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ALLYLIC OXIDATION OF α-PINENE OVER SUPPORTED SeO$_2$-BASED CATALYSTS

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***Abstract*—SeO$_2$-based samples were tested for the oxidation of α-pinene and of benzil alcohol using ethanol as solvent. Commercial SeO$_2$ was tested both at reflux and at 6 atm. of O$_2$. At conversion level of approximately 40%, the yield of myrtenal was much higher in the latter case (34.4%) than under reflux (18.0%). A palladium-promoted selenium dioxide-supported catalyst (Pd/SeO$_2$/SiO$_2$) was prepared. Characterization results indicated that selenium dioxide (14.4%) strongly interacts with silica support. The introduction of palladium (0.98%) modifies the reducibility of SeO$_2$, originating a selenium species activation towards allylic oxidation. A conversion level of 23% is attained over Pd/SeO$_2$/SiO$_2$ after 15 h of reaction time, using ethanol as solvent at 134°C the main product being myrtenal, obtained with a selectivity of 76%. Pd/SeO$_2$/SiO$_2$ allows to carry out a catalytic allylic oxidation of α-pinene, being the catalyst easy to handle and being possible its recovery and reuse after the reaction in liquid phase.**

***Keywords*— myrtenal, myrtenol, palladium, selenium dioxide.**

I. INTRODUCTION

Following the Green Chemistry and Sustainability Principles (Sheldon, 2007), heterogeneous catalytic process should be conceived for replacing traditional methods based on stoichiometric reactions.

Oxidation reactions are ubiquitous in organic synthesis. In large number of cases, oxidation allows the production of valuable products in the fine chemical and pharmaceutical industries. Terpenes play important roles in the synthesis of a wide variety of drugs. Besides, terpenoids obtained from the oxidation of terpenes, show improved or new biological activities (Maimone and Baran, 2007; Nagegowda and Gupta, 2020; Yang *et al.*, 2020). α-Pinene is abundant in natural essential oils (Noma, 2010; Becerra, 2020) and its allylic oxidation introduces an oxygen atom in the C-H bond adjacent to the double bond, giving rise to several products (Fig. 1). Amongst these products, myrtenal presents pharmacological activity against diabetes, cancer, and malaria (Becerra, 2020; Ayyasamy and Leelavinothan, 2016; Babu *et al.*, 2012; Lin *et al.*, 2017; Burgueño-Tapia *et al.*, 2010). Myrtenol shows anti-inflammatory and antinociceptive effects (Becerra, 2020; Gomes *et al.*, 2017; Silva *et al.*, 2014).

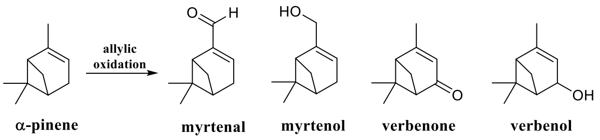

Figure 1: Main products from the allylic oxidation of α-pinene.

The oxidation of alcohols to carbonyl compounds is also an important organic transformation, which is of great interest not only for fundamental synthesis but also for the fine chemical industry (Sheldon *et al.*, 2000). In the case of the oxidation of benzyl alcohol, the products are benzaldehyde and benzoic acid. The former (bitter-almond odor) is the second most important aromatic molecule (after vanillin) in the cosmetics and flavors industries, pharmaceutical, dyestuff and agrochemicals. Benzoic acid its salts are used in the formulation of fragrance, pesticides, pH buffers, solvents, and in cosmetic products (del Olmo *et al.*, 2015; Jhonson *et al.*, 2017).

For the case of allylic oxidation of terpenes, the best know methodology is based on selenium dioxide (SeO$_2$), due to its relatively high regio- and chemoselectivity for the oxidation of the C-H bond in the α-position for the most substituted carbon of the double bond. Since the reactivity order is $CH_2 > CH_3 > CH$, myrtenal and myrtenol are mainly obtained, with higher selectivity to the alcohol than for the aldehyde (Nakamaura and Nakada, 2013; Bulman and McCarthy, 1991; Mlochowski and Wójtowicz-Mlochowska, 2015). SeO$_2$ is easy to handle with, however it presents many disadavantages: (**i**) stoichiometric relations or even high SeO$_2$/substrate ratios are needed to fulfill the reaction (Lempers and Sheldon, 1996; Tagawa, 2003); (**ii**) long reaction times are required (Tagawa, 2003); (**iii**) yields are not too high (Tagawa, 2003); (**iv**) reduced selenium in a colloidal form is produced in reaction conditions, (Mlochowski and Wójtowicz-Mlochowska, 2015; Lempers and Sheldon, 1996; Tagawa, 2003); (**v**) organoselenium compounds could be formed (Tagawa, 2003).

