



Conversion of limonene to limonene diol over activated carbon supported Ti catalyst

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Abstract

A series of activated carbon supported Ti-3,3'-ethylen bis(3,4-dihydro-2H-1,3-benzoxazine) complex catalysts (denoted Ti-Bz (0.25)/AC, Ti-Bz(0.37)/AC, and Ti-Bz (0.5)/AC) was evaluated in the conversion of limonene to limonene diol using H₂O₂ as oxidant. The opening of oxazine ring as a step to the titanium complex formation was highlighted, as far as we are aware, for the first time, by NMR analysis. A range of characterization methods, including SEM-EDS, nitrogen physisorption, ATR-FTIR, and XRD, showed that the procedure used in the preparation of these materials was reproducible. Parameters affecting the catalytic performances in the production of limonene diol, such as reaction temperature, amount of catalyst tested, and its catalytic stability, were studied. Ti-Bz (0.5)/AC was the most performant catalyst leading to limonene diol yield of 36.7%. The recyclability of the catalyst was evaluated along three catalytic consecutive tests that showed no significant difference of performance compared with that of fresh catalyst.

Keywords Limonene · Epoxidation · Biomass · Titanium catalyst

1 Introduction

Limonene is one of the most common monoterpenes with a wide application in creating high-quality chemicals. This is due to both the high reactivity of its two double bonds in the 1,2 and 8,9 positions which can be oxidized to its corresponding oxides and to its extraction in enormous amounts derived from waste of the orange juice industry, such as orange peels

[1, 2]. Oxidation of limonene (encompassing epoxidation) over metal-based catalysts with hydrogen peroxide or t-Butyl hydroperoxide or molecular oxygen [3] is one of the primary methods of converting it into useful compounds [4–9]. However, many side-reaction products such as 1,2-epoxylimonene diol, carveol, 8,9-epoxylimonene diol, carvone, and diepoxide can be obtained together with limonene 1,2-epoxide, which renders this process complex [10].

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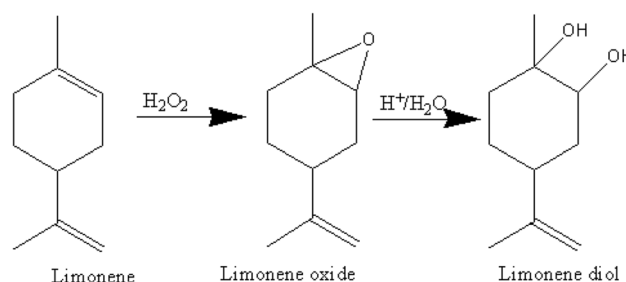
Considering that catalytic activity of vanadium-based catalyst in oxidation reaction is due to its change in oxidation state during reaction, Vaschetti et al. prepared V-MCM-41 by template-ion exchange with various loadings of V and tested them in the limonene oxidation with hydrogen peroxide at 70 °C for 7 h [11]. An increasing vanadium content up to 1 wt.% was accompanied by an increase in conversion of limonene till 13.5%. However, the stability of V-based catalyst was low and an impregnation on the surface of V-MCM-41 with titanium led to the mitigation of this drawback [11]. Besides the temperature, the polarity of solvent is another parameter that influences also significantly the catalytic performances in the process of oxidation limonene, with Ti-SBA-16 catalysts showing a higher catalytic activity in acetonitrile than in ethyl acetate [12].

Recently, Młodzi et al. reported the limonene oxidation to 1,2-epoxylimonene diol over activated carbon supported Fe using both hydrogen peroxide and tert-Butyl hydroperoxide as oxygen donor. The production of limonene diol is only noticed in the presence of hydrogen peroxide [13].

The increase in selectivity of epoxidation products using H_2O_2 as oxidant has also been highlighted by Vaschetti et al. in the limonene oxidation over Cu-MCM-41 catalyst [14]. On the other hand, an increase in the amount of copper incorporated into the siliceous structure or the use of t-Butyl hydroperoxide favored the formation of allylic products [14]. The production of allylic products using t-Butyl hydroperoxide was also reported by Li et al. in the allylic oxidation of limonene to carvone over cobalt-based zeolitic imidazolate framework [4]. From these works, the conversion of limonene to epoxidation products using H_2O_2 over catalysts with low transition metal content seems more indicated.

