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Acid Exchanged Montmorillonite Catalyzed Condensation Reaction of Fluoroalkyliodide onto Amines

AÏCHA HACHEMAOUI, MOHAMMED BELBACHIR* and AHMED YAHIAOUI
Université d'Oran, Faculté des Sciences, Département de Chimie
Laboratoire de Chimie des Polymères
BP 1524 El-Menouer 31000 Oran, Algeria
Fax: (213)(41)510057; E-mail: hachemaoui2002@yahoo.fr

The H-maghnite (Maghnia, Algeria), a montmorillonite sheet silicate clay was treated in different H_2SO_4 concentrations at 20°C. The aluminium and silicon were identified by ^{27}Al and ^{29}Si MAS NMR spectroscopy. Three different types of structural units were identified in acid-treated maghnite $Q^4(0Al)$ units of amorphous silica with three-dimensional cross-liked framework; $(SiO)_3SiOH$ and $Q^4(1Al)$ units. The catalytic activity of acid-treated maghnite was evaluated by reacting 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodo octane with several amines to yield perfluoro-alkylamines and no byproducts were obtained during the reaction. The structure of perfluoroalkylamines obtained was characterized by ^1H, ^{13}C and ^{19}F NMR.

Key Words: Montmorillonite, Maghnite, Catalyst, Self-condensation, Perfluorohexylethylene iodide, Amines.

INTRODUCTION

Selective organic transformation in the presence of various solid catalysts including metal cation-exchanged clay minerals is of current interest in making the synthetic processes comfortable and benign to the Earth[1]. The ability of variously exchanged montmorillonites to catalyze a range of organic reactions of synthetic and industrial significance remains attractive for chemists[2–4]. The catalytic activity could be explained in terms of either Lewis or Brönsted acid centres contributing to the reaction mechanism[5]. Clay catalysts have been shown to contain both Brönsted and Lewis acid sites, with the Brönsted sites mainly associated with the inter-lamellar region and the Lewis sites mainly associated with edge sites. The acidity of smectites is influenced by the quantity of water between the layers[6, 7].

Water molecules in the hydration spheres of exchangeable cations are proton donors (Brönsted acids). Hydration water dissociates under the polarizing effect of the metallic cation as follows:

$$[M(OH_2)_x]^{m+} \longrightarrow [M(OH)(OH_2)_{x-1}]^{(m-1)+} + H^+,$$

where x is the number of water molecules that directly coordinate with the metal cation M and m^+ is the charge on the cation.

The first step in the activation procedure, which is required for both natural and synthetic clay minerals, is to convert the mineral into the desired ion form. In the case of acid ions, this can be achieved relatively easily by ion exchange

using a concentrated solution of suitable acid followed by repeated washings to remove the excess acid.

There is still a great demand for heterogeneous catalysis under mild conditions and in environmentally friendly processes. Montmorillonites, a class of inexpensive and non-corrosive solid acids have been used as efficient catalysts for a variety of organic reactions. The reactions catalyzed by montmorillonites are usually carried out under mild conditions with high yields and high selectivities. The workup of these reactions is very simple; only filtration to remove the catalyst and evaporation of the solvent are required. Montmorillonite catalysts are easily recovered and reused[8, 9].

Some frequently used organic reactants containing reactive groups, such as aldehydes and ketones, require protection of these groups to avoid undesirable side reactions. Protection of aldehyde with acetic anhydride in the presence of montmorillonite catalyst is a suitable reaction for testing the catalytic activity of modified smectites[10]. An earlier assay showed that heated NH_4^+-MMT catalyzed protection of 3,4,5-trimethoxybenzaldehyde[11]. Recently, monomers were found to intercalate into lattice layers of montmorillonite clay, permitting *in situ* polymerizations yielding polymer/clay nano-composites. Several polymers, for example, polyamide (nylon-6)[12], polystyrene[13–17] and polystyrene-block-polyisoprene-block-polystyrene[18] have been prepared *via* this route.

