

Review

## Catalysts Supported on Carbon Materials for the Selective Hydrogenation of Citral

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Received: 14 August 2013; in revised form: 22 September 2013 / Accepted: 11 October 2013 /  
Published: 22 October 2013

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**Abstract:** The heterogeneously catalyzed selective-hydrogenation of citral is one of the more feasible ways for obtaining its appreciated unsaturated-alcohols, nerol and geraniol, which are present in over 250 essential oils. Thus, citral has very recently come to be produced petro-chemically in very large quantities, and so partial hydrogenation of citral has become a very economical route for the production of these compounds. However, the selective hydrogenation of citral is not easy, because citral is an  $\alpha,\beta$ -unsaturated aldehyde which possesses three double bonds that can be hydrogenated: an isolated C=C bond and the conjugated C=O and C=C bonds. For this reason, in catalyst selection there are several important issues which affect the product selectivity, for example, the active metal and metal particle size which are factors related to the catalyst preparation method, catalyst precursor, or support surface area, as well as other factors such as porosity, the addition of a second catalytic metal, and, of course, the type of catalyst support. About this last one, carbon materials are very interesting supports for this type of hydrogenation reaction due to their unique chemical and textural properties. This review collects and analyzes the results obtained in the selective hydrogenation of citral catalyzed by carbon material supported metals.

**Keywords:** citral; hydrogenation; activated carbon; graphite; carbon nanotubes

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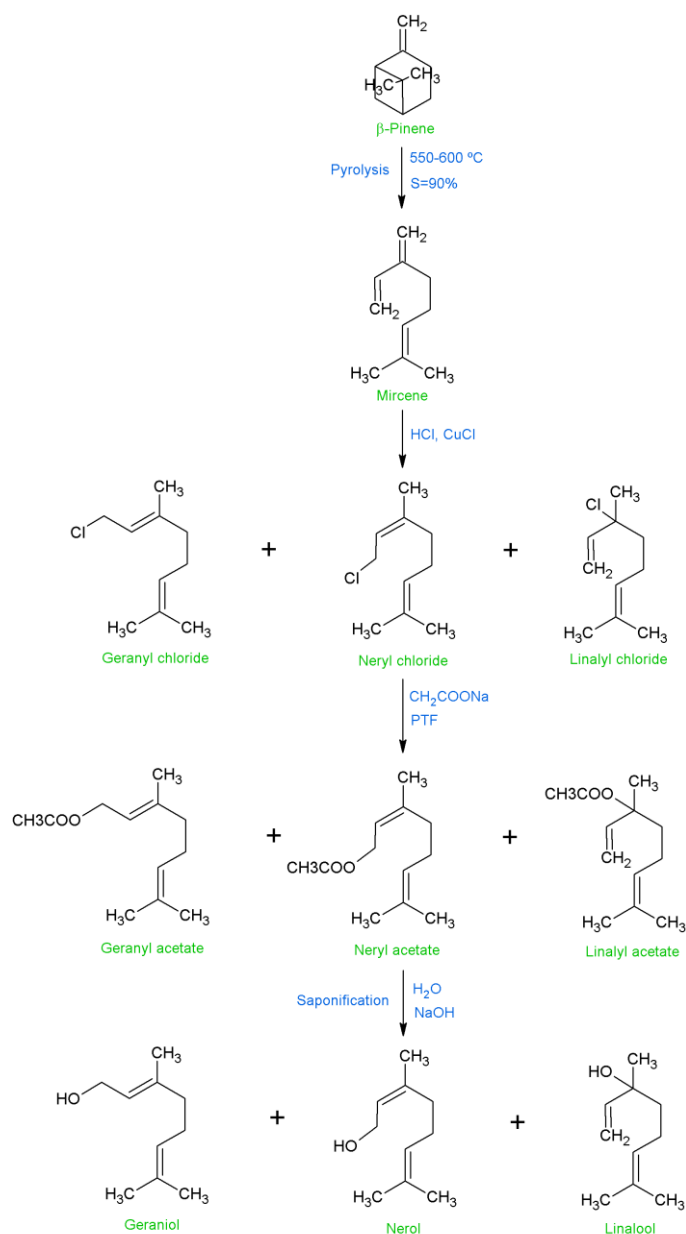
## 1. Introduction

Since ancient times, essential oils and extracts have been used for many different applications such as perfumes, air fresheners, cosmetics and medicinal substances. These compounds were mainly extracted by steam distillation or solvent extraction of different vegetable raw materials. These essential oils consist primarily in terpenes, where their unsaturated alcohols play a very important role. In particular, nerol and geraniol are present in over 250 essential oils as ninde oil (66.3%) [1], rose oil (59.0%) [2], palmarosa oil (80.9% geraniol in leaf) [3], monarda fistulosa oil (>95%) [4], citronella oil (24.8%) [5], among other essential oils.