For the case of benzyl alcohol oxidation, traditional methodology employs toxic stoichiometric compounds, generally based on chromium (Menger and Lee, 1981; Griffith 1992; Muzart, 1992).

Many heterogeneous catalysts have been studied in the allylic oxidation of α-pinene (Rauchdi *et al.*, 2018; Kholdeeva *et al.*, 2014; Kuznetsova *et al.*, 2007). For the

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most of the cases, high selectivity to verbenone and verbenol were observed. Rauchdi *et al.* (2018) employed water stabilized Ru nanoparticle, with acceptable high yield of verbenone (39%), although a co-catalyst (tert-butyl hydroperoxide) was used. Kholdeeva *et al.* (2014) have performed α-pinene oxidation over Cr-MOF and Fe-MOF, also using tert-butyl hydroperoxide. In this case, conversion level was low (22%) following 16 h. The selectivity was low: a mixture of several oxidation products, mainly verbenone and verbenol were produced (Kholdeeva *et al.*, 2014). Platinum, palladium, ruthenium, rhodium, and iridium catalysts supported on activated carbon have also been considered for the oxidation of α-pinene. For all the cases, verbenone, verbenal, and the corresponding epoxide were the observed products (Kuznetsova *et al.*, 2007). Summing up, the above-mentioned catalysts are active for the allylic oxidation, leading mainly verbenone and verbenol amongst others products, while the allylic oxidation through the stoichiometric reaction over selenium dioxide produces only myrtenal and myrtenol. In this context, it should be interesting to test a heterogeneous catalyst based on supported selenium dioxide in order to produce myrtenal and myrtenol in the oxidation of α-pinene.

A large number of heterogeneous catalysts have been studied for the oxidation of benzyl alcohol, mainly based on transition metals (Zhan *et al.*, 2012). The general observed trend is that the catalyst became deactivated during the reaction, and in several cases an added base is needed to reach acceptable conversion levels.

The present study deals with the preparation and characterization of supported SeO_2 samples and their test in two reactions: the allylic oxidation of α-pinene and the oxidation of benzyl alcohol. To our knowledge heterogeneous selenium-based catalysts have not been tested for oxidation reactions. Considering the SeO_2 high efficiency for oxidation, it could be envisaged that a that supporting selenium could give rise to an active catalyst.

The catalytic tests are carried out under batch conditions, with O_2 as oxidant, under initiators or admixtures free conditions. The activity and selectivity to the different products are measured. The characterization is performed by Transmission Electronic Spectroscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), and Temperature-programmed Reduction (TPR).

II. METHODS

A. Catalyst Synthesis and Characterization

Selenium dioxide from Merck (98.0%) was employed for carrying out the reaction. This sample is named SeO_2.

Silica (silica gel 60, SiO_2, 70-230 mesh, from Davison) was employed as the support for the selenium dioxide catalyst (SeO_2/SiO_2). Selenium was fixed to silica from the wet impregnation method (Singh *et al.*, 1997). Approximately 0.3 g of SeO_2 was dissolved in 20 mL of absolute ethanol (99.5%, Cicarelli), at 40°C under magnetic stirring for 24 h. 2 g of silica was added to the selenium solution. The solvent was then evaporated at 40°C under magnetic stirring. Afterwards, the solid was calcined at 400°C for 1 hour. SeO_2 concentration was measured by Induced Coupled Plasma Spectroscopy (ICP) in a Shimadzu Simultaneous 9000 apparatus, following EPA standard 200.7.

A binary selenium dioxide/palladium supported o silica catalyst ($Pd/SeO_2/SiO_2$) was also prepared. Based on previous experiments, it has been stablished that the silica support employed in the present retains no more than 1wt% of palladium, thus a 1wt% noble metal concentration was selected as the target concentration. Approximately 0.2 g of $Pd(AcAc)_2$ (Aldrich, 99.9%) was dissolved in 5 mL of toluene, at room temperature. This solution was added to the SeO_2/SiO_2 catalyst (2g). Following 24 h of contact, the solid was filtered and calcined at 400°C during 1 hour. The target concentrations correspond to a Pd/SeO_2 ratio lower than 0.1. Noble metal loading was measured by Atomic Absorption Spectroscopy in an A-Analyst Perkin Elmer equipment.

