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Limonene epoxidation by molecular sieves zincophosphates and zincochromates

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Abstract

Conversion of limonene in its derivatives has been an interesting process due to its high value for cosmetic, pharmaceutical and food industries. The use of molecular sieves based on transition metals in heterogeneous catalysis, and specifically in oxidative processes, has shown good results. Oxidation of limonene has been studied using zinc based catalyst, hydrogen peroxide as oxidative agent and *t*-butanol or tetrahydrofurane as solvents at different reaction times and temperatures. 1,2-Epoxi-limonene, carvone, carveol and limonene-1,2-diol were obtained as main products.
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Keywords: Limonene epoxidation; Zincophosphates; Zincochromates; Molecular sieves

1. Introduction

Limonene is a monoterpene that is extracted from citrus oils, being the largest component (90–95%) [1]. Limonene has been used in the production of paintings, cosmetics and secondary refrigerant fluid and in the cleaning industries. Indeed, the limonene epoxidation produces compounds used as an intermediate for the elaboration of flavors, perfumes, food additives, drugs and agrochemicals products [2]. Transformation of limonene in oxygenate products is an important industrial process in the world, because of commercial value of their products and the easy way to extract limonene from renewable natural sources [3].

Epoxidation of limonene still employs stoichiometric pathways with peracids, halohydrines or permanganates, although, environmental and economical trends make this method unacceptable [4]. In order to replace these process, it looks for alternatives routes like the catalytic processes with homogeneous catalyst like heteropolyacids and organometallic compounds containing W, Mo, Ti, Mn, Zn, Fe and Co that have proved advantages over stoichiometric routes, but it has problems like corrosion and the hard catalyst separation of the reaction mixture [5–11].

Due to the well known advantages of heterogeneous catalysis, it looks for new catalyst without problems of separation and recuperation, and with better conversions and selectivity for interesting products. In this way, it has carried out the oxidation of limonene with zeolite exchanged with transition metals like Fe, Co, Mo, and Mn [12], Y zeolite with Schiff complex bases containing Fe and Mn [13] and Ti-beta zeolite [14]; in all these systems O_2, H_2O_2 and/or yodo sil benzene, were used as the oxidant agent as well as solvents like methanol, *t*-butanol and dioxane.

Synthesis of catalyst with novel compositions has permitted the development of new applications and technologies, improving catalytic systems, which makes them more efficient and specifics [15]. Porous materials containing transition metals have potential applications similar to a catalyst in different chemical reactions; specifically zincophosphates and zincochromates molecular sieves that have interesting properties in condensation reactions, addition and oxidation [16,17], besides their acid surface [18], a property very important to limonene epoxidation. The aim of the present study was to evaluate the catalytic activity of three materials containing transition metals in limonene epoxidation; two molecular sieves zincophosphates, Hopeite and the chiral zincophosphate CZP with three-dimensional

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Table 1
Synthesis conditions of the catalyst

Catalyst	Gel molar composition	*T* (°C)	*t* (h)
CZP	1.0 NaOH:3 TMAOH:0.8 P_2O_5:1.1 ZnO:133 H_2O	4	5
Hopeite	1.0 NaOH:4.2 TMAOH:1.0 P_2O_5:2.4 ZnO:391 H_2O	4	5
ZnCr ϕy	ZnO:CrO_3:1.2 NH_4OH:172 H_2O	100	24

Table 2
Experimental design conditions

Reactive	Quantity
Limonene (95% Merck)	1 mL
H_2O_2 (30% Merck)	0.9 mL
Quantity of catalyst	0.100 g
Quantity of solvent	2 mL

Variable	Level
Catalyst	Hopeite, CZP, ZnCr ϕy
Solvent	*t*-Butanol, THF (Aldrich)
Temperature	40 and 60 °C
Time	6, 12, 18 and 24 h

structure, defined by 12 member rings [19,20]; and a layered zincochromate type Φy [21].

