Feasibility Analysis of Some Clays as Adsorbents for Styrene Purification

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Abstract: Characterization of five clays (kaolinite, Fuller earth's, bentonite, pansil and sepiolite) is presented herein emphasizing their properties as adsorbent in the purification of styrene monomer. Polymerization assays have been carried out in order to determine what clays are suitable for the styrene monomer purification by an adsorption process, without promoting styrene polymerization. Some adsorption experiments have been also carried out in order to determine adsorption capacities of the proposed clays.

Key words: Adsorbent, kaolinite, bentonite, pansi, sepiolite, polymerization.

1. Introduction

The purification of styrene monomer is a key aspect in the production of commercial rubbers. One of the most widely produced are SBR (styrene-butadiene derived rubbers), which are normally obtained by the block copolymerization of conjugated olefins (styrene and butadiene). The main problem when producing these polymers is that monomers, such as butadiene and styrene, are not very stable. They often react with themselves, even at ambient conditions, by a radical polymerization mechanism, with the risk of exothermic chain reactions. To avoid this, polymerization inhibitors such as TBC (*t*-butylcatechol) are usually added to the raw monomers during transport and storage. For this reason, when using the stabilized monomers to produce SBRs, these inhibitors as well as water, must be removed. On the contrary, polymerization could not be performed.

For this purpose, an adsorption process carried out onto an alumina bed is usually carried out [1, 2]. The main problem is that the lifespan of alumina beds is very short, so they must be continuously replaced, and the waste must be treated; what makes the process quite expensive [3]. The most probable cause of deactivation has been suggested to the chemisorption over the acid sites of the alumina is suggested as responsible of deactivation [4], although the real hydroxylation state of the alumina is not clear. One of the possible states could be the one represented in Fig. 1.

Reactions involving acid sites play an important role not only in alumina deactivation, but also in the reactivity of styrene. This monomer can be acidity activated to form active species by a dealkylation mechanism (benzene formation) [5-7] or radical polymerization [8, 9]. Therefore a previous study of chemical stability of the pairs styrene-adsorbent is needed in order to find out a cheap adsorbent material more suitable than alumina for styrene purification.

Commercial clays including sepiolite, Pansil, bentonite, kaolinite and Fuller's earth have been studied showing different behaviours in styrene solution. The objective of this work is to show that not all clays are suitable for their use as adsorbent in styrene liquid phase although some of them have great adsorption capacities.

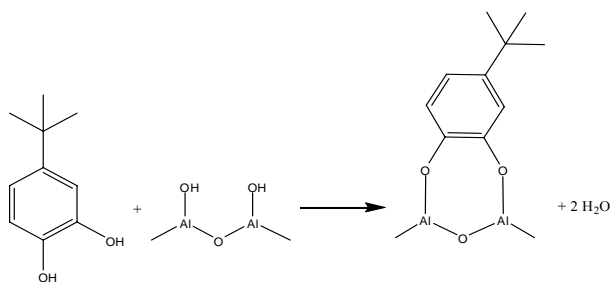**Corresponding author:** Gabriel Ovejero. E-mail: idiaz@quim.ucm.es.

Fig. 1 Alumina deactivation by TBC.

2. Materials and methods

2.1 Materials

Styrene was used in analytical grade and was purchased from Sigma-Aldrich.

The clays employed were: bentonite (from TOLSA), kaolinite (Fluka), sepiolite (TOLSA) and Pansil (TOLSA). Silica gel was purchased from Fluka and neutral alumina from Sigma-Aldrich as well as chitosan biopolymer.

Sepiolite sample was treated before being used in the experiments as follows [10] in order to remove possible impurities and the finest size fraction: one suspension containing 10g/L of sepiolite was mechanically stirred for 24 h at ambient temperature. After waiting two minutes, the supernatant was removed and the solid was washed again with distilled water. Later on, the solid samples were dried at 105 °C for 24 h. The other adsorbents (supposed as high purity materials), were used as received with no further purification.

2.2 Procedure

Polymerization assays with all the clays were conducted using 25 mL conical flasks immersed in a thermostatic bath at 30 ºC. The samples were stirred for 2 h. At the end of the reaction time, the system was left until complete phase separation was achieved and finally the liquid and solid phases were separated. Solid was left at ambient conditions for drying. After 24 h of drying TG analysis was carried out to determine if polystyrene was present or not.

Adsorption experiments were performed in the same way until equilibrium was reached (minimum time 2 h). Water content was determined by typical Karl-Fisher tritration (Mettler DL32). TBC content was measured by the reaction of the samples with the same volume of a NaOH-methanol mixture 0.15 N in NaOH. The system was left for 15 min becoming pink after complete reaction of TBC. Then UV/VIS determinations at 490 nm on Shimadzu spectrophotometer UV-2401 PC were performed to calculate the amount of TBC.

