A Protons Exchanged Montmorillonite Clay as an Efficient Catalyst for the Reaction of Isobutylene Polymerization

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Abstract: "Maghnite" a montmorillonite sheet silicate clay, exchanged with protons to produce "H-Maghnite" is an efficient catalyst for cationic polymerization of many vinylic and heterocyclic monomers (Belbachir, M. *U.S. Patent.* 066969.0101 –2001)**.** The structure compositions of both "Maghnite" and "H-Maghnite" have been developed. Isobutylene monomer, wich is polymerizable only by cationic process (Odian,G. *La Polymerisation :principes et Applications*; Ed.Technica: New York, 1994; pp 222-226), was used to elucidate the cationic character of polymerization.

The polymerization was performed under suitable conditions at isobutylene vaporization temperature (–7°C). Experiments revealed that polymerization induced by "H-Maghnite" proceed in bulk and in solution. In contrast to findings with methylene chloride CH_2Cl_2 as a polar solvent, polymerization yields with hexane C_6H_{14} non-polar solvent is very significant. In bulk polymerization, Isobutylene conversion increases with increasing "H-Maghnite" proportion.

Keywords: Maghnite, Montmorillonite, Catalyst, Isobutylene, Polyisobutylene.

Introduction

The use of 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 1960s [1]**.** And are still currently used in industrial processes such as the alkylation of phenols [2] and the dimerization and polymerization of unsaturated hydrocarbons [3].

Montmorillonites have both brönsted and Lewis acid sites and when exchanged with cations having a high charges density, as protons, produce highly-active catalysts for acid-catalysed reactions [4]. Inercalated 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 [3].

The present study is also concerned with polymerization and examines the catalytic activity of an Algerian proton exchanged montmorillonite clay called "Maghnite" via isobutylene polymerization to exhibit the cationic character of the reation [5]. The aim of this research is to extend the scope of other promising new field of polymer synthesis by the use of another catalyst system that has been shown to exhibit higher efficiency.

This paper concerns detailed analyses of "raw-Maghnite", "H-Maghnite" and polymerization products, effect of catalyst ration and solvent polarity on Isobutylene conversion.

Experimental

A. Materials

1) n-C_6H_{14} was refluxed with fuming sulfuric acid, washed neutral with distilled water, dried over molecular sieves, refluxed and distilled from CaH_2 under a nitrogen atmosphere on the day of the experiment.

2) CH_2Cl_2 was dried over molecular sieves, distilled over CaH_2, refluxed with triethylaluminium under nitrogen atmosphere overnight and freshly distilled on the day of the experiment.

3) "H-Maghnite xM": The acid forms of "raw-Maghnite" is prepared by shaking the material raw (raw-Maghnite) with solution of sulfuric acid until saturation achieved over two days at room temperature, washing the mineral with water until sulfate-free and drying. The concentrations 0.05M, 0.10M, 0.15M, 0.20M, 0.25M, 0.30M and 0.35M of sulfuric acid treatment solutions were used to prepare "H-Maghnite0.05M", "H-Maghnite0.10M", "H-Maghnite0.15M" , "H-Maghnite0.20M", "H-Maghnite0.25M","H-Maghnite0.30M" and "H-Maghnite0.35M" respectively.

4) Isobutylene (IB) was dried by passing the gas through a column packed with BaO, and condensing it under a nitrogen atmosphere.

5) Methanol was used as received

B. "Maghnite" and "H-Maghnite" characterization:

1) Samples for XRF analysis were prepared using the LiB_4O_7 fusion method. The resulting beads were analyzed on a Philips PW 2400XRF spectrometer in Laboratory of Inorganic Chemistry, Granada University, Spain

2) XRD profiles for pressed powder samples were recorded on a Philips PW 1710 diffractometer using Cu-Kα radiation (λ=1.5418A°)

3) IR absorption spectra were recorded on a ATI Matson FTIR N°9501165 spectrometer using the KBr pressed-disc technique, 0.5mg of sample was added to 300mg KBr and mixed for 3min in a vibratory grinder prior to pressing a 13mm disc.

4) High-resolution solid-state ^{29}Si and ^{27}Al MAS NMR spectra of untreated (raw-Maghnite) and acid treated (H-Maghnite0.25M) samples were recorded on a Brüker ASX 500 spectrometer at 59.6 and 130.3 MHz respectively. The sample spinning frequency was 4 KHz for ^{29}Si and 11.5 KHz for ^{27}Al.