2. Experimental

2.1. Synthesis

Three catalysts were prepared by hydrothermal synthesis, the molar composition of the gel, crystallization time and crystallization temperatures are given in Table 1. The procedure to obtain zincophosphates went as following: a solution of NaOH (Merck 99%), TMAOH (Aldrich 25%) and H_3PO_4 (Carlos Erba 85%) in deionized water was prepared and kept in an ice bath cooled at 4 °C and homogenized. In another vessel a solution of $Zn(NO_3)_2{\cdot}4H_2O$ (Merck 98.5%) was prepared in deionized water, and was cooled at the same temperature, then it was added drop by drop under stirring to the first solution. The formation of a thick gel was observed and after a while homogenization it poured into polypropylene bottles, which were kept in a refrigerated bath at 4 °C for 5 h. The precipitated solids were filtered and washed with deionized water and dried at 60 °C.

Zincochromate preparation went as follows: two aqueous solutions of $ZnCl_2$ (Merck 98%) and CrO_3 (Merck 99%)

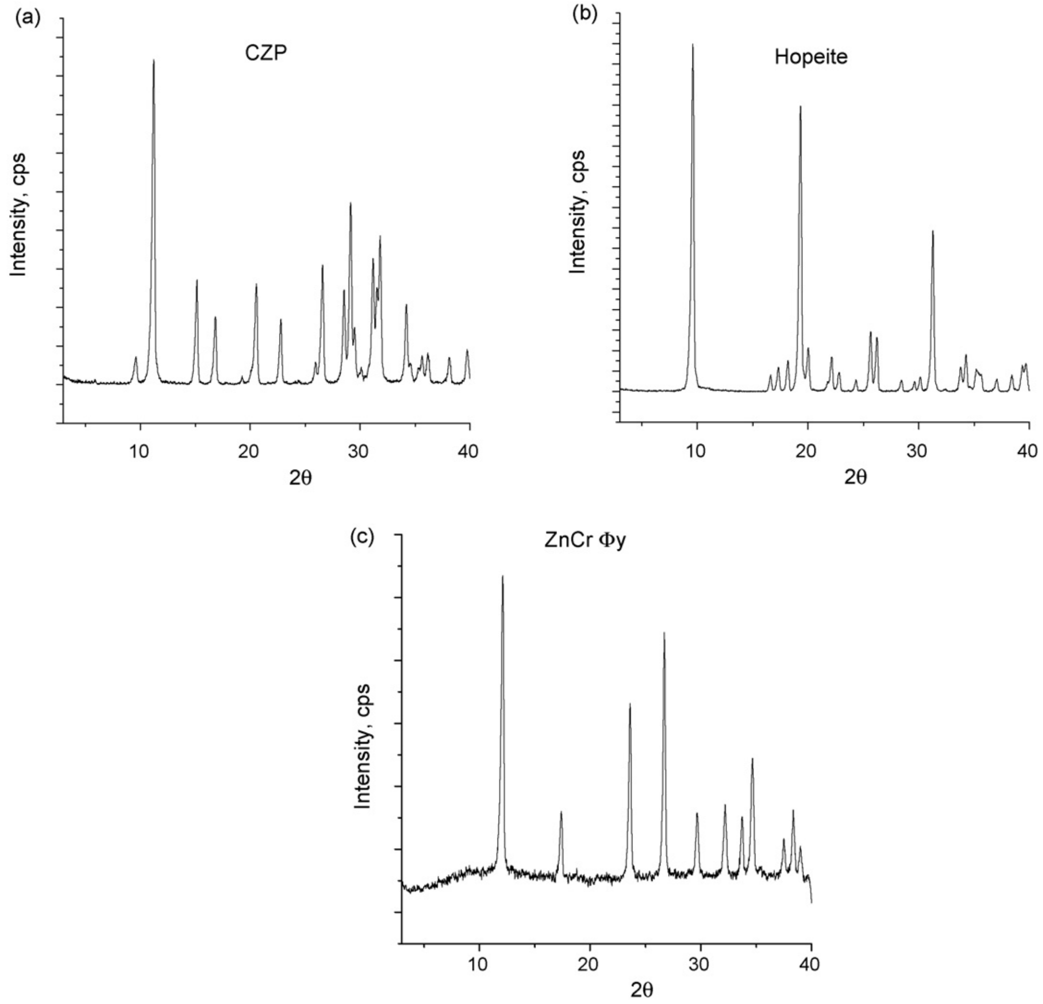

Fig. 1. (a) X-ray diffractograms for the CZP catalysts. (b) X-ray diffractograms for the Hopeite catalysts. (c) X-ray diffractograms for the ZnCr Φy catalysts.