2.3 Characterization of adsorbents

Textural characterization of clays was done by using N_2 adsorption-desorption at 77 K in a Micromeritics ASAP 2010 apparatus. The morphology of the solid samples was analyzed by SEM (scanning electron microscopy) at 15 kV using a JSM-6700F field emission scanning microscope. Sample preparation involved dispersing the solid onto a carbon film supported by copper grids and sputtered with gold. TGA (thermo gravimetric analysis) experiments were performed with a heating rate of 10 °C/min in inert atmosphere on a Seiko EXSTAR 6000 TGA Instrument from 20 to 900 °C with an helium flow rate of 30 mL/min. FTIR spectra were collected using a Nicolet Nexus-670 FTIR spectrophotometer with a resolution of 4 cm^{-1} in KBr tablets (2 mg of sepiolite/ 98 mg KBr). Mercury porosimetry data were obtained using a Thermo Finnigan PASCAL porosimeter. Nitrogen porosimetry experiments were carried out in a Micrometrics ASAP-2010 equipment. XRF (x-ray fluorescence) measurements were performed using a BRUKER S4 EXPLORER system, with software for data acquisition and analysis. At last, TPD (thermal programmed desorption) analysis of ammonia were performed in a TPDRO-1100 equipment with a previous treatment of 1h with He in order to remove all physisorbed ammonia.

3. Results and discussion

In this section characterization and polymerization

results are discussed in order to determine which clays are suitable for removing water and TBC from styrene. Although the properties of conventional clays are generally known [10], the specific characteristics of these ones studied here are a key aspect to apply them as specific adsorbents. In addition, their properties also vary depending on their origin and previous treatment. Therefore, it is necessary an exhaustive characterization before their application.

3.1 Characterization

3.1.1 Particle Size and Morphology

Kaolinite, Fuller's earth and bentonite clays suffer from aggregation during sieving, resulting in higher average diameter when using this technique for particle size analysis. The difference between the obtained results with both techniques is relatively low (< 10%) so both techniques can be suitable for determining average diameters, showing off if agglomeration is present. For bentonite, no aggregation is predicted and both size distrbution are very close. Sepiolite shows different distributions but the average diameters are very close.

Pansil has a fibrous structure so it is not possible to calculate an average diameter from SEM images and its aggregation properties make it difficult to sieve.

SEM and sieving of the samples determined that sepiolite has the largest average diameter (0.347 mm). For this clay, the fraction 0.294-0.250 mm was used in further experiments. The other clays used have an average particle diameter below 0.1 mm as it can be seen in SEM images (Figs. 2-5).
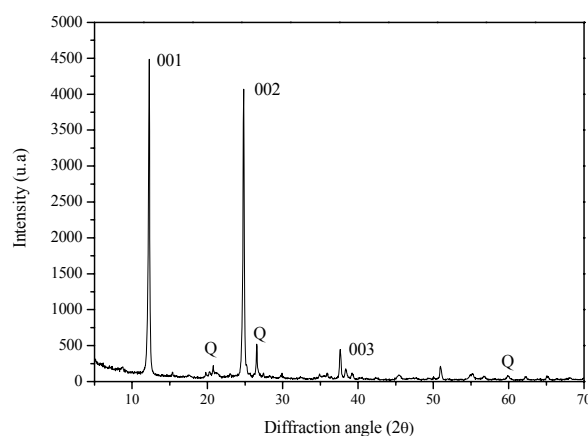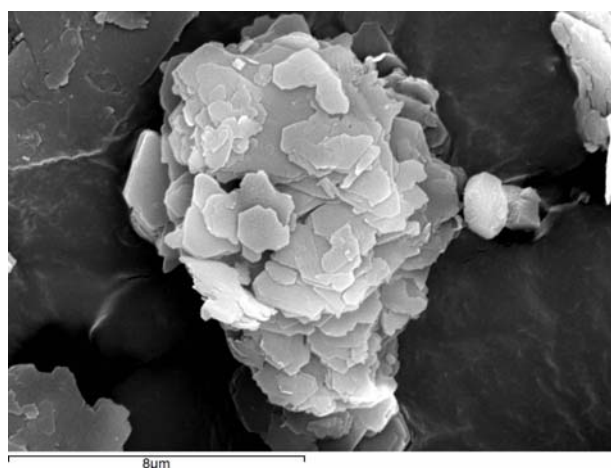

