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Investigation On $Pd/SeO_2/SiO_2$ For α-Pinene Oxidation. Characterization by Transmission Electron Microscopy (TEM)

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Myrtenal (**3**) has received a growing interest in research for its bioactive properties, and it was discovered that it exhibits a broad spectrum of biological activities [1, 2]. Allylic oxidation with selenium oxide (SeO_2) is one of the most used techniques in the traditional methodology, but it has several disadvantages, such as the use of high stoichiometric ratios, product mixes, very long reaction times and generation of colloidal selenium species that are difficult to eliminate, these being very toxic to the environment [3]. The heterogenization of oxidation reactions traditionally carried out following classical organic synthesis methodology presents a high impact in the context of the Green Chemistry principles.

In line with this, there are several reports regarding α-pinene (**1**) as a starting compound, molecular oxygen as oxidizing agent and catalysts based on supported metals, such as Pd, Pt, Fe, Ru and, Cr. However, this allylic oxidation produces verbenol (**4**), verbenone (**5**) and α-pinene epoxide (**6**), without the production or the desired myrtenal (Figure 1) [4 – 6].

To selectively obtain myrtenal, it is proposed to design a heterogeneous catalyst selective, active, stable with low selenium load, reusable and efficient to produce the expected aldehyde. In this work, a $Pd/SeO_2/SiO_2$ catalyst was prepared and tested for the allylic oxidation reactions of α-pinene to selectively obtain a good yield to the desired myrtenal product. To do this, we rely on the selectivity of SeO_2 and the oxidative capacity of Pd. The catalyst is made up of Pd nanoparticles supported on SeO_2 modified silica [7]. The $Pd/SeO_2/SiO_2$ catalyst characterization was carried out mainly by Transmission Electron Microscopy (TEM) and also by XRD, FTIR, and XPS. TEM study was performed for determining Pd particle size both over fresh and used catalyst.

Catalysts observation was performed in a TEM JEOL 100CX, operated at 100 kV. Digital Micrograph software was employed for measuring particles sizes. Micrographs and histograms of both fresh and used $Pd/SeO_2/SiO_2$ catalysts are showed in Figures 2 and 3, respectively. Pd particles are clearly observed. On the contrary, is not possible to distinguish SeO_2 from silica support, due to the similar electronic density of both oxides. Growth of Pd crystals is observed under reaction conditions. The average size determined were 2.9 and 3.5 nm for the fresh and used samples respectively. The increase in palladium particle size notably influences on catalytic activity and selectivity. The augmentation of palladium crystals leads to a decrease in the concentration of active sites, and concomitantly to an activity depletion [8].

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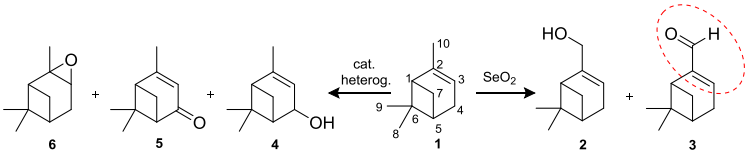

Figure 1. Allylic oxidation of α-pinene. Conventional and catalytic method

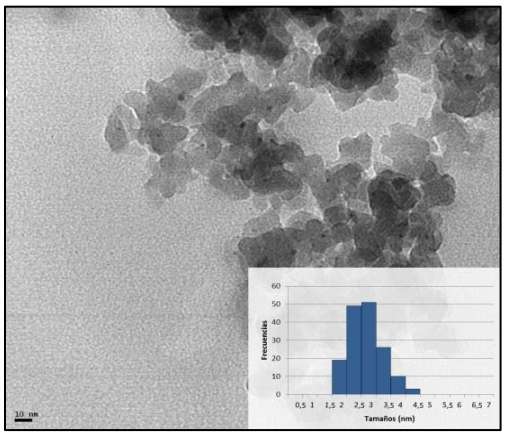

Figure 2. $Pd/SeO_2/SiO_2$ fresh

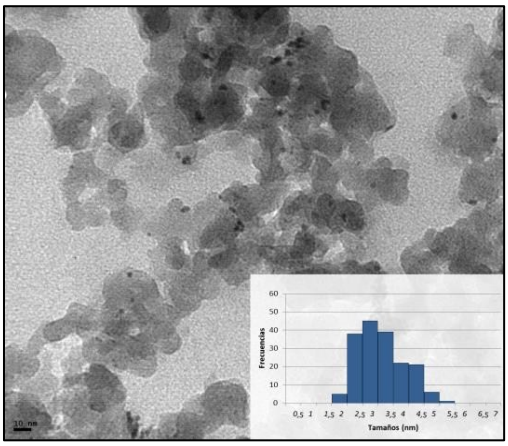

Figure 3. $Pd/SeO_2/SiO_2$ used

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