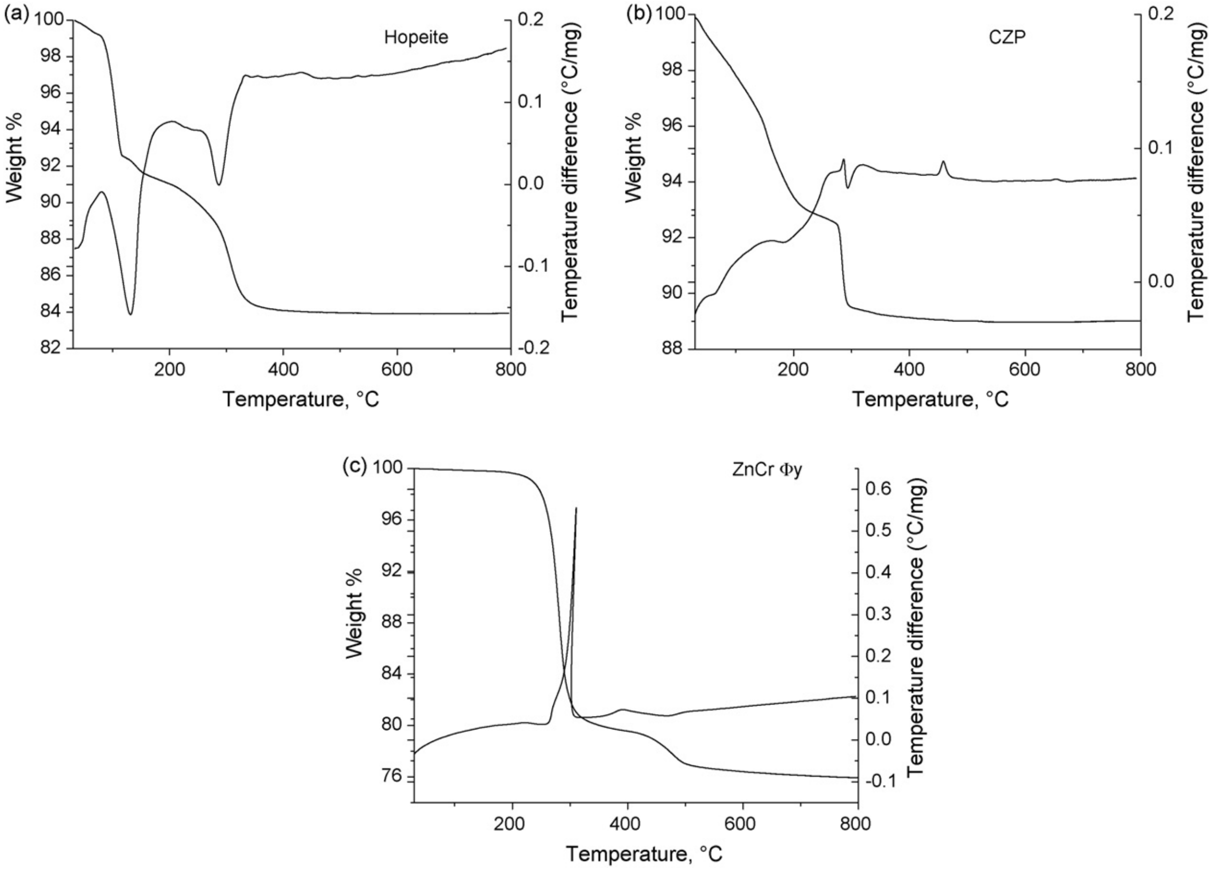

Fig. 2. (a) Thermal analysis of Hopeite catalysts. (b) Thermal analysis of CZP catalysts. (c) Thermal analysis of ZnCr Φy catalysts.