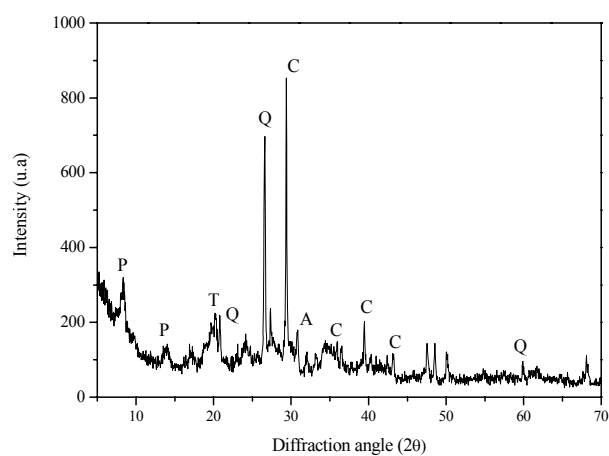**Fig. 2   Particle size, SEM image, FTIR and XRD analysis for kaolinite clay.**
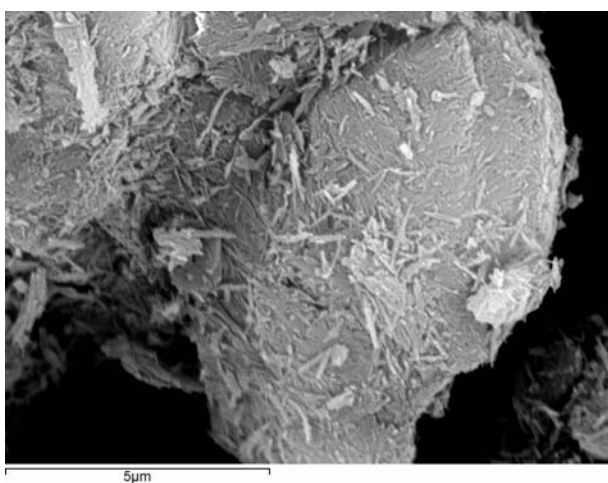

Fig. 3   Particle size, SEM image, FTIR and XRD analysis for Fuller's earth.
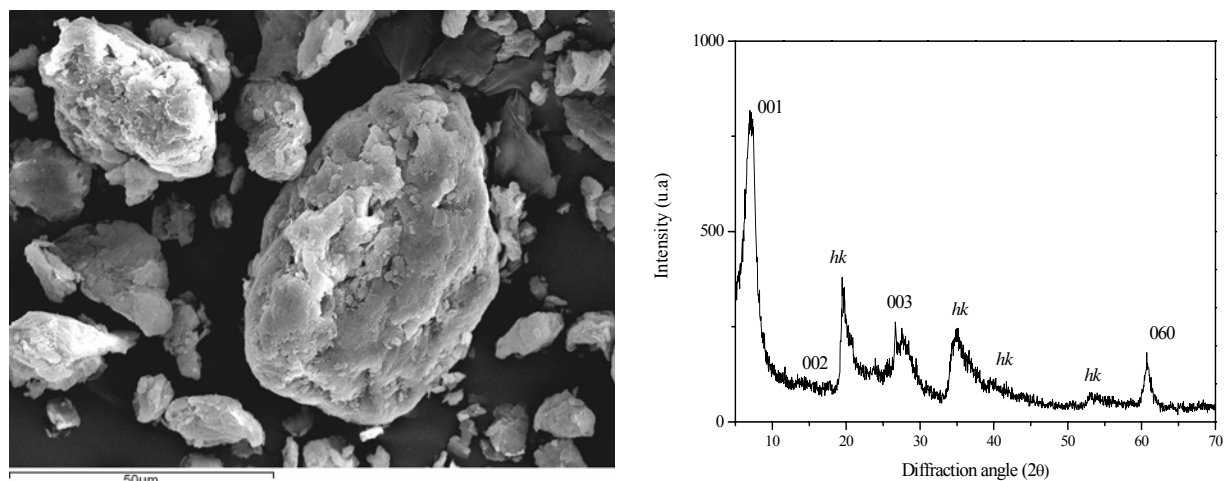
Fig. 4 Particle size, SEM image, FTIR and XRD analysis for bentonite clay.
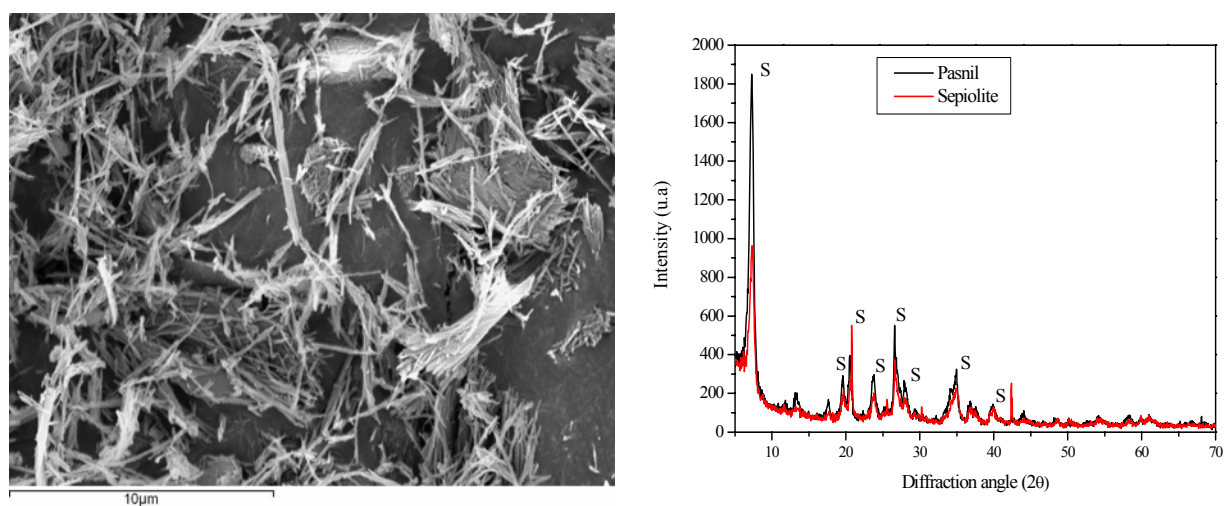

