H$_2$O$_2$ based α-pinene oxidation over Ti-MCM-41. A kinetic study

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ABSTRACT

α-Pinene oxidation with hydrogen peroxide using Ti-MCM-41, prepared by hydrothermal synthesis, with a Ti content of 1.12 wt.% was studied. The major products of reaction observed were: verbenone, verbenol and campholenic aldehyde which are used in the pharmaceutical, perfume and cosmetics industry. The effects of various parameters such as the concentration of reagents, catalyst and temperature on the reaction rate have been studied. The experimental results show that the surface chemical reaction onto the catalytic site controls the overall reaction rate. A kinetic model that includes the absorption of reactants, water and solvent on the catalyst was proposed. The analysis of the initial rates allowed to determinate that the reaction is first order regarding to the α-pinene, hydrogen peroxide and catalyst amount and zero order with respect to H$_2$O, with apparent activation energy of 67.5 kJ/mol. Under the study conditions, leaching of the active species is not observed. Finally, the catalyst can be used repeatedly without losing activity or selectivity, confirming that the reaction proceeds through a certainly heterogeneous process.

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1. Introduction

Essential oils of pine trees which generally contain more than 80% of terpenic olefins are a useful source as a cheap and renewable raw material for several high value industrial processes such as the synthesis of fragrances, flavors, drugs and agrochemicals [1,2]. Among the most important terpenes composing these oils are the α-pinene and β-pinene bicyclical hydrocarbons (C$_{10}$H$_{16}$), which are found in the turpentine. The turpentine is a by-product from the industrial plants of cellulose production, it has a low commercial value and it is considered a renewable raw material with a great potential to obtain a wide variety of fine chemicals [3,4].

Flavors and fragrances are important ingredients in food, chemical, cosmetic and pharmaceutical industries. Generally, oxidative functionalization of monoterpenes represents an important way to value these natural products since terpenic aldehydes, alcohols and esters can be produced. These compounds often show high volatility and desired organoleptic properties, for that reason they are present in the composition of a great number of modern fragrances [5]. Particularly, pinene oxidation produces numerous products of industrial interest such as verbenone, verbenol and campholenic aldehyde. Verbenone is used to obtain taxol, an important therapeutic agent [6,7], while campholenic aldehyde is an important intermediate for the synthesis of santalol, the main constituent of natural sandalwood oil [8–10].

The development of catalytic methods for the selective oxidation of α-pinene by heterogeneous catalysts using green oxidants is a challenging goal of fine chemistry. These methods allow reduce the chemically contaminated effluents that cause a great environmental impact [11,12]. Among the oxidants, the aqueous hydrogen peroxide can be the chosen because it is a quite cheap, atom-efficient, environmentally benign and produces water as the only byproduct. Usually, H$_2$O$_2$-based oxidations require a catalyst to achieve an acceptable reaction rate and selectivity. In this context, many catalytic materials have been reported in the literature, including both homogeneous and heterogeneous catalysts. The application of solid materials in catalytic reactions in liquid phase has been extensively studied with the aim of replacing the tradtional homogeneous systems. The heterogeneous catalyst shows technological and environmental advantages because of its easy recovery and recycling. In the literature, there are some studies reported on the catalytic oxidation of terpenes. Thus, alumina was used as a quite selective α-pinene epoxidation catalyst; however anhydrous conditions should be used [13,14]. Although the achievable level of selectivity in α-pinene epoxidation is rather hight, sufficient selectivity toward the allylic oxidation products, verbenol and verbenone, still remains a challenge. The allylic oxidation of α-pinene with t-butyl hydro peroxide was observed on silica-titania co-gels [15], chromium aluminophosphate-5 [16], Cr-pillared montmorillonite [17] and sol–gel Co/SiO$_2$ [18]. Recently Ajaikumar et al. have reported the use of bimetallic catalysts such as Au–Cu, Au–Co and Au–Ru supported on TiO$_2$ for the oxidation of α-pinene under liquid phase conditions at low temperature [19]. Meanwhile, Maksimchuk et al. [20] assessed the allylic oxidation of α-pinene with H$_2$O$_2$ on different materials

