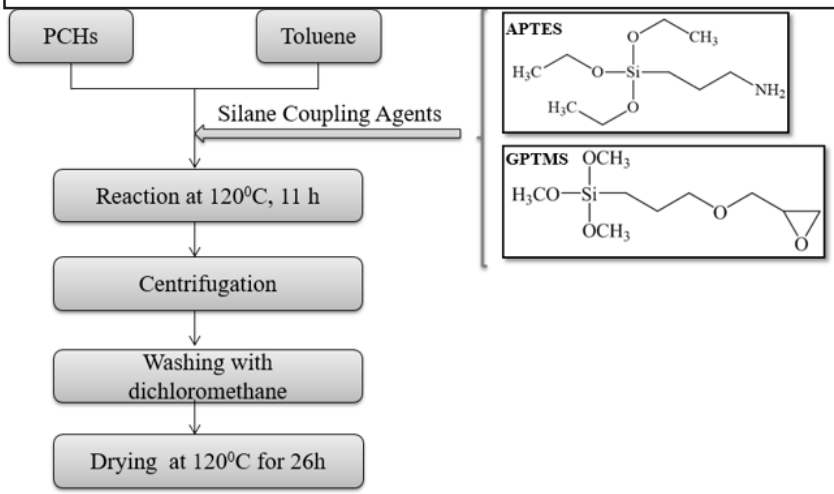


Fig.1. Chemical structures of raw materials



Scheme 1. The steps followed for the PCH modification with coupling agents.

Functionalization of PCH with APTES and GPTMS

Functionalization of PCH with amine and epoxy groups was accomplished by reacting the inorganic material with two silane coupling agents: 3-aminopropyl-triethoxysilane (APTES) and 3-glycidoxypropyl-trimethoxysilane (GPTMS) in toluene. Briefly, 1.6 g of PCH was reacted with 400 µL APTES/GPTMS in 15 mL toluene for 1L h under stirring at 120 ^{0}C (scheme 1). The modified PCHs were separated by centrifugation, washed with 60 mL dichloromethane and then the materials were dried at 120^{o}C for 26 h. The modified samples were abbreviated as Amine-PCH and Epoxy-PCH (scheme 2).

Characterization techniques

FTIR spectra were registered on a Bruker VERTEX 70 spectrometer using 32 scans with a 4 cm^{-1} resolution. The samples were analyzed from KBr pellets.

Thermogravimetric analysis (TGA) was performed on a Q 500 TA Instrument. The samples were heated from 20 to 800^{0}C at a scanning rate of 10^{0}C/min under a constant nitrogen flow rate.

XRD diffractograms were recorded on a X'Pert PRO MPD Panalytical equipment.

Textural parameters of unmodified PCH, Amine-PCH and Epoxy-PCH samples were recorded by nitrogen adsorption–desorption isotherms at -196^{0}C, using a NOVA 2200e Automated Gas Sorption instrument. Samples were pre-treated (degassed) under vacuum at 40^{0}C for 5 h.

Results and discussions

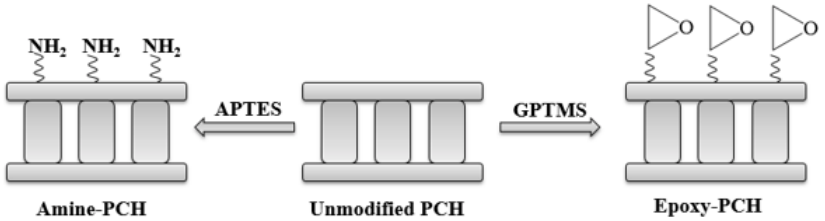
Characterization of functionalized PCHs

FTIR analysis

The modification of PCHs was firstly highlighted using FTIR spectrometry (fig.2). FTIR spectrum of unmodified PCH exhibits the following characteristic peaks: 3738 cm^{-1} (vibrations of isolated terminal silanol groups), 3649 cm^{-1} (vibration of geminal and associed terminal silanol groups), 3440 cm^{-1} (hydroxyl group stretching vibrations of water molecules adsorbed on PCH), 1630 cm^{-1} (bending vibration of adsorbed water molecules), 1084 cm^{-1} (formation of three dimensional silica network) [5,6]. The modification of PCH with silane coupling agents (APTES and GPTMS) was highlighted by the apearance of new peaks at 2927 cm^{-1} (APTES) and 2951 cm^{-1} (GPTMS) attributed to the streaching vibrations of C-H from CH$_2$ groups of the coupling agents. Similar results were reported for various inorganic clays (halloysite, montmorillonite, kaolinite, MCM) modified with silane coupling agents [9, 14-16].