Fig. 5 Particle size, SEM image, FTIR and XRD analysis for sepiolite and pansil.

With SEM images, apart from diameter distribution, the differences on morphology of the employed solids can be known. Bentonite and kaolinite show a typical laminar structure while Pansil, sepiolite and Fuller's earth show needle structures due to palygorskite type structure.

3.2 N_2 porosimetry

N_2 porosimetry gives an idea of micro and mesoporosity of solids. In this way, BET and t-plot theories were applied to such experiments taking out information about the specific surface due to micro and mesoporosity and the external area.

It can be seen in Table 1 that kaolinite is the clay with the less surface due to its pure laminar structure.

Fuller earth's and bentonite are the next (smectite type structure) in this serie.

Sepiolite and Pansil have the largest surface area because of it needle-like structure typical of this group of clays.

3.3 Hg porosimetry

From Hg porosimetry experiments (Table 2) carried out at 140 and 440 MPa, information about meso and macroporous was calculated as well as porosity and density values.

3.4 Infrared analysis (FTIR)

It is reported in literature that dioctahedric clays show an absortion shoulder of OH in 800-950 cm^{-1}

Table 1   N$_2$ porosimetry results.

	N$_2$	
	S^{BET} (m^2/g)	S$_{ext}$$^{t-plot}$ (m^2/g)
Kaolinite	7.0	4.4
Fuller's earth	77.4	63.9
Bentonite	82.6	64.5
Pansil	139.1	116.7
Sepiolite	157.6	146.0

Table 2   Hg porosimetry results.

	Hg			
	ε (%)	ρ$_{bulk}$ (g/cm^3)	S$_{spec}$ (m^2/g)	ρ$_{app}$ (g/cm^3)
Kaolinite	24	0.659	9.8	1.35
Fuller's earth	42	0.484	66.5	0.926
Bentonite	73	0.846	40.4	1.62
Pansil	43	0.206	5.0	0.280
Sepiolite	44	0.906	95.4	0.906

region [11]. In the case of trictahedric materials, this band moves to smaller wave numbers.

Fig. 6 shows that for kaolinite and Fuller's earth the IR absortion spectra is higher in 800-950 cm^{-1} region than in 600-700 cm^{-1}. Therefore these materials are supposed to be trioctahedric clays.

FTIR analysis for Fuller Earth's shows peaks at 881 and 915 cm^{-1} which are characteristic of AlFeOH and AlAlOH vibration modes. This confirms the dioctahedric nature (Al^{3+} and Fe^{3+} in the interlaminar space) of this clay.

In the case of bentonite, dioctahedric absorbtions were not found, but also Mg3OH vibration mode can be seen at 665 cm^{-1}.

Pansil and sepiolite show small absorbtions at 881 and 915 cm-1 but not so high as Fuller earth's and kaolinite.

Also, near 3600 cm^{-1} (Figure 6), octahedric cations vibration modes appear.

The sharpest peak at 3616 cm^{-1} is kaolinite's, which have much Al^{3+} substitutions in the octahedric layer. This peak is tipically related with the dioctahedric character of the material.

Fuller earth's peak appears at 3540 cm^{-1} which is reported to be associated with the presence of octahedric iron (FeMgOH and FeFeOH groups) [7].
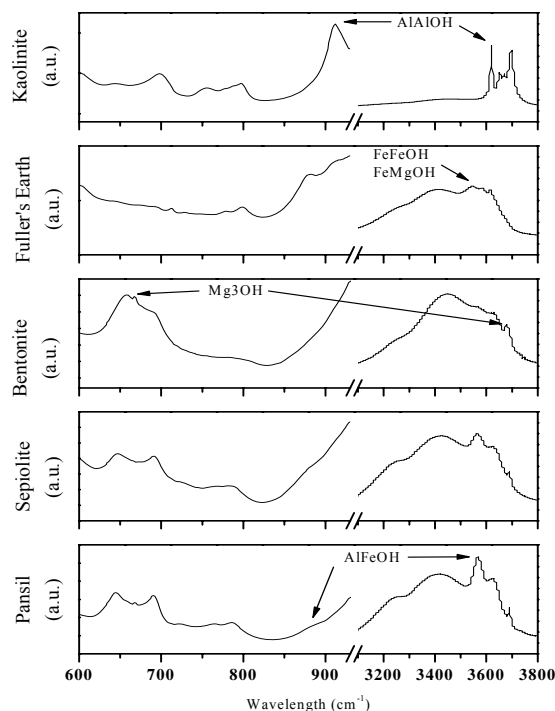
Fig. 6   FTIR analysis between 600-3800 cm^{-1}.