containing Ti (IV), Zr (IV) and Fe (III) ions isolated in inorganic matrixes such as hydrothermally stable silicates, mesoporous cellular foams and Kegging type heteropolytungstates. Mesoporous molecular sieves and mixed oxides containing highly dispersed transition metal ions have been reported as efficient catalysts for H_2O_2-based oxidation [21–32]. The MCM-41 family of mesoporous materials has acquired a great importance due to its hexagonal order of bi-dimensional pores and its high surface areas, due to the possibility of adapting its catalytic properties, such as type and force of acid and/or basic sites, hydrophilicity/hydrophobicity, structure and size of pores. Particularly, the incorporation of redox metallic ions as Ti in the network structure of MCM-41 molecular sieves gives activity for oxidation of voluminous olefins [24,33]. Recently, we reported the use of titanium containing mesoporous materials, synthesized by different methods, as catalysts for the oxidation of α-pinene with H_2O_2 [34,35]. In [34] we present the results of the oxidation of α-pinene in the liquid phase with hydrogen peroxide using Ti-MCM-41catalysts prepared by conventional hydrothermal synthesis. Conversions between 12 and 15% and, as majority products, campholenic aldehyde and verbenone were obtained. In [35] we reported the synthesis and the catalytic evaluation of Ti-containing mesoporous catalysts prepared using zeolite precursors as building blocks of the mesoporous network. These materials showed maximum conversion values of around 20% and high yields to epoxidation products.

On the other hand, the scope of chemical kinetics is to define the evolution with time of a reacting system. The information which can be acquired with this type of studies can be applied in different fields, such as the interpretation of reaction mechanisms and of the molecular behavior, the interpretation of catalytic phenomena, the optimization of catalysts formulations, the development of new chemical processes and reactors modelling and simulation. Therefore, the study of chemical reaction kinetics is of interest for both chemists and chemical engineers using and elaborating reaction rates data with different objectives and many books have been published on the subject [36–38].

Taking account for the major simplicity, the lower cost and the higher yield to allylic products that present the catalysts prepared by the conventional synthesis method, we chosen these materials in order to study the kinetics of the reaction of the α-pinene oxidation and to propose a reaction mechanism that fits the experimental results. Assessing the reaction heterogeneity and the possibility of reusing the catalyst is also stated.

2. Experimental

2.1. Catalyst synthesis

Ti-MCM-41 was prepared by hydrothermal synthesis using tetra-ethoxysilane (TEOS) (Fluka >98%) as a source of Si, Ti isopropoxide (IV) (Fluka >98%) as Ti source and ethanol solution of dodecyl trimethyl ammonium bromide (DTMABr) (Fluka) which was used as template, as described in [34]. Mole composition of the starting gel of the material used in this study was: Si/Ti = 60, OH/Si = 0.3, template/Si = 0.4, water/Si = 60. Template agent was evacuated from the sample by thermal desorption programmed under N_2 flow until 500 °C and maintained at this temperature for 6 h. Then the sample was calcined in air at 500 °C for 6 h.

2.2. Catalyst physicochemical characterization

The Ti content of the sample was determined by inductively coupled plasma emission spectroscopy (ICP-AES). The physico-chemical properties of the sample were characterized by powder X-ray diffraction (XRD), diffuse reflectance UV–vis spectroscopy (DRUV–vis) and specific surface area, whose analysis was presented in [39]. Moreover, DRUV–vis spectra of the fresh and used Ti-MCM-41 after calcination in air at 500 °C during 9 h were recorded using a JascoV-650 spectrometer in the wavelength range 200–500 nm.

2.3. Catalytic experiments

In a typical reaction, α-pinene ($C_{10}H_{16}$) (Fluka >95%) (7.17 mmol), hydrogen peroxide (H_2O_2) (Riedel de Haën, 35 wt.% in water) (1.79 mmol), acetonitrile (CH_3CN) (Sintorgan, 99.5%) (107.56 mmol) as solvent and Ti-MCM-41 (63 mg) were placed in a pirex glass reactor. This reactor, equipped with a condenser to reflux and magnetically stirred, was immersed in a thermally controlled bath at temperatures varying between 40 and 70 °C. Reaction progress was followed taking samples at different times by a lateral tabulation, without opening the reactor. Liquid samples were immediately filtered and analyzed by gas chromatography using a capillary column crosslinked methyl-silicone gum, 30 m × 0.53 mm × 2.65 mm film thickness and connected to a FID detector. The percentage of each component in the reaction mixture was calculated by using the method of area normalization employing response factors. The relative uncertainties of the measurements were tested with repeated determinations. The percent relative uncertainty (CV (%)) of the result was calculated by dividing the corresponding absolute uncertainty with the average of the measurements. Reaction products were identified by mass spectrometry in a Shimadzu GCMS-QP 5050. Mass spectral data (m/z/intensity ratio) for the identified products are the following: I: 137/15, 109/35, 83/34, 67/100, 55/42, 41/77. II: 152/1 [M+], 108/100, 93/91, 81/20, 67/48, 55/23. III: 134/10, 119/33, 109/40, 91/90, 81/33, 79/31, 55/38, 41/100. IV: 150/29 [M+], 135/55, 122/16, 107/100, 91/67, 79/50, 55/31, 41/85. V: 126/3, 111/3, 98/22, 83/66, 69/58, 55/36, 43/100. VI: 152/10, 137/17, 109/58, 94/21, 79/61, 59/100, 43/96.