The samples were analyzed by X-ray diffraction (XRD) with a PANalytical Empyrean 3 diffractometer using Ni-filtered CuKα radiation and a PIXcel 3D detector, operating at a voltage of 45 kV and a current of 40 mA, in the 2θ range from 10° to 80°, using a continuous scan mode with a scan angular speed of 0.02° min-1.

Fourier Transform Infrared Spectroscopy (FTIR) characterized the samples in a Nicolet Nexus apparatus. The spectra were obtained with a resolution of 2 cm^{-1} using 50 scans.

A Transmission Electronic Microscope (TEM) study was carried out for deterining Pd particle size. The equipement was a TEM JEOL microscope. The Digital Micrograph software was employed for measuring particle sizes. Palladium particle sizes were employing for determining palladium mole surface concentration following the relationship introduced by Aben (1968).

B. Liquid Phase Oxidation of α-Pinene and of Benzyl Alcohol.

For the case of α-pinene, the reaction test was carried out with the following conditions: (**i**) α-pinene (Riedel de Haden, 97%) in absolute ethanol (35 mL, 0.02M, 1 eq) with 2.5 eq of SeO_2; (**ii**) α-pinene in absolute ethanol (35 mL, 0.1M) employing 400mg of SeO_2/SiO_2, (**iii**) α-pinene in absolute ethanol (35 m L, 0.1M) employing 400 mg of $Pd/SeO_2/SiO_2$.

Two methodologies were followed: (**a**) the reaction was carried out in a round-bottomed flask, heated at reflux until the disappearance of the reactant. (**b**) the reaction mixture was placed in a 50 mL batch steel reactor, at 134°C, and at 6 atm. of oxygen. The stirring was set in 620 rpm .The stirring rate as well as the mass of the catalyst were previously varied in order to confirm the absence of external diffusion control for the selected parameters for carry out the catalytic test. For the case of benzyl alcohol oxidation, approximately 50 mg of the $Pd/SeO_2/SiO_2$ catalysts were tested in a 50 mL batch steel reactor, at 120°C, and at 6 atm. of oxygen, and with a 0.1M solution of benzyl alcohol in isopropanol. The stirring was set in 620 rpm.

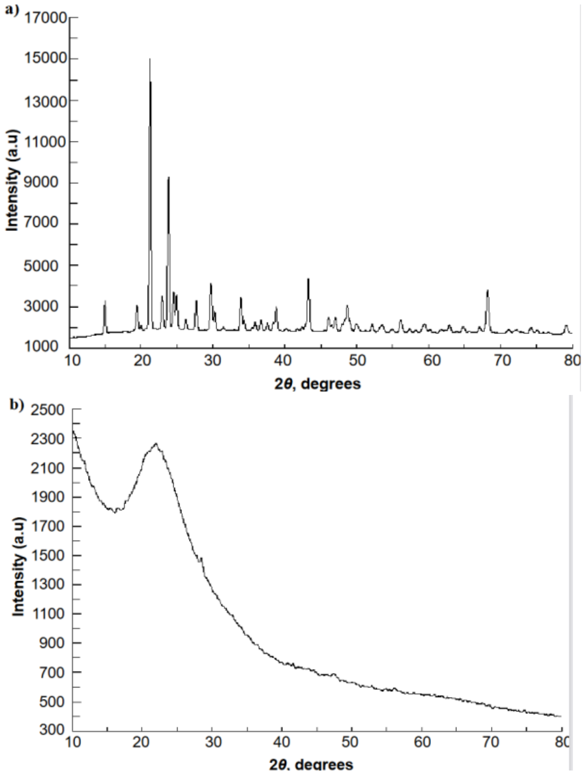

Figure 2: XRD patterns of: (**a**) SeO_2 and, (**b**) SeO_2/SiO_2.