Geraniol was isolated from palmarosa oil while nerol was obtained from the oil of neroli [6,7]. These monoterpenes are widely used in fragrance and flavour industries. A survey of consumer products between 1996–2001 revealed that they are present in 76% of 73 investigated deodorants on the European market—95% in vapo-spray deodorants, 91% in aerosol sprays deodorants and 46% in roll-on deodorants [8]—in the 41% of 59 investigated domestic and occupational products [9], and in the 33% of cosmetic formulations [10], their production in that year being more than 1000 metric tons [11]. In addition, recent studies revealed that geraniol exhibits various biochemical and pharmacological properties as a potential antimicrobial agent [12], an effective plant based insect repellent (currently being marketed by Fulltec<sup>®</sup> and BugBand<sup>®</sup>, for example) [13–15], an anti-inflammatory [16], anthelmintic [17,18], anti-oxidant [19,20] and anti-herpetic agent [21], and furthermore, geraniol exerts *in vitro* and *in vivo* antitumor activity against murine leukemia, hepatoma and melanoma cells [22–26]. Furthermore, this molecule is an important intermediate in the synthesis of other organic molecules with high added value [27] such as phellandrene, myrcene, ocimene, linalool and vitamins A and E [28].

This increase in the use of geraniol and nerol makes necessary a chemical synthesis of this compound. Actually, the industrial production of these compounds is mainly done from  $\beta$ -pinene by companies such as International Flavors and Fragrances (IFF), Pinova, DRT and TECNAL Corporation [29,30]. This process [31], shown in Figure 1, involves the pyrolysis of  $\beta$ -pinene, which yields 90% myrcene by passing it through a tube at 550–600 °C with a very short contact time. Then, in a second step (myrcene hydrochlorination), hydrogen chloride is added to myrcene in the presence of a small amount of cuprous chloride catalyst and an organic quaternary ammonium salt to effect a preferential addition at the allylic double bond resulting in the formation of a higher proportion of geranyl or neryl chloride, linalyl chloride and a little myrcenyl chloride. After removal of the catalyst, the crude mixture of chlorides is converted to a mixture of acetates (or formates) by addition of sodium acetate or sodium formate with a phase-transfer catalyst (PTC) or in the presence of a nitrogen base to give predominantly geranyl acetate (50%–55%), neryl acetate (40%–50%) and small amount of linalyl acetate. Saponification of the acetates or formates gives the corresponding alcohols and the sodium acetate or formate which is recycled. Fractionation of the crude alcohol mixture gives both geraniol and nerol products, usually as mixtures. Further fractional distillation yields about 98% geraniol [30,31].

**Figure 1.** Industrial-scale production process of nerol and geraniol. Powered by International Flavors and Fragrances (IFF), Pinova, and Dérivés Tecnaux Résiniques et Terpéniques (DRT). Adapted from [31].



The drawback of the industrial manufacturing process is the multitude of needed stages, including a pyrolysis, with the difficulties that it entails the need of large amount of reagents, and the corresponding loss of performance of each stage. For these reasons, the selective hydrogenation of citral is one of the more feasible ways for obtaining these unsaturated alcohols being a single step synthesis. Furthermore, citral has very recently come to be produced petrochemically in very large quantities, and so partial hydrogenation of citral has become a very economical route for the production of geraniol and nerol [31]. Therefore, the hydrogenation of citral is attracting the attention of a large number of scientists worldwide. Citral (3,7-dimethyl-2,6-octadienal) is a monoterpene found in plants and citrus fruits. It is an isomeric mixture of the acyclic aldehydes geraniol (citral E) and nerol (citral Z).

On the other hand, carbon materials show several advantages when they are used as supports in heterogeneous catalysis and especially in hydrogenation reactions [32]:

(i) Carbon surface is relatively inert, preventing the occurrence of unwanted reactions catalyzed by the support surface or reaction of the support with the active phase.

(ii) The cost of conventional carbon materials is lower than other conventional supports.