The α-pinene conversion was defined as the ratio of converted species to initial concentration. In order to study the possibility of reusing the catalyst, at the end of reaction, the catalyst was filtered off, washed with CH_3CN and calcined in air at 500 °C overnight to be used again with fresh reaction mixture in different catalytic cycles.

3. Result and discussion

3.1. Physicochemical characterization of catalyst

Table 1 shows the chemical composition and textural properties of Ti-MCM-41 material used in this study. DRX pattern of the sample, which is not presented here, is characteristic of an ordered hexagonal structure [39,40]. As it is shown in [39] the Ti ions were incorporated into the framework in tetrahedral isolated positions.

Table 1
Chemical composition, hexagonal-cell unit parameter, surface area and pore diameter of Ti-MCM-41 material.

Sample	Si/Ti[a]	Ti content (wt.%)[b]	A_0 (Å)	Area (m²/g)	d_{DFT} (Å)[c]
Ti-MCM-41	60	1.12	36.28	1546	27.25

[a] Mole ratio in starting gel.
[b] In calcined sample.
[c] Pore diameter corresponding to the maximum distribution by pores size obtained by the DFT method.
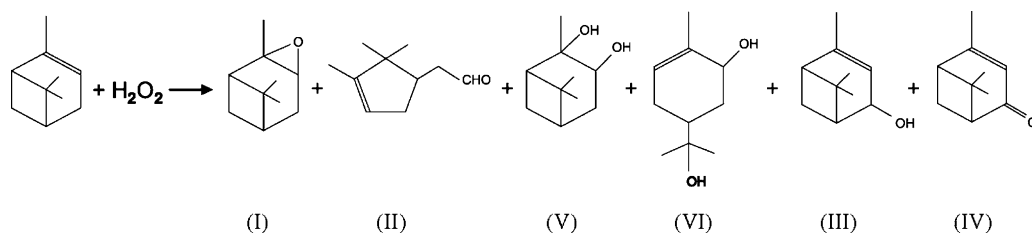
Fig. 1. Reaction products obtained from α-pinene oxidation: α-pinene oxide (I), campholenic aldehyde (II), 1,2 pinanediol (V), trans sobrerol (VI), verbenol (III) and verbenone (IV).

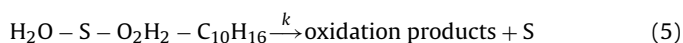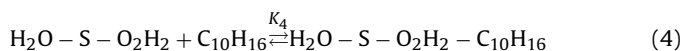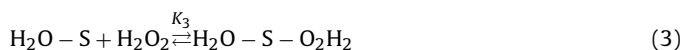### 3.2. Oxidation of α-pinene with H_2O_2

From GC–MS analyses, the products mixture is composed of species formed by oxidation of both allylic C–H and double bond (Fig. 1). The formation of product I is attributed to the oxidation of π bond, species II is formed by the rearrangement of I, whereas V and VI are formed by hydrolysis and opening of oxirane ring. Products III and IV are generated by oxidation of allylic C–H bond. Among these, the main products obtained by us on Ti-MCM-41, at 5 h of time reaction, were the verbenone (∼41%), the verbenol (∼16%) and the campholenic aldehyde (∼27%) at ∼15% conversion. On the other hand, Maksimchuk et al. [20] reached maximal values of total selectivity toward verbenol/verbenone of 80–82% at α-pinene conversion of 8–15% on a $H_5PW_{11}TiO_{40}$/silica catalyst in optimized reaction conditions (CH_3CN, 30 °C, α-pinene/H_2O_2 = 0.1 mmol/0.12 mmol). Nevertheless, using a titanium silicate Ti-MMM-2 prepared by hydrothermal synthesis, they reported a α-pinene conversion of 73% but with a total selectivity toward verbenol/verbenone of 23% and toward unidentified oligomeric/polymeric products of about 64%. Moreover, it is important to note that the turnover frequency, defined as TOF = (moles of α-pinene converted)/[(moles of active metal) × 5 h], reported by them was about 2.8 h^{-1} in contrast with the higher value found by us (14.3 h^{-1}), despite using a very higher α-pinene/oxidant molar ratio (4/1).

