



## SBA-15 with sulfonic acid groups as a *Green Catalyst* for the acetoxylation of $\alpha$ -pinene

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### ABSTRACT

The acetoxylation of  $\alpha$ -pinene was carried out over SBA-15 with sulfonic acid groups. The products of acetoxylation of  $\alpha$ -pinene are acetates ( $\alpha$ -terpinyl acetate, bornyl acetate and  $\beta$ -fenchyl acetate) and hydrocarbons (camphene, tricyclene, limonene,  $\gamma$ -terpinene, terpinolene and  $\alpha$ -terpinene).

Catalysts with different amount of sulfonic acid groups were prepared. It was observed that the activity increases with increase of the surface area and porous volume.

Catalytic stability of the sample that showed the highest activity (C1) was evaluated by performing consecutive batch runs with the same catalyst sample. After the fifth batch, the catalyst exhibited a good initial activity.

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### 1. Introduction

$\alpha$ -Pinene is a renewable raw material usually obtained either from pine gum or as a waste from the Kraft process [1–4]. Acid acetoxylation of terpenes are among the important synthesis routes to valuable terpenic esters which find applications in perfumery and pharmaceutical industry [5,6]. Traditionally, strong homogeneous acid catalysts, e.g. sulphuric acid, have been used [7], but the effluent disposal leads to environmental problems and economical inconveniences. These problems can be overcome by the use of solid acid catalysts. Beta zeolite [8,9] and heteropolyacids [10] have been used for the  $\alpha$ -pinene acetoxylation.  $\alpha$ -Pinene was converted to  $\alpha$ -terpinyl acetate in the presence of H-beta with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. It was observed that the rate of reaction of the  $\alpha$ -pinene is directly related to the zeolite  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio.  $\alpha$ -Pinene was converted to  $\alpha$ -terpinyl acetate at 29% yield in one step, with an H-beta zeolite catalyst in acetic acid at room temperature in 24 h. When the reaction temperature was increased, a decreased of the yield and selectivity of  $\alpha$ -terpinyl acetate was observed [8]. The acetoxylation of  $\alpha$ -pinene was also carried out in the presence of beta zeolites exchanged with metal cations such as silver, lanthanum, cerium, iron, cobalt, manganese, nickel, copper, zinc and strontium. Conversion levels were 62–100% and 72–100% for  $\alpha$ -pinene in the presence of glacial and aqueous acetic acid, respectively. Isomerisation and addition reactions were found

simultaneously in the system and bornyl acetate and  $\alpha$ -terpineol were the major products among addition products for glacial and aqueous acetic acid, respectively [9]. The acetoxylation of  $\alpha$ -pinene was also carried out in the presence of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , as the catalyst [10]. The heteropolyacid showed a much higher catalytic activity than the conventional acid catalysts such as  $\text{H}_2\text{SO}_4$  and Amberlyst-15.  $\alpha$ -Pinene was converted into  $\alpha$ -terpineol and  $\alpha$ -terpinyl acetate over 20%  $\text{PW}/\text{SiO}_2$  catalyst. The total concentration of the products in reaction mixture was reached  $0.37 \text{ mol L}^{-1}$ , corresponding to 9.3% substrate conversion, after 90 min of reaction, at 40 °C. When the reaction was carried out over 40%  $\text{PW}/\text{SiO}_2$  catalyst, it was obtained a total concentration of the products of  $0.86 \text{ mol L}^{-1}$ , corresponding to a 21% substrate conversion after 160 min of reaction, 25 °C [10].

Mesoporous materials, such as MCM-41 and SBA-15, have been used in heterogeneous catalysis as catalysts and catalyst supports, due to a combination of high surface areas and controlled pore sizes. The functionalisation of organic groups onto the surface of these materials can be performed either by grafting on the surface or by co-condensation. These modified mesoporous silicas have been used as catalyst in a wide range of chemical reactions [11–14]. The incorporation of organosulfonic groups over SBA-15 has generated effective solid acid catalysts with enhanced catalytic properties as compared with conventional homogeneous and heterogeneous acid catalysts [13]. These materials functionalised with organosulfonic acid groups have shown successful results for acid-catalysed reactions, showing better catalytic performances than the commercial sulfonated resins. Sulfonic acid-functionalised SBA-15 combines the high acid strength with a large surface area with

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interconnected mesopores and high accessibility of strong Brønsted acid sites to the reactants [11,13,14].

In the present work, we report the  $\alpha$ -pinene acetoxylation over SBA-15 with sulfonic acid groups. The influence of various reaction parameters, such as temperature, initial concentration of  $\alpha$ -pinene and catalyst loading, on the activity of the most active catalyst, is also studied.