A high selectivity in 1,2-epoxylimonene diol till 74 mol% was also highlighted by Wróblewska et al. using hydrogen peroxide to oxidize limonene over Fe/nanoporous carbon [15]. The metal catalysts assisted by activated carbon have undergone testing in a wide range of catalytic process such as reduction [16], hydrodeoxygenation [17], hydrogenolysis [18], transesterification [19], and oxidation [20, 21]. However, there are only few studies about the oxidation of limonene over such catalysts [22].

In light of the above considerations, in this study, we prepared, for the first time to the extent of our knowledge, activated carbon supported Ti-3,3'-ethylen bis(3,4-dihydro-2H-1,3-benzoxazine) complex and evaluated their catalytic performances, at different amount of loaded complex, in the liquid phase oxidation of limonene to limonene diol (Scheme 1) using a green oxidant such as H_2O_2 . On the other hand, the presence of nitrogen in the structure of the catalyst can increase the nearby carbon atoms' chemical reactivity leading to the formation the reactive oxygen species in the oxidation process [23]. The characterization by XRD, N_2 adsorption-desorption at $-196\text{ }^\circ\text{C}$,



Scheme 1 Oxidation of limonene to limonene diol

SEM-EDS, and FTIR of these catalysts in order to correlate their properties with their performance in production of limonene diol was another aim of this study.

2 Methods

2.1 Raw material and chemicals

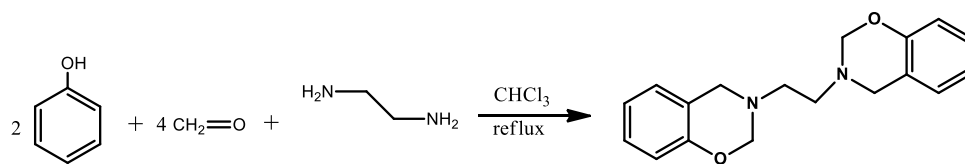
Waste coffee grounds (precursors to activated carbon) were obtained from the cafeteria of National University of Science and Technology Politehnica Bucharest. Phenol (Sigma-Aldrich), paraformaldehyde (Sigma-Aldrich), ethylenediamine (Sigma-Aldrich), ZnCl_2 , HCl 35% (Merck), AgNO_3 (Merck), dimethylformamide (Sigma-Aldrich), and hexane (Sigma-Aldrich) were used as purchased.

2.2 Catalysts preparation

2.2.1 3'-ethylen bis(3,4-dihydro-2H-1,3-benzoxazine) synthesis

The 1,2-bis(3,4-dihydro-2H-1,3-benzoxazin-3-yl) ethane monomer was prepared by Mannich condensation reaction from phenol, paraformaldehyde, and ethylenediamine; 10 g (0.106 mol) of phenol and 6.77 g (0.213 mol) of paraformaldehyde were dissolved in chloroform. After the dissolution was completed, 3.54 mL (0.053 mol) of ethylenediamine was added. The solution was then subjected to moderate stirring under reflux at 70 °C for 12 h to achieve the reaction as shown in Fig. 1.

After 12 h of stirring, the obtained solution was brought to room temperature and repeatedly cleaned with sodium hydroxide 1 M and distilled water in order to remove the unreacted reactants. The organic phase was separated and dried with MgSO_4 ; next, using vacuum conditions, the solvent evaporated. The structure of benzoxazine (Fig. 1) was highlighted by NMR technique (Figs. S1, S2).

Fig. 1 Synthesis of the benzoxazine monomer

2.2.2 Ti-3,3'-ethylen bis(3,4-dihydro-2H-1,3-benzoxazine) complex synthesis

A solution of 3,3'-ethylen bis(3,4-dihydro-2H-1,3-benzoxazine) (1 g) in 20 mL chloroform under stirring was added dropwise at various weight ratios of TiCl_4 beforehand dissolved in 20 mL chloroform in order to obtain metal/complexing agent molar ratios of 0.25, 0.37, and 0.5. Under reflux, the blend was heated to 60 °C for 6 h. The shift in hue from light yellow to orange when adding of TiCl_4 solution could be due to the desired complex formation [24]. The opening of oxazine ring after TiCl_4 addition was also highlighted, for first time to the best of our knowledge, by NMR analysis (Figs. S3, S4, S5). After cooling, chloride ions were removed by several washings with water and their absence was checked with AgNO_3 solution, then the organic phase was evaporated at room temperature. The complexes obtained were labeled as Ti-Bz (0.25), Ti-Bz (0.37), and Ti-Bz (0.5).

