



Kinetic study of α -pinene allylic oxidation over $\text{FePcCl}_{16}\text{-NH}_2\text{-SiO}_2$ catalyst



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ABSTRACT

The kinetic of α -pinene oxidation over an iron hexadecachlorinated phthalocyanine immobilized on modified silica ($\text{FePcCl}_{16}\text{-NH}_2\text{-SiO}_2$) with *t*-butyl hydroperoxide (TBHP) as oxidant is proposed. Reaction rates were calculated by the initial reaction rate method from the data obtained in a batch reactor, and compared with kinetic expressions proposed from mechanisms based on Langmuir Hinshelwood Hougen Watson (LHHW) and power-rate law models. The kinetic parameters were estimated from the experimental data by optimization using the Genetic Algorithm. A kinetic expression based on LHHW model with the adsorption of α -pinene, TBHP and the main reaction products (verbenone, α -pinene epoxide and verbenol) on the surface of the catalyst predicted the experimental data with good accuracy ($R^2 = 0.986$). The apparent activation energy of α -pinene allylic oxidation over $\text{FePcCl}_{16}\text{-NH}_2\text{-SiO}_2/\text{TBHP}$ was 40.08 kJ/mol. α -Pinene conversion of 83.7% was obtained after 23 h with a selectivity to verbenone of 23%. Under the reaction conditions leaching of the active species was not observed; however, the effect of radicals in the bulk liquid phase was demonstrated, confirming that the reaction involves a combination of both heterogeneous and homogeneous pathways. The catalyst can be used at least in seven cycles without loss of α -pinene conversion nor verbenone selectivity.

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1. Introduction

α -Pinene is a constituent of the turpentine oil obtained from pine plants, which can be converted into more valuable compounds, such as epoxides, alcohols, aldehydes and ketones [1–3]. The α -pinene allylic oxidation leads to the production of α,β -unsaturated compounds verbenol and verbenone (Fig. 1), raw materials in the production of flavors, insecticides, therapeutic drugs and food industry [3–9]. Although verbenone is a constituent of strawberry, raspberry, dill, vervain (20.5 wt.% [10]), rosmarinus (24.9 wt.% [11]) and spearmint flavor mixtures, the synthetic route from α -pinene oxidation to verbenone is of interest. However, during the oxidation of α -pinene two main competitive reactions are present: a) the epoxidation of the double bond to obtain α -pinene epoxide, and b) the allylic oxidation to produce verbenol and verbenone. The predominance of the reactions depends on the catalyst and the stability of the radicals formed during the oxidation [12].

The development of selective α -pinene oxidation using non-toxic solvents, efficient and environmentally friendly catalysts has

become a challenging goal in the chemical industry for productivity improvement [13]. Verbenone has been obtained using homogeneous and heterogeneous catalysts with moderate yields (Table 1) [14,15]; however, the requirement of expensive and toxic solvents [16–19], difficulty in catalyst recovery and product purification [20], inert atmosphere or large amount of catalyst and time, limit the application in some of those systems. Furthermore, in some cases reports do not include catalytic stability [21]. Hexadecachlorinated iron phthalocyanine immobilized on commercial silica $\text{FePcCl}_{16}\text{-NH}_2\text{-SiO}_2$ (Fig. 2), is an active catalyst for the synthesis of allylic ketones under mild reaction conditions (313 K, 24 h, acetone), with yields to verbenone above 22% using TBHP without not apparent activity loses in three reaction cycles [22]. Metallophthalocyanines (MPc) are structurally similar to metal porphyrins complexes, but more stable to degradation, and widely used as catalysts in several organic reactions, for example in the cyclohexene and cyclohexane oxidation [23–25].

In spite of the numerous reports about the heterogeneous catalytic allylic oxidation of α -pinene, there are few kinetic studies for this reaction. The proposed mechanism over $\text{Ti-MCM-41}/\text{H}_2\text{O}_2$ (which gave a 15% α -pinene conversion at 5 h, 343 K, acetonitrile) includes competitive adsorption of H_2O_2 , α -pinene, acetonitrile and H_2O from the H_2O_2 on the catalyst surface [26] and the sur-

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Table 1
Catalytic α -pinene allylic oxidation to verbenone systems.

Catalyst	Oxidant	^a Y _{VE} (%)	Solvent	Temp. (K)	Time (h)	Ref.
V-MCM-41	H ₂ O ₂	5	acetonitrile	343	7	[14] ^b
Co/SiO ₂	O ₂	14	–	333	24	[15] ^c
NaIO ₄	TBHP	18	acetone/pyridine	298	16	[16] ^d
Na ₂ Cr ₂ O ₇	N-hydroxyphthalimide	47	acetone	298	44	[17] ^e
Cr-MIL-100	O ₂ /TBHP	6	–	333	16	[18] ^f
UO ₂ ²⁺ /MCM-41	TBHP	52	acetonitrile	343	24	[19] ^g
Co(4-Me(C ₅ H ₄ N) ₂)Br ₂	O ₂	37	–	373	6.5	[20]
Fe-PILC/MA	TBHP	80	CH ₂ Cl ₂	313	50	[21] ^h

^a Y_{VE}: verbenone yield.

^b TBHP/ α -pinene mol ratio = 4, 9 g/L catalyst.

^c Co/SiO₂ (5 wt.%), 1 MPa (O₂).

^d α -pinene 18.6 mmol, 30 mmol catalyst, 20 mL TBHP, 32 mL acetone, 3 mL pyridine.

^e α -pinene/N-hydroxyphthalimide mol ratio = 1, 5 mmol catalyst/10 h.