## 2. Experimental

### 2.1. Catalysts preparation

The catalysts samples were prepared according to R. van Grieken et al. [15]. 4 g of Pluronic 123 were dissolved under gentle stirring in 125 g of 1.9 M HCl at room temperature. The solutions were heated to 40 °C and then tetraethylorthosilicate (TEOS) was added. A prehydrolysis time for TEOS species of 45 min was considered. Following this TEOS initial hydrolysis stage, mercaptopropyltrimethoxysilane (MPTMS) (0.004, 0.008 and 0.010 mol for C1, C2 and C3, respectively) and an aqueous solution of H<sub>2</sub>O<sub>2</sub> (30 wt.%, Merck) were added at once. The resulting mixtures were stirred at 40 °C for 20 h and aged at 100 °C for an additional time of 24 h under static conditions. After synthesis, the solid products were recovered by filtration and air-dried overnight. Template molecules were removed from as-synthesized materials by washing with ethanol under reflux for 24 h (2 g of as-synthesized material per 200 mL of ethanol).

### 2.2. Catalysts characterisation

The textural characterisation of the catalysts was based on the nitrogen adsorption isotherm, determined at 77 K with a Micromeritics ASAP 2010 apparatus.

Sulphur content was determined on CHNS Elemental Analyser 1112 series Thermo Finnigan instrument.

Cation-exchange capacities corresponding to the sulfonic acid mesostructured materials were determined using aqueous solutions of sodium chloride (NaCl, 2 M) as cationic-exchange agent. In a typical experiment, 0.05 g of solid was added to 15 g of aqueous solution containing the sodium salt. The resulting suspension was allowed to equilibrate and thereafter was titrated potentiometrically by dropwise addition of 0.01 M NaOH (aq.).

X-ray diffraction (XRD) patterns of the catalysts were obtained by using a Rigaku powder diffractometer with built-in recorder, using Cu K $\alpha$  radiation, nickel filter, 30 mA and 40 kV in the high voltage source, and scanning angle between 0.7° and 8° of 2 $\theta$  at a scanning rate of 1°/min.

Transmission electron microscopy (TEM) analyses were performed on a Hitachi S-2400 scanning electron microscope, at a current voltage of 25 kV.

### 2.3. Catalytic experiments

The catalytic tests were carried out in a batch reactor, at 60 °C. In a typical experiment, the reactor was loaded with 30 mL of acetic acid and 0.12 g of catalyst (SBA-15, C1, C2 and C3). Reactions were started by adding 6.3 mmol of terpene.

Stability tests of the C1 were carried out by running four consecutive experiments, using the same reaction conditions. Between the catalytic experiments, the catalyst was separated from the reaction mixture by filtration, washed with acetone and dried at 100 °C overnight.

Nonane was used as the internal standard. Samples were taken periodically and analysed by GC, using a KONIC HRGC-3000C instrument equipped with a 30 m  $\times$  0.25 mm DB-1 column.

The GC mass balance was based on the substrate charge. For each sample, the difference between the initial moles number of  $\alpha$ -pinene and the total moles number of all components ( $\alpha$ -pinene not converted, isomerisation products and addition products) present in reaction mixture was attributed to the formation of oligomers, which were not GC determinable. The products were identified by gas chromatography mass spectrometry (GC-MS) using a FISIONS MD800 (Leicestershire, UK) instrument, equipped with a 30 m  $\times$  0.25 mm DB-1 column.

The catalytic activity was calculated from the maximum slope of the experimental kinetic curve of  $\alpha$ -pinene divided by the catalyst amount.

## 3. Results and discussion

### 3.1. Characterisation of catalyst

Fig. 1A shows the nitrogen adsorption–desorption isotherms at 77 K of the samples. A typical IV adsorption isotherm with H1 hysteresis loop, as defined by IUPAC, is observed, which are consistent with mesoporous materials tailored by nonionic templates [16,17]. The textural properties of sulfonic acid-functionalised SBA-15 are shown in Table 1. Incorporation of sulfonic acid groups onto SBA-15 decreased the measured surface area ( $S_{\text{BET}}$ ) and pore volume. The decrease in the surface area can be attributed to the occlusion of some pores due to the agglomeration of the MPTMS groups in the mouth of the mesopores, such occlusion restrict the diffusion of N<sub>2</sub> inside the pores during surface area determination. Similar results