(iii) Carbon materials may be obtained in different forms (granules, pellets, fibers, foams, monoliths, fabrics, coatings, *etc.*).

(iv) The active phase, usually expensive, can be easily recovered by simple calcination of the support.

(v) They have a high surface area and its porous framework can be modified to obtain the pore size distribution (PSD) optimum for each particular reaction.

(vi) They are stable at high temperatures in non-oxidizing atmospheres (even above 700 °C).

(vii) Although carbon is usually a material with a hydrophobic nature, the chemical nature of their surface can be modified chemically to give them some hydrophilicity.

Despite all these advantages, carbon materials are not the main supports studied in the hydrogenation of citral as derived from the reviewed literature, being these mentioned only in 17% of the reviewed literature, and mainly they are used as reference materials. Within the carbon materials, the classical materials have been the most studied in the selective hydrogenation of citral (activated carbons and graphite were studied in the 57% and 19% of the citations, respectively). However, nowadays non-traditional carbon materials such as carbon nanotubes are widely being studied for this application (21% of the reviewed literature), and finally some works using advanced composite materials like Carbon-TiO<sub>2</sub> can also be found. Although carbon xerogels and aerogels are very interesting carbon materials especially as catalyst supports [33–37], we have not found works in the reviewed literature where they have been used in the selective hydrogenation of citral. Moreover, only a few works mention these materials for the hydrogenation of  $\alpha,\beta$  unsaturated aldehydes [38–40].

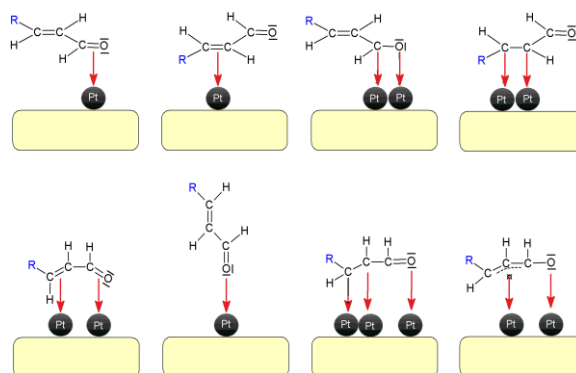
Finally, it should be mentioned that in the catalyst selection for the citral hydrogenation, there are several important issues which affect the product selectivity, such as the active metal [41–44], the metal-particle size [43,45–47], the support material or the use of bimetallic catalysts [45,48–50], as well as other factors relating to the operating conditions as the used solvent, which is important in the formation of acetals, the stirring, the operation temperature and pressure as well as the initial concentrations.

In this review, a widely used explanation about the different and possible reaction routes during the hydrogenation of citral, as well as a deep review of the role in the activity and selectivity of the main transition metal as catalyst in this reaction are shown. The more significant results using carbon materials, as catalyst supports in the selective hydrogenation of citral, have been collected. These results are shown and discussed by type of material, and finally, some challenges for the future are proposed.

## 2. Hydrogenation Selectivity

The selective hydrogenation of citral to nerol and geraniol is not easy, because citral is an  $\alpha,\beta$  unsaturated aldehyde which possesses three double bonds that can be hydrogenated: an isolated C=C



**Figure 3.** Adsorption modes of the  $\alpha,\beta$ -unsaturated aldehyde molecule. Adapted from [55].

The knowledge of the adsorption modes is very important for understanding the selectivity of the hydrogenation of the  $\alpha,\beta$ -unsaturated aldehydes. Basically, there are three basic ways to obtain the hydrogenation of the C=O bond and, hence, the desired unsaturated alcohol: (i) the first is to hinder the C=C molecular adsorption. This hindrance can be achieved by an increase of the repulsive electron interactions with the surface using metals with more extended d-orbitals like osmium or iridium, or increasing the {111} face presence in the metal surface, and finally, also using an electronically dense surface by means of an active support (*i.e.*, graphite). (ii) The second way is to favor the interaction of the C=O bond with the surface using Lewis acid promoters as for example the partially reducible oxides TiO<sub>2</sub> or CeO<sub>2</sub> in which new acid Lewis sites can be created by oxygen vacancies. (iii) The third way is a combination of both mentioned strategies, favoring the C=O adsorption and hindering the C=C adsorption at the same time. This would be achieved combining satisfactory electropositive and electronegative metals which produces a charge transfer between them that favors the electronic repulsion against the C=C adsorption, being equally created polarized sites  $\delta^+ - \delta^-$  that favor the interaction with the C=O bond [57].