Bentonite clay does not show strong peaks in this region, but it can be seen a specific peak at 3680 cm^{-1} which is related to Mg3OH group.

Sepiolite and Pansil show characteristic absorbtions at 3570 cm^{-1} associated to AlFeOH vibrations.

Water presence in clays can be also determined by a FTIR shoulder absorbtion near 3430 cm^{-1}. An increasing of the size and charge of the interlayer cations results in a displacement of this shoulder towards lower wave numbers for all 2:1 clays (kaolinite is 1:1 clay) [11, 12].

In this region, the studied clays follow the serie: Fuller's earth (3415 cm^{-1}), Pansil (3420 cm^{-1}), sepiolite (3425 cm^{-1}) and bentonite (3450 cm^{-1}).

The charge/size order of the interlayer cations usually present in 2:1 clay is Al^{3+}>Fe^{3+}>Mg^{2+}>Fe^{2+}>Ca^{2+}>Na^{+}>K^{+}. This agrees with the absortion peaks in Fuller earth's, so the presence of Al^{3+} and Fe^{3+} is confirmed. It is accepted that the higher the charge/size ration of the cation the more acidity, so it could be the reason of polymerization of styrene in the case of Fuller's earth and sepiolite.

3.5 X-ray fluorescence (XRF)

In Fig. 8 XRF analysis of studied clays is shown. It confirms that the iron content of Fuller's earth is higher than other clays. Kaolinita as expected has a great amount of aluminium in its structure while sepiolite, bentonite and Pansil show similar compositions in the octahedric positions.

3.6 Ammonia thermal programmed desorption (NH₃-TPD)

The acidity of the materials was measured by TPD analysis. The samples were saturated with ammonia and then heated up to 550 ºC. Because of its lack of selectivity all types of acid sites are titrated, even ammonia bonded by hydrogen bonds or dipolar interactions [23] so only the amount total sites are determined. In Fig. 9, it can be seen that, at higher temperatures, the total acidity of clays are related with the polymerization results (section 3.2). The density of acid sites is higher for Fuller's earth following by sepiolite and finally bentonite.

3.7 Adsorbent Unreactivity

Reactivity assays were carried out (following the procedure described in section 2) in order to show which clays were inert for styrene purification (did not catalyze styrene reactions).