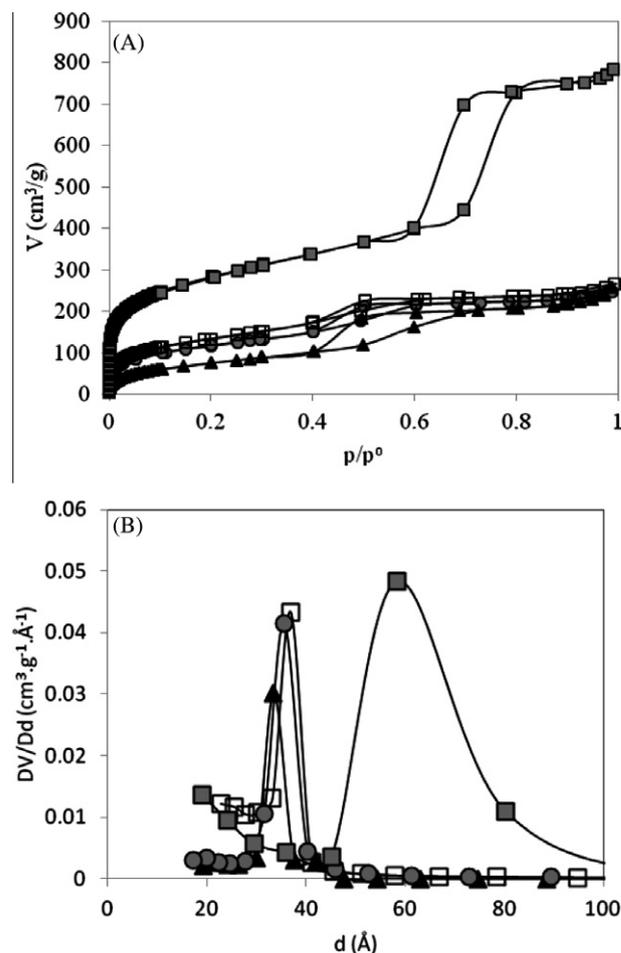


Fig. 1. (A) Nitrogen adsorption–desorption isotherms of catalysts; (B) Pore size distribution of catalysts. (■) SBA-15; (□) C1; (○) C2; (▲) C3.

**Table 1**  
Physicochemical characterisation of catalysts.

Sample	S content <sup>a</sup> (mmol/g)	H <sup>+</sup> (meq/g)	S <sub>BET</sub> <sup>b</sup> (m <sup>2</sup> /g)	Vp <sup>c</sup> (cm <sup>3</sup> /g)
SBA-15	–	–	744	0.91
C1	0.04	0.05	467	0.41
C2	0.14	0.16	413	0.38
C3	0.21	0.18	274	0.39

<sup>a</sup> Elemental analysis.

<sup>b</sup> BET.

<sup>c</sup>  $p/p_0 = 0.98$ .

were also observed by L.M. Yang et al. [18]. Fig. 1B shows the pore size distribution of SBA-15 with sulfonic acid groups. Pore size distributions were calculated using the desorption branch of the nitrogen adsorption–desorption isotherms and the BJH method. The SBA-15 sample has pore sizes around 5.8 nm. It is also observed that all catalysts samples (C1, C2 and C3) have pore sizes around 3.0–3.7 nm. This behaviour can be due to the incorporation of sulfonic acid groups on the SBA-15 surface. The decrease of the pore diameter is attributed to formation of a monolayer of the anchored group inside the pore channels which reduce the internal pore diameter, therefore the anchoring treatment inhibit the availability of some pores, and the total volume of pores measured by the adsorption of N<sub>2</sub> is also reduced. According to results reported by other authors, the reduction of surface area is around 30–45% of available surface area before anchoring of MPTMS group, and structural changes of SBA-15 frame are not observed since XRD patterns before and after thiol anchorage do not show significant changes [19].

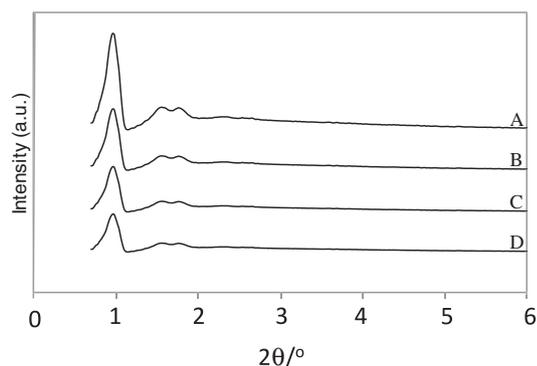
The powder X-ray diffraction patterns (Fig. 2) suggest that all samples exhibit well ordered SBA-15 structure. Comparing with the parent SBA-15, the functionalised samples seem to exhibit broadly similar degrees of long-range order, based on XRD peak widths and intensities. Similar results were also reported by Siril et al. [20].