C. Procedure and Polymer characterization

Polymerizations were carried out in stirred flasks at –7 °C. The catalyst was dried in a muffle at 120°C over night and then transferred to a vacuum desiccator containing P_2O_5. After cooling to room temperature under vacum, the mineral was added to the Isobutylene (10g) or IB (10g)-solvent (90ml) mixture preliminary keeped in stirred flask at Isobutylene boiling point temperature (-7°C). At the required time, an aliquot of the reaction mixture was then taken in such manner as to exclude any clay mineral and slowly added to methanol with stirring. The precipitated polymer was filtered off and dried at 35-40°C under vacuum and weighed. The polymers were redissolved in CH_2Cl_2 and precipitated into methanol for characterization and molecular weight measurement.

Molecular weights were determined by a Waters high pressure GPC instrument (Model 6000A Pump) having a serie of ultra-Styragel columns (100, 500, 10^3, 10^4, 10^5 A°), a Differential Refractometer 2401 and a UV absorbance Detector Model 440. The flow rate of tetrahydrofuran (THF) was 1 ml/min. The calibration curve was made with well-fractionated polyisobutylene standards.

^{1}H NMR spectra were recorded on an AM 300 FT Bruker instrument using $CDCl_3$ as solvent, and tetramethylsilane (TMS) as internal standard.

Results and Discussion

Catalyst Structure

Various methods of analysis, such as ^{27}Al and ^{29}Si MAS NMR, show that "Maghnit" is a montmorillonite sheet silicate clay. The elementary analysis of the selected samples obtained using XRF and monomer conversions obtained from the reaction of 1g of each sample with 10g of Isobutylene during 3 hours in a bulk polymerization at –7°C, are as settled in the following Table 1.

It is necessary to report that the best value of isobutylene conversion was obtained with "H-Maghnite0.25M", for this reason we kept this sample to study the effect of catalyst proportions and solvent on isobutylene polymerization. Acid treatment of ''Raw-Maghnit'' cause reduction in octahedral content (Al_2O_3) resulted in an increase in the proportion of silica (SiO_2) observed.

The X-Ray powder diffraction profiles (Figure 1 and Table 2) exhibited the presence of other crystalline phases as quartz, feldspath and calcite in "raw-Maghnit" By treatment acid, all trace of calcite was removed in "H-Maghnite".

Table1 Elementary compositions of Protons exchanged samples "H-Maghnite"

sample	Compositions wt%											IB conversion %
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3	As	PF*	
Raw-Maghnite	69.39	14.67	1.16	0.30	1.07	0.50	0.79	0.16	0.91	0.05	11	00
H-Mag0.05M	70.75	14.67	1.05	0.30	1.01	0.49	0.78	0.16	0.75	0.04	10	2
H-Mag0.10M	71.00	14.60	1.00	0.30	0.98	0.39	0.78	0.16	0.55	0.04	10.2	3.21
H-Mag0.15M	71.58	14.45	0.95	0.29	0.91	0.35	0.77	0.15	0.42	0.03	10.1	10
H-Mag0.20M	71.65	14.20	0.80	0.28	0.85	0.30	0.77	0.15	0.39	0.01	10.6	13.7
H-Mag0.25M	71.70	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	0.01	11	65
H-Mag0.30M	73.20	13.85	0.70	0.27	0.78	0.20	0.76	0.13	0.31	0.02	9.78	30
H-Mag0.35M	75.31	13.52	0.71	0.26	0.78	0.18	0.75	0.13	0.32	0.01	8.03	27