2.2.3 Activated carbon (AC) synthesis

Firstly, a particular amount of ZnCl_2 dissolved in 30 mL of distilled water was combined with 3 g of ground coffee that had been dried to create a 1:1 ratio of parched coffee to ZnCl_2 . Before being carbonized in a horizontal oven with a nitrogen flow (20 mL/min) and a rate of warmth of 10 °C / min up to 1000 °C and a keeping time of 120 min, the resulting slurry was uniformized, heated to 60 °C for an hour, and then dried at 120 °C for an additional night. The carbon obtained was treated with HCl 10% at 110 °C for 4 h under stirring and then washed with deionized water in order to

remove the zinc chloride. Finally, the acid functional groups on the surface of carbon (Figure S6) were obtained via its treatment with 65% HNO_3 at 50 °C for 6 h.

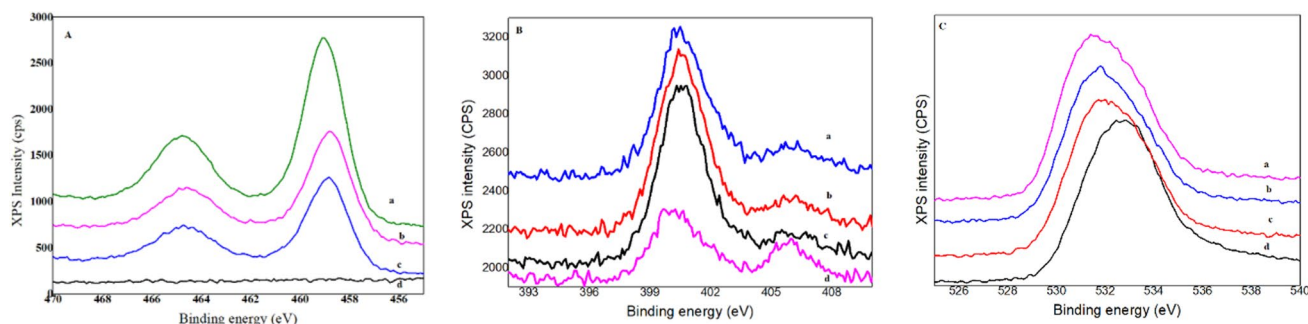
2.2.4 Preparation of activated carbon supported Ti-3,3'-ethylen bis(3,4-dihydro-2H-1,3-benzoxazine) complex

The anchoring of Ti-complex on the surface of activated carbon was carried out in dimethylformamide at 80 °C under stirring for 3 days at a Ti-benzoxazine complex/activated carbon mass ratio of 1:1. The materials (Ti-Bz (0.25)/AC, Ti-Bz (0.37)/AC, and Ti-Bz (0.5)/AC) obtained were washed with hexane, and the presence of Ti on the surface of activated carbon was highlighted both by SEM-EDS (Figure S7) and XPS analysis (Fig. 2).

2.3 Characterization techniques

The nuclear magnetic resonance (NMR) spectra of the obtained samples were performed on a Bruker Avance III HD 600 MHz spectrometer (Bruker, Rheinstetten, Germany). The samples were dissolved using CDCl_3 as a solvent, and the spectra were registered and processed with TopSpin 3.5.pl6 spectrometer software. The chemical shifts were referenced to CDCl_3 .

The structural characterization was performed with a Bruker D8 Advance diffractometer equipped with a Linxeye XE-T detector. K_{α} line of Cu (0.15418 nm) was used with the cathode operated at 30 mA and 40 kV. The acquisition procedure was recorded in the 5–80° (2 theta) range, with a

**Fig. 2** XPS spectra of the Ti (2p) (A), N (1 s) (B), and O (1 s) (C) level for (a) Ti-Bz(0.5)/AC, (b) Ti-Bz(0.37)/AC, (c) Ti-Bz(0.25)/AC, and (d) AC

0.015° as increment step, and 0.15 s integration time. The data was examined using EVA software (Bruker).