TEM images (Fig. 3) of the catalysts exhibit the existence of well-ordered nanochannels, and the nanochannels are arranged on 2D hexagonal structure and appear to be continuous over very large scales.

The sulfur content of the sulfonic acid-functionalised SBA-15 materials was analysed by elemental analysis and the number of accessible organosulfonic acid groups in the mesoporous silica was determined quantitatively by acid–base titration. The results are given in Table 1. It was observed that the amount of surface sulfonic acid sites increased with the amount of MPTMS in the synthesis gel. Similar results were also obtained by S. Hanoudi et al. [21].

### 3.2. Catalytic experiments

The products of  $\alpha$ -pinene (1) acetoxylation were  $\alpha$ -terpinyl acetate (2), bornyl acetate (3),  $\beta$ -fenchyl acetate (4), camphene (5),



**Fig. 2.** X-ray diffractograms of (A) SBA-15; (B) C1; (C) C2; (D) C3.

tricyclene (6), limonene (7),  $\gamma$ -terpinene (8), terpinolene (9) and  $\alpha$ -terpinene (10) (Scheme 1) [4].

Fig. 4 shows the initial activity of the catalysts in  $\alpha$ -pinene acetoxylation. It was observed that the catalytic activity increases in the series: C3 < C2 < C1. This behaviour can be due to the higher surface area (Table 1) observed for C1 catalyst. Although SBA-15 presents some catalytic activity in this reaction, the difference in conversion clearly demonstrates the advantage of introducing the sulfonic groups in the material. It is also observed that the catalytic activity decreases when the sulfonic acid amount increases (Table 1). In this case probably there is a decrease of accessibility to the active sites, also related to the change in the textural properties of the materials.

Table 2 shows the  $\alpha$ -pinene conversion and selectivity to the products obtained by the reaction of  $\alpha$ -pinene with acetic acid over SBA-15 with sulfonic acid groups, after 30 h of the reaction. The oligomer/polymer amount present in reaction mixture, which was not GC determinable, was determined by the difference between the initial moles number of  $\alpha$ -pinene and the total moles number of all components ( $\alpha$ -pinene not converted, isomerisation products and addition products). It can be seen that sample C1 presents the highest conversion. After 30 h of reaction time, the  $\alpha$ -pinene conversion was 83%, with a selectivity of 20% to  $\alpha$ -terpinyl acetate. Similar values of selectivity were also found by Gainsford et al. [9]. However, when the acetoxylation of  $\alpha$ -pinene was carried out over ionic-exchange beta zeolite, it was observed that the selectivity to the  $\alpha$ -terpinyl acetate is 2–12%, at 70% of  $\alpha$ -pinene conversion [8]. This behaviour can be explained considering the side reactions that occurred under acetoxylation conditions such as, isomerisation and polymerisation.

The sulfonic acid groups present on SBA-15, acting as a Brønsted acid catalyst, not only promotes the addition of acetic acid to  $\alpha$ -pinene but also many side reactions such as double bond isomerisation and oligomerisation of the substrate. The reaction network may be represented by Scheme 2. The acetoxylation of  $\alpha$ -pinene proceeds via two parallel pathways, one of which resulting in bicyclic products (route A) and the other in monocyclic products (route B). The reaction initiates by protonation of the  $\alpha$ -pinene double bond to form the pinyl ion. The pinyl ion can rearrange into the bornyl ion and into the terpinyl ion. From the bornyl ion is yield bornyl acetate,  $\beta$ -fenchyl acetate, camphene and tricyclene, while from the terpinyl ion is yield  $\alpha$ -terpinyl acetate, limonene,  $\gamma$ -terpinene, terpinolene and  $\alpha$ -terpinene [4].

Fig. 5 represents the conversion and total amount of isomerised and addition products for all catalysts. It can be observed from the figure that the amount of the addition products increase with the amount of sulfonic acid groups.

Figs. S1–S4 (Supporting information) show the selectivity values for acetates products during different reaction times, over SBA-15, C1, C2 and C3 catalysts. It was observed that the selectivity to  $\alpha$ -terpinyl acetate increased with reaction time. Similar results were also obtained by Gainsford et al. [9]. The formation of acetates can be explained by the reaction network represented by Scheme 2.

In order to optimise the reaction conditions, the effect of different parameters (catalyst loading, initial concentration of  $\alpha$ -pinene and temperature) on the acetoxylation of  $\alpha$ -pinene over C1 catalyst was studied.