Also, other factors relating to the catalytic system should be considered such as the solvent. The solvent is important not only for preventing the formation of acetals, but also because it could affect the selectivity and the hydrogenation rates. Generally, the higher the polarity of the solvent, the higher is the hydrogenation rates, due to an increase of the H<sub>2</sub> solubility in the solvent [58–60]. Related to the product distribution, some authors have obtained a trend modifying the polarity of the solvent. Polar solvents activated the C=O hydrogenation whereas non-polar solvents favored the C=C bond hydrogenation over non acidic catalysts to avoid the acetals formation over alcohol solvents [59,61,62]. Additionally, supercritical CO<sub>2</sub> has been used as non-conventional solvent due to its important benefits such as: (i) the higher solubility of hydrogen than conventional solvents; (ii) much easier separation after reaction; (iii) and the improvement of selectivity in the C=O hydrogenation. The higher selectivity towards the unsaturated alcohols using supercritical CO<sub>2</sub> has been ascribed to specific interactions between CO<sub>2</sub> and the citral molecules [63–65].

Another way to favor the C=O interaction with the catalyst may be achieved by adding a water film to the surface of the catalysts. In this sense, Jiang *et al.* [66] used a combination of Ru/AlO(OH) and water improving the catalyst activity and its selectivity to geraniol and nerol. The interactions between water molecules and the surface hydroxyl groups of the support made possible a water film adhesion around the catalyst particles. This water favoured the citral adsorption throughout the C=O bond due to

its more polarized bond character. In a similar way, with SLPC (supported liquid-phase catalyst) the selectivity towards the unsaturated alcohols can be modified adding water (or another polar solvent) to an organic media [67,68]. The drawback of this type of methodology is that the entire surface should be covered by water in order to maintain the desired selectivity [67].

### 3. The Type of Transition Metal as Catalytic Phase

In the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes, usually transition metals supported on oxides or carbon materials are used as catalysts. The selection of the catalytic phase is very important due to its influence on the product's selectivity. In general, Ir and Os catalysts show moderately high selectivities to C=O hydrogenation, while Pt, Ru and Co possess moderate selectivities and Pd, Rh and Ni are unselective or poorly selective to the un-saturated alcohol. These trends were confirmed by Sokolskii *et al.* [69,70] in the crotonaldehyde hydrogenation with catalysts supported on carbon finding the following selectivity trend to the un-saturated alcohol: Os > Ir > Ru > Rh  $\approx$  Pt  $\approx$  Pd, and also by Giroir-Fendler *et al.* [41] in the hydrogenation of cinnamaldehyde using coal and graphite as supports finding the trend Ir > Pt > Ru > Rh > Pd with both supports. This increase of selectivity is attributed to an electronic effects according to theoretical calculations of Delbecq and Soutet and semi-empirical calculations of Hückel [54,57]. According to these authors, the selectivity to the unsaturated alcohol can be correlated with the metal d-band width. With increasing electron density and, hence, d-orbital population, the repulsive four electron interaction of the C=C double bond with the metal surface increases, however, the interaction of the metal surface with the C=O  $\pi$ -system is favored [52,55]. Thus, the binding of unsaturated molecules on metal surfaces is based on the distinction between stabilizing two-electron (of the C=O) and destabilizing four-electron interactions (of the C=C) [71]. The C=C coordination is very sensitive to Pauli repulsion with the surface. A metal with more diffuse orbitals will increase the Pauli repulsion and therefore weaken the C=C adsorption. This is the case of Ru and Os which have a large radial expansion of the d orbitals and therefore give a good selectivity to un-saturated alcohol. In contrast, Pd has more contracted d orbitals, and in this case the molecule can easily approach the surface and a flat  $\eta^4$  mode is preferred [72]. As a result, Pd gives a poor selectivity in unsaturated alcohol. The calculated metal d-band width is Ni < Pd < Ru < Pt < Ir, Os, which is in agreement with the experimentally obtained selectivities toward the un-saturated alcohol [57,73].