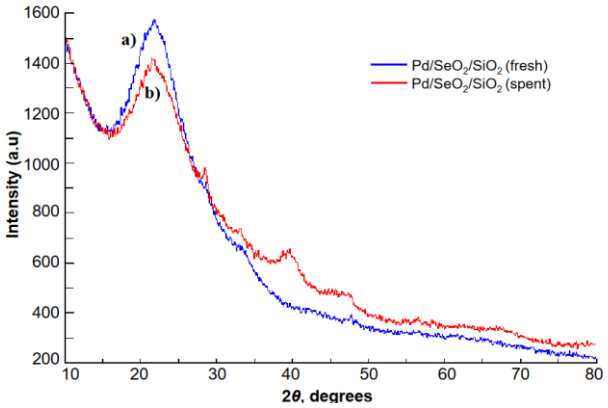

Figure 3: XRD pattern of: (**a**) fresh and, (**b**) spent $Pd/SeO_2/SiO_2$ catalysts.

The reaction products were identified using a GC/MS Perkin Elmer CLARUS 500 gas chromatograph coupled with a mass spectroscopy detector, provided with an Elite-5 MS column (60 m, 0.25 mm ID). The identification of chromatographic peaks was achieved according to the NIST MS library with global matches higher than 900. It was considered that the chromatographic detector response factors corresponding to the reactant α-pinene and allylic oxidation products are the same.

The specific activity of the $Pd/SeO_2/SiO_2$ catalyst, was calculated as the rate of moles of the reactant converted per second and per mole of Pd (s^{-1}) was measured.

III. RESULTS

A. Catalysts Preparation and Characterization

The target SeO_2 loading for both the SeO_2/SiO_2 and the $Pd/SeO_2/SiO_2$ catalysts was 15%. The selenium dioxide concentration was slightly lower than that theoretical concentration, being 14.6 and 14.4 wt% for SeO_2/SiO_2 and for $Pd/SeO_2/SiO_2$ respectively, as measured by ICP. The palladium loading in the $Pd/SeO_2/SiO_2$ sample is 0.98%, which is also quite similar to the nominal concentration (1 wt%).

In Figs. 2a and 2b, the XRD patterns corresponding to commercial SeO_2 sample and to the SeO_2/SiO_2 catalyst, respectively, are shown. Diffractions peak assigned to selenium dioxide and to selenious acid (JCPDS card Nº 00-041-0259 and JCPDS card Nº 00-022-1314 for H_2SeO_3 and SeO_2, respectively) are observed in the spectrum of the commercial sample. A wide peak, due to silica is observed (Khan *et al*., 2016) in the case of the /supported selenium dioxide sample. No peaks corresponding to selenium species were detected, probably due to the high dispersion that these species present on silica.

The as prepared and the used $Pd/SeO_2/SiO_2$ samples were both characterized by XRD. Figure 3 shows the corresponding patterns. For the fresh sample, the pattern is quite similar to the one of SeO_2/SiO_2, while the peaks due to palladium or palladium oxide are not detected. This is would be due to the low particle palladium size, under the detection limit of the technique. On the contrary, theXRD pattern corresponding to the used catalyst, following the catalytic test, shows the signals due to metallic palladium at 39.5 and 47.3 degrees of 2θ° and to palladium oxide (28.6 degrees of 2θ°). It is proposed that palladium crystals are originally highly dispersed in the fresh catalyst, while following the liquid phase oxidation, a sintering of the particles takes place, giving rise to larger palladium crystals assigned to XRD peaks.

FTIR results corresponding to SeO_2, SiO_2 and SeO_2/SiO_2 are shown in Figs. 4 a-c. SeO_2 (Fig. 4a) show the bands at 871 and 668 cm^{-1} due to Se-O stretching, while those at 1248 and 1150 cm^{-1} are due Se-OH (Falk and Siguére, 1958).

FTIR results corresponding to SiO_2 show many signals (Fig. 4b). Bands at 1193 and 1118 cm^{-1} are originated in Si-O stretching (Khan *et al*., 2016). Both of these bands are shifted and their relative intensity is modified in the FTIR spectrum of SeO_2/SiO_2. These modifications are originated in the high SeO_2-SiO_2 interaction. Furthermore, the bands at 894 and 671 cm^{-1} due to selenium dioxide species are observed in the case of the SeO_2/SiO_2 sample.