Introduction of fluorine into an organic molecule often leads to significant changes in biological activity and organofluorine compounds have been utilized in pharmaceuticals, agrochemicals and as mechanistic probes for biochemical processes[19]. The aminoperfluoroalkyl iodides have a wide range of use and can be used for the synthesis of intermediates, particularly as auxiliaries in the textile industry, for example, as hydrophobic, oleophobic, anti-spotting agents and in the preparation of dyestuffs. They have surface tension properties which can also be used as surface active agents[20, 21].

The aim of this work was to prepare an acid exchanged montmorillonite called (Maghnite-H^+)[22–24] from Na^+-form by acid exchange and to test catalytic activity of this material for the condensation reaction of fluoroalkyliodide onto amines.

EXPERIMENTAL

Perfluorohexylethylene iodide was obtained from commercial source (PECK) and used without further purification. The several amines, *viz.*, diethanolamine $HN(CH_2CH_2\text{-}OH)_2$, diethyl amine $HN(CH_2CH_3)_2$ and morpholine C_4H_9ON, were purchased from Merck and purified by vacuum distillation before use. Organic solvents such as chloroform and diethyloxide were purified by usual methods[25]. Montmorillonite clay or raw-maghnite was obtained from ENOF Maghnia (Western Algeria). The protonated forms of montmorillonite (Mag-H^+) were prepared by shaking 2 g of clay in 4 mL of sulfuric acid solution at 20°C until saturation was achieved (normally after 2 d at room temperature). The cation-exchanged clay was then recovered by filtration and again suspended in deionized water. This process was repeated until no sulfate ions were indicated present in

the filtrate using $BaCl_2$. The Mag-H^+ was then isolated by filtration, dried at 105°C and then finely ground. The cation exchange capacity (CEC) of the clay was found to be 84 mEq $(100\ g)^{-1}$ of dried clay. Sulfuric acid of concentrations 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35 M were used to prepare the samples, respectively, denoted Mag-H^+ 0.05, Mag-H^+ 0.10, Mag-H^+ 0.15, Mag-H^+ 0.20, Mag-H^+ 0.25, Mag-H^+ 0.30 and Mag-H^+ 0.35 M.

Reactions were performed without solvent at 20°C. The procedure was identical in both cases, a mixture of $HN(CH_2\text{-}CH_2OH)_2$ (4.2 g, 0.04 mol) and 2 g of catalyst was stirred under vacuum for 1 h. The mixture was then agitated with (9.5 g, 0.02 mol) of $C_6F_{13}CH_2CH_2I$ for 2 h. The reacting solution was washed several times by chloroform and a viscous product, a quaternary ammonium salt, was obtained.

After having prepared 100 cm^3 of an aqueous solution of KOH (10%), the ammonium salt was added in small quantities. The mixture was left under stirring overnight. A homogeneous solution was obtained and the aminoperfluoroalkyl was extracted by ether. Two phases were formed, which were separated by decantation and perfluoroalkylamine was obtained by evaporation of ether (yield 82%).

^1H and ^{13}C nuclear magnetic resonance measurements were carried out on a 400 MHz Bruker NMR spectrometer equipped with a probe BB 05 mm, in $CDCl_3$. Tetramethylsilane (TMS) was used as the internal standard. ^{19}F nuclear magnetic resonance measurements were carried out on a 400 MHz Bruker spectrometer equipped with a probe QNP 5 mm in $CDCl_3$, and $CFCl_3$ was used as the internal standard. Thermal gravimetric (TGA) characterizations were performed under nitrogen using a Dupont model 9900 thermal analyzer at a heating rate of 20°C min^{-1}. Maghnite and Mag-H^+ samples were characterized by XRF (a Philips PW 2400 XRF spectrometer at the Laboratory of Inorganic Chemistry, Granada University, Spain) using the LiB_4O_7 fusion method. XRD profiles for pressed powder samples were recorded on a Philips PW 1710 diffractometer using Cu-K_α radiation (λ = 1.5418 Å). IR absorption spectra were recorded on an ATI Matson FTIR No. 9501165 spectrometer using the KBr pressed discs. High-resolution solid-state ^{29}Si and ^{27}Al MAS NMR spectra of untreated (raw-maghnite) and acid treated (Mag-H^+ 0.25 M) 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.