Two experimental techniques have been employed for testing the activity of clays. The first one is FTIR analysis. By comparison of the pure sepiolite, with
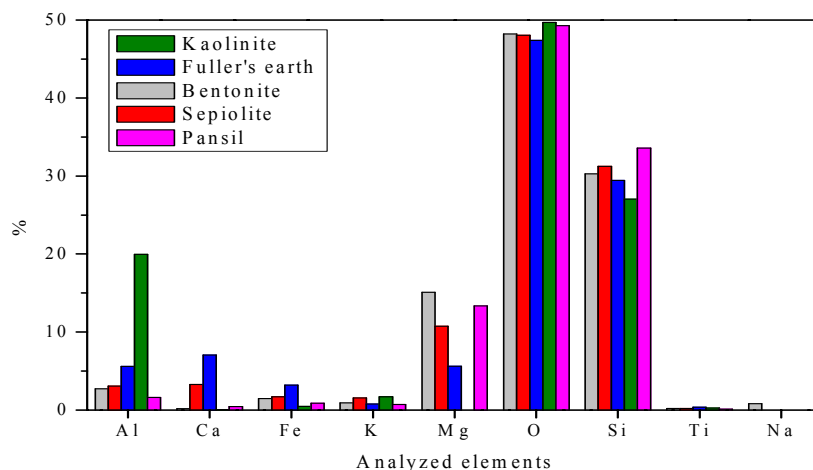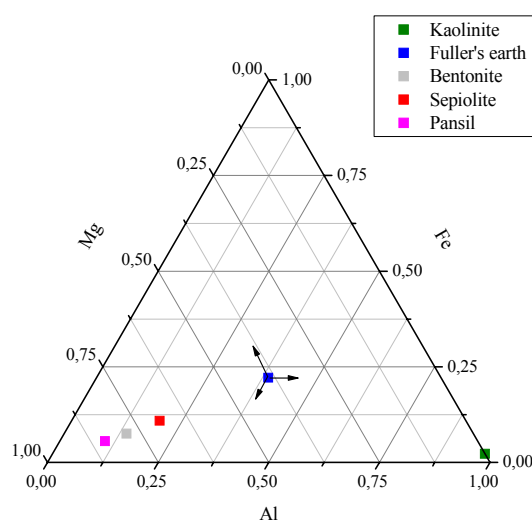
Fig. 7   Elemental XRF analysis.
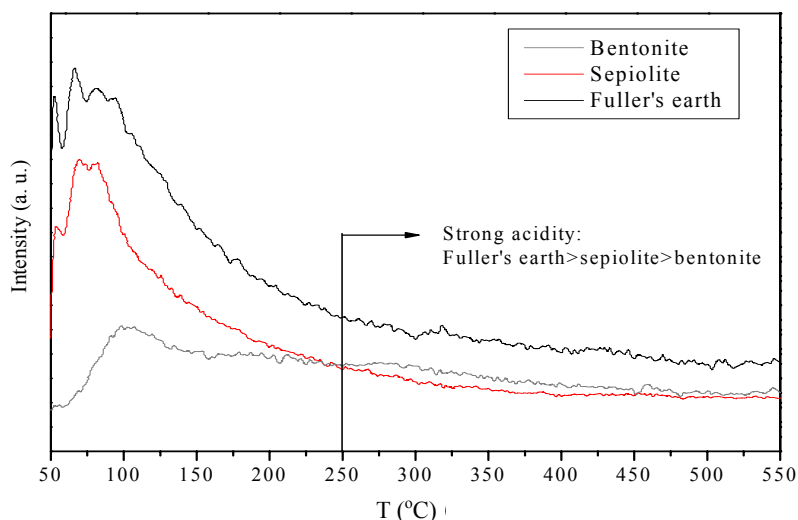
Fig. 8   Octahedric cations proportion.

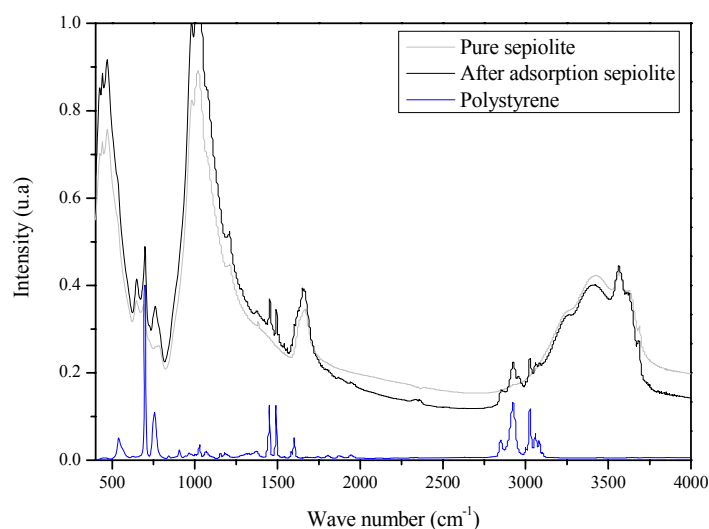**Fig. 9   NH$_3$-TPD analysis of bentonita, sepiolite and Fuller's earth.**

Fig. 10   FTIR analysis of pure sepiolite, after adsorption sepiolite and polystyrene.

the sepiolite after adsorption and pure polystyrene, it can be seen that after the adsorption sepiolite spectrum is a mixture as a result of adding to pure sepiolite spectrum the characteristic peaks for pure polystyrene (Fig. 10). In this way, it is shown that 24 h after the reaction assays (volatile compounds removed), the remaining product on the clay is polystyrene.

From DTG/DTA analysis as shown in Fig. 11, it can be seen that near 400 ºC there is a strong difference between the pure sepiolite analysis and the sepiolite after adsorption analysis, with an exothermic process as it is deduced for a peak in DTA. It has been reported that, under helium conditions, thermal decomposition of polystyrene takes place near 400 ºC [24]. So, when

this kind of peaks in DTA analysis of the after adsorption clays were present, polymerization of styrene takes place and that clay it is not suitable as adsorbent for the purification of styrene monomer.

The identification of the species resulting from decomposition was made by mass spectrometry/TG analysis. As is shown in Fig. 12, it can be seen that water is desorbed mostly at temperatures lower than 100 ºC but also bound, zeolitic and crystalline water appears at higher temperatures. Because of acidity of sepiolite, the dealkylation of styrene to benzene can be produced. This reaction is very common in this kind of in catalysis of this kind of alkylaromatic compounds [5-7]. Near 400 ºC, the great amount of

styrene is desorbed which agrees with the assumption of thermal decomposition of polystyrene.

