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Acid-Activated Algerian Montmorillonite as Heterogeneous Catalysts for Cationic Polymerization of Styrene

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In this work, the styrene polymerization catalyzed by maghnite, an Algerian typical montmorillonite sheet silicate clay is reported. As a first step, the physicochemical variation in maghnite by sulfuric acid activation and the catalytic efficiency of maghnite (Mag) and maghnite-H⁺ (Mag-H) were studied. Acid activated maghnite were characterized by X-ray fluorescence, X-ray diffraction and FTIR. Then, the polymerization of styrene catalyzed by Mag-H was investigated. It was found that the cationic polymerization of styrene is initiated by Mag-H at ambient temperature in bulk. The effect of the amount of Mag-H, the temperature and the solvent was studied. The conversion increased with increase in the temperature and the proportion of catalyst and it was larger in nonpolar solvents. These results indicated the cationic nature of the polymerization. It was suggested that both the Lewis and the Brønsted acid sites are responsible for the catalytic activity. However, acid treatment of maghnite increases the catalytic activity and the polymerization of styrene was initiated mainly by H⁺.

Keywords: Catalyst, Cationic polymerization, Clay, Montmorillonite, Styrene.

INTRODUCTION

Styrene polymerization is one of the oldest, most studied of all vinyl polymerizations. It spontaneously generates free radicals upon heating above 100 °C and polymerizes yielding amorphous polystyrene (PS) [1,2]. Styrene can also be polymerized by other mechanisms (anionic, cationic, free radical, or Zeigler-Natta). Commercially, the polystyrene is produced *via* free radical chemistry and mostly *via* continuous solution polymerization processes.

The polymerization of styrene by clay was largely studied [3-8]. Solomon and Rosser [3] studied the polymerization of styrene on neutral mineral surfaces [2]. They suggested that the catalytic activity is related with catalyst structure.

A study was made on the polymerization of styrene by using various bentonite samples [7]. The results of this study showed that the most active bentonite samples were those which had been treated thermally for 2 h at 550 °C and a sample which was treated with H₂SO₄ (35 %). The polymerization of styrene with acid clay catalyst has been studied in toluene and 1,2-dichloroethane at temperature from -70 to +60 °C [8]. Molecular weights were 500-2000, depending on solvent, catalyst quantity; monomer concentration and temperature, monomer conversions approached 100 %. The reaction rate is

rapid at 0 °C and at ambient temperatures and is severely inhibited by water and other proton acceptors. The initiation mechanism of styrene by acid clay was studied. The results showed that the polymerization was initiated by Brønsted acid sites and then progressed *via* a cationic.

The use of the acid treated clays, as a solid source of protons in a number of industrial significant reactions, continue because they constitute a widely available, inexpensive solid source of protons, *e.g.*, they were employed as cracking catalysts until the 1960 s [9] and are still currently used in industrial processes such as the alkylation of phenols [10] and the dimerization and polymerization of unsaturated hydrocarbons [11]. Montmorillonite has both Brønsted and Lewis acid sites and when exchanged with cations having a high charges density, as protons, produce highly-active catalysts for acid-catalyzed reactions [12]. Intercalated organic molecules are mobile and can be highly polarized when situated in the space between the charged clay layers. These exchanged montmorillonites have been successfully used as catalysts for the reactions of polymerization [12]. Clays have also been used widely for the preparation of polymer/clay nanocomposites (PCNs). In recent years, much attention has been paid to polymer/clay nanocomposites as advanced plastic materials prepared *via in situ* intercalative polymerization and montmorillonite (MMT) is

the most widely used clay. Intercalative compounding by bulk, solution, suspension and emulsion polymerization, have been studied widely. Noh and Lee [13] and Kim *et al.* [14] have synthesized intercalated PS/MMT nanocomposites by emulsion polymerization in the presence of pristine montmorillonite. Fu and Qutubuddin [15] have prepared polystyrene/reactive organoclay intercalated nanocomposites by emulsion polymerization. Kim *et al.* [16] synthesized a series of montmorillonite nanocomposites with polystyrene.

The purpose of this study, on one hand, the physico-chemical behaviour of maghnite during the activation process by sulfuric acid and on the other hand the cationic polymerization of styrene by maghnite clay (Mag), a non-toxic cationic catalyst for vinyl monomers [12,17-19]. Mag-H can be easily separated from the polymer product and regenerated by heating to a temperature above 100 °C [12]. The effect of some factors such as the amount of the Mag-H, the temperature or the dielectric constant of solvent and the mechanism of initiation are discussed.

