Catalytic conversion of propylene oxide on a super acid sulfonic clay (SASC) system

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Abstract

Trifluoromethanesulfonic acid (triflic acid) and montmorillonite type clay were used to prepare a super acid sulfonic clay (SASC) with Ho < −12.75 (Hammett acidity function). The clay activity was evaluated in the propylene oxide conversion including solvolysis with a series of alcohols, at O°, 20° and 25°C, yielding high conversion (88.9 to 99.8%) and selectivity (27.6 to 80.8%) to monomer formation. The clay was regenerated at least three times, recovering the total activity level after drying the catalyst 24 h at 110°C, under vacuum. The main properties of the acidic clay were characterized by X-ray diffraction, Hammett indicators technique and other spectroscopic and analytical methods. © 1997 Published by Elsevier Science B.V.

Keywords: Super acid clay; Acid activated clay; Catalysis; Solvolysis; Bentonite catalyst; Cellosolves

1. Introduction

Natural clay montmorillonites have been used in the chemical industry to promote acid catalyzed organic reactions involving both Brønsted and Lewis acid sites [1]. Some examples of those reactions are alkenes with alcohols, thiols, carboxylic acids, [2] dehydration of alcohols, polymerization, [2,3] oxirane solvolysis, [4] cracking of petroleum fractions, [5] and ethers formation [2–4,6]. Most of these catalytic reactions have been performed with heterogeneous catalysts, i.e. acidic and/or metal–ion–exchanged–montmorillonites [6].

Considering the wide range of applications of acidic clays in all those organic reactions, together with the availability of bentonite raw materials, the aim of the present work was to evaluate these layered silicates as potential catalysts for several reactions which might be of interest in oil refining [5]. The modification of the surface acid properties of the original clays, by means of the deposition of super acids, i.e. triflic acid, was aimed to increase the acid strength of these materials, which in turn might have an impact on their catalytic properties.

The super acidic sulfonic clay (SASC) having a Hammett function Ho < −12.75 was developed in this work and it was used as a

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promoter in the propylene oxide solvolysis with different alcohols. Additionally, a multitechnique characterization of the solid catalyst was realized comprising X-ray diffraction, electron microscopy, IR-spectroscopy and EDS. The catalytic activity evaluation was performed in a batch type microreactor using a Jeol GC-Mass Spectrometry for the product analysis.

2. Experimental

200 g of a clay mineral (DCBS) from Durango, México, was purified by sedimentation from a 4 l suspension of bidistilled water, in order to eliminate quartz impurities and other solid materials. The clay suspension was treated with NH_4OH concentrated solution, stirred until constant pH = 11.3 and aged during one week. The alkaline suspension was centrifuged and washed several times with bidistilled water, dried at 80°C and mechanically grounded into a fine powder.

The super acid sulfonic clay (SASC) was prepared by suspending 50 g of the clay in bidistilled water (300 ml) and upon stirring during 72 h, concentrated (100%) trifluoromethane sulfonic acid (Aldrich, 27 g) was added until pH = 1.2. After 24 h, the suspension was dried at 100°C under vacuum, in order to remove the acid excess, then it was grounded into a fine powder and used as catalyst to promote the solvolysis reactions showed in Table 1.

All the reactions in this study were performed in a Teflon-coated 20 ml stainless steel reactor. First the reactor was charged with the sulfonic clay (0.25 g) together with propylene oxide (5 ml, i.e. 0.07 mol) which were solvated with 0.07 mol of alcohol i.e. EtOH, MeOH. All the reaction mixtures were analyzed using a gas chromatograph, (Tremetrics model 9000) fitted with a 60 m (J & W) gas capillary column, having a film thickness of 0.25 μ, coated with DB-1 methyl silicon 100% and QB-5, 5% phenyl, 95% methyl silicon and an internal di-

Table 1
Oxirane promoted reactions with a super acid sulfonic clay

			Conversion (%)	Selectivity Monomers	Dimers	Trimers
	(oxirane)	Sulfonic Clay, 20 °C, 120 min	99.8		50.6	
	MeOH	Sulfonic Clay, 20 °C, 120 min	99.8	42.1	48.6	9.0
	EtOH	Sulfonic Clay, 20 °C, 120 min	98.4	37.4	30.8	12.8
	n-C₆H₁₁OH	Sulfonic Clay, 20 °C, 120 min	98.9	80.8	18.1	-
(oxirane) +	~~OH	Sulfonic Clay, 20 °C, 120 min	98.7	38.9	36.0	23.8
	≡—CH₂OH	Sulfonic Clay, 20 °C, 120 min	99.8	22.7	20.2	18.5
	OH	Sulfonic Clay, 20 °C, 120 min	88.9	36.6	32.6	14.4
	(cyclohexane)	Sulfonic Clay, 20 °C, 240 min	96.0	44.1	46.5	6.4
	—OH	Sulfonic Clay, 20 °C, 120 min	93.8	27.6	19.3	16.23