The FTIR analysis of the $Pd/SeO_2/SiO_2$ catalyst showed a similar result to the SeO_2/SiO_2 sample (Fig. 5). The spent catalyst, following the catalytic test, was also studied by FTIR, and no differences with the fresh sample are detected. It is worth noting that bands due to the C-H, C=O, or C-OH groups were not detected over the sample used, which would indicate that no irreversible adsorption of reactants, intermediates, or products occurs during the reaction. Such adsorption was observed over used catalysts employed for liquid phase reactions involving aldehyde, alcohols, and acids over metal supported catalysts, and it would be responsible for catalyst deactivation (Piqueras *et al*., 2016).

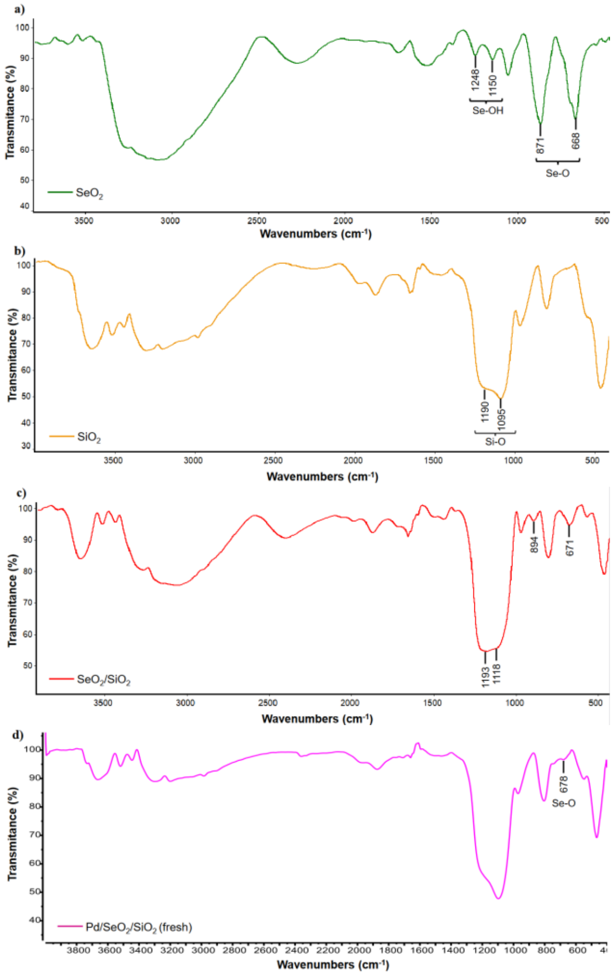

Figure 4: FTIR spectra of; (**a**) SeO_2, (**b**) SiO_2, (**c**) SeO_2/SiO_2 and, (d) fresh $Pd/SeO_2/SiO_2$

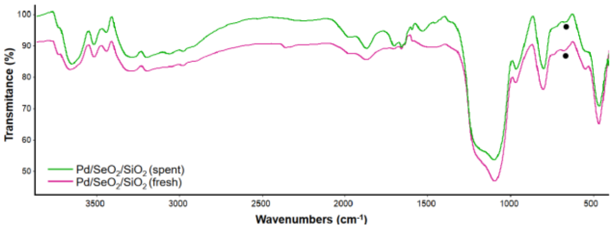

Figure 5: FTIR spectra of: (**a**) fresh and, (**b**) spent $Pd/SeO_2/SiO_2$.

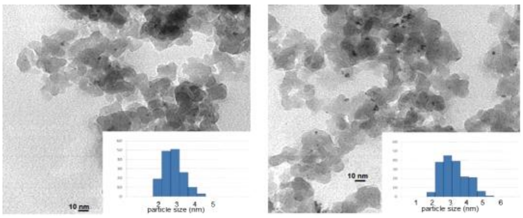

Figure 6: TEM images of; (**a**) fresh and, (**b**) spent $Pd/SeO_2/SiO_2$ catalysts.

TEM characterization was carried out over SeO_2/SiO_2 sample, but it was not possible to observe any difference between the silica support and the selenium species. Similar electronic densities of the both oxides would be the responsible for the low contrast between silica and selenium species.

Table 1. Allylic oxidation of α-pinene employing SeO_2 under reflux (methodology (**i**)).[a]

Entry	**Time (h)**	**X[b] (%)**	**Sol[c] (%)**	**Sal[d] (%)**
1	5	18	72	28
2	7	23	65	35
3	9	34	59	41
4	11	41	56	44
5	13	50	44	56

[a] 1 eq. of α-pinene, 2.5 eq. of SeO_2, 35 mL of ethanol
[b] Conversion of α-pinene. [c] Selectivity to myrtenol.
[d] Selectivity to myrtenal.