### 3.3. Effect of the catalyst loading

In order to study the effect of the C1 catalyst loading on the  $\alpha$ -pinene conversion, different catalytic experiments were carried out, at 60 °C. The initial concentration of  $\alpha$ -pinene (0.2 mol dm<sup>-3</sup>) was kept constant. Fig. 6 shows the conversion of the  $\alpha$ -pinene versus time. It was observed that when the catalyst loading increases,

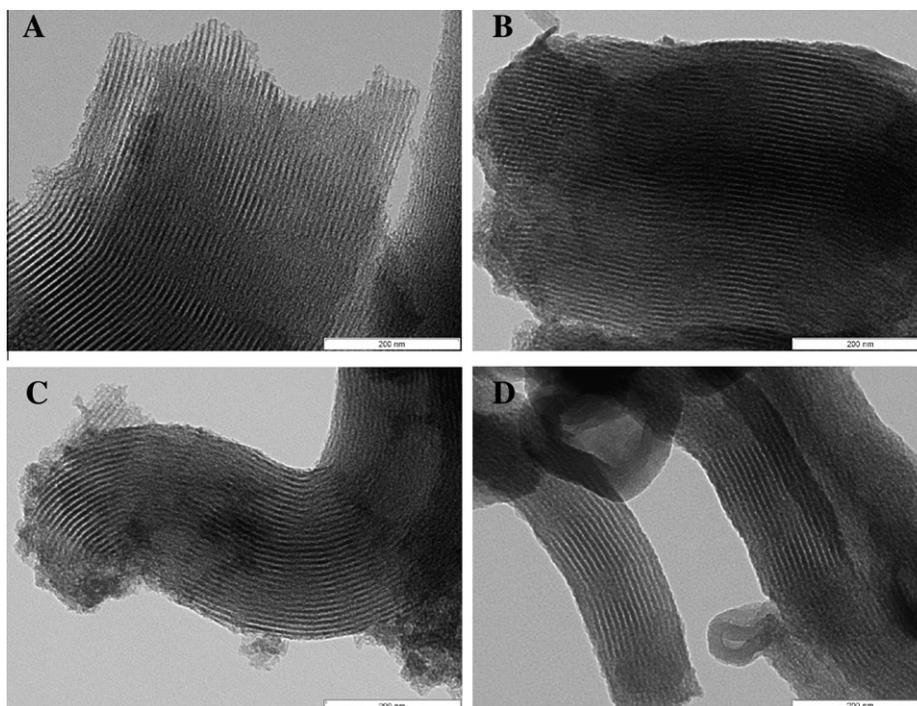
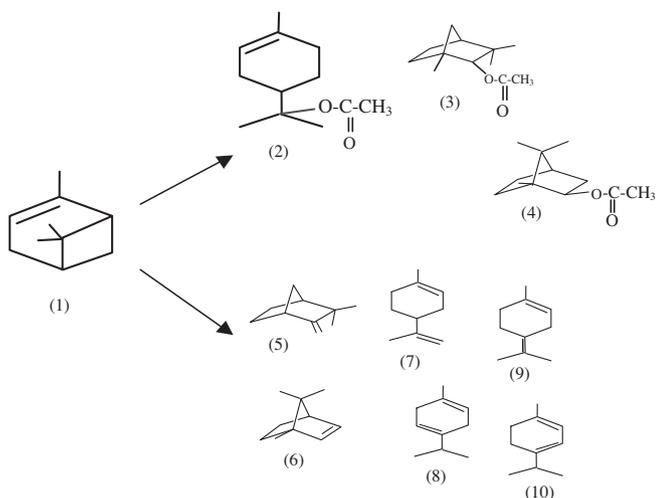


Fig. 3. Transmission electron microscopy (TEM) images of SBA-15 with sulfonic acid groups. (A) SBA-15; (B) C1; (C) C2; (D) C3.



Scheme 1. Acetoxylation of  $\alpha$ -pinene with acetic acid.

the equilibrium conversion is achieved more quickly, which can be explained due to the increase of the total number of the active sites. However, when the catalyst amount increases from 0.12 to 0.18 g, only a slight increase on the  $\alpha$ -pinene conversion was noticed. It was also observed that the catalyst loading has no effect on the equilibrium conversion (Fig. 6).

The selectivity does not vary much in all the catalytic experiments over different amount of C1, yielding similar values of  $\alpha$ -terpinyl acetate selectivity (about 18%) at 80% of  $\alpha$ -pinene conversion.