3.3. Kinetics of the oxidation

The α-pinene oxidation with H_2O_2 may therefore be described by the following simplified reaction scheme:

$$H_2O_2 + C_{10}H_{16} \rightarrow C_{10}H_{16}O + H_2O$$

$$H_2O_2 \rightarrow H_2O + 1/2 O_2$$
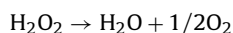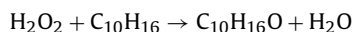
where $C_{10}H_{16}O$ includes all the possible oxidation products. Assuming that the reaction takes place in a heterogeneous catalytic system, the steps of the global reaction can be represented as a sequence of different elementary steps, as follows:

$$S + CH_3CN \underset{}{\overset{K_1}{\rightleftarrows}} CH_3CN - S \qquad (1)$$

$$S + H_2O \underset{}{\overset{K_3}{\rightleftarrows}} H_2O - S \qquad (2)$$

$$H_2O - S + H_2O_2 \underset{}{\overset{K_3}{\rightleftarrows}} H_2O - S - O_2H_2 \qquad (3)$$

$$H_2O - S - O_2H_2 + C_{10}H_{16} \underset{}{\overset{K_4}{\rightleftarrows}} H_2O - S - O_2H_2 - C_{10}H_{16} \qquad (4)$$

$$H_2O - S - O_2H_2 - C_{10}H_{16} \overset{k}{\longrightarrow} \text{oxidation products} + S \qquad (5)$$

S symbolizes an empty site on the surface, where solvent (CH_3CN), H_2O and H_2O_2, can be adsorbed in a competitive way. These species adsorbed were designated as CH_3CN–S, H_2O–S and H_2O–S–O_2H_2, respectively. This last specie represents the Ti–peroxo complex stabilized by H_2O through hydrogen bonding.

Then, the olefin approximates to this complex to give rise the intermediate H_2O–S–O_2H_2–$C_{10}H_{16}$. k is the kinetic rate constant and K_i represents the adsorption equilibrium constant for each reaction step described above.

The kinetic law equation was determined introducing two useful hypotheses on a theoretical basis: (1) the hypothesis of the existence of a rate-controlling step; (2) the assumption of the stationary state approximation for the unstable intermediates appearing in the mechanism. Considering that the surface chemical reaction is the controlling step of the rate, the following reaction rate can be written:

$$r = k[H_2O - S - O_2H_2 - C_{10}H_{16}] \qquad (6)$$

$$r = kK_2K_3K_4[S][H_2O][H_2O_2][C_{10}H_{16}] \qquad (7)$$

To obtain [S] the balance of the catalyst sites was performed. Considering that $[S]_0$ represents the initial concentration of active sites on the catalyst, which is directly proportional to the amount of catalyst used, the following expression can be written:

$$[S]_0 = [CH_3CN - S] + [H_2O - S] + [H_2O - S - O_2H_2]$$
$$+ [H_2O - S - O_2H_2 - C_{10}H_{16}] + [S] \qquad (8)$$

Taking this into account, Eq. (7) is transformed into the following expression:

$$r = \frac{kK_2K_3K_4[S]_0[H_2O][H_2O_2][C_{10}H_{16}]}{1 + K_1[CH_3CN] + K_2[H_2O](1 + K_3[H_2O_2](1 + K_4[C_{10}H_{16}]))} \qquad (9)$$

To find a kinetic law equation as a function of measurable properties, able to reproduce the evolution with time of reactants and products, the initial rates method was applied. The experimental kinetic data were adjusted using the Micro Math Scientists for Window software. To study the order regarding to the catalyst a set of experiments was performed, where the H_2O_2, H_2O, solvent and α-pinene initial concentration remained constant varying only the catalyst amount. Under this condition, the Eq. (9) was reduced to the following expression:

$$r_0 = a[S]_0 \qquad (10)$$

with $a = \frac{kK_2K_3K_4[H_2O]_0[H_2O_2]_0[C_{10}H_{16}]_0}{1 + K_1[CH_3CN]_0 + K_2[H_2O]_0(1 + K_3[H_2O_2]_0(1 + K_4[C_{10}H_{16}]_0))}$

Fig. 2 shows α-pinene conversions obtained from different catalyst amounts. From these results the initial rates were calculated at the different catalyst amounts. The results given in Fig. 3 clearly show that the reaction is first order with respect to the number of active sites.