Table 2. Allylic oxidation of α-pinene employing SeO_2 (methodology (**ii**), batch reactor, at 6 atm O_2).[a]

Entry	**Time (h)**	**X[b] (%)**	**Sol[c] (%)**	**Sal[d] (%)**
1	2	5	58	42
2	3.5	21	29	71
3	5	41	16	84

[a] 1 eq. of α-pinene, 2.5 eq. of SeO_2, 35 mL of ethanol, 134°C. [b] Conversion of α-pinene. [c] Selectivity to myrtenol. [d] Selectvity to myrtenal.

Table 3. Allylic oxidation of α-pinene employing $Pd/SeO_2/SiO_2$ (methodology (**ii**), batch reactor, at 6 atm O_2).[a]

Entry	**Time (h)**	**X[b] (%)**	**Sol[c] (%)**	**Sal[d] (%)**
1	2	5	58	42
2	5	16	38	62
3	8	18	30	70
4	15	23	24	76

[a] α-pinene in ethanol (35 mL, 0.1M), 400 mg of $Pd/SeO_2/SiO_2$, 134°C. [b] Conversion of α-pinene. [c] Selectivity to myrtenol. [d] Selectvity to myrtenal.

A TEM study was also carried out for $Pd/SeO_2/SiO_2$, for both the fresh and the spent samples (Fig. 6). The mean size of the palladium particles in the fresh sample 2.9 nm, while the one of the used catalyst is 3.5 nm. Morphological modification developed under reaction conditions, leads to the increase in palladium particle size.

B. Catalytic Test

α-pinene allylic oxidation

The reaction using ethanol as the solvent, at reflux (78°C), yielded mainly myrtenol at short reaction times. The yield of the minor product, myrtenal , increases with time at expense of myrtenol, showing that the aldehyde is being formed from the oxidation of the alcohol. At 13 h the selectivity to myrtenal does not surpass 56%, yielding 28% (Table 1). This yield is lower than the one reported by Lin *et al.* (2017), who have performed the oxidation with 1,4-dioxane.

Besides, the oxidation of α-pinene was performed employing SeO_2 in batch conditions, under oxygen pressure (6 atm.), and at 78°C and at higher temperature than in the previous case (134°C). The catalytic pattern corresponding to the lower temperature was similar to the one observed when the reaction was carried out following the methodology (i). On the other hand, at 134°C , the level of conversion was 41% and it was attained at shorter times than for the reaction being carried out at reflux (5 h against 11 h). Myrtenal and myrtenol were the only products, being the the selectivity to the aldehyde quite high (84%) (Table 2).

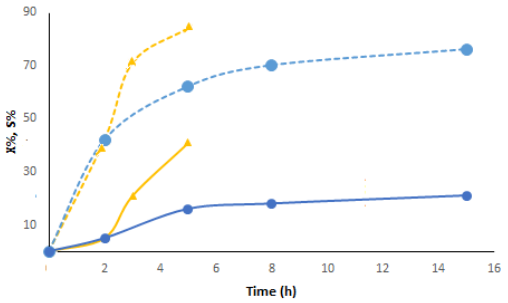

Figure 7: The allylic oxidation of α-pinene over: (●) Pd/SeO_2/SiO_2 and, (▲) SeO_2. Percentage of conversion (X%,—) and selectivity to myrtenal (S %, ----) following methodology (ii), 134°C and 6 atm of O_2.

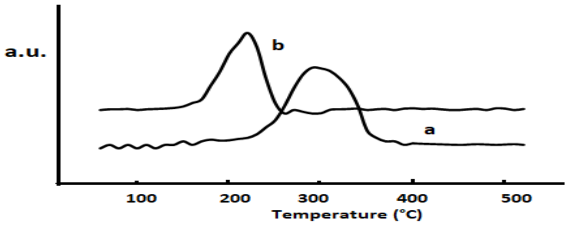

Figure 8: TPR profiles of: (**a**) SeO_2/SiO_2 and, (**b**) Pd/SeO_2/SiO_2.