ameter of 0.25 mm. The carrier gas was He (Matheson), at linear velocity of 30 cm/s; the injector temperature was 180°C with flow splitter 1:100, the amount of sample was 0.2 μl, and the initial oven temperature was set at 35°C for 5 min, increasing the temperature program up to 300°C at a 10°C/min rate. The GC was coupled to a Jeol-JMS-AX-505WA mass spectrometer in order to characterize all the reaction products by electron impact at 70 eV, alternatively chemical ionization with isobutane at ionization temperatures in the source of 200° and 150°C were used respectively. All the products were identified by means of a computer matching method, using EIGC-MS data and comparing them with those of the NBS library of mass spectral data.

X-ray diffraction was used to assess the structural integrity of the clays as well as their expandibility degree. A Siemens D-500 diffractometer fitted with monochromator and $\lambda_{Cu(1.54}$ $_{\text{Å})}$ was used with this purpose. Also, a FTIR-Nicolet 7000 spectrometer was used to characterize the type of surface acid sites of the clay before and after impregnation. The surface acid strength was determined by means of the Hammett titration method, using a series of organic bases with different pK_a values [7]. The sub-

surface chemical composition was determined by means of energy dispersive spectroscopy (EDS) in the electron microscope (Jeol-100 CX) fitted with Si/Li Tracor 5500 X-ray detector.

The analysis by this technique was performed in two ways. First a global analysis was made from an area of about 5 μm $\times$ 5 μm of extension which gave the 'bulk' chemical composition of the sample, i.e. average composition which is comparable to the atomic absorption analysis. In the second case, a point analysis was made from regions of about 200 Å $\times$ 200 Å, which allowed to assess the local chemical composition of clay flakes at edges and faces respectively.

3. Results and discussion

Bentonites and other ion-exchanged layered clays have been used in the past as catalysts for the transformation of oxirane rings into diols, dioxanes, dioxolanes, cellosolves or crown ethers; all those reactions reached high selectivities under different conditions [2,4,8]. The ring epoxide opening reactions, usually proceed with aluminum-exchanged bentonite (0.5 g) on a 20 ml steel reactor, using 2.5 to 5 ml of epoxide and similar amounts of nucleophilic reagents, at 100–110°C and 4 to 6 h reaction time. The yields vary commonly between 24 to 84% of oxirane conversion [2]. Improved results have been drawn for the same reaction using catalysts based on acidic montmorillonite type clays, with or without thermal activation [4]. Surprisingly, the above results disagree with the fact that larger interlamellar distances, which are induced by ion–metal-intercalation, should favor the conversion rates.

On the other hand, homogeneous catalysis via wet acids and super acids, also promote the oxirane transformation, but they exhibit some disadvantages in the process, when compared with heterogeneous catalysts. The last ones become classified as *envirocats* (environmentally safe catalysts), which are safe for handling,

pollution free, easy waste disposable, as well as simple for recovery from the products or raw materials [9].

The super acid sulfonic clay, as described here, afforded the production of alkyl cellosolves as displayed in Table 1, from propylene oxide and alcohols, leading to higher yields. The clay support represents an option to improve the handling of the sulfonic super acids that in turn is of interest due to the low environmental impact, corrosion level, etc., also, the use of special and costly equipment might be reduced. Additionally, the materials can be stored several months at room temperature, without loosing fumes or acid activity.

In comparison with the previously described montmorillonite-type clays employed as promoters [4], the super acid sulfonic bentonite, used here, is superior as catalyst. The clay Brønsted and Lewis acid strength increase after the treatment with trifluoromethanesulfonic acid ($H_o < -14$, triflate super acid) [10] yielding a super acid clay with a Hammett acidity function of $H_o < -12.75$ [9]. Due to the high acidity of the catalyst, the reaction time and temperature for the oxirane solvolysis decreased remarkably. When the ring opening is carried out with methanol and ethanol, the reaction becomes highly exothermic and violent and, after 1.5 h at 0°C, the epoxide is completely transformed. The epoxide opening is generally promoted in a very short time, as compared with other acidic clays, thus affording high conversion and giving the isomeric monomers in better yields. Dimers and trimers are formed as secondary compounds in substantial quantities, from the epoxide transformation.

In order to know more about the catalyst properties, an evaluation was made by changing the contact time, i.e. by reducing the clay catalyst mass, in a set of reactions between propylene oxide and 2-propanol at 20°C.