RESULTS AND DISCUSSION

The elementary analysis of the selected samples obtained using XRF is as given in Table-1. It is necessary to report that the best value of perfluoroalkylamine (FAA) yield was obtained with Mag-H^+ 0.25 M; for this reason we kept this sample in all reactions. Acid treatment of raw-maghnite was indicated to cause a relative reduction in the content of octahedrally spaced Al_2O_3 and a relative increase in silica (SiO_2).

TABLE-1
ELEMENTARY COMPOSITIONS OF PROTON EXCHANGED SAMPLES
MAGHNITE COMPOSITIONS (WEIGHT %)

Sample	Composition (wt %)										
	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
H-Mag 0.05M	70.75	14.67	1.05	0.30	1.01	0.49	0.78	0.16	0.75	0.04	10
H-Mag 0.10M	71.00	14.60	1.00	0.30	0.98	0.39	0.78	0.16	0.55	0.04	10
H-Mag 0.15M	71.58	14.45	0.95	0.29	0.91	0.35	0.77	0.15	0.42	0.03	10
H-Mag 0.20M	71.65	14.20	0.80	0.28	0.85	0.30	0.77	0.15	0.39	0.01	10
H-Mag 0.25M	71.70	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	0.01	11
H-Mag 0.30M	73.20	13.85	0.70	0.27	0.78	0.20	0.76	0.13	0.31	0.02	9.78
H-Mag 0.35M	75.31	13.52	0.71	0.26	0.78	0.18	0.75	0.13	0.32	0.01	8.03

*PF: Pert in Fire

Fig. 1 (A and B) and Table-2 show X-ray diffraction patterns of raw-maghnite and Mag-H^+, respectively. The basal spacing of the raw-maghnite was exhibited 15.02 Å. The titration of raw-maghnite with 0.25 H_2SO_4 resulted in the exchange of exchangeable cations for H^+ in the interlayer. The X-ray powder diffraction of the dried Mag-H^+ (Fig. 1(B)), exhibited 00*l* reflections corresponding to basal spacing of 12.5 Å. Yun Kwon *et al.*[26] reported that the decrease in the basal spacing indicates a loss of the interlayer H_2O upon the replacement of Na^+ for H^+. In particular, although the X-ray peak of the montmorillonite did not change substantially before or after the acid treatment, there was a decrease in the basal spacing. This implies that the original structure was well preserved after the acid treatment.

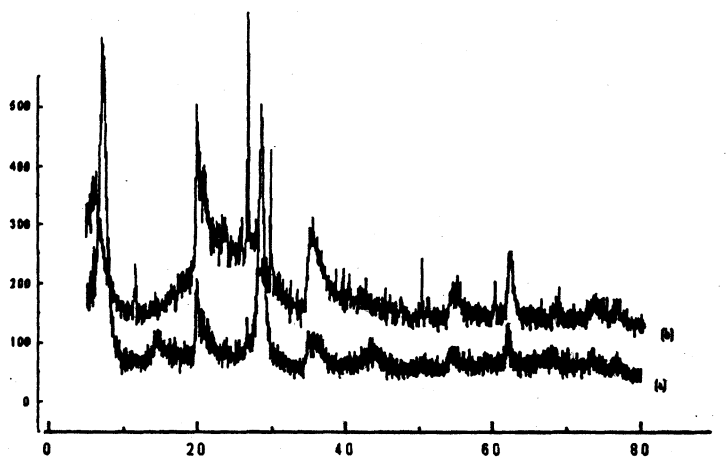


Fig. 1. X-ray powder diffraction of (A) raw-maghnite and (B) Mag-H^+ 0.25 M

TABLE-2
RX CHARACTERISTIC OF RAW-MAGHNITE AND MAG-H^+ 0.25 M

Samples	d_{hkl} (Å)	hkl	Nature of sample
Raw-Maghnite	12.50	001	Montmorillonite
	4.47	110	Montmorillonite
	4.16	110	Quartz
	3.35	110	Quartz
	3.21	110	Feldspar
	3.03	110	Calcite
	2.55	200	Montmorillonite
	1.68	009	Montmorillonite
	1.49	060	Montmorillonite
H-Maghnite 0.25M	15.02	001	Montmorillonite
	4.47	110	Montmorillonite
	4.16	110	Quartz
	3.35	110	Quartz
	3.21	110	Feldspar
	3.03	110	Calcite
	2.55	200	Montmorillonite
	1.68	009	Montmorillonite
	1.49	060	Montmorillonite