In the selective hydrogenation of citral, the above mentioned tendency was also shown by Vannice and Singh [53] who examined the influence of the active metal on the activity and selectivity in the liquid phase hydrogenation of citral at 300 K and 1 atm using silica as support. These researchers found the following trend in activity Pd > Pt > Ir > Os > Ru > Rh > Ni > Co >> Fe and in selectivity was found that Os showed high selectivity to unsaturated alcohols (88%), the Ru and Co showed moderate selectivity (55%) and Rh, Ni and Pd were more selective to citronellal and isopulegol (0% unsaturated alcohols). In turn, Manikandan *et al.* [74] analyzed Pt and Ru catalysts intercalated in a silicate (Mantmorillonite) obtaining a selectivity of 60% for Pt and 45% for Ru. Taking into account the literature review collected in Table 1 and the results obtained by Vannice and Singh, a reasonable activity trend for the most  $\alpha, \beta$ -unsaturated aldehydes independently of the support and the conditions employed would be the following: Ni < Pd <<< Rh < Ru, Pt, Co < Ir, Os.

With regard to the selectivity, the susceptibility of the Ir to the formation of un-saturated alcohols in the hydrogenation of citral as well as with other aldehydes [52] is not clear. Comparing the results (Table 1) for Ir/TiO<sub>2</sub> in the same operating conditions, some authors achieved selectivities as high as 91%–100% while others get a moderate selectivity of 60%, whereas using other supports like SiO<sub>2</sub>, very different selectivities among 100%, 40% or 15% were obtained. However, it seems clear that with Ir catalyst, low conversions are achieved (5%–10%). Thus, despite that Os and Ir seem to be the most selective to un-saturated alcohols in the hydrogenation of citral, they are the least active. On the other hand, Pt and Ru are the most employed in the literature (they are present in 68% of the reviewed papers): Pt because it shows moderate activity and selectivity, and Ru because it combines an acceptable catalytic performance with the cheapest price among the best metals. Obviously, the ideal would be to achieve a high selectivity with a great conversion without losing sight of the economic factor. For this reason, the challenge is to improve the selectivity of Pt and Ru by adding a second metal or enhancing electronic effects of the support.

**Table 1.** Effect of the type of metal on the selectivity toward the un-saturated alcohol in the selective hydrogenation of citral.

Metal	Support	T <sup>a</sup> (°C)	P (Bar)	S (%)	C (%)	Ref.
Rh	TiO <sub>2</sub>	70	70	10	100	[75]
Rh	TiO <sub>2</sub>	70	70	11	94	[76]
Rh	SiO <sub>2</sub>	35	1	5.2	100	[77]
Pt	TiO <sub>2</sub>	70	70	58	98	[75]
Pt	TiO <sub>2</sub>	90	100	68	95	[78]
Pt	SiO <sub>2</sub>	100	20	56	30	[79]
Ir	TiO <sub>2</sub>	90	6.2	100	11.2	[80]
Ir	SiO <sub>2</sub>	90	6.2	47	5	[81]
Ir	Nb <sub>2</sub> O <sub>5</sub>	90	6.2	82	15	[82]
Ir	SiO <sub>2</sub>	90	6.2	44	3	[82]
Ir	TiO <sub>2</sub>	90	6.2	91	10	[81]
Ir	SiO <sub>2</sub>	70	4	100	10	[83]
Ir	TiO <sub>2</sub>	70	4	100	10	[83]
Ir	SiO <sub>2</sub>	27	1	15	5	[44]
Os	SiO <sub>2</sub>	27	1	88	5	[44]
Co	TiO <sub>2</sub>	90	70	50	80	[42]
Co	C	120	10	60	17	[84]
Au	TiO <sub>2</sub>	80	40	16	6	[85]
Ru	TiO <sub>2</sub>	80	40	22	15	[85]
Ru	TiO <sub>2</sub>	126	50	42	76.8	[86]
Ru	Al <sub>2</sub> O <sub>3</sub>	126	50	48	12.2	[86]
Pd	TiO <sub>2</sub>	80	40	8	27	[85]
Pd	SiO <sub>2</sub>	130	70	0	100	[87]
Ni	Al <sub>2</sub> O <sub>3</sub>	70	1	0	n.d.	[88]
Ni	Cr <sub>2</sub> O <sub>3</sub>	120	40	0	n.d.	[89]
Ni	Graphite	50	50	0	100	[90]



## 4. Carbon Materials as Supports

In heterogeneous catalysis, the active phase is deposited on a support material which normally is catalytically inert. These supports are usually metal oxides or carbon with the aim of maximizing the specific surface area to achieve a greater dispersion of the active phase. However, the use of micro-mesoporous supports may not be suitable for hydrogenation reactions in liquid phase where hydrogen solubility in the solvent is small, because when very active metals are used, isomerization reactions may occur to a greater extent than the desired ones due to an immediate decrease of the hydrogen concentration on the active site [91,92]. Sometimes, we find in the literature that selectivity results in these types of reactions—including citral hydrogenation—can be affected by the above mentioned process, but the explanation is attributed to other factors.