EXPERIMENTAL

Raw-maghnite: Algerian montmorillonite clay, was procured from "BENTAL" (Algerian Society of Bentonite). All products were purchased from Aldrich. Styrene was purified by stirring over CaH₂ for about 24 h and then distilled under reduced pressure over CaH₂ and was finally stored under nitrogen atmosphere. Then, 40 g of styrene was washed with 80 mL of aqueous solution of NaOH (1.25 N), after a strong agitation, in a bulb to decanted, we separates the two phases; the white phase and the yellow phase that contains the styrene to which one adds an excess of anhydrous magnesium sulfates, to eliminate draws them of water. Methanol was dried over magnesium sulphate. Toluene was washed successively with concentrated sulfuric acid, distilled water, 5 % aqueous sodium hydroxide and then dried over anhydrous magnesium sulfates. Toluene was distilled and stored. Dichloromethane was washed successively with conc. sulfuric acid, distilled water, 5 % aqueous sodium hydroxide and distilled and dried over anhydrous calcium chloride. Dichloromethane was distilled from calcium hydride and stored. Carbon tetrachloride, chloroform, nitrobenzene, acetonitrile and acetone were used as received.

Characterization

Characterization of maghnite: The BET surface area and pore volume of acid activated maghnite were determined by nitrogen sorption at 77 K using an ASAP 2020 V3.04 E from Micromeritics.

The chemical compositions of raw and acid activated maghnite were determined by X-ray fluorescence (XRF) using a PW 2400 Philips Analytical wavelength-dispersive sequential XRF spectrometer with SuperQ PANalytical software.

X-ray powder diffraction spectra were performed on oriented samples with a Bruker AXS D8 Advance diffractometer equipped with LynxEye linear detector, with Co K_{α1} radiation ($\lambda = 1.54056 \text{ \AA}$) and a scanning interval of $2\theta = 0^\circ$ to 70° and a scanning speed of $0.02^\circ/\text{s}$, at room temperature. The FTIR spectra were recorded on an Alpha FTIR Bruker spectrometer ($4000\text{-}400 \text{ cm}^{-1}$).

Characterization of polystyrene: The ¹H NMR spectra were recorded in CDCl₃ solution under ambient temperature on an AM 300 FT Bucker spectrometer using tetramethylsilane (TMS) as internal standard. The FTIR spectra were recorded on an Alpha FTIR Bruker spectrometer ($4000\text{-}400 \text{ cm}^{-1}$).

Viscosity and molecular weight (M_v): Viscosity measurements were carried out with an Ubbelohde capillary viscosimeter (viscologic TI1, version 3-1 Semantec). Intrinsic viscosity, $[\eta]$ (mL/g), was measured at 25 °C in toluene. We established a calibration curve which is: $\log(M_v) = f(\log \eta)$, for a series of samples of standard polystyrene, isomoleculaire of quite precise molecular weight, going from 580 up to 11200 in toluene at 25 °C. Thus, we measured intrinsic viscosities of our products under the same conditions and then we projected them on the calibration curve to determine the corresponding weights. The calibration curve has as an equation: $Y = 2.0011 + 2.0022X$; $Y = \log(M_v)$, $X = \log \eta_{\text{moy}}$.

Gel permeation chromatography (GPC): The molecular weight and its distribution were determinate respectively by gel permeation chromatography, using a Spectra physics RI SP8430 equipped with a polystyrene gel column (96000) and with tetrahydrofuran (THF) as an eluent at a flow rate of 0.80 mL/min at 25 °C.

Kinetics procedure: The polymerization of styrene was carried out in a heterogeneous system. Each mixture was prepared with quantities of styrene and Mag-H (% w/w to monomer) and were introduced in several (6-8) sealed tubes. The mixture was stirred with a magnetic stirrer under dry nitrogen. After a definite time, a quantity of dichloromethane was then added and the content was dried *in vacuo* to eliminate Mag-H. In the next step, a given quantity of phenol was added as an external standard to the filtrate and the solution was analyzed using high pressure liquid chromatography HPLC (standard spherisorb ODS column, mean diameter of particles: 5 mm, column length: 25 cm; eluent: methanol; $\lambda = 254 \text{ nm}$). The consumption curve of the monomer is plotted

Preparation of clay catalysts

Maghnite (Mag): The maghnite is cleaned by separation of clay phase and of rude phases. The maghnite is put in suspension in distilled water, the solid/liquid report is about 1/10. Suspension is then sieved on a sieve 0.02 mm in diameter of pores to eliminate rude material and pebbles. It is then poured into test tubes and left in rest during 2 h. The separation of the clay phase of rude fraction which stays at the bottom is made by siphoning. Recovered suspension is then centrifuged in 4500 tr/min during 20 min then maghnite was separated.

Maghnite-H⁺ (Mag-H): The preparation of the Mag-H was carried out by using a method similar to that described by Belbachir and Bensaoula [12]. The raw-maghnite (20 g) was grinded for 20 min using a Prolabo ceramic balls grinder. It was then dried by backing at 105 °C for 2 h. The maghnite was then weighed and placed in an Erlenmeyer flask together with 500 mL of distilled water. The maghnite/water mixture was stirred using a magnetic stirrer and combined with analytical grade H₂SO₄, with concentrations varying between 0.1 and 2 N, until saturation was achieved over 2 days at room temperature, the mineral was washed with water and then dried at 105 °C.