To determine the order of the reaction with respect to α-pinene, the concentration of H_2O_2, solvent and catalyst amount were kept constant, and only the initial concentration of α-pinene was varied between 0.50 and 1.22 mol L^{-1}. The $C_{10}H_{16}$/H_2O_2 molar ratio was always superior to 1 to avoid the leaching of Ti atoms from the solid
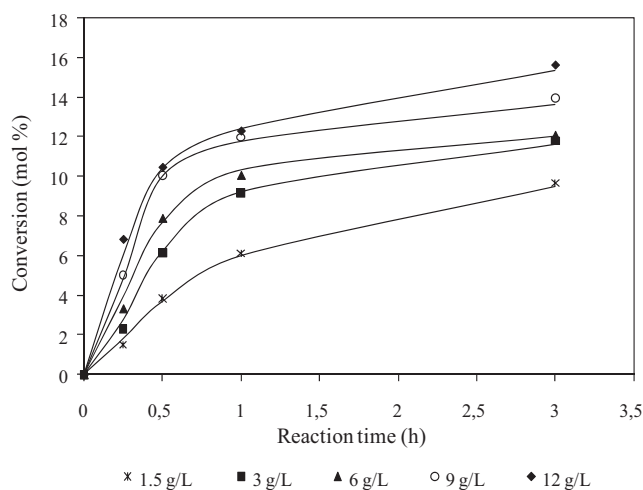
Fig. 2. Influence of the catalyst amount on the α-pinene oxidation reaction. Reaction conditions: 70 °C, $[C_{10}H_{16}] = 1.02 \, mol \, L^{-1}$, $[H_2O_2] = 0.25 \, mol \, L^{-1}$, $[CH_3CN] = 15.36 \, mol \, L^{-1}$.

catalyst to the reaction medium [41]. Under these conditions the Eq. (9) is reduced to the following expression

$$r_0 = \frac{b[C_{10}H_{16}]_0}{c + d[C_{10}H_{16}]_0} \tag{11}$$

or,

$$r_0 = \frac{[C_{10}H_{16}]_0}{(c/b) + (d/b)[C_{10}H_{16}]_0} \tag{12}$$

where $b = kK_2K_3K_4[S]_0[H_2O]_0[H_2O_2]_0$, $c = 1 + K_1[CH_3CN]_0 + K_2[H_2O]_0 + K_2K_3[H_2O]_0[H_2O_2]_0$ and $d = K_2K_3K_4[H_2O]_0[H_2O_2]_0$

Plotting the reciprocal values of the initial rate versus $l/[C_{10}H_{16}]_0$ (Fig. 4), it can be observed that the oxidation is first order regarding to the substrate. Table 2 shows the values of the parameters obtained from the adjusted rate equations. Analyzing the values of the parameters c/b and d/b, the order observed can be confirmed.

To determine the order of reaction regarding to the oxidant, the H_2O_2 concentration was varied between 0.12 and 0.75 mol L^{-1}, keeping constant the concentration of α-pinene, solvent and catalyst amount. Moreover, taking into account that the H_2O_2 is used as a solution in water of concentration 35 wt.%, the concentration
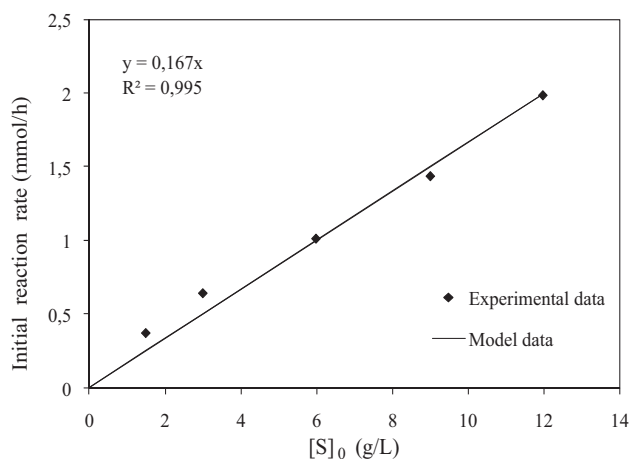
Table 2
Values of the parameters of the adjusted equations.

Parameters	Value[a]	Standard deviation[a]	R^2
a	0.167	±0.005	0.995
c/b	0.048	±0.022	0.994
d/b	0.000	±0.074	
f/e	0.028	±0.004	0.996
g/e	0.000	±0.006	
i/h	0.000	±0.001	0.999
j/h	0.044	±0.021	

[a] Intervals calculated with a 99% confidence.

of water in the system should also be kept constant. Under these conditions the Eq. (9) can be reduced to the following expression:

$$r_0 = \frac{e[H_2O_2]_0}{f + g[H_2O_2]_0} \tag{13}$$

or,

$$r_0 = \frac{[H_2O_2]_0}{(f/e) + (g/e)[H_2O_2]_0} \tag{14}$$

where $e = kK_2K_3K_4[S]_0[H_2O]_0[C_{10}H_{16}]_0$, $f = 1 + K_1[CH_3CN]_0 + K_2[H_2O]_0$, $g = K_2K_3[H_2O]_0(1 + K_4[C_{10}H_{16}]_0)$

In Fig. 5, the reciprocal values of the initial rate versus $l/[H_2O_2]_0$ are shown. The linearity observed determines that the reaction is first order regarding to the oxidant. As in the previous cases, the values of the f/e and g/e parameters obtained from the adjustment of the Eq. (14) (Table 2) confirm the order observed.