The effects of the acid activation process on the FTIR spectrum of the treated maghnite (Fig. 2) are summarized as follows: The intensity of the absorption band at 3630 cm^{-1} (AlAlOH coupled by AlMgOH stretching vibrations) decreases with acid treatment. The bands at 3425 and 3200 cm^{-1} (absorption of interlayer water) become more diffuse with acid treatment[27]. The intensity of the Si—O out-of-plane and Si—O—Si (2 bands) in-plane stretching bands at 1116, 1043 and 999 cm^{-1} have not been affected by acid treatment. The AlAlOH (920 cm^{-1}), $AlFe^{3+}OH$ (883 cm^{-1}) and AlMgOH (846 cm^{-1}) deformation bands decrease with acid treatment. The

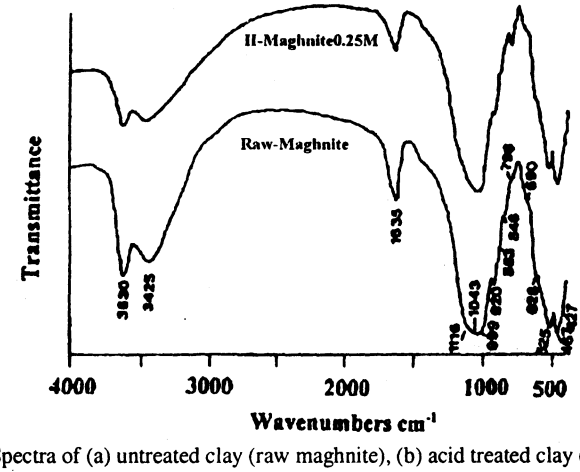


Fig. 2. IR Spectra of (a) untreated clay (raw maghnite), (b) acid treated clay (Mag-H^+ 0.25 M)

intensity of the band at 796 cm^{-1} increases with treatment, reflects alterations in the amount of amorphous silica in accordance with the earlier findings[28, 29]. The intensity of the band at 628 cm^{-1} (either Al-OH or Si-O bending and/or Al-O stretching vibration) gradually decreases with acid treatment in good agreement with the findings of Komadel[30]. The intensity of the band at 467 cm^{-1} (Si-O-Al and Si-O-Mg coupled by OH vibrations or Si-O bending vibrations) is essentially unchanged.

^{27}Al NMR spectra of raw-maghnite and Mag-H^+ 0.25 M are given in Fig. 3. The spectra of maghnite exhibits mainly the typical resonance at 2.9 ppm of octahedral aluminium (^{6}Al) in a phyllosilicate but also small but significant contributions at 60 and 68 ppm assigned to aluminium tetrahedrally coordinated to oxygen (^{4}Al)[31, 32].

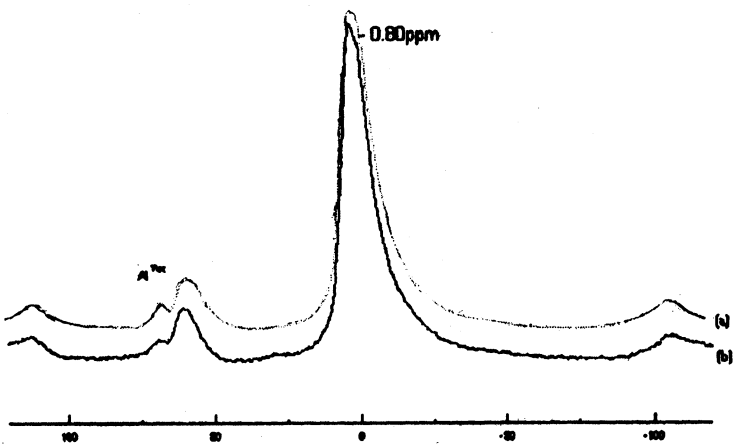


Fig. 3. Al MAS NMR spectra of (a) raw maghnite, (b) Mag-H^+ 0.25 M

The ^{29}Si MAS NMR spectra for the raw-maghnite and Mag-H^+ 0.25 M are shown in Fig. 4. The dominant resonance at –93.5 ppm corresponds to Q3 (O-Al)