TGA tests

Thermogravimetrical analysis also confirmed the modification of PCHs (fig.3). TG curve of unmodified PCH involves two main steps: **(1)** dehydroxylation process of hydroxyl groups situated in the pillars (300-500 ^{0}C) and **(2)**



Scheme 2. Functionalization of PCH with silane coupling agents (APTES, GPTMS)

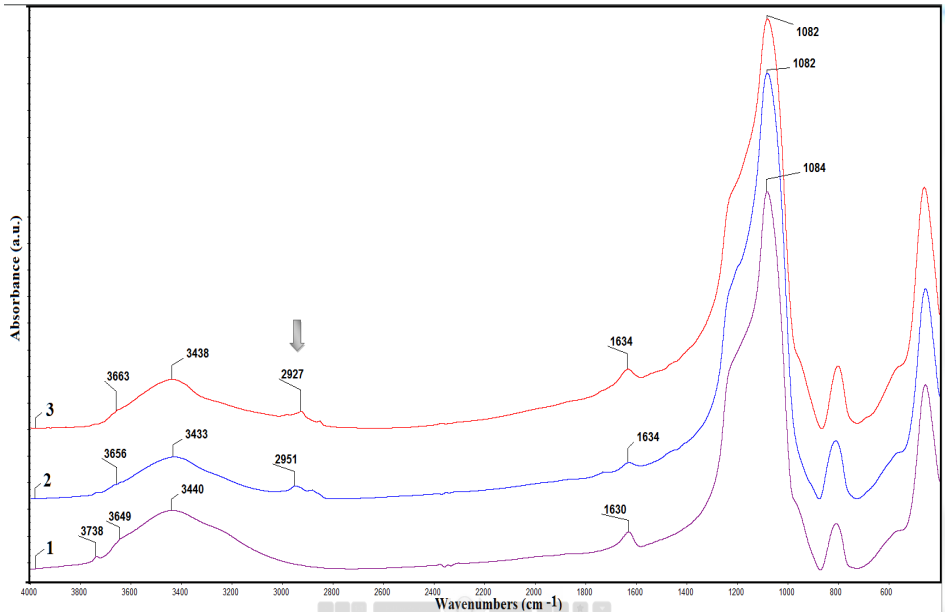


Fig.2. FTIR spectra of 1- unmodified PCH, 2-Epoxy-PCH, 3-Amine-PCH

dehydroxilation process of hydroxyl groups located between the tetrahedral sheets of MMT (500-800 ^{0}C) [5,6].

The TG curves of modified PCHs (Epoxy-PCH, Amine-PCH) samples show a different profile that included three degradation steps: (1) dehydration, due to the physically adsorbed water (20-200^{0}C), (2) degradation of organic coupling agents (200-500 ^{0}C) and (3) dehydroxylation process of hydroxyl groups located between the tetrahedral sheets of MMT (500-800 ^{0}C) [9, 17]. A higher weight loss value (8.8 % for Amine-PCH and 13% for Epoxy-PCH) of modified PCHs samples confirmed the presence of organic fraction that was introduced into PCHs during the functionalization step.

XRD Analysis

X-ray diffractograms of unmodified PCH and modified PCHs (Epoxy-PCH, Amine-PCH) are shown in figure 4. The results of the XRD analysis indicated that the structure of the modified PCHs (Amine-PCH and Epoxy-PCH) is influenced by the functionalization reaction with different silane coupling agents. The modified PCH with GPTMS (Epoxy-PCH) exhibits an intercalated structure highlighted