The structural study of the samples was carried out using FTIR spectroscopy. The measurements were assessed on a Vertex 70 Bruker FTIR spectrometer (USA), equipped with an attenuated total reflectance (ATR) accessory. The spectra of each sample were collected using ATR-FTIR mode, at room temperature with 32 scans and a resolution of 4 cm⁻¹ in domain from 600–4000 cm⁻¹.

The presence and dispersion of titanium on the surface of activated carbon highlighted by SEM–EDS measurements were performed using Thermo Scientific™ Apreo SEM equipped with an Octane Elite Super Silicon Drift Detector (SDD) and TEAM™ EDS Analysis System.

Using an adsorption analyzer from Micromeritics ASAP 2020 Plus, N₂ physisorption was carried out at –196 °C. Prior to measurement, the 0.4-g samples were vacuum-degassed and held at 150 °C for a full day. Using the BET method, the specific surface area (SBET) was calculated in the relative pressure range of 0.05 to 0.20. The t-plot method was also utilized to determine the micropore volumes (V_{μp}) and the exterior surface area (S_{ext}).

A Surface Science Instruments (USA) SSX 100/206 spectrometer fitted with a monochromatized and microfocused Al X-ray source (powered at 20 mA and 10 kV) was utilized for X-ray photoelectron spectroscopy (XPS) studies. Approximately 10⁻⁶ Pa was the pressure in the analysis compartment. Around 1.4 mm² was the zone under analysis, and the pass energy was set at 150 eV for the overall spectra and 30 eV for the elementary spectra. The charge was stabilized using an electron cannon set to 8 eV and a nickel grid positioned 3 mm above the samples' surface. All of the binding energies were calculated using the surface adventitious carbon peak, C 1 s, at 284.8 eV, as a reference. When necessary, spectra were broken down using the CasaXPS software (Casa Software Ltd., UK) by subtracting a non-linear Shirley baseline and then applying 85/15 Gaussian/Lorentzian product functions.

2.4 Limonene oxidation

The oxidation reaction with 30% H₂O₂ over the activated carbon supported Ti-3,3'-ethylen bis(3,4-dihydro-2H-1,3-benzoxazine complex catalysts was performed under stirring into an oil-bath-immersed glass reactor with a reflux condenser attached, using 3 mL of acetonitrile as solvent. Typically, 0.6 mL of limonene, 0.6 mL of 30% H₂O₂, and from 0.03 to 0.06 g of catalyst were charged into the glass reactor and heated at 50 or 70 °C for 4 or 6 h. The products of the reaction were examined by GC–MS (Agilent 7890 A GC–MS/ MS TRIPLE QUAD, equipped with a DB-FFAP column (30 m × 0.32 mm ID × 0.25 μm film thickness, Agilent, Santa Clara, USA). At a flow rate of 1 mL/min,

helium was utilized as the carrier gas. The temperature of the injector was 250 °C, and the oven temperature was set as follows: 50 °C for 2 min, and then 4 °C/min to 230 °C. The peaks were highlighted with the NIST MS database, and their quantification calibration curves obtained using standard solutions were used. The experimental procedure for testing the recyclability of the catalysts was performed for three catalytic cycles as follows: after the first run, the catalyst, recovered by centrifugation, was examined using identical circumstances in the next reaction.

The catalytic activity of titanium-benzoxazine complex (Ti-Bz(0.5)) on the conversion of limonene to limonene diol was evaluated as follows: the mixture of 0.02 g Ti-Bz(0.5) in 0.6 mL of limonene and 0.6 mL of 30% H₂O₂ in 3 mL acetonitrile was charged into the glass reactor and heated at 70 °C for 6 h.

The following equations were used to determine the yields and conversion:

$$\text{Conversion (\%)} = \frac{\text{amount of limonene consumed}}{\text{amount of limonene introduced}} \times 100 \quad (1)$$

$$\text{Product yield (\%)} = S \times C \quad (2)$$

S selectivity

C conversion

3 Results and discussion

3.1 Catalyst characterization

Table 1 shows the textural characteristics of the tested catalysts. The anchoring of Ti-Bz complex on the surface of activated carbon led to a reduction in the specific surface area. An increase in titanium/benzoxazine molar ratio only led to minor difference of textural properties from one catalyst to another (Table 1).