*PF : Pert in Fire

The increase in basal spacing from 12.5 Å in "raw-Maghnite'', characteristic of one water layer between the sheets, to value of 15.02 Å in ''H-Maghnite'', where there are two interlamellar water layers, subsquent to acid treatment reflects the change in interlayer cation and its associated hydration state [6].
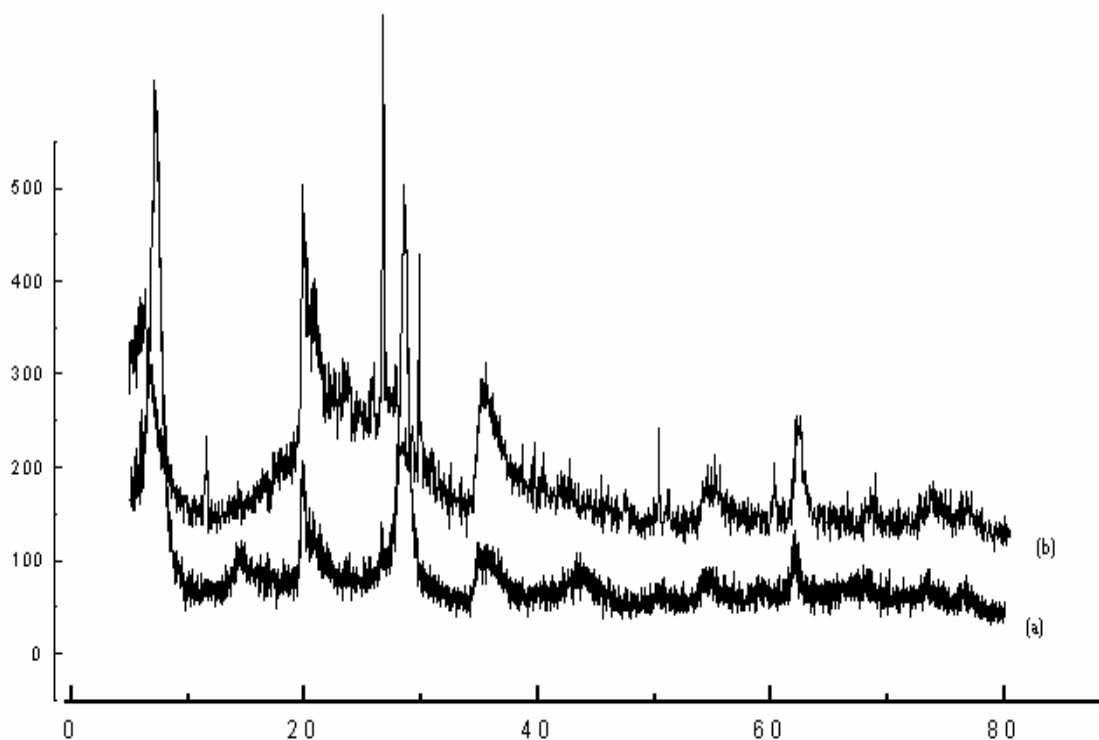
**Figure 1.** X-ray Power Diffraction of (a) "Raw-Maghnite" and (b) "H-Maghnite0.25M"

Table 2 RX characteristic of Raw-Maghnite and H-Maghnite0.25M.

| samples	d_{hkl} (Å)	hkl	Nature of sample
Raw-Maghnite	12.50	001	Montmorillonite
	4.47	110	Montmorillonite
	4.16	,,	Quartz
	3.35	,,	Quartz
	3.21	,,	Feldspath
	3.03	,,	Calcite
	2.55	200	Montmorillonite
	1.68	009	Montmorillonite
	1.49	060	Montmorillonite
H-Maghnite0.25M	15.02	001	Montmorillonite
	4.47	110	Montmorillonite
	4.16	,,	Quartz
	3.35	,,	Quartz
	3.21	,,	Feldspath
	3.03	,,	Calcite
	2.55	200	Montmorillonite
	1.68	009	Montmorillonite
	1.49	060	Montmorillonite

The IR Spectra of Raw-Maghnit and H-Maghnite0.25M (Fig. 2) are in good agrement with literature [7]. The characteristic vibrations of hydroxy groups, the silicate anion and the octahedral cations were observed in the IR spectra of both montmorillonites. The most intense band near 1040 Cm^{-1} is attributed to the Si-O stretching vibrtations of the tetrahedral layer and the bands near 522 and 466 Cm^{-1} are assigned to Si-O bending vibrations of smectites. A low intensity band near 800 Cm^{-1}, assigned to four-coordinated silica [8], indicates the presence of amorphous silica. Compareson of Raw-Maghnite and H-Maghnite0.25M spectra show a small increasing in the SiO_2 band intensity near 800 Cm^{-1} in H-Maghnite0.25M, reflects alterations in the amount of amorphous silica [9].