This produces a mixture of monomeric isomers, i.e. isopropoxypropanol, (Fig. 1). The best yields to monomers, ca 52%, was obtained after 60 min on stream, with 0.150 g of catalyst,

Propylene oxide and isopropyl alcohol reaction conversion with a super acid clay
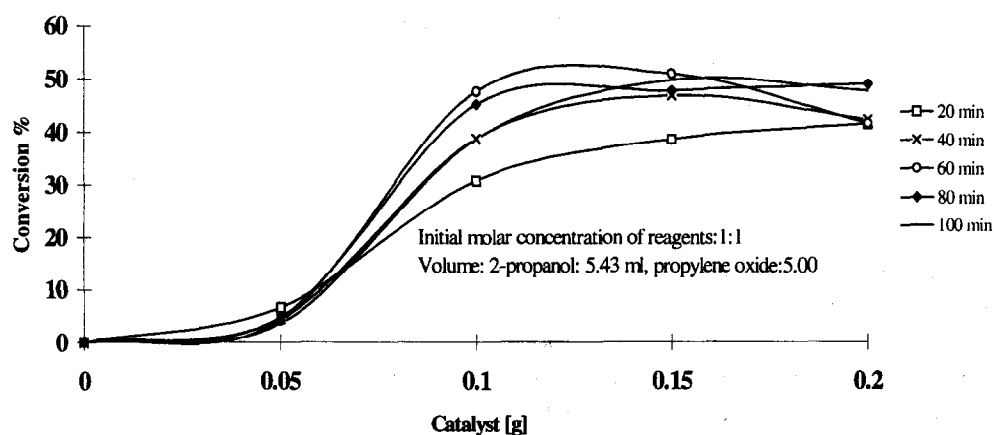

Fig. 1. Propylene oxide and isopropyl alcohol reaction conversion with a super acid clay.

whereas more than 45% was formed in the first 25 min, with 0.125 g of clay (Fig. 2).

After reaction, the clay residue was recovered and washed with methanol, then dried at 100°C under vacuum. The same catalyst was used an recovered during three cycles, giving a total conversion of 44.18% of monomers.

On the other hand, the pure three membered cyclic-ether (propylene oxide), was put in contact with the sulfonic clay and transformed se-

lectively, giving the cyclodimerization reaction which produces the dimethyl-1,4-dioxane isomers in high yields. This reaction is similar to the liquid super acid catalytic action over the ethylene oxide, as reported by Kobayashi et al. [11].

The X-ray diffraction comparison between the natural (a) and acidic clay (b) (Fig. 3), showed a relative destruction of the stacked structure of the clay after acidification. How-

Kinetic behavior of propylene oxide and isopropyl alcohol reaction catalyzed with a super acid sulfonic clay
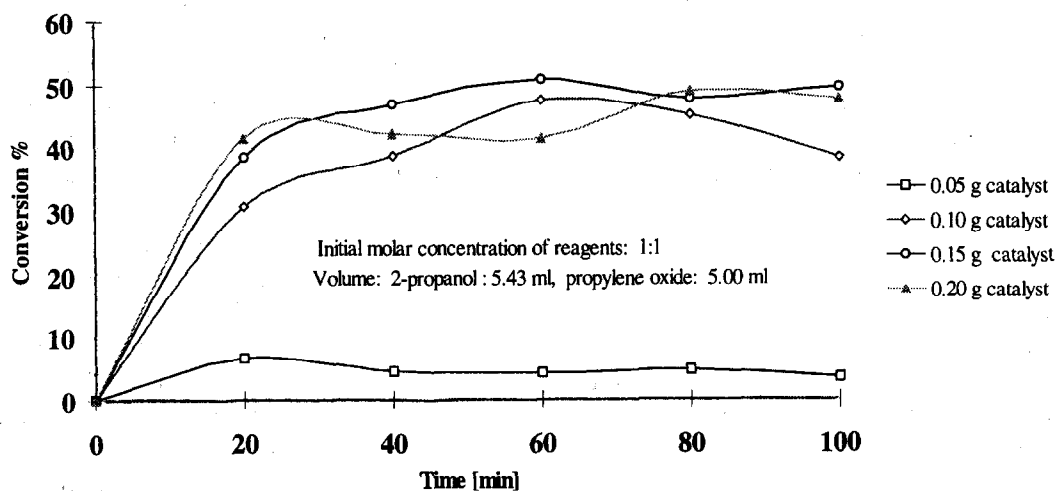