The functionalization of carbon surface with -COOH group due to its treatment with 65% HNO₃ solution was

Table 1 The examined catalysts' textural properties

Catalyst	Specific surface area (m ² /g)	Pore size (nm)
AC	1192	1.9
Ti-Bz(0.25)/AC	621	1.8
Ti-Bz(0.37)/AC	636	1.8
Ti-Bz(0.5)/AC	655	1.8

highlighted by the band at 1736 cm^{-1} . The bands at 1093 and 1382 cm^{-1} could be associated with the C–O–Ti and Ti–O stretching vibrations [25, 26] as a result of the anchoring of titanium-benzoxazine complex on the surface of activated carbon while that at 2927 cm^{-1} is characteristic for vibrations of CH_2 of the oxazine ring [27]. Moreover, the C–N stretching vibration and Ti–N stretching vibrations at 1441 cm^{-1} [28] and 1045 cm^{-1} , respectively [29], present for both the titanium complex and activated carbon supported titanium complex may indicate that titanium was anchored on the surface of carbon as a complex. The band at 750 cm^{-1} attributed to ortho di-substituted aromatic ring [30] gives evidence of benzoxazine stability even after its complexation with titanium. Regarding the bands around 900 and 1200 cm^{-1} in the FTIR spectrum of Ti-3,3'-ethylen bis(3,4-dihydro-2H-1,3-benzoxazine) complex assigned to the stretching vibration of C–O of oxazine ring and C–O–C symmetric stretching, respectively [31], these could be buried in the spectrum of Ti-Bz/AC taking into account that the band from 750 cm^{-1} , the most intense band of Ti-Bz complex spectrum, is very small in the spectrum of Ti-Bz/AC (Figure S6).

The both activated carbon supported and unsupported Ti-Bz complex samples' structures are amorphous and the two reflexions at 23.8 and 43.3° correspond, in accord with the literature, to 002 and 010 planes of the disorganized graphitic carbon [32]. The most intense peak at 23.8° is assigned to the carbon interlayer-stacking arrangement while the reflexion at 43.3° corresponds to the hexagonal carbon structure [33]. It is also worth noting that the diffraction lines corresponding to the titanium complex (Fig. S8) are not observed which supposes a high dispersion of titanium over carbon surface [34].

The Ti 2p XPS spectrum showed only one component at 458.8 eV assigned to Ti^{4+} [35]. For O 1s spectra (Fig. 2c), the component at binding energy (532.4 eV) [36] is attributed to hydroxyl group C–OH present on the surface of the carbon. The formation of Ti–O–C bond as for the activated carbon supported Ti-Bz complex led to a shift of the peak from 533 eV (for activated carbon unsupported) to lower binding energy [37].

The N 1s spectra show similar behavior as that of O 1s spectra. The peak at 399.8 eV assigned to nitrogen pyrrolic is shifted to higher binding energy which corresponds to C=N bond as due to the opening of oxazine ring occurring during the formation of the Ti-Bz complex [24]. All the more, no peak at around 402 eV , assigned to N–C=O [38], was highlighted in our XPS analysis.

3.2 Catalytic performances

The treatment of the activated carbon with the nitric acid led to an increase of its acidity due to the generation of lactonic,

carbonyl, and phenolic groups on the surface of the carbon [39]. Moreover, taking into account that 1,2-oxide of limonene can be hydrolyzed to 1,2-diol of limonene over acid sites [4], an increase in limonene diol yield, from 11.7 to 36.7%, was noticed (Fig. 3), in agreement with the amount of titanium supported on the carbon surface. Conversely, though, the catalytic activity of non-supported titanium-benzoxazine complex (Ti-Bz(0.5)) was much lower than the one supported as highlighted by a limonene diol yield of 8%, which suggests the necessity of the anchoring of the complex on the surface of activated carbon. Using a microporous catalyst such as titanium silicalite TS-2 in the oxidation of limonene in methanol with H_2O_2 , Wróblewska et al. [40] reported, compared with our study, a higher conversion of limonene of 70% but with a low selectivity of limonene diol of only 6% due to the small size (about 0.5 nm) of these microporous materials (TS-2) which supposes a hindering of the limonene access to the active sites located in the inside of the catalyst pores [41].