Polymerization procedures

Polymerization of styrene by maghnite and Mag-H:

Prior to use, maghnite was dried at 120 °C overnight and then transferred to a vacuum desiccator containing P₂O₅ and cool to room temperature overnight. The mixture was prepared with a quantity of styrene and a percentage, by weight relative to styrene, of catalyst (Table-2) and was introduced into a 100 mL flask. The mixture was then stirred at room temperature with a magnetic stirrer under dry nitrogen. After a time, a quantity of dichloromethane was added, the resulting mixture was then filtered to remove the clay and the product was precipitated in methanol at 0 °C. Finally, the polymer (white powder) was isolated and was dried in a vacuum oven before submitting them GPC, FTIR and ¹H NMR analysis.

RESULTS AND DISCUSSION

Natural montmorillonite clay has been used. Mag-H was obtained by treating the raw maghnite (Mag) with H₂SO₄ concentrations of 0.1, 0.3, 0.5, 1 and 2 N. After the activation process and filtration, the samples were washed until pH close to 7 and dried at 105 °C overnight and characterized by XRF, XRD and FTIR.

BET characterization: Mag-H⁺ was found to have a BET surface area (SSA) of 59.45 m²/g, an average pore diameter of 62.46 Å and total pore volume of 0.00772 cm³/g.

XRF characterization: This analysis was performed to know the chemical compositions of the minerals that are present in maghnite and Mag-H. Table-1 shows that the alumina and silica oxide are present in major quantities while other minerals are present in trace amounts and that maghnite clay contains mainly Al³⁺ with some Fe³⁺ and Mg²⁺ as octahedral cations and Ca²⁺, K⁺ and Na⁺ as exchangeable interlayer cations.

Results show, firstly, a dissolution (wt %) of cations, in particular Al³⁺, thereby resulting to a decrease of the Lewis

sites and increase (wt %) of SiO₂ in maghnite clay after acid treatments and, secondly, an increase in the yield to reach a maximum (67 %), for a concentration of 0.5 N H₂SO₄ and then decreases. This is explained by the fact that the Brønsted acid site (surface area) of montmorillonite increases up to a maximum value (Mag-H 0.5 N) after which it decreases [20,21].

XRD characterization: The XRD pattern of the raw and acid-treated maghnite (0.1, 0.3, 0.5 and 0.7 N) (Fig. 1) shows peak positions, observed in the range 2θ (0-40°), characteristic of montmorillonite. Furthermore, maghnite samples treated with H₂SO₄ showed a decrease in peak (001) which exhibited structural disorganization due to the excessive removal of Al, Fe and Mg from the structure, as seen in Table-1. Acid treatment is known to cause the progressive dealumination and degradation of the octahedral clay layers thus resulting in the smectite structure [22-26].

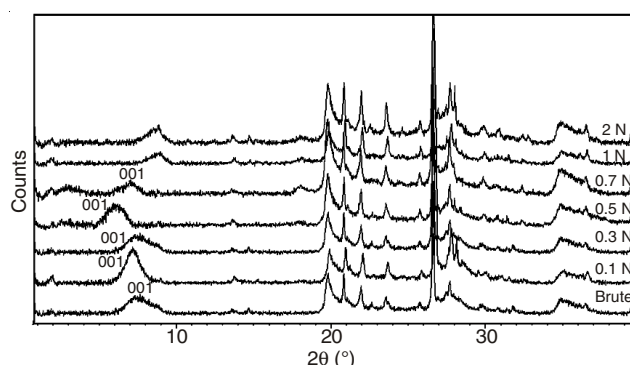


Fig. 1. XRD pattern of natural and activated montmorillonite

FTIR characterization: Fig. 2a and 2b show the FTIR spectra of raw and acid activated Algerian montmorillonite by different concentrations of sulfuric acid, all montmorillonite characteristic bands are present, while Table-2 shows the assignments of the vibration modes.

TABLE-1
CHEMICAL COMPOSITION OF RAW AND ACID ACTIVATED MAGHNITE
(FOR YIELD OF POLYSTYRENE; Styrene: 48.07 mmol, 3 % OF MAGHNITE, 6 h, 20 °C)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	SO ₃	Organics/ Water	Yield of PS (%)
Raw maghnite	61.21	15.01	3.87	1.44	3.46	1.24	1.71	0.16	0.44	11.21	0
Mag-H 0.1 N	61.98	14.88	3.73	1.42	3.32	1.37	1.66	0.18	0.43	10.73	Trace
Mag-H 0.3 N	63.32	14.68	3.47	1.39	3.05	1.36	1.49	0.18	0.48	10.50	10.0
Mag-H 0.5 N	64.13	14.48	3.23	1.42	2.80	1.40	1.47	0.21	0.42	10.54	67.0
Mag-H 0.7 N	64.52	14.22	3.16	1.37	2.66	1.38	1.32	0.19	0.43	10.60	27.0
Mag-H 1 N	65.17	14.09	3.05	1.41	2.44	1.30	1.06	0.19	0.77	10.39	15.0
Mag-H 2 N	66.73	13.58	2.82	1.34	2.15	1.24	0.73	0.17	0.62	10.50	12.7