### 3.4. Effect of the initial concentration of $\alpha$ -pinene

The initial concentration of  $\alpha$ -pinene was varied from 0.1 to 0.3 mol dm<sup>-3</sup>, while the reaction temperature ( $T = 60$  °C) and the catalyst loading ( $m = 0.12$  g) were kept constant. The  $\alpha$ -pinene acetoxylation was carried out over C1. The results are shown in Fig. 7. After the same reaction time, it was observed that the

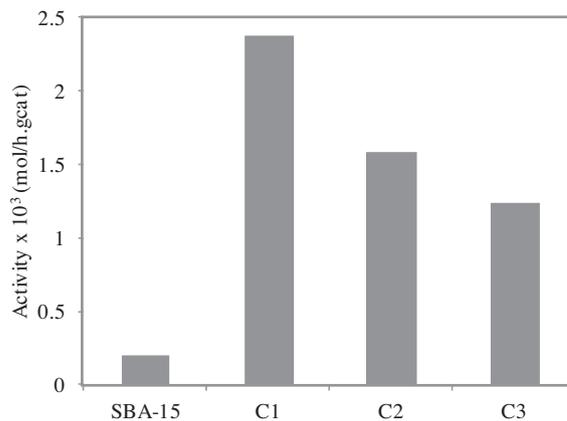


Fig. 4. Acetoxylation of  $\alpha$ -pinene over SBA-15 with sulfonic acid groups. Initial activities taken as the maximum observed reaction rate, calculated from the maximum slope of the  $\alpha$ -pinene kinetic curve. Reaction conditions: initial concentration of  $\alpha$ -pinene = 0.2 mol dm<sup>-3</sup>; Temperature = 60 °C; catalyst loading = 0.12 g.

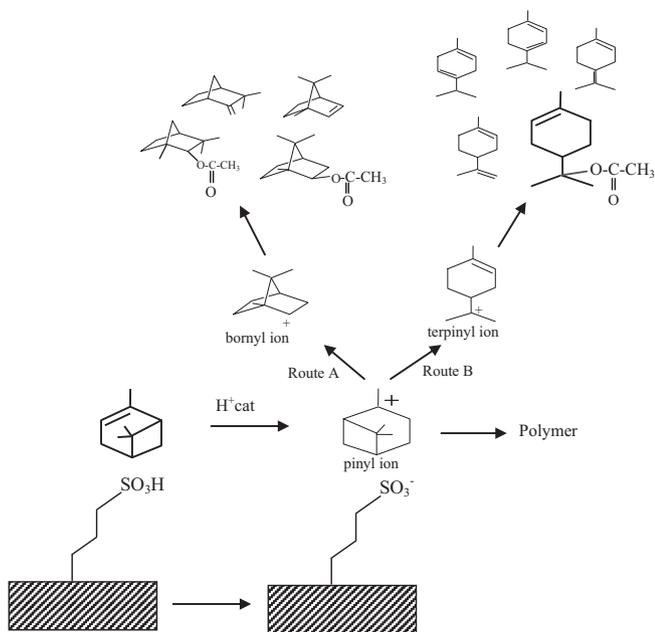
Table 2

Conversion and selectivity to the products of the acetoxylation of  $\alpha$ -pinene over SBA-15 with sulfonic acid groups, at 60 °C.

Catalyst	Conversion (%) <sup>a</sup>	Selectivity (%)						
		(5)	(7)	(9)	(3)	(2)	Others	Polymer
SBA-15	15	12	12	6	6	18	3	43
C1	83	12	14	5	5	18	5	41
C2	60	10	15	6	5	21	9	34
C3	50	11	16	5	7	23	7	31

<sup>a</sup>  $\alpha$ -pinene conversion after 30 h of reaction.

$\alpha$ -pinene conversion increases when the initial concentration of  $\alpha$ -pinene increases, under otherwise identical conditions. This behaviour may be a result of the increase of the reaction rate with  $\alpha$ -pinene concentration.



Scheme 2. Mechanism of acetoxylation of  $\alpha$ -pinene with acetic acid.

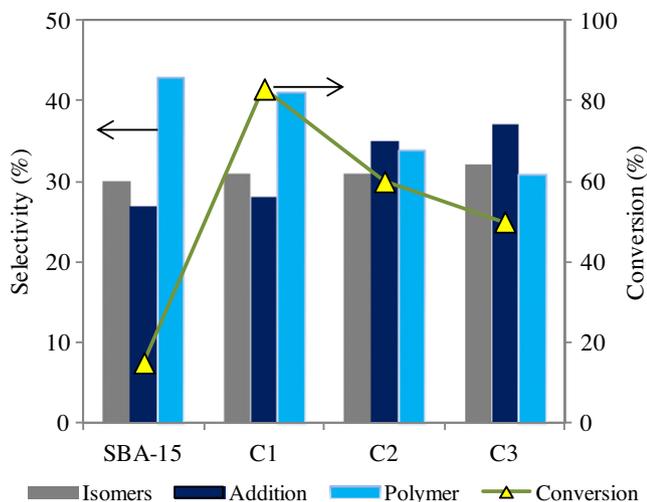


Fig. 5. Acetoxylation of  $\alpha$ -pinene over SBA-15 with sulfonic acid groups. Isomers, addition products and polymer. Reaction conditions: initial concentration of  $\alpha$ -pinene =  $0.2 \text{ mol dm}^{-3}$ ; Temperature =  $60^\circ\text{C}$ ; catalyst loading =  $0.12 \text{ g}$ ; time reaction =  $30 \text{ h}$ .