Wróblewska et al. [10] showed the impact of temperature during reaction in the conversion of limonene to limonene diol, the highest limonene conversion of 12% being obtained at 120°C for 3 h. On the other hand, in our study, we noticed an increase both in limonene conversion from 18 to 44.6% and yield in limonene diol from 6.3 to 36.7% by an increase in reaction temperature from 50 to 70°C (Fig. 4). Moreover, an increase in reaction temperature led to a decrease in 1,2-epoxylimonene yield followed by an increase in limonene diol as it results from hydration of 1,2-epoxylimonene to diol (Fig. 4).

Besides the reaction temperature and amount of activated carbon supported titanium complex, the catalytic performances were also by being affected by the catalyst quantity that was evaluated when limonene was converted. Indeed,

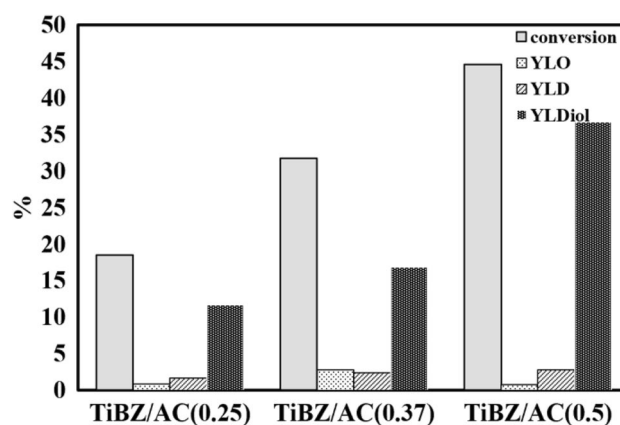


Fig. 3 The conversion of limonene to limonene-1,2-diol (0.6 mL limonene, 0.6 mL of 30% H_2O_2 , 0.06 g catalyst, 70°C , 6 h; YLO, yield in limonene oxide; YLD, yield in limonene dioxide; YLDi, yield in limonene diol)

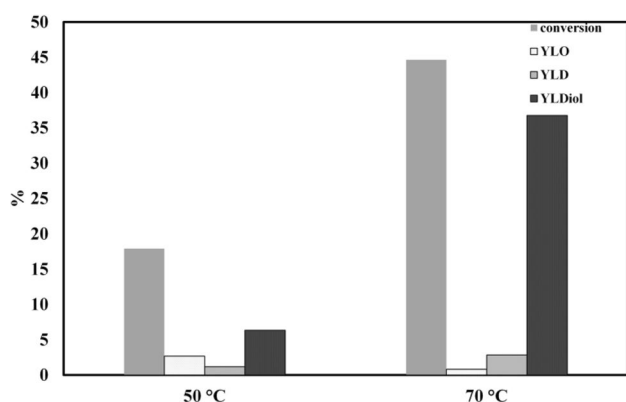


Fig. 4 The conversion of limonene to limonene-1,2-diol (0.6 mL limonene, 0.6 mL of 30% H_2O_2 , 0.06 g TiBz/AC(0.5), 6 h; YLO, yield in limonene oxide; YLD, yield in limonene dioxide; YLDiol, yield in limonene diol)

an increase of the catalyst amount from 0.03 to 0.06 g was accompanied by an improvement of catalytic performances (Fig. 5). The efficiency of Ti-based catalyst such as silica supported titanium in the production of limonene diol was also highlighted by Palumbo et al. [42]. Similar yields in limonene diol were reported by Resul et al. [43] in the oxidation of limonene with H_2O_2 using tungsten-based polyoxometalates as catalyst in a shorter reaction time (2 h). Moreover, the hydrolysis of the epoxide to diol depended on the presence and polarity of the solvent; using acetonitrile, an increase of limonene diol yield from 0 (without solvent) to 25% was noticed indeed. On the other hand, these results required the use of both soluble catalyst in the aqueous phase and H_2SO_4 in order to increase in limonene diol yield due to increase of the reaction medium acidity.