The ^{27}Al MAS NMR spectra of both Raw–Maghnite and H-Maghnite-0.25M (Fig. 3) show Aluminium in two tetrahedral environments with resonances centered at 60 and 68 ppm, in addition to the main contribution from the octahedral aluminium at 2.9ppm. These values and assignments concur with those published in literature [6,10,11].
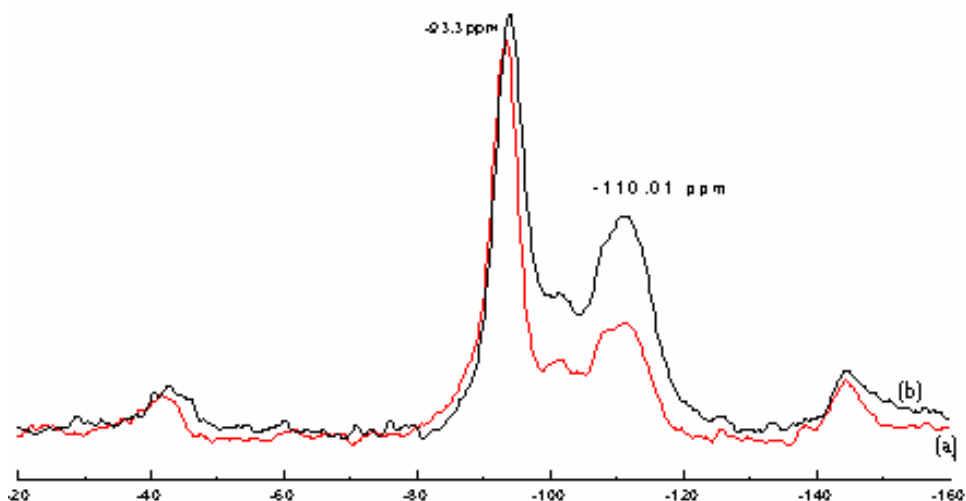
The ^{29}Si MAS NMR spectra for the Rw-Maghnite and H-Maghnite0.25M are shown in Fig 4. The dominent resonance at – 93,5 ppm corresponds to Q^3(OAl) units,i.e SiO_4 groups crosslinked in the tetrahedral sheets with no aluminium in the neighbouring tetrahedral [12]. The resonance at –112 ppm corresponds to three-dimensial (3D) silica with no aluminium present, designed Q^4 (OAl) [6,13].
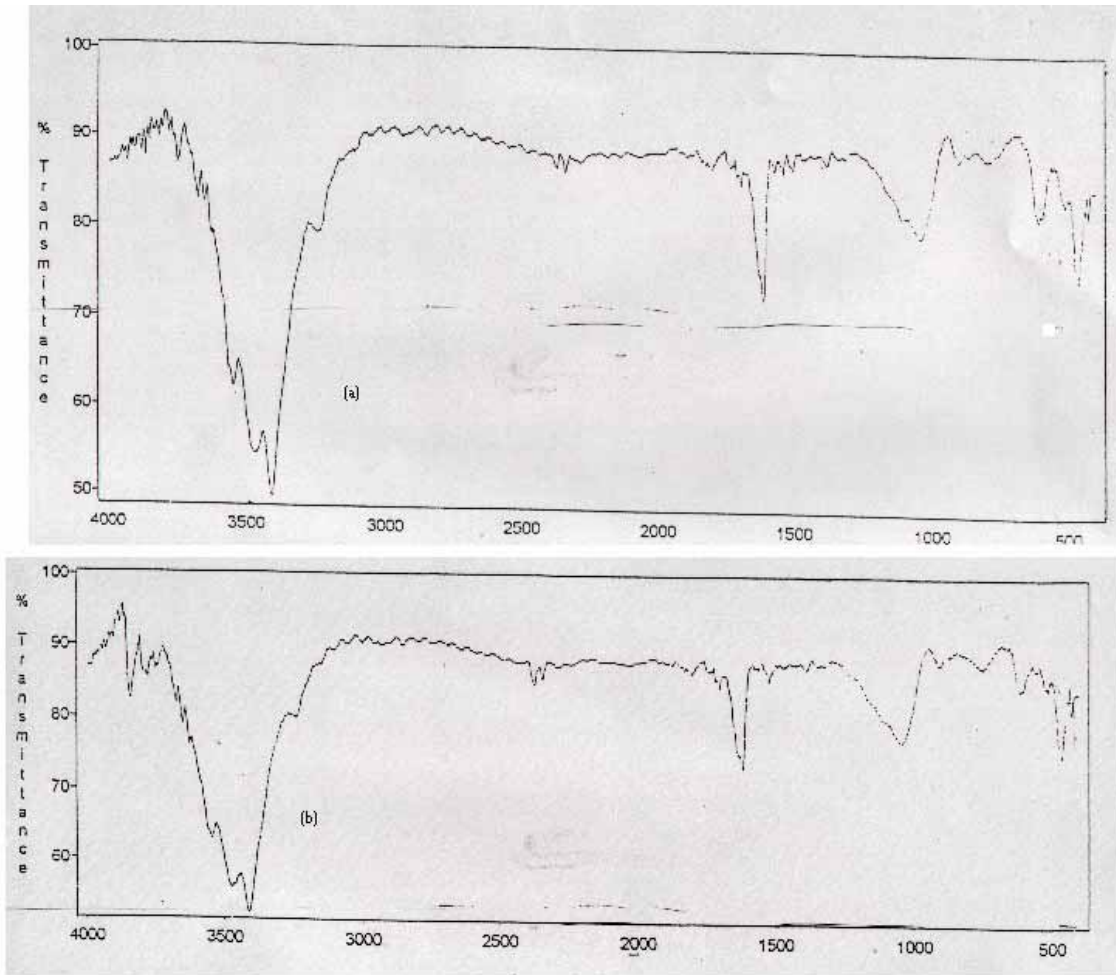
Figure 2. IR Spectra of (a) untreated Clay "Raw-Maghnite" and (b) Acid treated Clay "H-Maghnite0.25M"
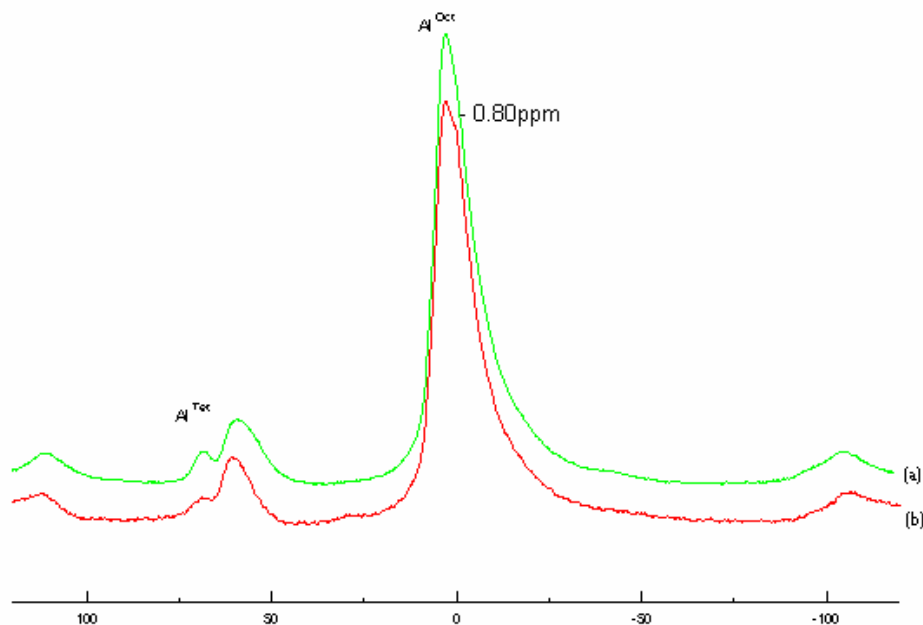
Figure 3. ^{27}Al MAS NMR spectra of (a) "Raw-Maghnite" and (b) "H-Maghnite0.25M"