previously prepared, were mixed under stirring. Then NH_4OH was added to obtain a gel that was homogenized during 30 min. The gel was packed in a Teflon lined stainless steel autoclave and heated at 100 °C under autogenous pressure for 24 h. A yellow solid was recovered by filtration and washed with deionized water and drying at 60 °C.

2.2. Characterization

Catalysts were characterized by X-ray diffraction (XRD), thermal analysis (TGA and DTA), scanning electronic microscopy (SEM) and elemental analysis. XRD powder pattern of the solids were recorded at room temperature with a diffractometer Rigaku Miniflex Cu Kα_1 (λ = 1.5418 Å) working at 40 kV and 30 mA, between 5° and 40° in 2θ, with a scan rate of 2°/min. TGA was performed in a Hi-Res TA instrument 2920 equipment and the DTA in a TA Instrument 2950 equipment, both in a range from room temperature to 800 °C, under N_2 and heat rate of 10 °C/min. SEM was carried out with a Phillips XL 30 and a JEOL JSM 5910 LV apparatus with detector BES and SEI. Elemental analyses (Zn, P, Na, Cr) were performed by atomic absorption (AA) in a Unicam 969 Solaar equipment.

2.3. Catalytic tests

Catalytic tests were carried out in a glass batch reactor, into a thermal oil bath with temperature and magnetic stirrer controlled. A factorial experimental design was made using Statgraphics plus 4.1, and it was analyzed the influence of temperature, time, solvent and catalyst over the conversion of limonene and selectivity toward interest products. Table 2 shows the experimental design condition. For the oxidant agent and solvents selection, environmental parameters were considered. The oxygen peroxide was titrated in order to verify its concentration. Duplicate tests were performed in all cases. With this experimental procedure a good reproducibility was get.

Quantification of reaction products was done by the ratio of area method, conversion is expressed as (Σ(area of products × 100)/[(Σ(area of products)) + (Σ(area of reactive))]; and selectivity is expressed as (area of product *i*) × 100/[(Σ(area of products))]. All oxidation products were analyzed using an Agilent 6890N with flame detector ionization (FID), with capillary column HP-5 of 30 m length and 0.32 mm of diameter; it used N_2 like carried gas. The reactants and products were identified chromatographically using external standards.

Table 3
Catalysts chemical composition

Catalyst	Chemical formula
CZP	$NaZnPO_4{\cdot}H_2O$
Hopeite	$Zn_3(PO_4)_2{\cdot}1.4H_2O$
ZnCr Φy	$(NH_4OH)_{3/2}(ZnCrO_4)_2$