In aqueous media, it is well known that the activity of solid catalyst can decrease due to the strong hydration of their acid sites [44]. The low interaction between water

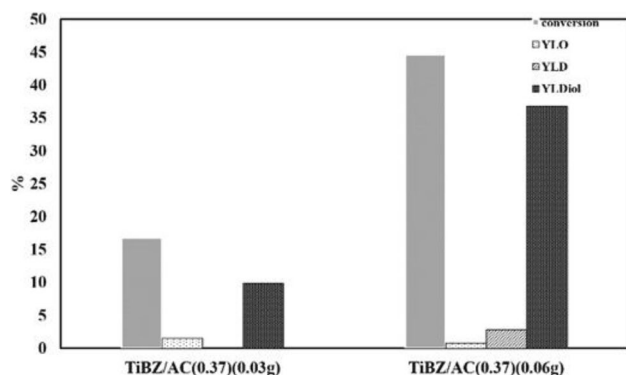


Fig. 5 The conversion of limonene to limonene-1,2-diol (0.6 mL limonene, 0.6 mL of 30% H_2O_2 , 6 h; YLO, yield in limonene oxide; YLD, yield in limonene dioxide; YLDiol, yield in limonene diol)

molecules and unsaturated Ti^{4+} sites (Lewis acid sites) [45] allowed the reusability of TiBz/AC (0.37) for three catalytic cycles without a notable reduction in catalytic activity in conversion of limonene to limonene diol (Fig. 6). Moreover, after three catalytic cycles, the presence of titanium on the surface of activated carbon highlighted by SEM-EDS analysis (Fig. 6) showed an excellent stability of the catalyst in the limonene oxidation process as well as a uniform distribution of Ti species on the surface of activated carbon. The stability of titanium-based catalyst in the oxidation of limonene with hydrogen peroxide was also reported by Wróblewska et al. [10].

4 Conclusions

This study showed the oxidation of limonene over activated carbon supported Ti-3,3'-ethylen bis(3,4-dihydro-2H-1,3-benzoxazine) complex to limonene diol. The formation of titanium complex was highlighted by NMR analysis while interaction of the complex with the oxygen of the surface groups was revealed by XPS analysis. The catalytic performances of the materials prepared were evaluated by varying some parameters such as reaction temperature and amount of catalyst tested, and the main oxidation product was limonene-1,2-diol. The catalyst with the best behavior was TiBz/AC (0.5) which reached at 70 °C for 6 h approximately 45% of conversion and 36.7% of yield in limonene diol while the catalytic activity of titanium-benzoxazine complex (Ti-Bz(0.5)) non-supported was very low reaching only 8% yield of limonene diol. Without losing its action, the catalyst may be recycled three times. The presence of

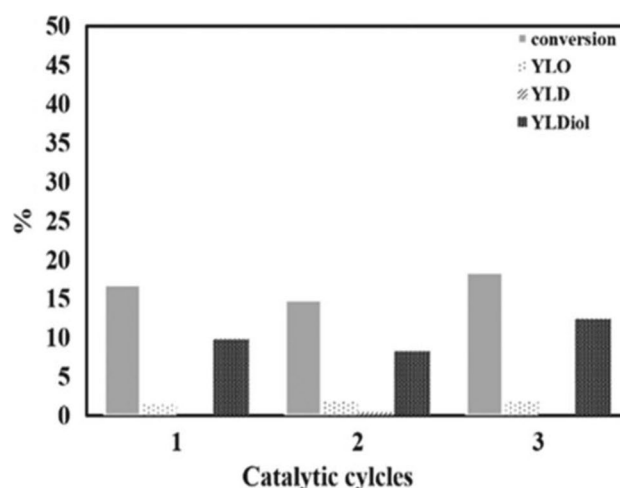


Fig. 6 The conversion of limonene to limonene-1,2-diol (0.6 mL limonene, 0.6 mL of 30% H_2O_2 , 0.03 g TiBz/AC (0.37), 6 h; YLO, yield in limonene oxide; YLD, yield in limonene dioxide; YLDiol, yield in limonene diol)

titanium as well as its uniform distribution on the surface of activated carbon after three catalytic cycles is highlighted by SEM–EDS analysis.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s13399-024-05966-8>.

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Author contribution Maria Minodora Marin: methodology, validation, writing—original draft; Iuliana Elena Biru: methodology, writing—original draft; Cristina Elena Stavarache: investigation, writing original draft; Sorin Marius Avramescu: writing—review and editing, resources; Gabriel Vasilievici: investigation; Adriana Marinoiu: investigation; Marius Dumitru: investigation; Francois Devred: investigation; Eric M. Gaigneaux: supervision, writing—review and editing; Marian Nicolae Verziu: conceptualization, supervision, writing—original draft, writing—review and editing.

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Declarations

Conflict of interest The authors declare no competing interests.

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