Sepiolite was treated with the aim of lixiviating all active cations. A reduction from 1.7% to 0.7% was observed for iron from from pure sepiolite to acid treated sepiolite (1N HNO$_3$, 1h, 25 ^{o}C), but also polymerization activity increases (DTG between 300 and 400 ºC, where polymerization products desorb) as it can be seen in Figure 13. So it is deduced that polymerization is related with the total acidity of the

clay, which increases when hardening the acid treatment, and not only with the amount of iron present in the adsorbent, although its presence is a contribution to the catalytic (acid) activity.

The assays show that the other clays do not give significant styrene polymerization as it can be seen in Figure 14-16. So bentonite, kaolinite and pansil are suitable as adsorbents for the purification of styrene. Fuller's earth gives strong polymerization resulting in a viscous paste so DTG/DTA analysis were not possible.
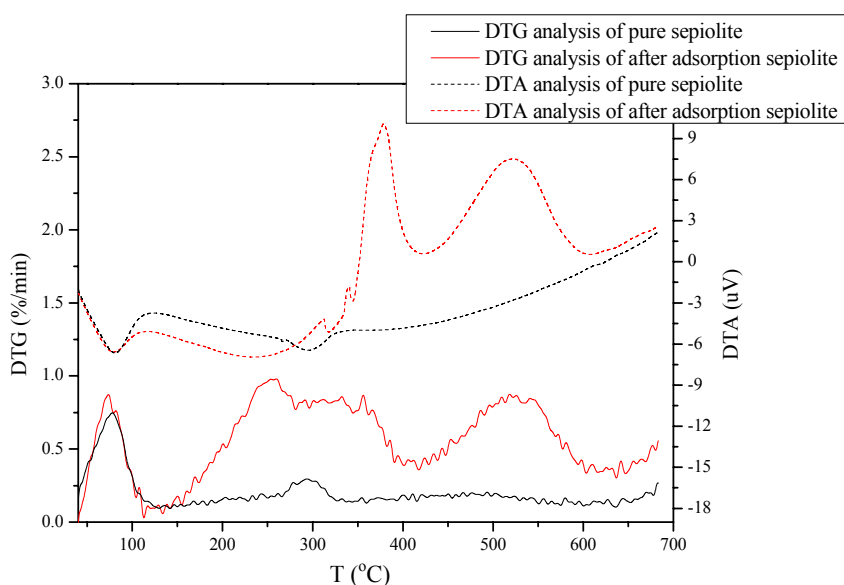

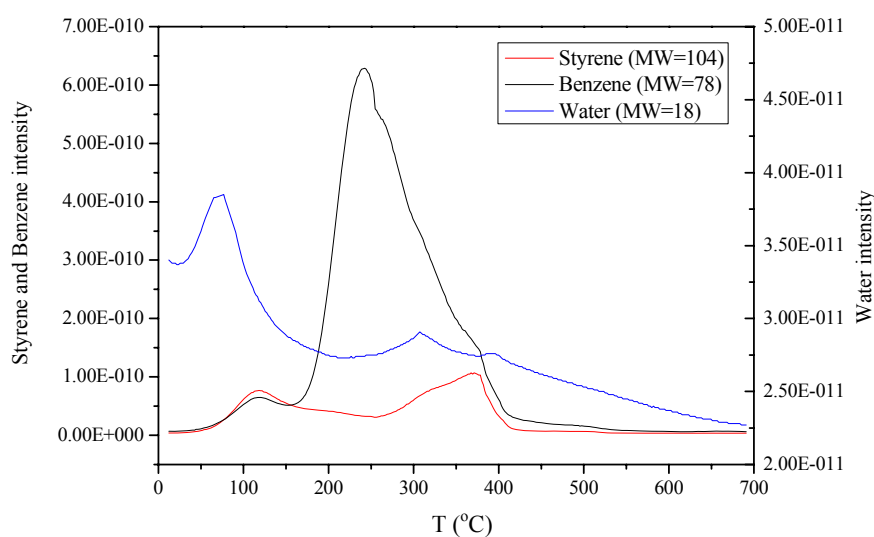**Fig. 11   DTG/DTA analysis of sepiolite pure and after adsorption.**