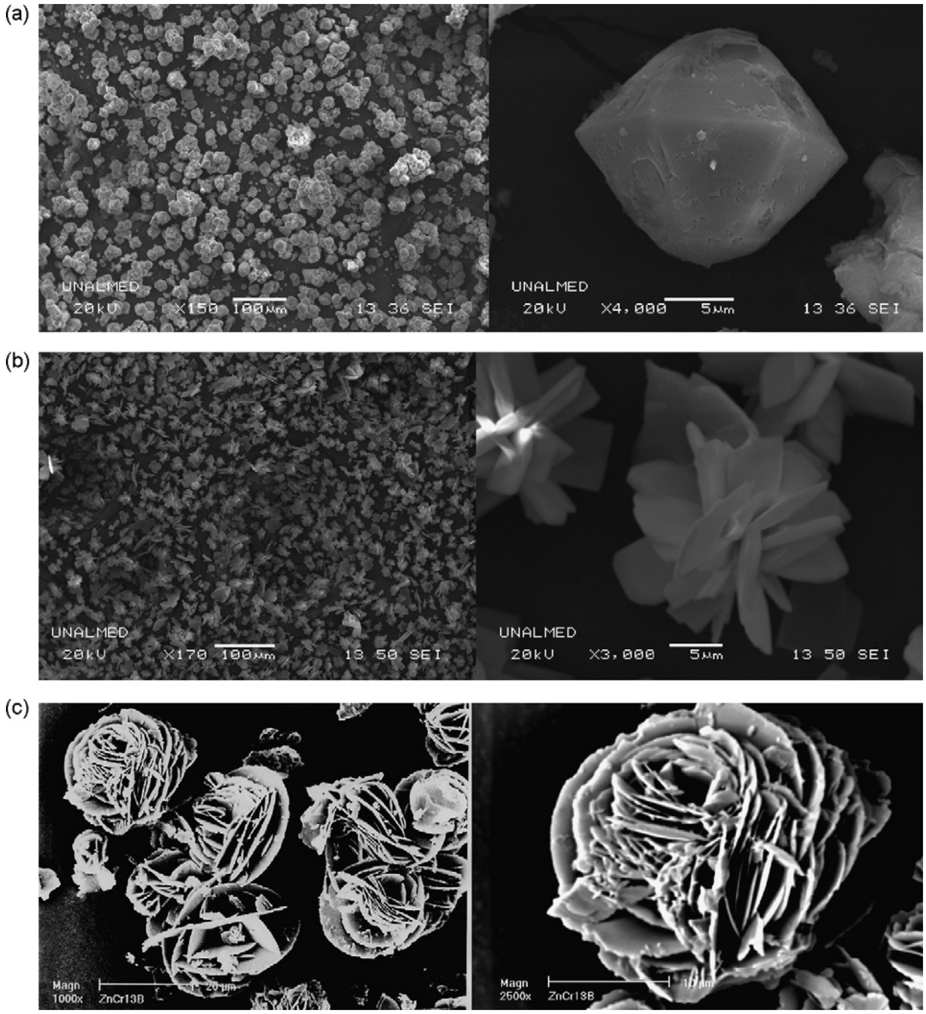

Fig. 3. (a) Scanning electronic microscopy for CZP catalysts. (b) Scanning electronic microscopy for Hopeite catalysts. (c) Scanning electronic microscopy for ZnCr Φy catalysts.

3. Results and discussion

3.1. Synthesis and characterization

Diffractograms for catalyst are shown in Fig. 1a–c, materials with high crystallinity can be observed without amorphous or crystalline impurities, which correspond to the previous reported. The thermal and chemical analysis allowed determining the chemical formula as shown in Table 3.

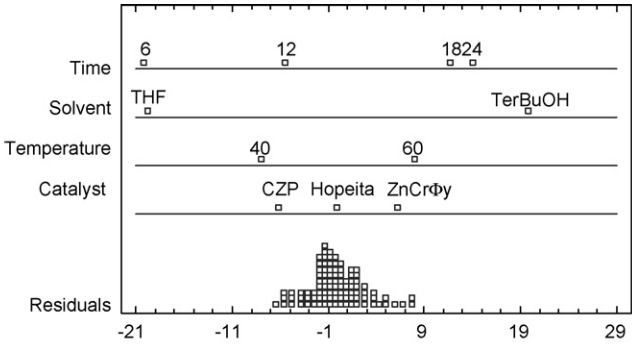

Fig. 4. Graphical ANOVA for conversion.

In Fig. 2a the thermal analysis results for the Hopeite catalysts are shown; in the TG and DT analysis two events were observed, both endothermic, first from room temperature to 120 °C, attributed humidity in the sample. A second event from 120 to 350 °C presents 9% weight loss ascribed to crystallization water desorption, which corresponds to 1.4 mol of water by formula. The TGA and DTA for the CZP can be observed in Fig. 2b, where two weight losses are presented, the first one with 4.5% due to humidity and the second one with