Figure 4. ^{29}Si MAS NMR spectra of (a) "Raw-Maghnite" and (b) "H-Maghnite0.25M"

Polymerization and Products characterization

   The results of experiments of Isobutylene polymerization induced by "H-Maghnite0.25M" are reported in Table 3. For all these experiments the temperature was kept constant at –7°C for 3 hours.

Table 3. Polymerization of IB induced by the "H-Maghnite0.25M"

| Experiment	Solvent	IB g	[IB] mol/l	"H-Maghnite0.25M"(g)	Yield %	M_n	M_w	M_w/M_n
1	Bulk	10	-	0.5	47	728	3269	4.49
2	Bulk	10	-	1.0	65	713	3020	4.24
3	Bulk	10	-	1.5	72	520	2410	4.63
4	CH_2Cl_2	10	2	1.0	37	3270	3839	1.17
5	C_6H_{14}	10	2	1.0	50	3690	4291	1.16

Effect of "H-Maghnite0.25M" proportion

   We can see from Table 3 that, the conversion of monomer increases with increasing "H-Maghnite0.25M" proportion (experiments 1,2,3). This lead was followed up by a serie of deeper experiments in which the conversion of Isobutylene with the time has been observed at various amounts of catalyst. Table 4 and Figure 5 show that increasing the "H-Maghnite0.25M" amounts yielded higher Isobutylene conversions. This phenomena is probably the result of number of "initiating active sites " responsible of inducing polymerization, this number is prorata to the catalyst amount used in reaction.

Table 4. Isobutylene conversions with time : for 10g of Isobutylene, the amounts of H-Maghnite0.25M were: a)0.5g   b)1g   c) 1.5g