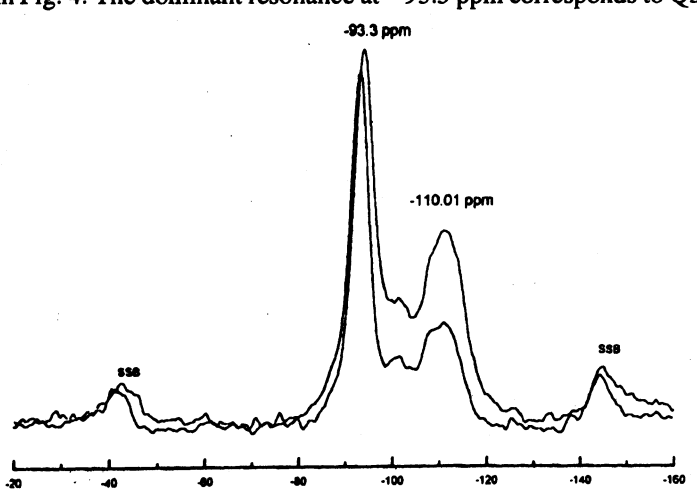
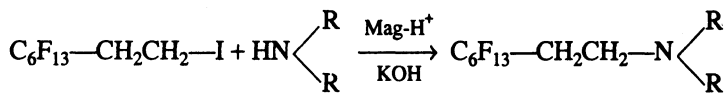


Fig. 4. ^{29}Si MAS NMR spectra of (a) raw maghnite, (b) Mag-H^+ 0.25 M

units, *i.e.*, SiO_4 groups cross-linked in the tetrahedral sheets with no aluminium in the neighbouring tetrahedral[33]. The weak resonance at –105 ppm correspond to Q4 (^{1}Al) units, *i.e.*, framework SiO_4 tetrahedral with one Si-O-Al linkage to neighbouring tetrahedrally coordinated Al. The resonance at –112 ppm corresponds to three-dimensional silica with no aluminium present, designed Q4 (O-Al). This value is in good agreement with the data for silica gel[34].

The reactions of fluorohexyletheylene iodide with some amines such as diethanol amine, diethyl amine and morpholine, without solvent were carried out at ambient temperature in the presence of Mag-H^+ as catalyst. These amines react with perfluorohexylethylene iodide under very mild condition to give a series of fluorohexylethylenamine (**Scheme-1**).



Scheme-1. Reaction of perfluorohexylethylene iodide with amines in the presence of Mag-H^+

The most probable reaction mechanism is that the amine groups activated by the acid centres present on the catalyst, followed by a nucleophilic attack of the fluoroalkyliodide molecule. This reaction is considered to be a suitable alternative for preparation of fluoroalkylamine from amines, with the advantage of selectivity, operational simplicity, high yields, short reaction times and minimal environmental impact. The results obtained for these reactions are summarized in Table-3.

TABLE-3
YIELDS OF REACTION OF R-AMINES WITH R_f-CH_2CH_2I CATALYZED WITH Mag-H^+ 0.25 M

No.	Amine	ϕ Amine (g)	ϕ $C_6F_{13}C_2H_4I$ (g)	Time (h)	Yield (%)
TP1	Diethanolamine	4.20	9.50	2	82
TP2	Diethylamine	1.96	9.48	2	62
TP3	Morpholine	2.70	9.48	2	89

ϕ: Quantity.

The acid-treated (Mag-H^+) catalyst is highly active in the acid-catalyzed condensation reaction of fluoroalkyliodide onto amines due to either the amount or the accessibility of the surface acid sites. The importance of active site accessibility in catalysts of this type was illustrated for Friedel-Craft reactions catalyzed by K10, a series of pillared clays and metal cation-exchanged montmorillonite catalyzed protection of aromatic aldehydes with acetic anhydride[35]. The reaction was diffusion-controlled in the pillared clay catalysts and the superior activity of the Mag-H^+ was due largely to the wider pores and more accessible acid sites in montmorillonite[36]. Although the acid exchanged catalyst used here exhibit smaller pores than the pillared clays, it is likely that diffusion control is more important in these catalysts than in Mag-H^+.