TABLE-2
FTIR RESULTS OF RAW AND ACID ACTIVATED MONTMORILLONITE

Wavenumber (cm ⁻¹)	Attribution
3624	Stretching vibrations due to hydroxyl group bonded with Al ³⁺ cations
3415	OH groups stretching vibration of physisorbed water molecules
1630	OH, bending of water molecules due to hydration
1450	Absorption of calcite
1114	Si–O stretching, out-of-plane or presence of cristobalite
1006-990	Si–O–Si stretching [Ref. 28]
915, 883 and 840	Al ₂ OH stretching, AlFeOH and AlMgOH hydroxyl bending vibrations
515-460	Stretching and bending vibrations of the Si–O–Al and Si–O–Si groups respectively

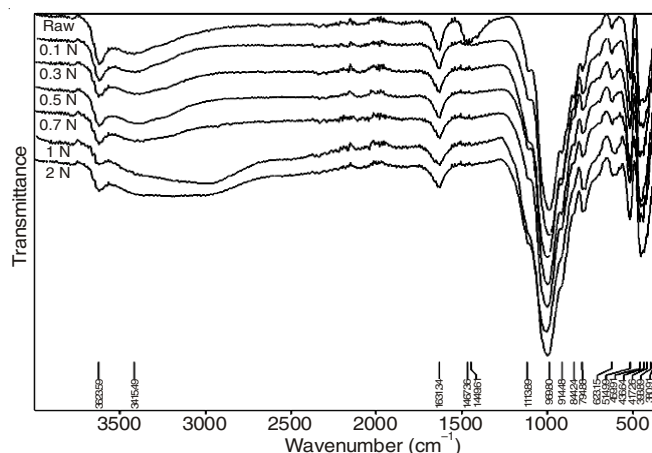


Fig. 2a. FTIR spectra of the raw and acid activated Algerian montmorillonite

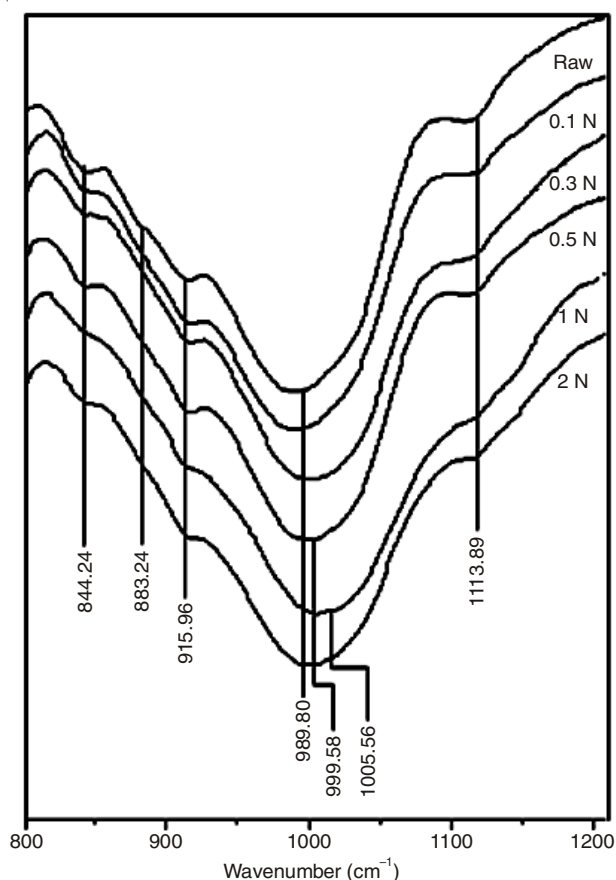
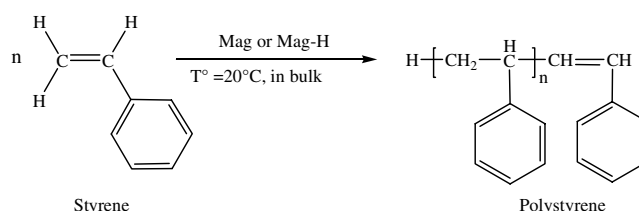


Fig. 2b. FTIR spectra of raw and treated montmorillonite clay

Fig. 2a shows an increase in the intensity of 3419 cm^{-1} band after acid treatment. The result meant that parts of Si-O-Si bonds may be destroyed and therefore additional Si-OH_2^+

groups were formed on the surface of acid activated montmorillonite [27]. Fig. 2a also shows the disappearance of the carbonate band at 1450 cm^{-1} after the acid treatment. The FTIR bands at 915 , 883 and 840 cm^{-1} were attributed to Al_2OH , AlFeOH and AlMgOH vibrations, respectively. An O-H stretching band located around 3620 cm^{-1} has been reported Al-enriched dioctahedral smectite [28-31]. All of these decreased in intensity after acid treatment (Fig. 2b) and these results reflect the leaching of octahedral cations such as Al^{3+} , Mg^{2+} and Fe^{3+} as shown in Table-1. The Si-O stretching band at 989 cm^{-1} in raw montmorillonite increases to 1006 cm^{-1} after acid treatment. This shows that there is a change in Si environment (Fig. 2b).