### 4.1. Activated Carbons

The activated carbons are the supports most studied in hydrogenation of citral. These materials do not present electronic effect like the partially reducible oxides, or graphite which could enhance the selectivity towards un-saturated alcohols, but due to their high surface areas they are very interesting for the preparation of bimetallic catalysts. For these reasons, most authors who used activated carbon as support, used them for preparing bimetallic catalysts, or as reference materials.

Galvagno *et al.* [43,93,94] studied the influence of Ru particle size, type or metal precursor and the reaction media, using a commercial activated carbon with a surface area between 900 and 1100 m<sup>2</sup>/g by impregnation with RuCl<sub>3</sub> and different metal loading. Due to the high surface area of the carbon support, Ru could be dispersed better than using other supports such as Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>. Metal particle sizes among 3.7 and 10.3 nm, with Ru loading among 0.5 and 10 wt.% were obtained treating the impregnated catalysts at 300 °C in H<sub>2</sub>. They found that the specific catalytic activity per Ru surface atom as well as the product distribution did not depend of Ru particle size supported on the activated carbon. On the other hand, making a catalytic comparison among the supports activated' carbons, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> [43,94], the authors explained that due to the hydrophobic nature of the carbon support, which leads to a weaker interaction between the catalyst and the solvent (ethanol), the poisoning effect on the Ru active sites decreased, and higher amounts of unsaturated alcohols were also obtained.

On the other hand, in other works activated carbons were used to prepare bimetallic catalysts [48,84,95–100] employing their high surface areas to improve the dispersion of the bimetallic clusters. Vilella *et al.* [99] studied the influence of the addition of different Ge and Sn loading to Pt/activated carbon catalysts. These catalysts were prepared by successive impregnation of the precursor salts (H<sub>2</sub>PtCl<sub>6</sub> and SnCl<sub>2</sub> or GeCl<sub>4</sub>). They used a commercial carbon with an apparent surface area of 987 m<sup>2</sup>/g and high ash content. The activated carbon was demineralised and a fraction of this was oxidized with a HNO<sub>3</sub> treatment. Pt-Sn catalysts worked better than Pt alone increasing both activity and selectivity towards reaching 78% of selectivity at 70% of conversion. By contrast, the addition of Ge forming the Pt-Ge clusters decreased the activity and the selectivity towards unsaturated alcohols, which was ascribed to very few oxidized Ge species being placed near Pt in order to polarize the carbonyl group of the citral molecule. This can explain the catalysts' low selectivity to unsaturated

alcohols. Moreover, the formation of unsaturated alcohols did not improve with the addition of Ge because this would be mainly located over the support without modifying either electronically or geometrically the Pt sites. In order to enhance the numbers of Pt-Ge clusters, these catalysts were again prepared by controlled surface reactions which could ensure a contact between Pt and Ge [97] and using the oxidised activated carbon, in this case, a clear improvement of the selectivity to unsaturated alcohols was detected.

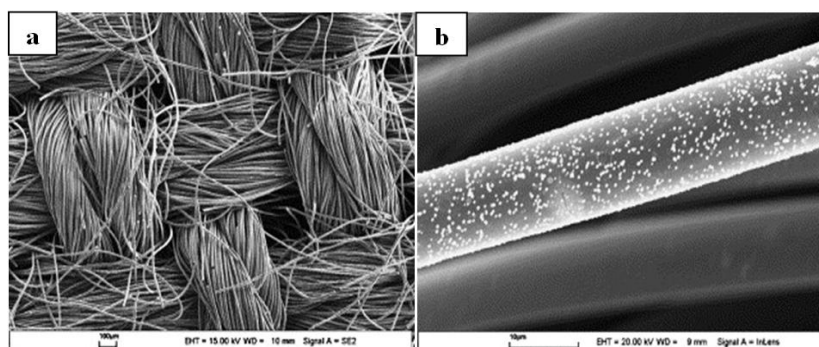
Vilella *et al.* [100] also studied the catalytic performance of two different activated carbon-based supports using Pt and Pt-Sn clusters: an activated carbon in powder shape against a commercial activated carbon felt. Differences in selectivity to unsaturated alcohols were found, which were ascribed to the different surface acid characteristics of the supports as well as to the presence of  $\text{Sn}^{\circ}$  species, being the catalysts supported on carbon powders (equilibrium pH 10) more selective than that supported on carbon felts (equilibrium pH 7) and obtaining a larger amount of isopulegol than the latter.  $\text{Sn}^{\circ}$  species produced blocking or dilution of de Pt particles. This effect was produced mainly on the felts based catalyst which provoked that this catalyst were less active and selective (80% and 68% of selectivity, for activated carbon and carbon felt, respectively, at 95% of conversion)