Catalytic activities of ion-exchanged clay minerals in both Brönsted and Lewis acid-catalyzed reactions reflect the surface acidities of the catalysts. The trend in Brönsted acidity can be explained in terms of the abilities of the exchangeable

cation in the catalyst to polarize the coordinating water molecules and hence generate protons. Na^+-MMT and other forms with alkali and alkaline earth cations gave very low yields and in control experiment without any catalyst no reaction occurred. The catalysts in these forms show the lowest activity, confirming that the exchangeable cations are indeed the active sites. Experiment with initiating reaction by adding the amine to premixed catalyst Mag-H^+ plus fluoroalkyliodide showed no difference in the results of catalytic activity. The yields obtained with different amines show that the reaction yield depends on the reactivity of the amine molecule, which is connected with the substituents rather than on the basicity of the amine, thus proving the mechanisms shown in **Scheme-1**.

Catalytic activity of the prepared material was tested in the reaction of preparation of perfluoralkyl (R-amine) from R-amine (R = CH_2CH_2OH, morpholine and CH_2CH_3). The reactants in these three reactions contain the same functional groups and so the factors associated with the active sites on the catalyst are likely to be similar.

The effect of the substitution of amines on the catalyzed reaction involves electron donating force of the substituting group. The morpholine, in contrast to the diethanolamine and diethylamine groups, has more reactivity because of molecule planarity effect and therefore the expected order of reactivity for substituted amines was:

Morpholine > Diethanolamine > Diethylamine

The results obtained evidently support this order and average difference in the yield of reaction between experiments with various amines was *ca.* 8% for diethanolamine and morpholine while *ca.* 24% for diethaolamine and diethylamine.

Concerning the role of the catalyst, it is well stated that reactions on montmorillonites generally involve previous adsorption and diffusion of reactant through the pores and interlayers. However, in the present liquid phase reaction, the acid sites on the external surface of the catalyst play a crucial role in the activation of reactant molecules, particularly with large and bulky compounds. In fact, under these conditions, the interlayer spaces are completely filled with reactant and product molecules and the curvature effects on the external surface of the clay catalyst are likely to promote reagent activation and process selectivity[36–38].

The structure of the perfluoroalkylamines obtained was identified by ^1H, $_{13}C$ and ^{19}F NMR.

Perfluorohexylethylenediethanolamine: The spectrum ^1H NMR (Fig. 5) shows four characteristic peaks at δ 2.7 ppm (t, 6H, N-CH_2), 3.6 ppm (t, 4H, CH_2-O), 2.45 ppm (t, 2H, C_6F_{13}-CH_2) and 3.3 ppm (s, 2H, O-H). The spectrum ^{13}C NMR (Fig. 6) shows δ 36 ppm ($\underline{C}H_2$-C_6F_{13}), 56 ppm ($\underline{C}H_2$-N), 60 ppm (CH_2-O), 106–125 ppm (C_6F_{13}). The spectrum ^{19}F NMR (Fig. 7) shows: δ –127 ppm (s, 2F); –124 ppm (t, 2F); –123 ppm (s, 2F); –122 ppm (s, 2F); –116 ppm (s, 2F); –82 ppm (t, 3F).

Perfluorohexylethylenemorpholine: ^1H NMR ($CDCl_3$) δ: 2.8 ppm (m, 6H, N-CH_2), 3.7 ppm (t, 2H, C_6F_{13}-CH_2) and 3.7 ppm (t, 4H, CH_2-O). ^{13}C NMR