Table 4
Systems to obtain higher conversion

Catalyst	*T* (°C)	*t* (h)	Solvent	Conversion (%)
ZnCr Φy	60	18	*t*-Butanol	30.2
ZnCr Φy	40	18	*t*-Butanol	26.6
ZnCr Φy	60	24	*t*-Butanol	24.6
Hopeite	60	18	*t*-Butanol	22.9
CZP	60	24	*t*-Butanol	20.5
CZP	60	12	*t*-Butanol	20.4
ZnCr Φy	40	24	*t*-Butanol	20.4
Hopeite	60	24	*t*-Butanol	19.7
ZnCr Φy	40	12	*t*-Butanol	19.7

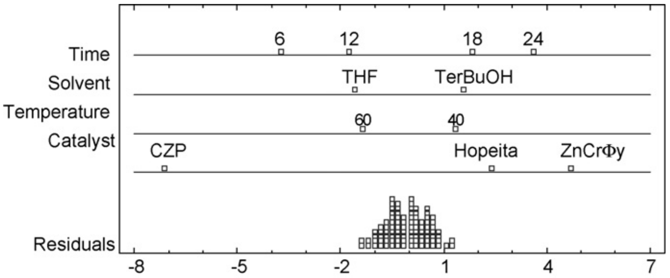

Fig. 5. ANOVA graphic for 1,2-epoxi-limonene selectivity.

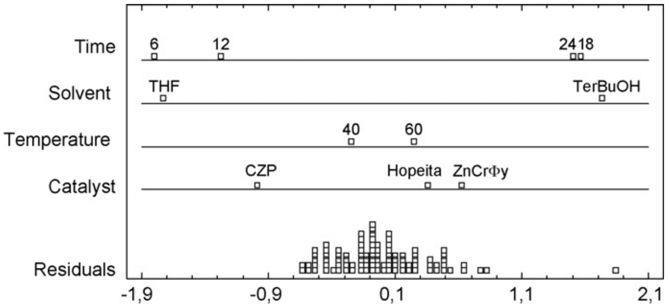

Fig. 6. ANOVA graphic for carveol selectivity.

8.2% due to the crystallization water, according to chemical formula. Finally, for the ZnCr Φy the TGA and DTA curves (Fig. 2c) there is a first weight loss that is explained like the desorption of 3/2 mol of NH_4OH by formula and a second event attributed to the catalyst thermal decomposition.

In Fig. 3a–c, SEM pictures shows that the catalysts size are between 5 and 10 μm, with homogeneous particle size and without crystalline or amorphous impurities; Hopeite assumes an orthorhombic habit, while the CZP and the ZnCr Φy are shown as small particle agglomerates that give place to different shapes.

Table 5
Systems to obtain higher 1,2-epoxi-limonene selectivity

Catalyst	*T* (°C)	*t* (h)	Solvent	Selectivity
ZnCr Φy	60	18	*t*-Butanol	18.0
CZP	60	24	*t*-Butanol	24.0
ZnCr Φy	40	18	*t*-Butanol	18.2
ZnCr Φy	60	24	*t*-Butanol	18.3
ZnCr Φy	40	24	*t*-Butanol	21.3
ZnCr Φy	40	12	*t*-Butanol	20.6
ZnCr Φy	40	12	THF	23.5

Table 6
Systems to obtain higher carveol selectivity

Catalyst	*T* (°C)	*t* (h)	Solvent	Selectivity
ZnCr Φy	60	18	*t*-Butanol	13.9
ZnCr Φy	60	24	*t*-Butanol	11.1
ZnCr Φy	40	18	*t*-Butanol	8.5
CZP	60	24	THF	8.2
CZP	60	24	*t*-Butanol	10.4
ZnCr Φy	40	24	*t*-Butanol	10.4

Table 7
Systems to obtain higher carvone selectivity

Catalyst	*T* (°C)	*t* (h)	Solvent	Selectivity
ZnCr Φy	60	18	*t*-Butanol	18.8
ZnCr Φy	40	18	*t*-Butanol	20.8
ZnCr Φy	60	24	*t*-Butanol	18.9
ZnCr Φy	40	12	*t*-Butanol	22.8
ZnCr Φy	40	24	*t*-Butanol	21.2