Finally, the effect of water was also studied by adding different amounts of water to a typical reaction mixture which contains 0.87 mol L^{-1} of water. Thus, we kept constant the concentration of α-pinene, oxidant, solvent and catalyst amount and the only change was the initial concentrations of H_2O between 0.87 and 2.28 mol L^{-1}. In this case the rate expression is reduced to:

$$r_0 = \frac{h[H_2O]_0}{i + j[H_2O]_0} \tag{15}$$

or,

$$r_0 = \frac{[H_2O]_0}{(i/h) + (j/h)[H_2O]_0} \tag{16}$$

where $h = kK_2K_3K_4[S]_0[H_2O_2]_0[C_{10}H_{16}]_0$, $i = 1 + K_1[CH_3CN]_0$, $j = K_2(1 + K_3[H_2O_2]_0(1 + K_4[C_{10}H_{16}]_0))$
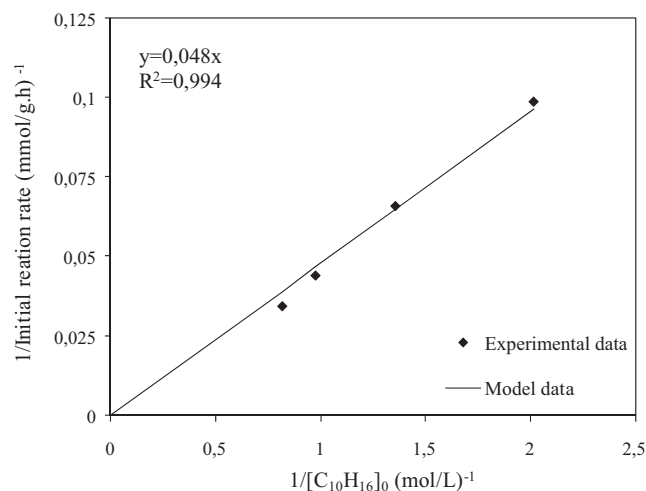

Fig. 3. Effect of the catalyst amount on the initial reaction rate of the α-pinene oxidation. Reaction conditions as in Fig. 2.

Fig. 4. Plot of $1/r_0$ vs $1/[C_{10}H_{16}]_0$. Influence of substrate concentration on the initial reaction rate for α-pinene oxidation. Reaction conditions: 70 °C, [cat] = 9 g L^{-1}, $[H_2O_2] = 0.25 \, mol \, L^{-1}$, $[CH_3CN] = 15.36 \, mol \, L^{-1}$.
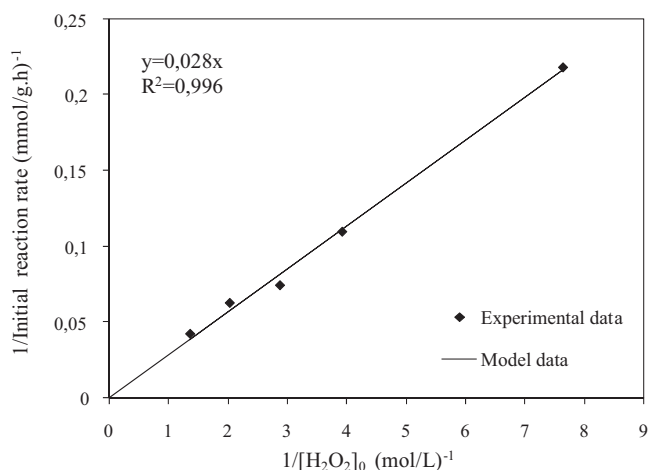
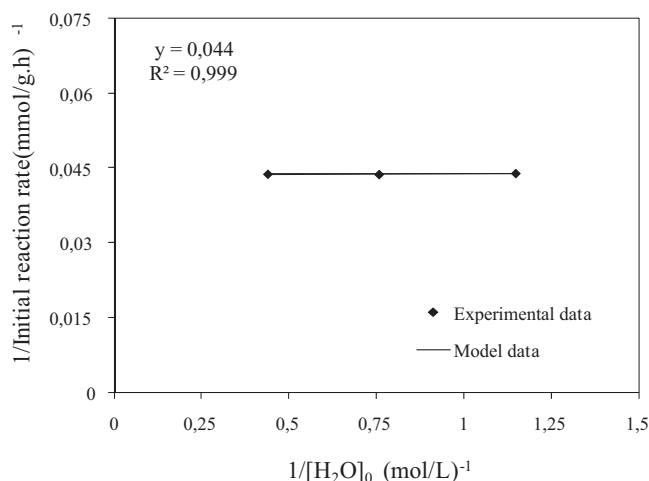**Fig. 5.** Plot of $1/r_0$ vs $1/[H_2O_2]_0$. Effect of the initial concentration of oxidant on the initial reaction rate for α-pinene oxidation. Reaction conditions: 70 °C, [cat] = 9 g L⁻¹, [C₁₀H₁₆] = 1.02 mol L⁻¹, [H₂O] = 2.6 mol L⁻¹, [CH₃CN] = 15.36 mol L⁻¹.