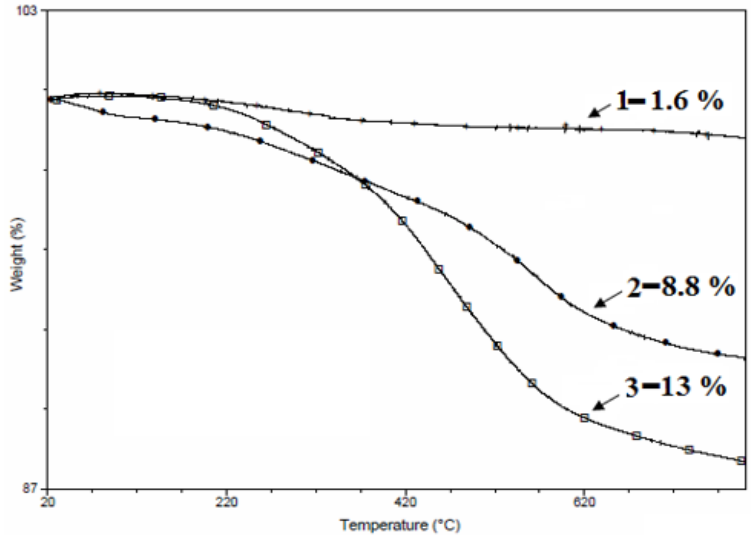


Fig.3. TGA curves of: 1 unmodified PCH, 2- Amine-PCH, 3- Epoxy-PCH

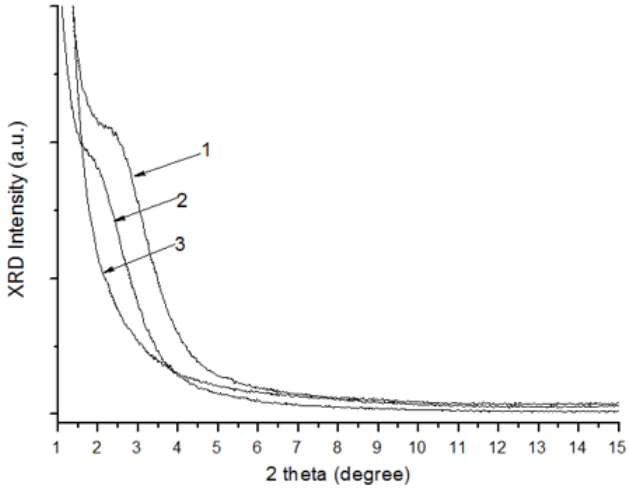


Fig. 4. X-ray diffractograms of: 1-Epoxy-PCH, 2-unmodified PCH, 3-Amine-PCH

by the presence of the shoulder/ characteristic peak d_{001} that exists in MMT structure. Comparing to Epoxy-PCH, in the case of modified PCH with APTES (Amine-PCH), X-ray diffractogram indicated an exfoliated structure proved by the absence of the d_{001} peak assigned to the interlayer distance.

BET analysis

Textural properties of unmodified PCH and modified PCHs (Epoxy-PCH, Amine-PCH) were determined in order to point out the modification of PCHs with silane coupling agents (APTES and GPTMS). Figure 5 shows the nitrogen adsorption-desorption isotherms for unmodified and modified PCHs. The BET results indicated that the modified samples are charaterized by lower values of specific surface area (S_{BET}=381- 91 m^2/g) and total pore volume (V_t=0.2- 0.3 cm^3/g) than unmodified PCH (S_{BET}= 628 m^2/g and Vt= 0.8 cm^3/g). According to these results it can be concluded that silane coupling agents are located inside the pores and also on the surface of PCHs.Similar results were obtained for mesoporous silica modified with different silane couplig agents [15, 18-20].

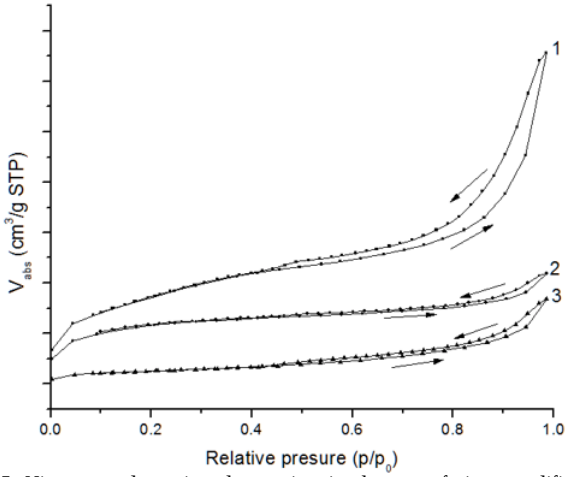


Fig. 5. Nitrogen adsorption-desorption isotherms of: 1-unmodified PCH, 2- Epoxy-PCH, 3- Amine-PCH

Table 1

TEXTURAL PROPERTIES OF UNMODIFIED PCH AND MODIFIED PCHS (EPOXY-PCH, AMINE-PCH)

Samples	S_{BET} (m^2/g)	Vp (cm^3/g)
Unmodified PCH	628	0.8
Epoxy-PCHs	381	0.2
Amine-PCHs	91	0.3

Conclusions

All the results confirmed the modification of PCHs samples with silane coupling agents (APTES and GPTMS).