Styrene polymerization: With the aim to propose a probable mechanism of the styrene polymerization catalyzed by maghnite, different catalysts are tested. The polymerization of styrene was examined in the presence of maghnite and Mag-H powder, as catalyst, in bulk and at room temperature ($T = 20 \pm 2^\circ\text{C}$) (**Scheme-I**). Results are shown in Table-2.



Scheme-I

Table-3 shows that Mag-H gives the best yield of polymer, therefore, the continuation of the paper will deal with the use of Mag-H as catalyst.

Polymer characterization: All polystyrene obtained have similar FTIR spectra (Fig. 3). They all show, a band at 2920 cm^{-1} corresponding to aliphatic CH and bands at 3020 cm^{-1} and $1600\text{--}1500\text{ cm}^{-1}$ corresponding, respectively to the aromatic CH and aromatic double bond. The polymerization was confirmed by the disappearance of the vinyl double bond, from styrene, expected to 1630 cm^{-1} .

The proof for the styrene polymerization, using the Mag-H as a catalyst, obtained by ^1H NMR spectroscopy, is shown in Fig. 4. The different polystyrene characteristics signals are present with formation of a double bond at the chain end. Indeed, the termination proceeds by disproportionation.

Effect of amount of maghnite and Mag-H on the polymerization: Table-3 shows the effect of the amount of catalyst on the polymerization yield. Indeed, using various amounts of catalyst by weight, the polymerization was carried out in bulk at 20°C . The polymerization yield increased with

TABLE-3
POLYMERIZATION OF STYRENE (5 g: 48.07 mmol) WITH CLAY CATALYST

Catalyst	Weight of catalyst (%)	Time (min)	Polymer yield (%)	M_n	M_v	M_w	PD
Mag	5	1440	0	-	-	-	-
	10	1440	12	1790	3577	4067	2.27
	20	1440	33	1418	3011	3446	2.43
Mag-H	5	Spontaneous	94	863	1016	1230	1.42
	3	360	67	1470	1868	2059	1.40
	1	360	12	1636	2019	2239	1.35

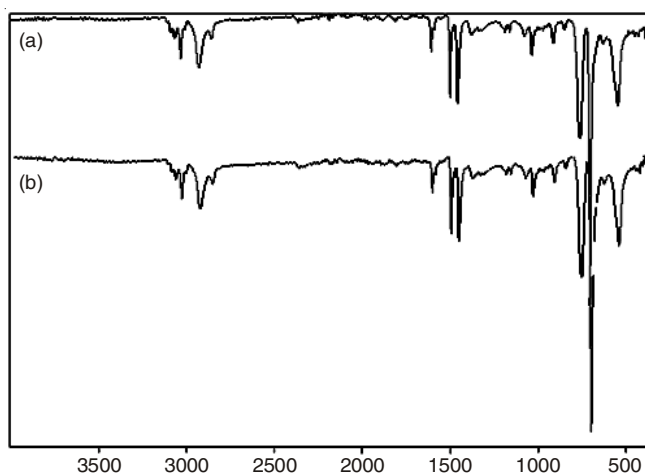
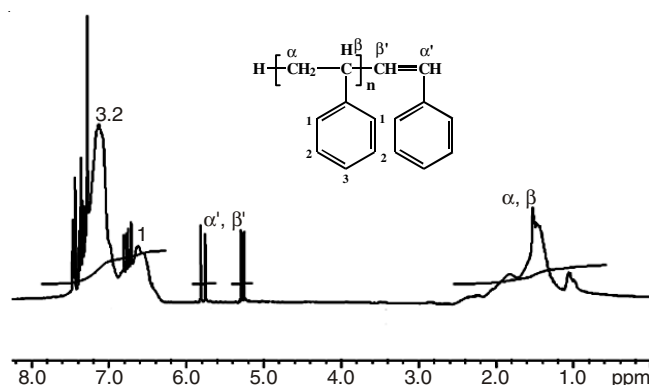


Fig. 3. FTIR spectra of polystyrene, catalyst: (a) Mag, (b) Mag-H

Fig. 4. ^1H NMR spectra (CDCl_3) of polystyrene (PS) with maghnite (St: 48.07 mmol, Mag-H: 5 %; $T = 20^\circ\text{C}$)

the amount of maghnite or Mag-H, thus clearly showing the effect of catalyst. This phenomenon is probably the result of an increase in the number of “initiating active sites” responsible of inducing polymerization, this number is prorating to the catalyst amount used in reaction. Similar results are shown by Meghabar *et al.* [18] and Moulkheir *et al.* [19] in the cationic polymerization, respectively, of N-vinyl-2-pyrrolidone and α -methylstyrene initiated by Mag-H. The molecular weight was found to decrease, depending on the amount of catalyst (*i.e.*, M_n decreases when amount of maghnite increases), with the increase in quantity of the catalyst. This finding is in good agreement with the presumption that maghnite and Mag-H are present as the active initiator species since the number of those species should be related to their surface area. These results indicate that, in the case of maghnite as catalyst, the catalytic activity of montmorillonite is related to aluminium in octahedral coordination at crystal edges and that the mineral is acting as a Lewis acid [6,32]. Thus the drying operation removes coordinated water molecules which are acting as a Lewis base and so makes the acid site available for styrene (Fig. 5). Thus, the mechanism of vinyl monomers polymerization by Mag-H is cationic [12,17-19]. When the catalyst was activated by acid, both the Lewis and the new Brønsted acid sites produced could be responsible for the catalytic activity [6,32]. Thus, acid treatment of maghnite increases the catalytic activity and the polymerization of styrene was initiated mainly by H^+ , as shown in the mechanism scheme (eqns. 1-3 *i.e.*, initiation, propagation and termination).