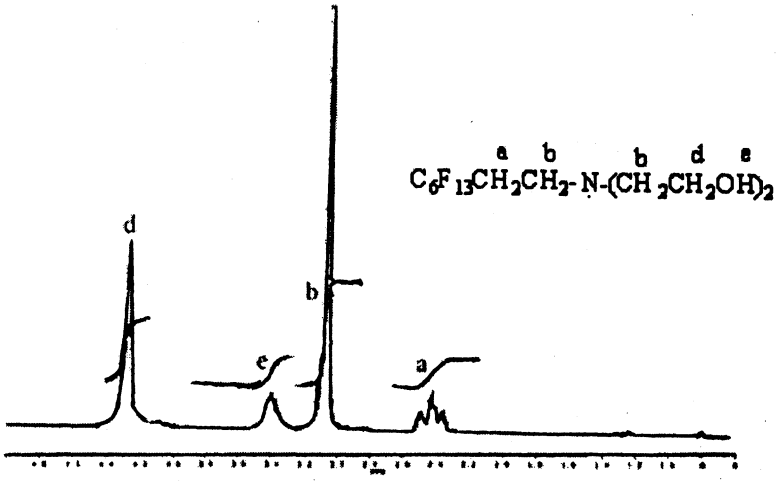


Fig. 5. Spectrum ^{1}H-NMR of perfluorohexylethylene diethanolamine in $CDCl_3$

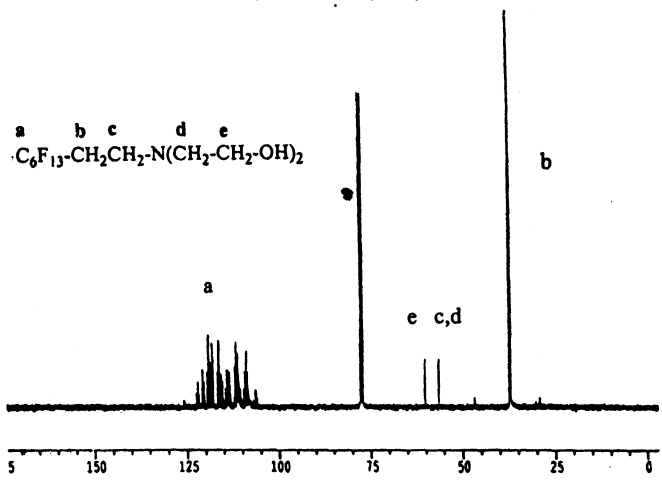


Fig. 6. Spectrum ^{13}C-NMR of perfluorohexylethylene diethanoamine in $CDCl_3$

($CDCl_3$) δ: 44 ppm ($\underline{C}H_2$-C_6F_{13}), 47 ppm (CH_2-N), 68 ppm ($\underline{C}H_2$-O), 100–125 ppm ($\underline{C}_6$-F_{13}). ^{19}F NMR ($CDCl_3$) δ: –126 ppm (s, 2F); –124 ppm (t, 2F); –123 ppm (s, 2F); –122 ppm (s, 2F); –115 ppm (s, 2F); –81 ppm (t, 3F).

Perfluorohexylethylenediethylamine: ^{1}H NMR ($CDCl_3$) δ: 4 ppm (t, 2H, C_6F_{13}-CH_2), 0.97 ppm (t, 6H, CH_3) and 2.43 ppm (m, 6H, N-CH_2). ^{13}C NMR ($CDCl_3$) δ: 36 ppm ($\underline{C}H_2$-C_6F_{13}), 23 ppm ($\underline{C}H_3$), 56 ppm ($\underline{C}H_2$-N), 105–125 ppm ($\underline{C}_6F_{13}$). ^{19}F NMR ($CDCl_3$) δ: –127 ppm (s, 2F); –124 ppm (t, 2F); –123 ppm (s, 2F); –122.5 ppm (s, 2F); –116 ppm (s, 2F); –82 ppm (t, 3F).

Mechanism

Scheme-2 shows a proposed mechanism for the formation of Perfluoroalkylamines (PA) products. The ion exchange of Maghnite by H^+ will afford