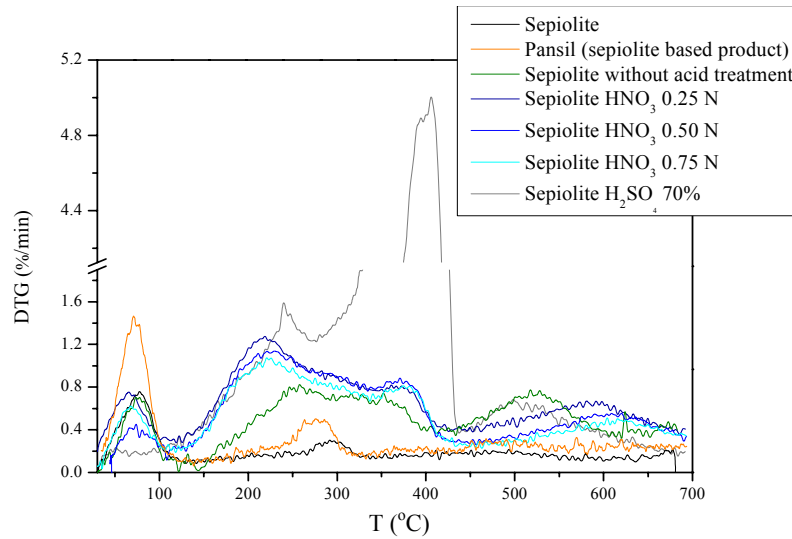**Fig. 12   Mass spectrometry/TG analysis of after adsorption sepiolite.**
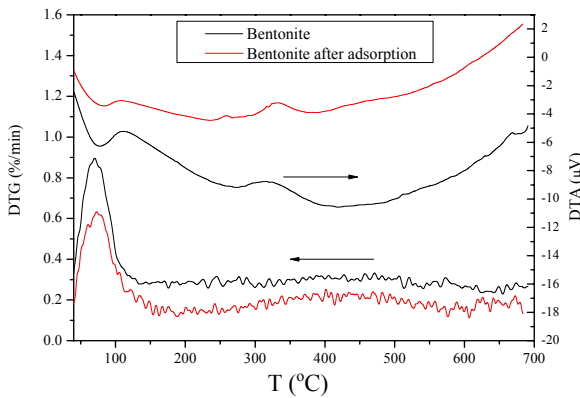
Fig. 13   DTG analysis of some sepiolite treatments.

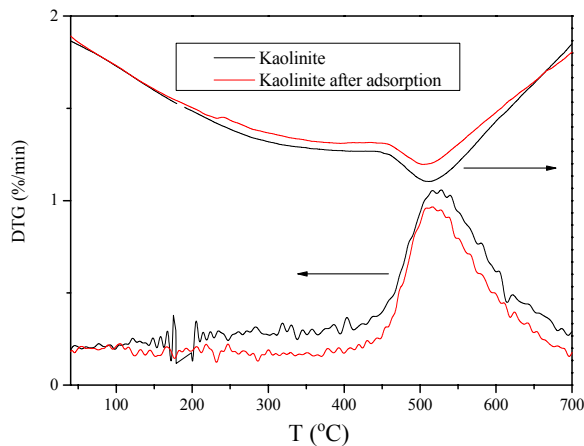**Fig. 14   DTG/DTA analysis for bentonite clay.**

Fig. 15   DTG/DTA analysis for kaolinite clay.

3.8 Adsorption capacities

Some adsorption equilibrium experiments have been carried out in order to determine which adsorbent would be used for further study. Thus, bentonite clay

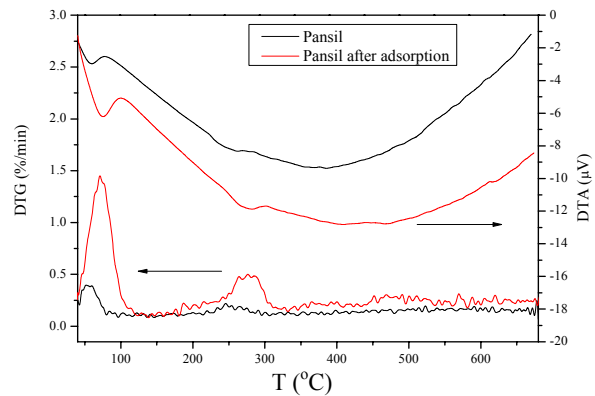has exhibited the highest capacities for the systems water-clay and TBC-clay as it can be seen in Table 3 and Table 4.

Fig. 16   DTG/DTA analysis for pansil clay.

Table 3   Water adsorption capacities of clays.

q_e (mg/g)				
Water (ppm)	Kaolinite	Bentonite	Pansil	Sepiolite
25	<2	3.1		
30	<2	4.0	4	5
50	<2	7.6		7
65	<2	10.3		
75	<2	12.0		10
80	<2	12.8	8	

Table 4   TBC adsorption capacities of clays.

q_e (mg/g)				
TBC (ppm)	Kaolinite	Bentonite	Pansil	Sepiolite
100	<2	23.9	9	
120	<2	24.5		3
180	<2	25.7		5
200	<2	25.9		

4. Conclusions

The clays studied show that a replacement of commercial alumina for the purification of styrene monomer is possible. Between all of these clays, bentonite exhibits the best behaviour in terms of adsorption equilibrium capacity. Its low price as well as its abundance make bentonite a good option for the purification studied. From the polymerization assays, it can be seen that acid sites in clays are responsible for the polymerization activity. Thus, non ferric clays as pansil, kaolinite and bentonite could be used.

Acknowledgments

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