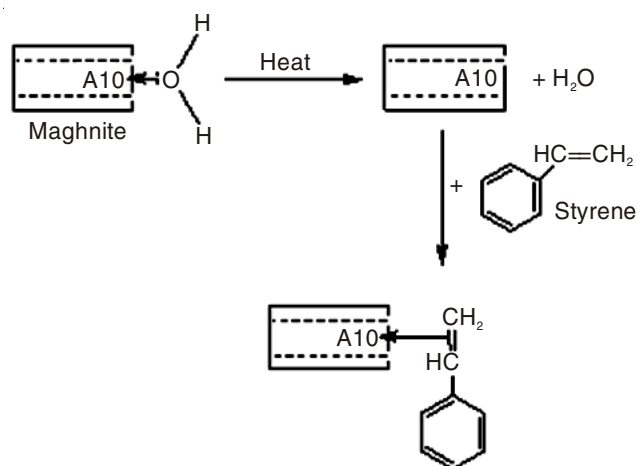
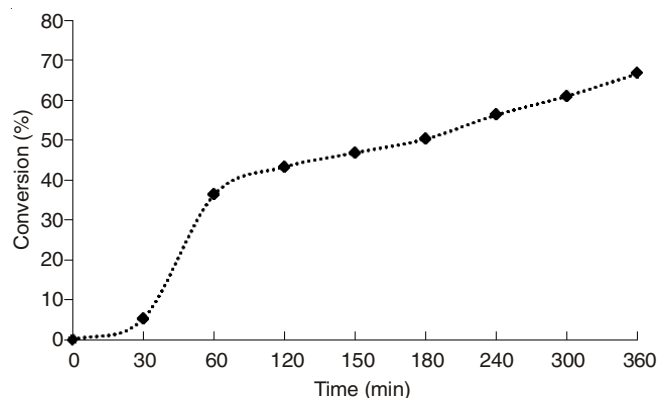


Fig. 5. Initiation mechanism of styrene polymerization by Lewis acid

Polymerization of styrene by Mag-H: According to this development, we have studied the cationic polymerization catalyzed by Mag-H. Fig. 6 shows the evolution of styrene polymerization, in the presence of Mag-H, over time. We observe from the obtained results, that after the first 30 min, the reaction is very slow and then it suddenly accelerates until it reaches 36.68 % of conversion after 1 h. Beyond, the development of the conversion becomes almost linear. Similar results are shown in polymerization, respectively, of isobutylene [17], N-vinyl-2-pyrrolidone [18] and α -methyl styrene [19], with Mag-H.

Fig. 6. Polymerization of styrene by Mag-H (St: 48.07 mmol, Mag-H: 3 %, $T = 20^\circ\text{C}$)

Effect of amount of maghnite on the polymerization:

Fig. 7 and Table-4 show the effect of the Mag-H amount on the styrene polymerization rate. Indeed, using various amounts of Mag-H by weight, the polymerization of styrene was carried in bulk at 20°C . The polymerization rate increased with the amount of Mag-H, in which the effect of Mag-H as a cationic catalyst of styrene is clearly shown. This is mainly due to the number of active sites, because the latter are proportional to the amount of the catalyst. More the active sites; the more opportunities for contact with the monomer. These results are in good agreement with those found by Tsubokawa [33], in the case of the cationic polymerization of α -methyl styrene initiated by carbon black. On the other hand, the effect of Mag-H proportion on average viscosimetric molecular weight was studied (Table-4). Increasing the Mag-H amounts yielded lower

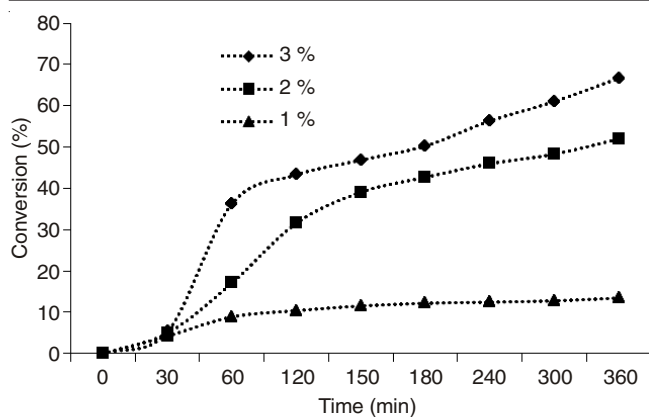


Fig. 7. Effect of the amount of Mag-H on polymerization of styrene (St: 48.07 mmol, T = 20 °C)

Time (min)	Mag-H (%)	$[\eta] \cdot 10^{-2}$ (dl/g)	M_v (g/mol)
Spontaneous	5	3.18	1016
Spontaneous	4	3.40	1162
300	3	4.31	1868
300	2	4.41	1959
300	1	4.48	2019

polystyrene M_v 's. Molecular weight viscosity is inversely proportional to the amount of Mag-H. This can be explained by the fact that increasing the amount of catalyst, results in growth of the initiating active sites, which will result in an increase in the number of chain growth and therefore a decrease in number average degree of polymerization.