At 5 h, the yield of myrtenal was higher when the reaction is carried out under oxygen pressure (34%) than at reflux (18%). If comparisons are carried out at equal conversion (21-23%), the yield of myrtenal is also higher for the reaction carried out under oxygen pressure (15%), than for the case performed at reflux (8%). The high yield of myrtenal reached would be due to both the higher reaction temperature and the improved oxygen concentration in the liquid phase.

The above commented results, for both methodologies, correspond to a stoichiometric process, SeO_2 being reduced during reaction. For increasing conversion, higher amount of SeO_2 should be employing, increasing notably the SeO_2/α-pinene ratio, which is a notable drawback.

For circumventing stoichiometric reactions, the employement of a supported heterogeneous catalyst was envisaged. Thus SeO_2 was fixed to SiO_2 originating the SeO_2/SiO_2 sample. No noticiable conversion was attained during the allylic oxidation of α-pinene, even for 18 h of reaction, at 134°C under oxygen pressure (6 atm). Probably, the active selenium species are diluted in an inert support, which results in an insufficient active phase amount.

Upon the fixation of Pd to the selenium dioxide/silica binary system was effective, since the Pd/SeO_2/SiO_2 catalyst is quite active (see Table 3 and 4). At 5 h, the conversion was 16%. The catalyst shows a relatively high selectivity to myrtenal (62%), being myrtenol the other product. It is worth to note that no other co-product was detected.

Table 4. Oxidation of benzyl alcohol employing Pd/SeO_2/SiO_2 (methodology (**ii**), batch reactor, at 6 atm O_2).[a]

Entry	Time (min)	X^b (%)	Sal^c (%)	Sac^d (%)
1	45	10	45	55
2	120	24	28	72
3	180	43	18	82

[a] benzyl alcohol in isopropanol (35 mL, 0.1M), 50 mg of Pd/SeO_2/SiO_2, 120°C. [b] Conversion of benzyl alcohol. [c] Selectivity to benzaldehyde. [d] Selectvity to benzoic acid.

In Fig. 7 the conversion and selectivity results for both Pd/SeO_2/SiO_2 and unsupported SeO_2 are shown. Although the former catalyst is less active than the pure SeO_2, it is interesting to note that the amount of selenium species is notably low in the Pd/SeO_2/SiO_2 catalyst. If the conversion is expressed in a selenium mole basis, the binary catalyst is much more active than the pure SeO_2 one. For explaiing this fact one could argue that palladium is promoting selenium oxide activity or that noble metal sites are also active for carry out the allylic oxidation,

The production of myrtenal over the Pd/SeO_2/SiO_2 catalyst is a another quite interesting result, since previous reports, corresponding to Pd (or any other noble metal) based catalysts, indicated that the main products are verbenone, verbenol, and verbenoic acid (Rauchdi *et al.*, 2018; Kholdeeva *et al.*, 2014; Kuznetsova, 2007). It seems that the allylic oxidation using Pd/SeO_2/SiO_2 is determined by selenium species, leading to the allylic oxidation in α-position for the most substituted carbon of the double bond and that palladium plays a promotional role on SeO_2. Still another interpretation of the selectivity results over the binary palladium /selenium oxide catalysis could be postulated: SeO_2 could promote a change in the Pd regioselectivity if Pd is the active site. In any case, the binary catalyst present active site for the allylic oxidation of the terpene, leading to a relative high production of myrtenal.

The reducibility of the catalysts was analyzed by a TPR study (Figs. 8 a-b). Based on the fact that the allyic oxidation is a redox reaction, it is considered that in TPR results can throw some light in the redox properties of the palladium/selenium oxide binary catalyst A change in the reduction pattern of supported SeO_2 upon the noble metal introduction can be observed. In the TPR profile of SeO_2/SiO_2 (Fig. 8a) a peak with a maximum at 290°C is detected, which would be due to the reduction of selenium dioxide. In the binary Pd/SeO_2/SiO_2 catalyst this peak appears at a lower temperature, 270°C (Fig. 8b). In this sense, it is proposed that the palladium promotional effect on SeO_2 is originated from a high interaction between both species. Such an interaction would give rise to active sites for the production of myrtenal.