Time (minutes)		0	30	60	90	120	150	180	240	300
	a	0	15	25	35	38	43	47	54	56
Yield%	b	0	30	40	47	55	60	65	75	83
	c	0	35	48	55	63	68	72	80	81
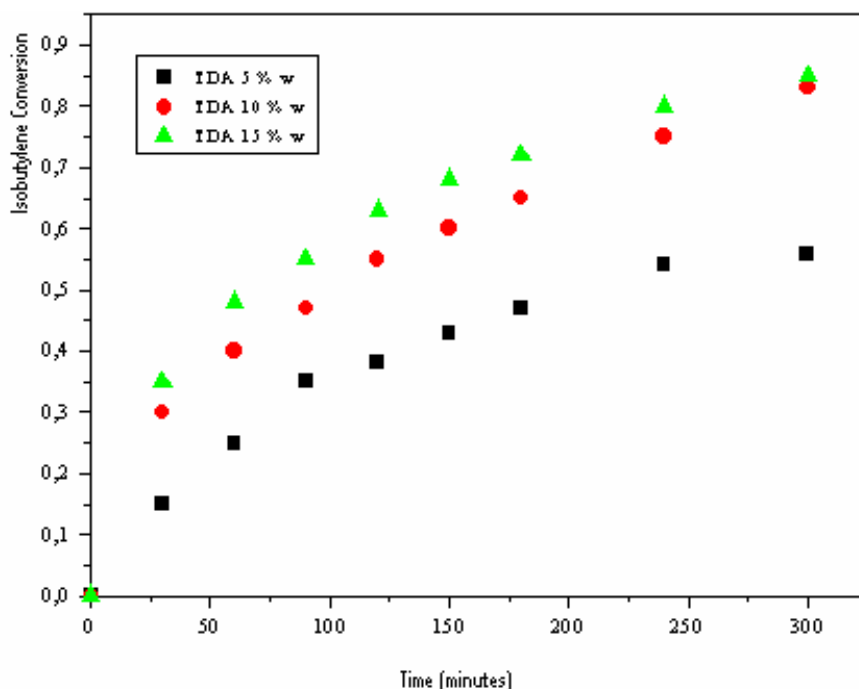
Figure 5. Effect of catalyst proportion upon the conversion of Isobutylene

Effect of solvent:

Data in Table 3 show that polymerization carried out in solution leaded to higher molecular weights and narrower MWDs (M_w/M_n) . However conversions in solution were smaller than the ones obtained in bulk polymerization. Low conversions in solution polymerization may be explained by the difficult contact in heterogeneous phase, between monomer particles and the "initiating active sites" of "catalyst" surface.

Conversion of monomer obtained in non-polar solvent (C_6H_{14}) was more important than the ones obtained in polar solvent (CH_2Cl_2), this result is due to "catalyst" structure. As all minerals clay, it shows an affinity over polar particles, in this case, adsorbed molecules of polar solvent (CH_2Cl_2) occupied "initiating active sites", and led to low Isobutylene conversions.
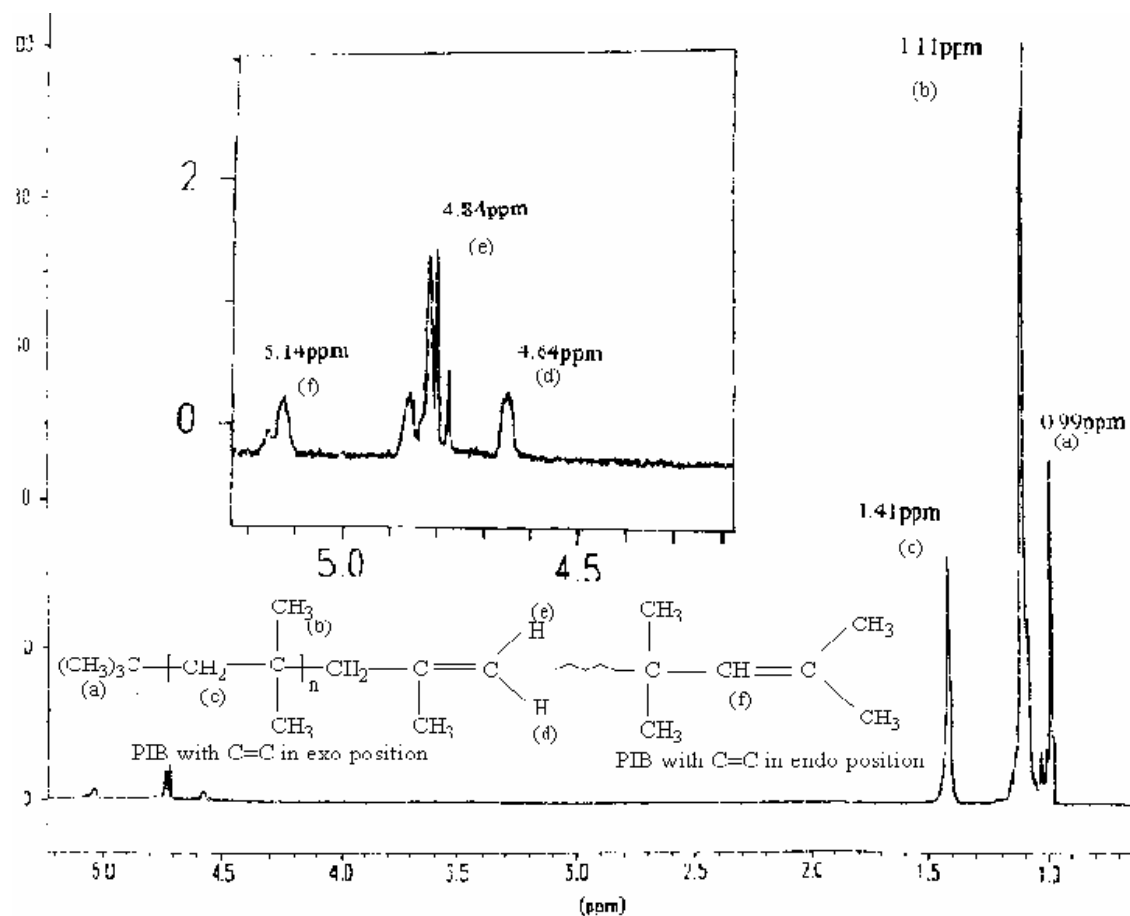
Characterization of products