Effect of temperature on the polymerization: In the presence of Mag-H, the polymerization of styrene in bulk was carried out at -10, 0, 20 and 40 °C and the effect of temperature on polymerization was examined. The results are shown in Fig. 8 and Table-5. Rate of polymerization was found to increase and the viscosimetric molecular weights decrease with the increase of polymerization temperature. Indeed, when the temperature decreases, problems of exothermy and transfers to monomer or polymer are limited. Similar results were found, in the case of the cationic polymerization of N-vinyl-2-pyrrolidone [18], α -methyl styrene [33] and isobutene [34], initiated, respectively, by Mag-H, carbon black and aluminum trichloride.

Effect of solvent on the polymerization: Mag-H is an efficient catalyst for polymerization of styrene. The bulk polymerization of styrene proceeds by an exothermic and spontaneous reaction at room temperature ($T = 20 \pm 2$ °C), using 4 to 5 % of Mag-H. Such bulk reactions are difficult to control due to the uncontrollable rise in temperature observed during these polymerizations; for this reason, we have studied the polymerization of styrene in some solvent (Table-6). Results show that, contrary to polar solvents, nonpolar solvents have no effect on the styrene polymerization. Indeed, polar solvents inhibit the catalyzed polymerization of styrene by clay minerals; polar compounds are stronger Lewis bases than styrene and compete successfully for the Lewis and Brønsted acid sites [6].

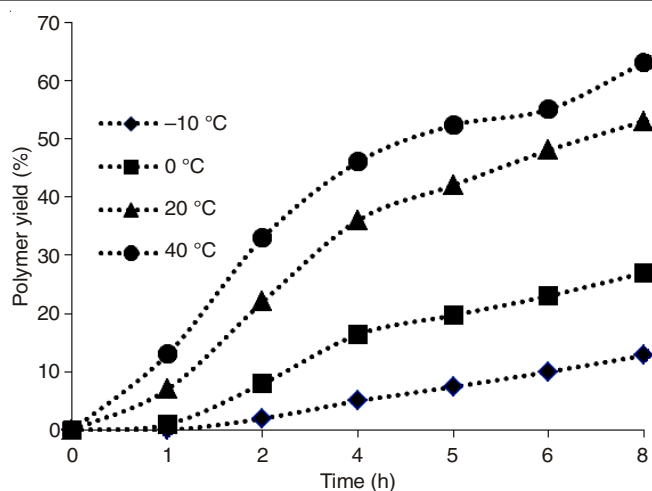


Fig. 8. Effect of the temperature on polymerization of styrene in bulk (St: 48.07 mmol, Mag-H: 3 %)

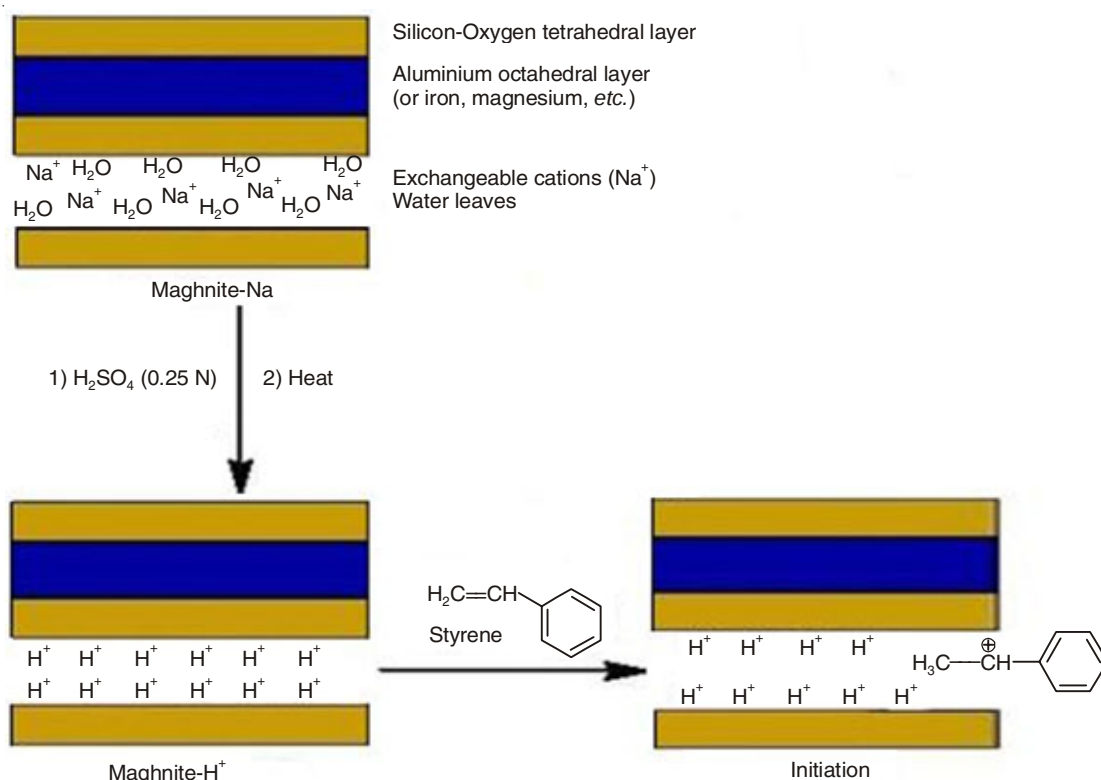
Temperature (°C)	Polymer yield (%)	$[\eta] \cdot 10^{-2}$ (dl/g)	M_v (g/mol)
-10	07.4	4.94	2455
0	19.7	4.64	2166
20	42.0	4.31	1868
40	52.3	4.25	1816