FTIR spectra showed the presence of the organic fraction in PCHs samples through the appearance of new peaks attributed to the silane coupling agents.

Thermogravimetric analysis also confirmed the modification of PCHs. A higher weight loss than unmodified PCHs can be attributed to the presence of the organic fraction into PCHs.

The results of the XRD analysis indicated that the structure of modified PCHs is influenced by the type of the silane coupling agents.

Textural parameters suggested that the modified PCHs show lower value of specific surface area and a decrease of total pore volume than unmodified PCHs. These results indicated that the incorporated amine and epoxy gropups are located inside the pores and also on the surface of PCHs.

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References

1. GALARNEAU, A., BARODAWALLA, A., PINNAVAIA, T.J., Nat., **374**, 1995, p. 529–531.
2. CECILIA, J.A., GARCIA-SANCHO, C., FRANCO, F., Microporous and Mesoporous Mater., **176**, 2013, p. 95–102.
3. QU, F., ZHU, L., YANG, K., J. Hazard. Mater., **170**, 2009, p. 7–12.
4. GAREA, S.A., MIHAI, A.I., VASILE, E., VOICU, G., Rev. Chim.(Bucharest),**65**, no. 6, 2014, p.649
5. GAREA, S.A., MIHAI, A.I., GHEBAUR, A., NISTOR, C., SÂRBU, A., Int. J. Pharm., **491**, 2015, p. 299–309.
6. GAREA, S.A., MIHAI, A.I., VASILE, E., NISTOR, C., SARBU, A., MITRAN, R., Mater. Chem. and Phys., **179**, 2016, p. 17-26.
7. GARCYA, N., BENITO, E., GUZMAN, J., TIEMBLO, P., MORALES, V., GARCYA, R.A., Microporous and Mesoporous Mater., 106, 2007, p. 129–139
8. NAKANISHIA, K., TOMITAA, M., KATOB, K., J. Asian Ceram. Soc., **3**, 2015, p. 70–76
9. MBAYE, A., DIOP, C. A. K., MIEHE-BRENDLE, J., SENOCQ, F., MAURY, F., J. Clay Miner., **4**, 2014.
10. MORITZ, M., LANIECKI, M., Appl. Surf. Sci., **258**, 2012, p. 7523–7529.
11. IRAJI, S., RASHIDI, L., GANJI, F., Iranian J. of Chem. Eng., **4**, 2015, p. 93-100.
12. HARTONO, S.B., QIAO, S.Z., LIU, J., JACK, K., LADEWIG, B.P., HAO, Z., LU, G.Q.M., J. Phys. Chem., **114**, p. 8353–8362.
13. WEI, L., HU, N., ZHANG, Y., Mater., **3**, 2010, p. 4066-4079.
14. GAREA, S.A., GHEBAUR, A., CONSTANTIN, F., IOVU, H., Polym.-Plast Technol. Eng., **50**, 2011, p. 1096–1102.
15. HUANG, Z., WU, P., GONG, B., DAI, Y., CHIANG, P.C., LAI, X., YU, G., PLoS ONE, **11**, 2016, p. 1-18.
16. WANG, Y., SUN, Y., WANG, J., YANG, Y., LI, Y., YUAN, Y., LIU, C., ACS Appl. Mater. Interfaces, **8**, 2016, p. 17166–17175.
17. SHI, Y.F., TIAN, Z., ZHANG, Y., SHEN, H.B., JIA, N.Q., Nanoscale Res. Lett., **6**, 2011, p. 1-7.
18. HAKEEM, A., DUAN, R., ZAHID, F., DONG, C., WANG, B., HONG, F., OU, X., JIA, Y., LOU, X., XIA, F., The Royal Soc. of Chem., 2014, p.1-18.
19. LUAN, Z., FOURNIER, J.A., WOOTEN, J.B., MISER, D.E., Microporous and Mesoporous Mater., **83**, 2005, p. 150–158.
20. OTHMAN, Z.A., APBLETT, A.W., Mater. Lett., **63**, 2009, p. 2331–2334

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