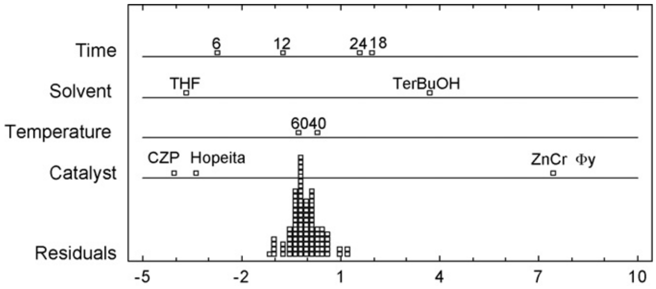

Fig. 7. ANOVA graphic for carvone selectivity.

3.2. Catalytic test

The main oxidation products from experimental studied systems, according to chromatographic analysis were 1,2-epoxi-limonene, carvone, carveol and limonene-1,2-diol. The higher conversions were obtained always at 18 and 24 h, using as catalyst the ZnCr Φy, and *t*-butanol as solvent; these results are shown on the ANOVA graph for conversion, Fig. 4, given by statistical analysis. The ZnCr Φy and the Hopeite, reached maximum conversion at 18 h, while the CZP was at 24 h. In Table 4 the systems with highest conversions obtained are shown.

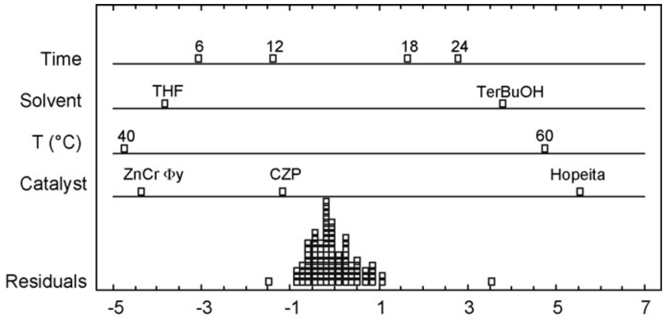

Fig. 8. ANOVA graphic limonene-1,2-diol selectivity.

Table 8
Systems to obtain higher limonene-1,2-diol selectivity

Catalyst	*T* (°C)	*t* (h)	Solvent	Selectivity
Hopeita	60	18	*t*-Butanol	24.2
CZP	60	24	THF	21.1
Hopeita	60	24	*t*-Butanol	27.6
CZP	60	12	*t*-Butanol	15.2

Table 9
Previous reports for catalytic activity

Catalyst	*T* (°C)	*t* (h)	Solvent	Conversion (%)	Selectivity to epoxide (%)[a]
Ti-MCM-41	70	8	Acetonitrile	50	60 [23]
MPA/C	60	7	Acetonitrile	6.9	24 [23]
MPA/Al	60	7	Acetonitrile	10.7	37 [24]
TPA/C	60	7	Acetonitrile	4	33.9 [24]
TPA/Al	60	7	Acetonitrile	10.5	54.9 [24]
PW11/c	60	7	Acetonitrile	11.8	71.6 [24]
PW-Amberlita	38	24	CH_3-CN	84	85 [25]

[a] Between brackets is the reference.

Although that highest selectivities towards the 1,2-epoxi-limonene and carveol were reached with THF as solvent, (26.7 at 40 °C and 24 h and 13.9% at 40 °C and 6 h, respectively) its conversion is low. Generally, the production of epoxide is favored at 40 °C, with reaction times of 18 and 24 h when ZnCr Φy and CZP were used; while Hopeite presented a very low selectivity towards this product. Carveol is favored at 18 and 24 h with Hopeite and ZnCr Φy, getting the higher selectivity at 40 °C, but yield was higher at 60 °C, on the contrary, the CZP catalyst is less selective towards this product. In Figs. 5 and 6, ANOVA graphs are shown for the 1,2-epoxi-limonene and carveol products, and Tables 5 and 6 show the systems that reached the highest selectivities.