Solvent	Dielectric constant (ϵ)	Dipolar moment μ^d (D)	Results	Polymer yield (%)
Carbon tetrachloride	2.24	0.00	+	52.7
Chloroform	4.81	1.15	+	42.6
Dichloromethane	8.93	1.55	+	27.5
Acetone	20.70	2.86	-	Trace
Nitrobenzene	34.80	4.02	-	Trace
Acetonitrile	37.50	3.45	-	Trace

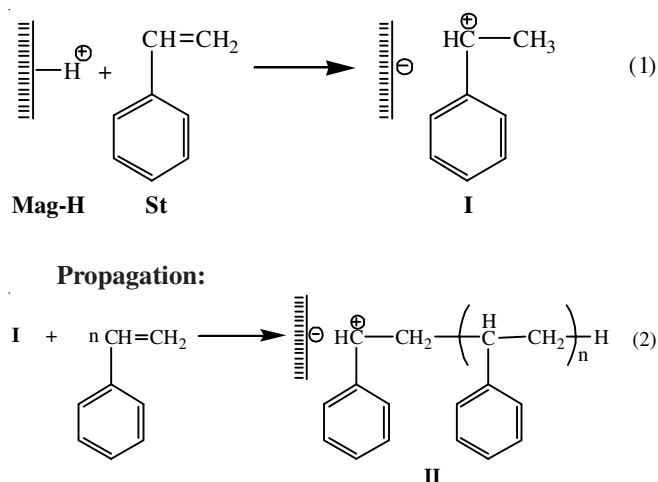
(+) = Non-polar solvent has no effect on the polymerization.
(-) = Polar solvent inhibits the reaction.

Mechanism of polymerization with Mag-H: The Mag-H lattice is composed of layers made up of two silica tetrahedral sheets with a central alumina octahedral sheet [12]. Thus, the polymerization of styrene is considered to be initiated, between the maghnite lamellae (*in situ*), simultaneously with the Brønsted acid and the Lewis acid but mainly by Brønsted acid. However, the protons carried by Mag-H in the interlayer space induce, in large part, styrene cationic polymerization and the maghnite sheets play the role of counter-anions (**Scheme-II**). Propagation and termination then take place by conventional cationic mechanism. Termination occurs by proton transfer to monomer and/or to initiator produced by unsaturation as shown in the reaction **Scheme-I** and in ^1H NMR spectra (Fig. 4).

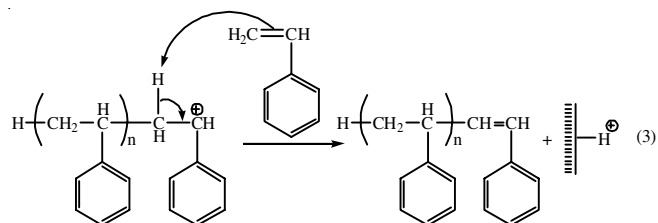
Initiation: Initiation is done between initiator and a first molecule of styrene to form the active species.



Scheme-II



Termination: There was formation of a double bond, as shown in Fig. 2, at the end of the chain of polystyrene by spontaneous transfer.



Conclusions

On the basis of the results obtained during this study, the cationic polymerization of styrene was found to be initiated

by maghnite powder in heterogeneous phase. The polymerization was considered to be initiated, mainly, by the proton addition, in the case of maghnite- H^+ , to monomer and the propagation proceeds with maghnite as counter-ion. The following conclusions have been also drawn:

- Maghnite is a non-toxic cationic catalyst for cationic polymerization.
- This heterogeneous reaction method is environmentally friendly for the ease of separation of polymers.
- Maghnite may be regenerated by simple filtration and washing
- The maximum yield is for a concentration of 0.5 N H_2SO_4 .
- Concentrated acid treatment causes a change in the clay structure.
- The polymerization is therefore consistent with a concerted Brønsted/Lewis acid catalyzed mechanism.
- The synthesized H^+ -exchanged clay showed a significant catalytic activity.
- The values of the molar masses average ($M_w < 5000$) show clearly that the polymerization is confined between the layers (polymerization *in situ*).

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