Fig. 7. Parity graph. Reaction Conditions: (◆): [C₁₀H₁₆] = constant, [H₂O₂] = 0.125–075 mol L⁻¹, [cat] = 9 g L⁻¹, T = 70 °C. (▲): [H₂O₂] = constant, [C₁₀H₁₆] = 0.50–1.22 mol L⁻¹, [cat] = 9 g L⁻¹, [H₂O] = 2.6 mol L⁻¹, T = 70 °C.

Fig. 6. Plot of $1/r_0$ vs $1/[H_2O]_0$. Effect of the initial concentration of water on the initial reaction rate for α-pinene oxidation. Reaction conditions: 70 °C, [cat] = 9 g L⁻¹, [C₁₀H₁₆] = 1.02 mol L⁻¹, [H₂O₂] = 0.25 mol L⁻¹, [CH₃CN] = 15.36 mol L⁻¹.

Fig. 8. Arrhenius plot for the reaction of α-pinene oxidation over Ti-MCM-41. Reaction conditions: [cat] = 9 g L⁻¹, [C₁₀H₁₆] = 1.02 mol L⁻¹, [H₂O₂] = 0.25 mol L⁻¹, [CH₃CN] = 15.36 mol L⁻¹.

Thus, Fig. 6 shows $1/r_0$ versus $1/[H_2O]_0$ where it can be seen that the reaction is zero order regarding to the water concentration.

In the parity graph shown in Fig. 7, a very good correlation between the initial rates obtained by adjusting Eq. (9) and the ones calculated from the experimental data can be observed. The experimental data were obtained keeping constant the temperature, catalyst amount, solvent, water and one of the reactives.

The effect of temperature on the initial rate of reaction was studied in the range of 40–70 °C, under the conditions of the typical reaction. The initial rate was then calculated for different reaction temperatures and the logarithm of the initial rate versus reciprocal of temperature, in K, has been plotted in Fig. 8. It should be noted here that since the reaction conditions were the same, the slope is equal to E_a/R where E_a is the apparent activation energy. From the slope of the straight line of plot, the apparent activation energy obtained is 67.5 kJ/mol. This activation energy is close to the 76.4 kJ/mol reported by Villa de et al. [42] for the oxidation of limonene by hydrogen peroxide on PW-Amberlite.
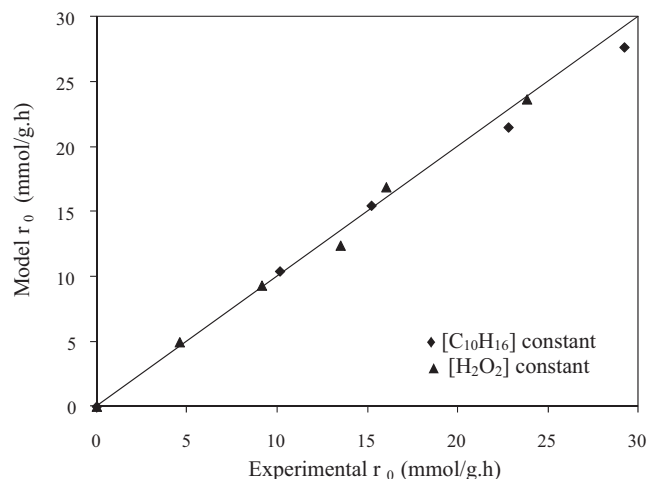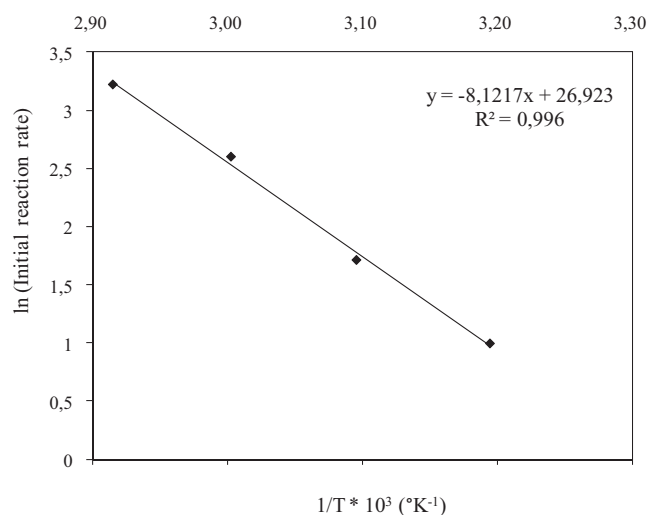
3.4. Stability and recycling of catalyst