The initial concentration of  $\alpha$ -pinene has also an effect on the selectivity of C1 to  $\alpha$ -terpinyl acetate. After 30 h, it was observed an increase of the selectivity with the initial concentration of  $\alpha$ -pinene (about 15%, 18% and 23%, at 41 %, 83% and 95 % of  $\alpha$ -pinene conversion, for  $C = 0.1 \text{ mol dm}^{-3}$ ,  $C = 0.2 \text{ mol dm}^{-3}$  and  $C = 0.3 \text{ mol dm}^{-3}$ , respectively).

### 3.5. Effect of the temperature

The effect of the temperature on the  $\alpha$ -pinene acetoxylation was also studied. The catalytic experiments were carried out at different temperature over C1 catalyst, while the initial concentration of  $\alpha$ -pinene ( $0.2 \text{ mol dm}^{-3}$ ) and the catalysts loading ( $m = 0.12 \text{ g}$ ) were kept constant. Fig. 8 shows the influence of the temperature on the  $\alpha$ -pinene acetoxylation. It was observed that the  $\alpha$ -pinene

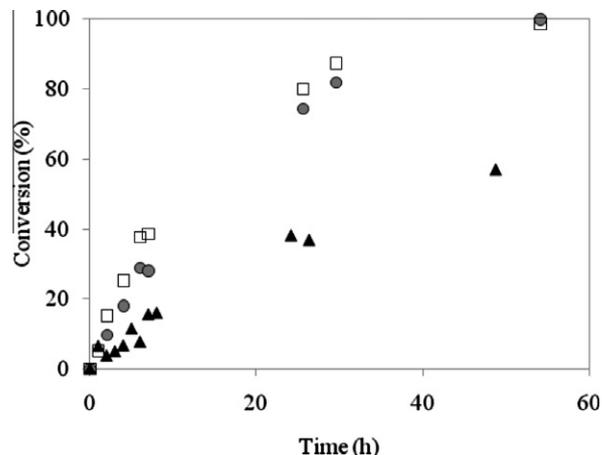


Fig. 6. Acetoxylation of  $\alpha$ -pinene over SBA-15 with sulfonic acid groups (C1 catalyst). Effect of catalyst amount. Conversion (%) versus time (h): ( $\blacktriangle$ )  $m = 0.06 \text{ g}$ ; ( $\circ$ )  $m = 0.12 \text{ g}$ ; ( $\square$ )  $m = 0.18 \text{ g}$ . Reaction conditions: initial concentration of  $\alpha$ -pinene =  $0.2 \text{ mol dm}^{-3}$ ; Temperature =  $60^\circ\text{C}$ .

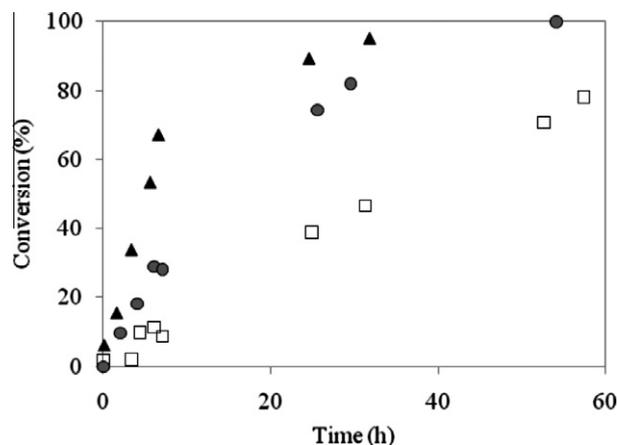


Fig. 7. Acetoxylation of  $\alpha$ -pinene over SBA-15 with sulfonic acid groups (C1 catalyst). Effect of initial concentration of  $\alpha$ -pinene. Conversion (%) versus time (h): ( $\blacktriangle$ )  $C = 0.3 \text{ mol dm}^{-3}$ ; ( $\circ$ )  $C = 0.2 \text{ mol dm}^{-3}$ ; ( $\square$ )  $C = 0.1 \text{ mol dm}^{-3}$ . Reaction conditions: catalyst amount =  $0.12 \text{ g}$ ; Temperature =  $60^\circ\text{C}$ .