An investigation was devoted to the analysis of the polymer from experiment 2 in Table 3 by ^{1}H NMR spectroscopy at 300MHz (Table 5 and Fig. 6).

Table 5. Results of product analysis by ^{1}H NMR spectroscopy

Proton type	(a)	(b)	(c)	(d)	(e)	(f)
δ in ppm	0.99	1.11	1.41	4.64	4.84	5.14

Figure 6. ^{1}H NMR spectra of polyisobutylene product of experiment 3 in Table 3.

Chains of Polyisobutylene present two types of unsaturation. Spontaneous termination and transfer involving proton abstraction lead to the expected exo/endo terminal double bonds (Structures A, B). The integration of ^{1}H NMR peaks of protons carried by terminal double bonds is necessary to determinate proportions of these structures (A, B).

A 32%   B 68%
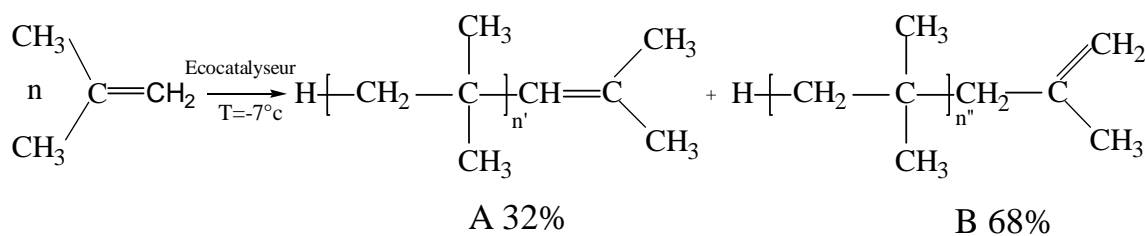
According to the work published by Francis and Archer [14], and Stanly et al. [15], ^{1}H NMR spectroscopy at 300 MHz (Solvent $CDCl_3$) (Fig. 6) showed different peaks, the methyl groups of the main chain at 1.11ppm, the methylene groups at 1.41ppm, the terminal tert-butyl groups at 0.99ppm. Besides these well-known resonances, analysis shows at 5.14ppm the characteristic resonance of the proton borne by the double bond of the terminal trisubstituted unsaturation PIB-C**H**=C(CH$_3$)$_2$, at 4.64ppm the proton at a cis position of the methyl group belonging to the function PIB-C(CH$_3$)=C**H$_2$** and at 4.84ppm the multiplet of the proton at a trans position of the same function.

Mechanism of the reaction

Isobutylene is an monomer witch is polymerizable only by cationic way. According to the foregoing discussion and the results of product analysis, we may suggest a cationic mechanism for the resulting reaction of polymerization induced by "H-Maghnite0.25M".