Fig. 2. Kinetic behavior of propylene oxide and isopropyl alcohol reaction catalyzed with a super acid sulfonic clay.
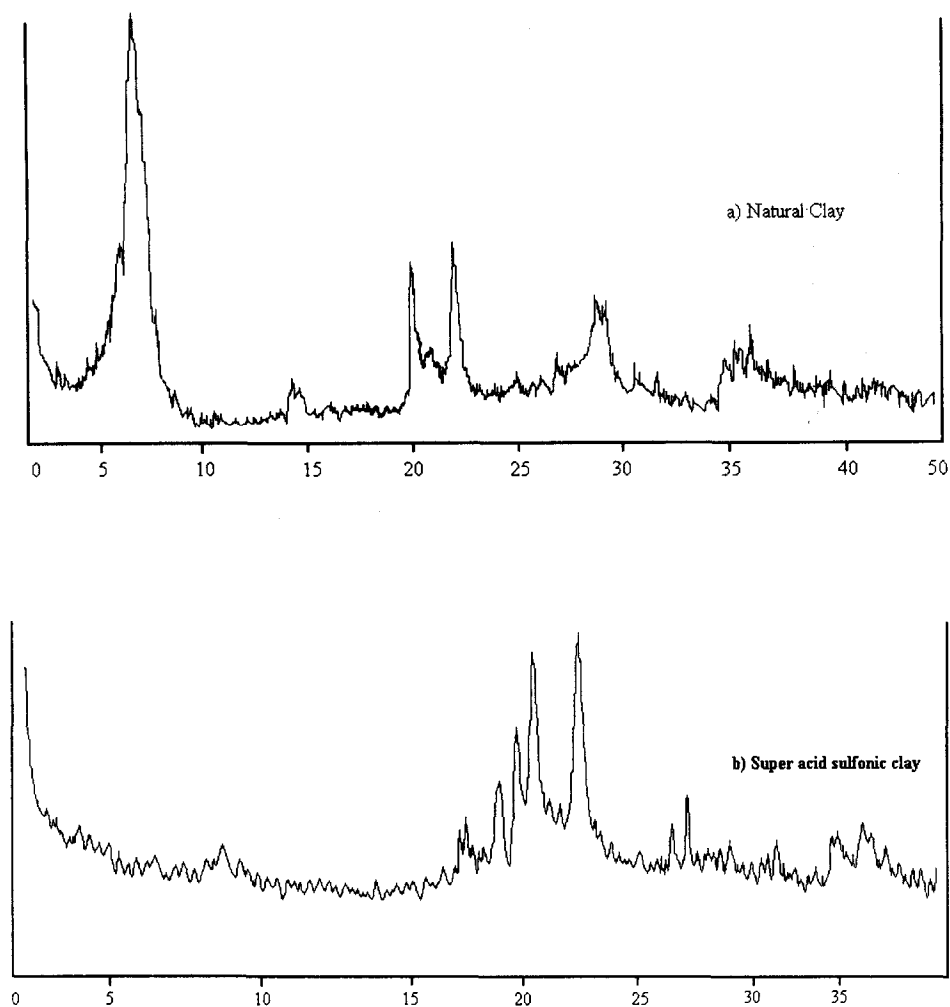
Fig. 3. (a) Natural clay. (b) Super acid sulfonic clay.

ever, the results obtained and reported here, prompted us to search other ways of clay treatments in order to avoid the delamination and also to optimize the F_3CSO_3H–SiO_2–Al_2O_3 composition, but these studies are underway and will be published elsewhere.

The result of EDS, are shown in Table 2, where one observes the global composition (GL) plus the average of the point analysis in surface and the edge composition of the natural clay M1 after triflic treatment. It is clear that upon triflic acid deposition, the alkaline cations are exchanged and leave the clay support. On the other hand, sulfur is present in all the samples, being greater for the global and random type analysis, i.e. GL and P1 analysis in Table 2. However, for specific point analysis of faces and clay edges a significant reduction of the

Table 2
Clays (EDS) microanalysis [a]

Sample	S	Si	Al	Mg	Ca	Fe	K	Na
Clay MI	—	63.88	23.35	3.40	0.73	8.50	0.14	—
SASC (GL) [b]	18.4	60.55	10.03	—	—	11.02	—	—
P1 [c]	23.48	60.02	8.37	0.31	—	7.82	—	—
FM [d]	14.48	60.01	10.32	0.06	0.62	14.48	—	—
EP [e]	16.64	64.75	12.0	—	—	6.6	—	—

[a] Average of five chemical analysis.
[b] Global.
[c] Point.
[d] Faces.
[e] Edges local chemical analysis.

sulphur content was recorded, i.e. FP and EP. This probably means that sulphur containing species are spread out around the clay flakes. Another interesting result of the EDS analysis is the sudden increase of iron content (Table 2), i.e. this figure rises from 2% of Fe_2O_3 in the natural clay to about 6.5% wt in the edge point analysis (EP). This result means that original iron is part of the skeletal structure of the clay layers and it is extracted out to the clay flakes surface, thus increasing the average content recorded by the EDS technique, i.e. a sub-surface analysis [12].

Acknowledgements

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