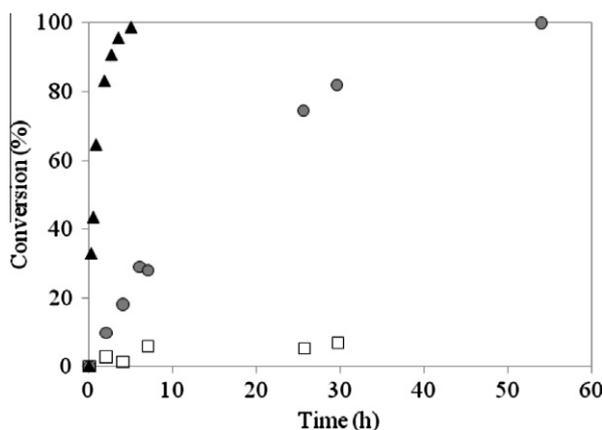
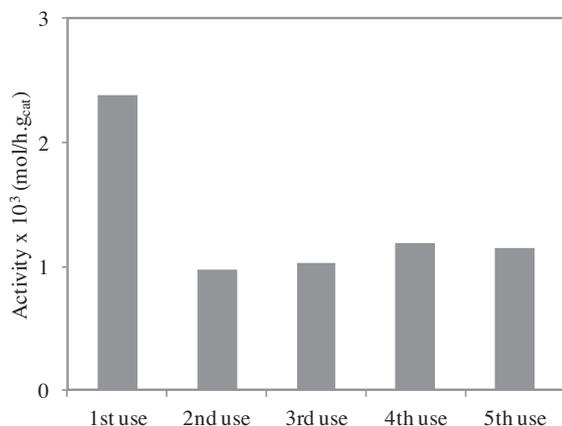


Fig. 8. Acetoxylation of  $\alpha$ -pinene over SBA-15 with sulfonic acid groups (C1 catalyst). Effect of temperature. Conversion (%) versus time (h): ( $\blacktriangle$ )  $T = 120^\circ\text{C}$ ; ( $\circ$ )  $T = 60^\circ\text{C}$ ; ( $\square$ )  $T = 30^\circ\text{C}$ . Reaction conditions: initial concentration of  $\alpha$ -pinene =  $0.2 \text{ mol dm}^{-3}$ ; catalyst amount =  $0.12 \text{ g}$ .

conversion increases with the temperature, at a fixed reaction time under otherwise identical conditions.



**Fig. 9.** Stability studies on C1 catalyst sample. Initial activities taken as the maximum observed reaction rate, calculated from the maximum slope of the  $\alpha$ -pinene kinetic curve.

At the different temperatures considered, after 5 h, a decrease of the selectivity occurs with the increase of temperature ( $T = 30\text{ }^{\circ}\text{C}$ , 17%;  $T = 60\text{ }^{\circ}\text{C}$ , 11%;  $T = 120\text{ }^{\circ}\text{C}$ , 7%).

### 3.6. Catalyst stability and reusability

In order to study the catalytic stability of the C1, different batch runs, with the same catalyst sample at same conditions, were carried out. Before reused, the catalyst was carefully washed with acetone to ensure maximum elimination of any product or polymer that could be adsorbed in it. It was observed that the catalytic activity decreases from the first use to the second use. This behaviour can be explained due to some leaching of sulfonic acid groups unbound to the SBA-15 support. After the second use, the catalyst C1 remained the activity (Fig 9). After five cycles, the selectivity of C1 sample to  $\alpha$ -terpinyl acetate remained 18%, at 80% of  $\alpha$ -pinene conversion.

## 4. Conclusions

The products of  $\alpha$ -pinene acetoxylation were  $\alpha$ -terpinyl acetate, bornyl acetate, fenchyl acetate, limonene, terpinolene and camphene.

SBA-15 containing sulfonic acid groups were used, as catalysts, in the acetoxylation of  $\alpha$ -pinene. The conversion increased with the increase of surface area and porous volume of the catalysts, probably due to the increases of  $\alpha$ -pinene accessibility to the active sites. The introduction of the sulfonic groups promotes the conversion to the desired products.

In order to optimise the reaction conditions, different parameters, such as catalyst amount, initial concentration of  $\alpha$ -pinene and temperature were studied.

The catalytic stability of C1 sample was also studied. After the second use, the catalytic activity of C1 remained constant.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.micromeso.2012.07.028>.

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