Protons carried by montmorillonite sheets of "H-Maghnite0.25M" induced the cationic polymerization, these montmorillonite sheets take place as counter-anions. Propagation and termination then take place by conventional cationic mechanism. Termination by proton transfer to monomer and/or to initiator produced unsaturations onto polyisobutylene chains.
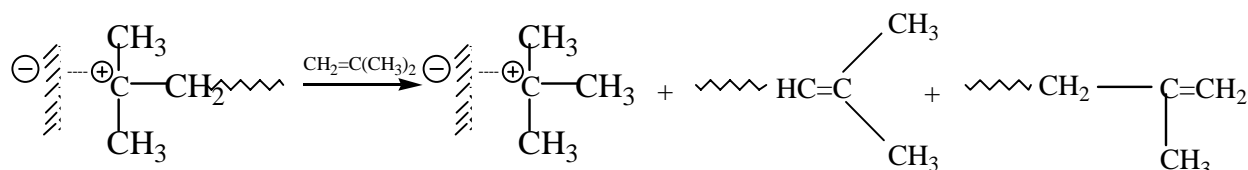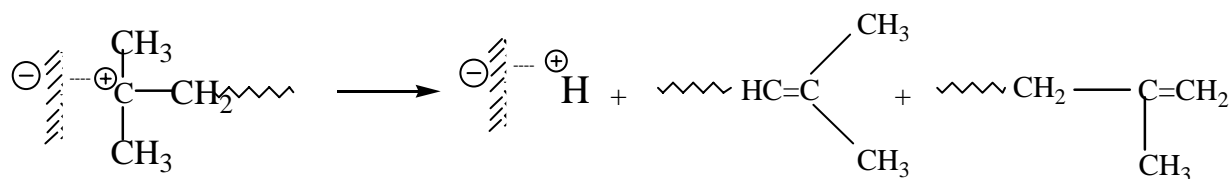
Initiation:
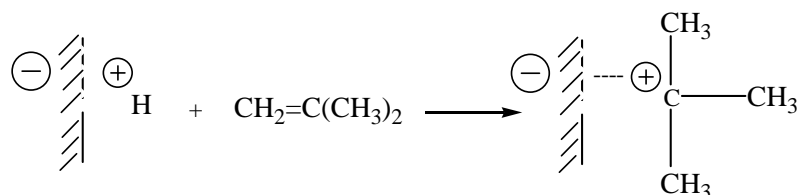
Propagation:
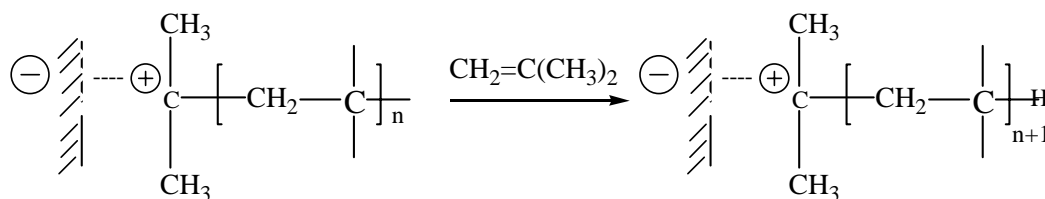
Termination:

Transfer to monomer:

Transfer to initiator:

Conclusion

The present work shows that Isobutylene polymerization can be induced in heterogeneous phase by a proton exchanged montmorillonite clay called "H-Maghnite". Polyisobutylenes were produced accordingly by an easy-to-handle procedure in one batch process. This new chemistry for cationic polymerization will be explored deeply in forthcoming work.

References

1. Thomas, C.L.; Hickey, J.; Stecker,G. *Ind. Eng. Chem.* **1950**, *42*, 866.

2. Kaplan, H.; *U.S.Patent.* 3287422.1966.

3. Hojabri, F.*; J. Appl. Chem. Biotechnol*. **1971**, *21*, 87.

4. Ballantine, J.A.; Davies, M.; Purnell, H. Chemical conversions using sheet silicates: novel interlamellar dehydrations of alcohols to ethers and polymers. *J. C. S. Chem. Comm.* **1981**, 427-428.

5. Odian,G. *La Polymerisation: principes et Applications*; Ed.Technica: New York, **1994**; pp 222-226.

6. Breen ,C.;Madejovà,J.; Komadel, P. *J.Mater.Chem.***1995**, *5(3)*, 496-474.

7. Farmer,V.C. In *Infrared Spectra of Minerals*, V.C. Farmer, Ed.; Mineralogical Society: London, **1974**, p.331.

8. Moeke, H.H.W. In *Infrared Spectra of Minerals*, V.C. Farmer, Ed.; Mineralogical Society: London, **1974**, p.365.

9. Madejovà ,J.; Bednànikovà, E.; Komadel, P.; Cicel, B. *in Proc.11th Conf. Chem. Miner. Petrol. Ceske Budéjovica 1990*; J. Konta, Ed.; Charles University: Prague, **1993**; p. 267.

10. Komarneni ,S.; Fyfe, C.A.; Kennedy, G. J.; Strobhl, H. *J. Am. Ceram. Soc.* **1986**, *69*, 645.

11. Samajovà ,E.; Kraus, I.; Lajcàkovà, A. *Geol. Carpath. Ser. Clays*. **1992**, *42*, 21.

12. Thompson ,J.G. *Clay Miner.* **1984**, *19*, 169.

13. Tkàc ,I.; Komadel, P.; Müle, D. *Clay Miner*. **1994**, *29*, 11.

14. Francis,S.A.; Archer, E.D. *Anal.Chem.* **1963**, *35*, 1363–1369.

15. Stanley, L. M.; Ingham, J. D.; Miler, J. A. *J. Org. Magn. Reson*. **1977,** *10*, 198.