Neri *et al.* [95] have also studied bimetallic Pt-Sn catalysts supported on activated carbon, prepared by co-impregnation (2 wt.% of Pt), obtaining an increase in selectivity towards unsaturated alcohols (from 40%–90%) by increasing the Sn loading from 0–0.82 wt.%.

Another bimetallic catalyst supported on carbon is Pt-Co. Bertero *et al.* [84] prepared Pt/C, Co/C and Pt-Co/C catalysts using a sub-bituminous carbon of high surface area ( $1300 \text{ m}^2/\text{g}$ ) by impregnation of acetylacetonate precursor salts. The catalysts were reduced at  $150 \text{ }^{\circ}\text{C}$  and  $500 \text{ }^{\circ}\text{C}$  in  $\text{H}_2$  flow. The activity and selectivity of the bimetallic catalysts were higher than the monometallic ones, suggesting the creation of new polarized sites which would activate the  $\text{C}=\text{O}$  bond hydrogenation. Moreover, secondary reactions such as decarbonylation and hydrogenolysis observed with the monometallic catalysts would be inhibited using the bimetallic ones.

Active carbon cloths (Figure 4) also have been employed in the selective hydrogenation of citral. Aumo *et al.* [101,102] studied Pt catalysts supported on carbon cloth and on woven active carbon fiber. Unsaturated alcohols selectivities of 80%–100% for carbon fiber catalysts were reached against a selectivity of 49%–62% for the activated carbon catalysts used for comparison. However, the authors mentioned that the price of these types of cloths is still a limiting factor for extended use.

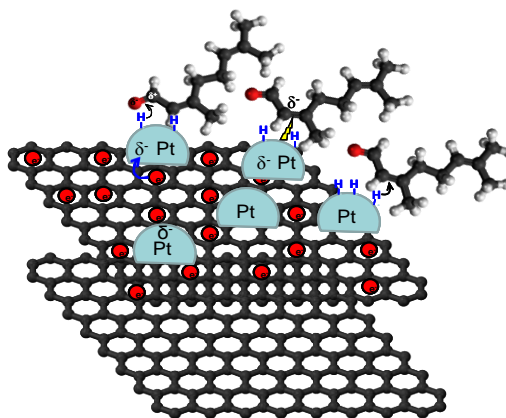
**Figure 4.** SEM images of the (a) woven activated carbon and (b) Pt-woven activated carbon catalyst [102].



#### 4.2. Graphite

In general, the literature shows that graphite-supported catalysts are more selective towards the unsaturated alcohol than other conventional supports (alumina, activated carbon, or silica). This higher selectivity would be explained on the basis of electron transfer from the graphitic support to the metal particles located at the edges of the basal planes (Figure 5). The increased charge density on the metal particles would decrease the probability of adsorption via the C=C bond, and therefore hindering its hydrogenation [103].

**Figure 5.** Electron transfer from the graphitic support to the metal particles.



Steffan *et al.* [104] studied the catalytic behaviour of Pt catalysts supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, activated carbon and graphite. The reaction was carried out at 140 °C, 70 bar H<sub>2</sub>, 1.5 g of catalyst and an initial citral concentration of 0.56 M in n-hexane, as reaction media. They found the following trend in selectivity to unsaturated alcohols Pt/AC < Pt/Al<sub>2</sub>O<sub>3</sub> < Pt/SiO<sub>2</sub> < Pt/G. For the carbon based catalysts Pt/G and Pt/AC, the use of graphite as support yielded a higher selectivity towards geraniol and nerol compared to activated carbon, in agreement with previous results for the hydrogenation of cinnamaldehyde [105]. However, this work also showed that Pt catalysts supported on graphite were much more selective to nerol and geraniol than those supported on other conventional supports such as silica or alumina.