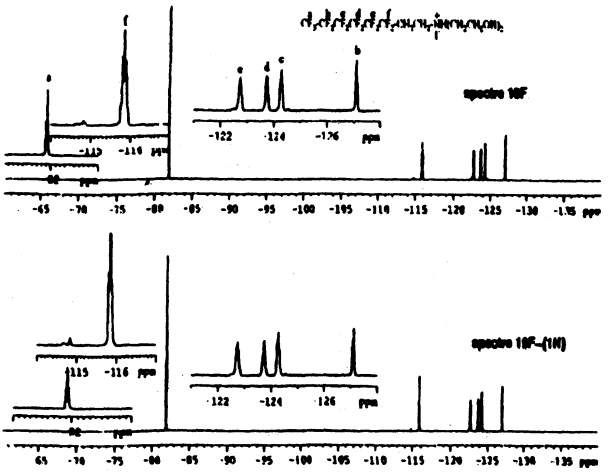
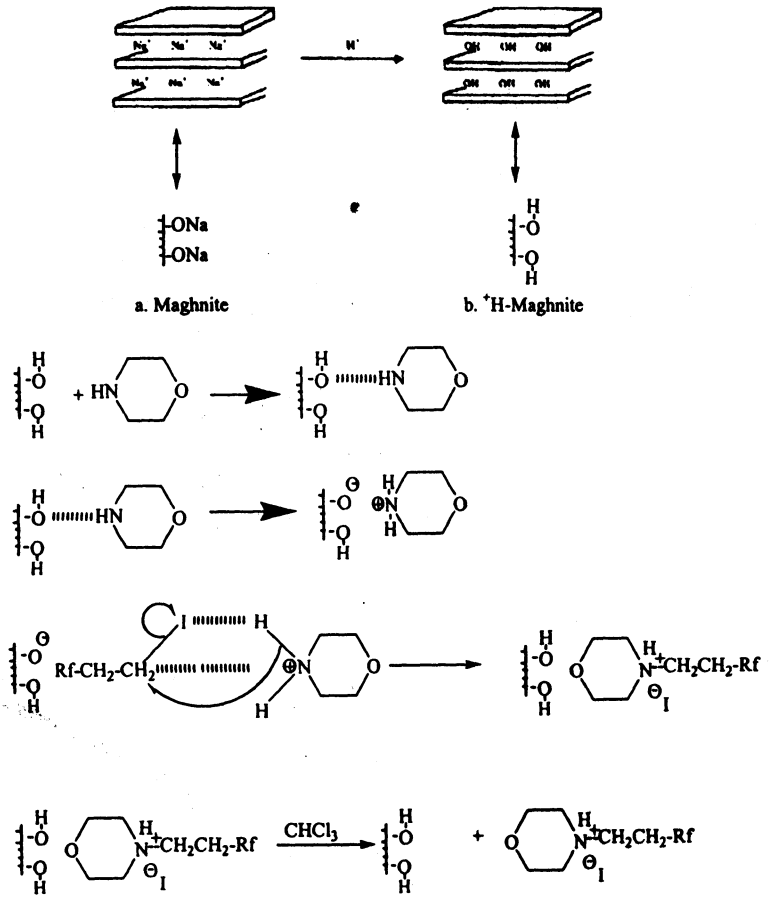


Fig. 7. Spectrum ^{19}F-NMR of perfluorohexylethylene diethanolamine



Scheme-2. Mechanism for the formation of perfluoroalkylamines

interaction sites accessible to amino alcohol by forming silanol groups **(Scheme-2b).** The reaction between H-Maghnite and amino alcohol solution forms an intercalate with a lamellar layer of amino alcohol molecules. The addition of perfluoroalkyl iodide to this intercalated derivative and after extraction with $CHCl_3$ lead to perfluoroalkylammonium iodide.

Conclusion

In the course of acid leaching of maghnite, the ^{27}Al MAS NMR showed that the small amount of Al present in maghnite occurs as both Al^{6+} and Al^{4+}. The final reaction product of H_2SO_4-treated maghnite is amorphous silica formed by a three-dimensional cross-linked SiO_4 framework. Catalytic activity of acid-exchanged maghnites was tested for the preparation of perfluoroalkylamines by condensation reaction of perfluorohexylethylene iodide onto amines; we have found that the best value of perfluoroalkylamine yield is obtained with Mag-H^+ 0.25 M; for this reason we kept this sample in all reactions. The simplicity of the methods, good yields and the ready availability of inexpensive precursors make this an attractive method for the perfluoralkylation of amines.

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Contact:
L. Van't Dack
Department of Chemistry, University of Antwerp
Universiteitsplein I, B-2610 Antwerp, Belgium
Tel.: 3-820.23.43; Fax: 3-820.23.76
E-mail: luc.vantdack@ua.ac.be
Website: http://www.euroanalysisxiv.ua.ac.be/