Finally, a comment on the reuse of the Pd/SeO_2/SiO_2 should be carried out. The spent catalyst, following the reaction, was withdrawn from the reactor, washed with fresh solvent, dried under air at 70°C, and a new catalytic test was performed. The activity of the catalyst was almost the same following 8 h of reaction time, showing that the reuse could be accomplished. The morphological modifications observed for Pd/SeO_2/SiO_2 related with the larger palladium particle size, as measured from TEM analysis, for the spent than for the fresh catalyst seems to

Table 5. Cayalytic propierties of Palladium based catalysts.[a]

Catalyst	X[b] (%)	Sol[c] (%)	Sac[d] (%)	Rate (s^{-1})
Pd/SeO$_2$/SiO$_2$	10	45	55	24
Pd/Al$_2$O$_3$	4	30	51	10
Pd/SiO$_2$	5	38	59	11

[a] benzyl alcohol in isopropanol (35 mL, 0.1M), 50 mg of catalyst, 120°C, 6 atm O_2, stirring rate 650 rpm, 45 min. [b] Conversion of benzyl alcohol. [c] Selectivity to benzaldehyde at 10% of conversion level. [d] Selectvity to benzoic acid at 10% of conversion level.

have no effect on the catalytic properties of Pd/SeO$_2$/SiO$_2$.

It is concluded that Pd/SeO$_2$/SiO$_2$ is an active catalyst for carrying out the oxidation of α-pinene, which shows a relatively high selectivity towards myrtenal. In addition, a practical advantage arises due to the employment of a supported material, which is easy to both handle and separate from the reactive mixture by comparison with the SeO$_2$ sample.

Oxidation of benzyl alcohol

Taking into account the Pd/SeO$_2$/SiO$_2$ is active for terpene oxidation, the same catalyst was evaluated for the oxidation of benzyl alcohol. The benzyl alcohol oxidation reaction has been performed as a characterization tool in order to analyze Pd-SeO$_2$ interactions that could play a role in an oxidation reaction.

The conversion and selectivity to benzaldehyde and to benzoic acid at different reaction time are shown in Table 4.

Relatively high conversion levels are obtained at 180 min, while selectivity to benzaldehyde decreases along with time, due to over oxidation. Besides benzaldehyde and benzoic acid, toluene was also detected in minor amounts, with a nearly constant selectivity of 1-2% (these products were not considered for calculating S% values in Table 4). From the conversion measured at 45 min, the specific rate of the reaction, expressed as mole of benzyl alcohol converted per g of palladium and per second was calculated. This value corresponds to 24 s^{-1}, being this rate quite high. For the sake of comparison two selenium free samples were tested under the same experimental conditions corresponding to Pd/SeO$_2$/SiO$_2$. These two samples are unpromoted palladium catalysts supported on alumina and on silica: Pd(0.98%)/Al$_2$O$_3$ (Neyertz *et al*., 2004) and Pd(1.1%)/SiO$_2$. Both catalysts developed both lower conversion levels at the same reaction time and lower specific activity, expressed as rate in Table 5 (measured at low conversion levels) than the one corresponding to Pd/SeO$_2$/SiO$_2$ (Table 5).

It is interesting to note that the selectivity pattern is different for the selenium containing sample than for the other one. The selectivity to benzaldehyde is high for Pd/SeO$_2$/SiO$_2$ than for both Pd/Al$_2$O$_3$ and Pd/SiO$_2$, probably due to the modifications introduced by selenium oxide over palladium particles. It is concluded that Pd-SeO$_2$ interactions modifies the both activity and selectivity values by comparison with the monometallic palladium catalysts. This issue is being studied in on going studies.

V. CONCLUSIONS

An effective supported catalyst for the allylic oxidation of α-pinene and for the oxidation of benzyl alcohol was studied.

The supported SeO$_2$ catalyst modified with Pd leads to the oxidation in the α-position for the most substituted carbon of the double bond, with a reactivity order $CH_2 > CH_3 > CH$, giving only the terpenes of biological and pharmaceutical interest, myrtenal and myrtenol, showing no overoxidation products or epoxide formation. This result is quite different from the one obtained over other metal supported catalysts, which lead to the allylic oxidation, giving mainly verbenone and verbenol amongst others products.

The present results are promising regarding the substitution of the conventional allylic oxidation methods for α-pinene by a catalytic transformation, being in line with Green Chemistry Principles.

The oxidation of benzyl alcohol over Pd/SeO$_2$/SiO$_2$ shows peculiar catalytic parameters that indicates that selenium oxide strongly modifies palladium.

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