The catalyst that showed important selectivities and conversion towards carvone was the ZnCr Φy, when *t*-butanol was used as solvent and the reaction was carried out at 18 and 24 h. In Table 7 the best selectivity results are shown; these observations are derived by the ANOVA graph in Fig. 7.

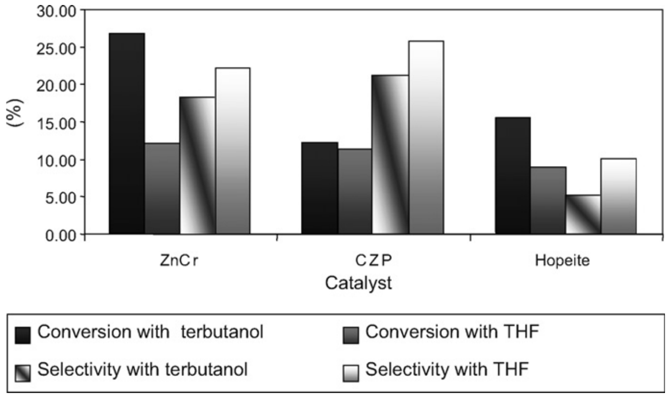

Fig. 9. Production of 1,2-epoxi-limonene at 40 °C and 18 h.

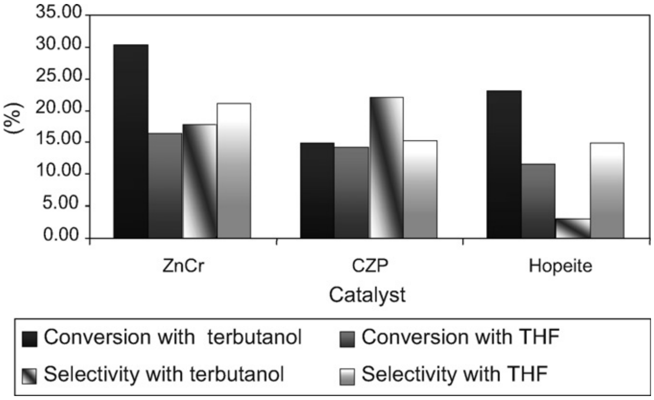

Fig. 10. Production of 1,2-epoxi-limonene at 60 °C and 18 h.

At 60 °C, using Hopeite and CZP as catalyst, and *t*-butanol as solvent, limonene-1,2-diol production was favored, which is a 1,2-epoxi-limonene hydrolysis product [22]. In Table 8, the best systems for obtaining this product are shown and in Fig. 8 the ANOVA graph is shown. This product has acquired great importance during the last years for its potential as catalyst for asymmetrical hydrolysis of epoxides [22]. Fig. 9 shows the conversion and selectivity for the main product, 1,2-epoxi-limonene at 40 °C and 18 h, while in Fig. 10 shows at 60 °C and 18 h.

In Table 9 systems previously reported for heterogeneous catalyst in which H_2O_2 was used as oxidant agent for conversion of limonene and the selectivity to 1,2-epoxi-limonene are shown. Even though some conversion and selectivity results presented in Table 9 are higher than ones obtained in this work, it is remarkable that the experimental conditions under environmental considerations were chosen; both the nature of solvents and oxidant agent used, as the small quantity of them in the reaction, make this process less dangerous for the environment.

4. Conclusions

The CZP, Hopeite, and ZnCr Φy catalysts were successfully synthesized by the hydrothermal method and correspond to previously reported phases, they present a good crystallinity without evidence of impurities.

The main oxidation products were: 1,2-epoxi-limonene, carvone, carveol and limonene-1,2-diol. The catalyst that presented the best behavior was the ZnCr Φy, which reached approximately 30% of conversion and 23% of selectivity towards 1,2-epoxi-limonene. The conditions of this reaction for the highest conversion were gotten using *t*-butanol like solvent, time and temperature of 18 h and 60 °C, respectively, while at 40 °C the best selectivities were obtained.

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