An important aspect to be studied in the oxidation process in liquid phase with solid catalysts is the stability of the catalyst to the leaching of the active species, the heterogeneity of the reaction and the possibility of catalyst recycling. We have measured the Ti loading in the solid and liquid phases, before and after the reaction by ICP-AES. The Ti content remained constant in the used catalyst and it was not detected in the liquid phase considering the detection limits of the used technique (0.5 ppb).

Fig. 9 displays the DRUV–vis spectra of the fresh and used Ti-MCM-41 after calcination in air at 773 K during 20 h. No significant changes were observed between the DRUV–vis spectra of the fresh and used catalysts, indicating the maintenance of the structure of the Ti⁴⁺ sites after the reaction.

Therefore no Ti leaching has been observed in our reaction conditions, which confirms that the Ti incorporated to matrix is responsible for the substrate oxidation, and also that the Ti-MCM-41 material operates as heterogeneous catalyst. These results were corroborated since the catalyst activity remained constant when it

Table 3
Catalytic performances of the recycled Ti-MCM-41 in the oxidation of α-pinene with H_2O_2.

Catalytic cycles	α-Pinene conversion (mol%)[a,b]	Selectivity (mol%)[c]				
		I	II	III	IV	V + VI
1	14.7	6.2	26.9	16.0	40.5	10.4
2	14.6	6.9	26.8	15.5	40.9	9.8
3	14.4	6.9	26.6	15.8	40.7	9.9
4	14.2	7.0	26.9	15.5	40.9	9.7

Reaction conditions: 70 °C, $[C_{10}H_{16}] = 1.02$ mol L^{-1}, $[H_2O_2] = 0.25$ mol L^{-1}, $[CH_3CN] = 15.36$ mol L^{-1}, $[cat] = 9$ g L^{-1}, reaction time = 5 h.
[a] Maximum possible α-pinene conversion = 25 mol%
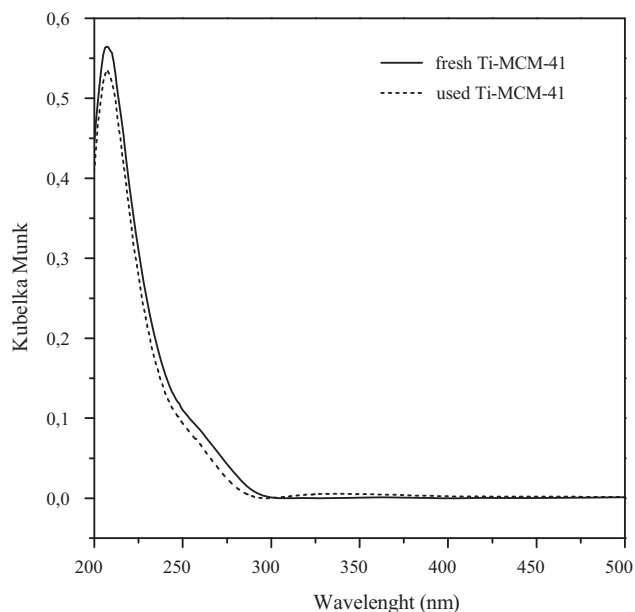[b] Relative uncertainty of measurements CV (%) < 7%.
[c] CV (%) < 5%.

Fig. 9. Diffuse reflectance spectra in the UV–visible region of fresh and used Ti-MCM-41.

was reused in several cycles of reaction. As it is shown in Table 3, the material does not exhibit a significant loss of catalytic activity or selectivity for at least four catalytic cycles, which confirms that the Ti-MCM-41 material operates as heterogeneous catalyst and can be recycled.

4. Conclusion

The kinetics of α-pinene oxidation with H_2O_2 on Ti-MCM-41, prepared by hydrothermal synthesis, was studied. Taking into account all the adsorption equilibria and including the competence of the solvent and the water with the oxidant for the active sites, a general kinetic equation was obtained. It was found that the reaction rate is first order regarding to the concentrations of α-pinene, hydrogen peroxide and catalyst amount, and zero order with respect to H_2O. The effect of reaction temperature on the kinetics of pinene oxidation has been determined, and apparent activation energy of 67.5 kJ/mol was obtained.

Ti-MCM-41 material can be used repeatedly without significant loss of activity or selectivity, confirming that the reaction is certainly heterogeneous under the reaction conditions studied, with no leaching of the active species.

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