^f 1.5 mL α -pinene, 1 bar (O₂), 0.02–0.03 mmol TBHP, 26 mg catalyst.

^g 50 mg UO₂²⁺/MCM-41 (50), TBHP/ α -pinene mol ratio = 2, 10 mL solvent.

^h Argon atmosphere, 6% mol catalyst, TBHP/ α -pinene mol ratio = 10.

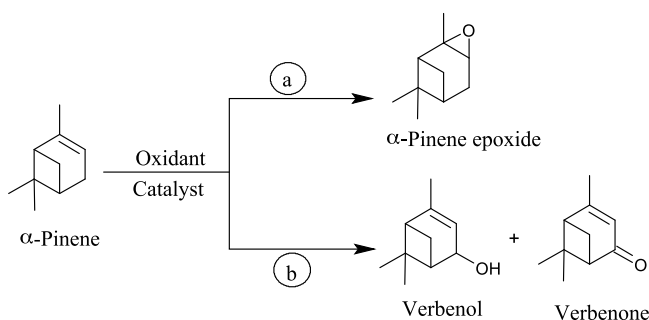


Fig. 1. Competitive reactions from α -pinene oxidation: (a) epoxidation, (b) allylic oxidation.

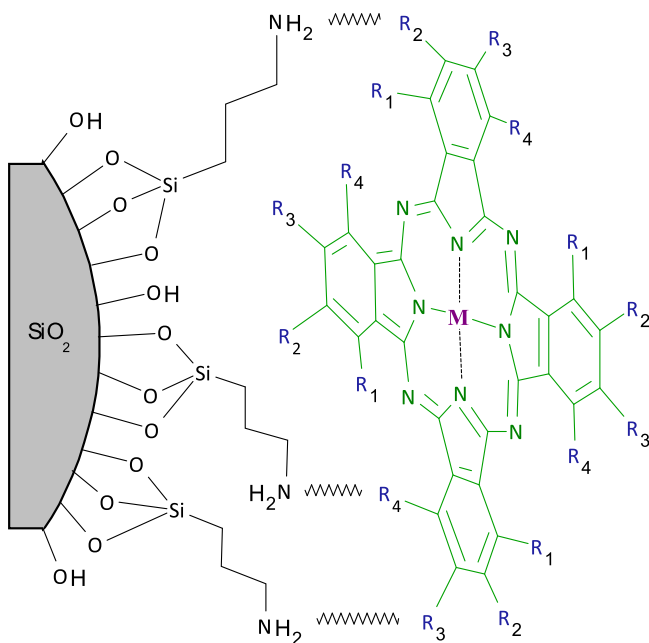


Fig. 2. Representation of MPCl_n supported on NH₂-SiO₂ catalyst. Center metal M = Fe, peripheral groups R_n = R₁ = R₂ = R₃ = R₄ = Cl.

face chemical reaction as controlling step; using the stationary state approximation for the intermediates, the authors found that the reaction rate was first order respect to the concentrations of α -pinene, H₂O₂ and catalyst, and zero order respect to H₂O. However, the formation of oxidation products was not clearly detailed [26]. In other study, a proposed mechanism for α -pinene liquid-phase

oxidation by O₂ over Pd/C catalyst (343–393 K and 0.5–6 bar O₂ pressure) involves two consecutive steps: (i) α -pinene oxidation by O₂ to verbenyl hydroperoxide (VHP) intermediate and α -pinene epoxide and (ii) selective reduction of VHP to verbenol by H₂ over the catalyst [27]. The mechanism was proposed as a set of radical chain steps. The authors suggested for the step (i) a kinetic equation of first order regarding to the O₂ pressure and half order respect to VHP concentration [27]. Until now, there are no reports about the kinetic of the α -pinene allylic oxidation to verbenone considering both the radicalary mechanism and the heterogeneous catalytic process.

In this paper a kinetic study of α -pinene allylic oxidation was performed with the catalytic system FePcCl₁₆-NH₂-SiO₂/TBHP, using several kinetic expressions based on LHHW reaction mechanism; furthermore, the role of the heterogeneous catalyst and radicals was studied. The kinetic parameters were estimated by optimization using the Genetic Algorithm in Matlab[®]. In addition, the heterogeneity and stability of FePcCl₁₆-NH₂-SiO₂ catalyst was evaluated using leaching and reusing tests.

2. Experimental

2.1. Reagents

All commercial reagents were used without any further purification: (1R)-(+)- α -pinene 98%, *tert*-butyl hydroperoxide solution (70% aqueous), tetrachlorophthalic anhydride 96%, (3-aminopropyl) triethoxysilane 99%, fumed powder SiO₂, 2,4-di-*tert*-butylphenol 99% and triphenyl phosphine \geq 98.5% from Sigma–Aldrich. Acetone ACS reagent \geq 99.5%, *n*-decane anhydrous \geq 99%, urea ACS reagent and FeCl₂·4H₂O from Merck. Ammonium heptamolibdate tetrahydrate from J.T. Baker.

2.2. Catalyst preparation

The phthalocyanine complex FePcCl₁₆ was synthesized using a well-grounded mixture of urea (11.7 g), tetrachlorophthalic anhydride (16 g), FeCl₂·4H₂O (2.8 g) and ammonium heptamolibdate tetrahydrate (0.1 g) [28]. Before the complex immobilization, the support was modified with 3-aminopropyltriethoxysilane (APTES) following a reported procedure [29] and named as NH₂-SiO₂. The final material was called FePcCl₁₆-NH₂-SiO₂ (detailed procedure in the Supplementary data, section 1. Catalyst preparation).

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