Bachiller-Baeza *et al.* [106] studied Ru and Ru-Fe catalysts supported on a high-surface-area graphite ( $S_{\text{BET}}$  295 m<sup>2</sup>/g) and activated carbon ( $S_{\text{BET}}$  964 m<sup>2</sup>/g). The activated carbon was demineralised by acid treatments, and the graphite was treated in He at 900 °C in order to remove the surface oxygen groups. Monometallic catalysts were prepared by incipient wetness of the supports with an aqueous solution of RuNO(NO<sub>3</sub>)<sub>3</sub>, and bimetallic catalysts were prepared by a co-impregnation method with aqueous solution of RuNO(NO<sub>3</sub>)<sub>3</sub> and Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O. The catalysts were reduced in H<sub>2</sub> flow at 400 °C for 2 h. The liquid-phase hydrogenation of citral was carried out in isopropanol at atmospheric pressure under H<sub>2</sub> at 60 °C, 850 rpm of agitation. A citral/Ru molar ratio of 30 was used. Contrary to what was expected the initial activities and the selectivity to unsaturated alcohols (~38%) for both monometallic Ru catalysts were similar. Authors ascribed this behaviour to the absence of oxygen groups at the surface of the graphite during the impregnation which would restrain the metal-support interaction. Oxygen groups were not present on the support before impregnation, but they were introduced into the carbon materials during the catalyst preparation procedure due to the

very high oxidizing character of the ruthenium precursor ( $\text{RuNO}(\text{NO}_3)_3$ ). The presence of these oxygen functional groups at the surface of the graphite also impeded the electron donor effect of the macro-ligand graphite. On the other hand, using Fe as promoter, the selectivity was enhanced due to the bimetallic effect. However, bimetallic catalysts supported on graphite achieved higher selectivity to unsaturated alcohols than those on activated carbon probably due to the lower oxygen content and the maximum electronic transfer from support to the metals. This work clearly shows the importance of the surface chemistry of carbon materials in the selective hydrogenation of citral.

Asedegbega-Nieto *et al.* [90] studied the catalytic behaviour of Ru-Cu and Ni-Cu bimetallic catalysts supported on a high surface area graphite. Bimetallic catalysts with different Cu loadings were prepared by a co-impregnation method employing ethanolic solutions of ruthenium acetylacetonate and copper acetate for the Ru-Cu system, and nickel nitrate and copper nitrate for the Ni-Cu system. The graphite was treated under inert atmosphere at 900 °C in order to remove oxygen groups before its impregnation, and the catalysts were treated in hydrogen flow at 350 °C, for the Ru-Cu system, and 350 °C for the Ni-Cu system, both for 2 h. The reaction were carried out at 50 bar of pressure, 50 °C, initial citral concentration of 0.03 M in isopropanol under 500 rpm of stirring. Regarding the Ru-Cu system, the monometallic catalyst (only Ru) produced citronellal and unsaturated alcohols. The addition of Cu did not modify the activity, but the selectivity to unsaturated alcohols decreased probably due to a poor Ru-Cu interaction where the Cu phase would be mainly covering the Ru particles. Regarding the Ni-Cu system, the saturated aldehydes were the main product obtained, and when Cu was added, changes in the selectivity were not observed. Therefore, Cu did not enhance selectivity to unsaturated alcohols in any case.

Court *et al.* [107] prepared Ni-M (M=Al, Cr, Cu, Co, Mo) bimetallic catalyst supported on graphite by incipient wetness using an aqueous solution of the appropriated composition of the two metal salts, and later reduction with naphthalene sodium. Hydrogenations were carried out at 80 °C under constant hydrogen pressure (1.01 MPa) using a citral concentration in 2-propanol of 0.195 M. It was expected that Ni-Cr catalysts were more selective to citronella1 whereas Ni-Mo catalysts were more selective to citronellol. However, in none of the cases, the bimetallic catalysts modified the selectivity of Ni to unsaturated alcohols.

Cerro-Alarcón *et al.* [108] studied the behaviour of Ni catalysts supported on a high surface area graphite (200 m<sup>2</sup>/g) and 3 wt.% oxygen surface content. Two different metal salts were used, namely,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , and with different pre-treatment: reduction in H<sub>2</sub> at 400 °C for 2 h, and hydrazine based treatments; reduction of the impregnated support directly with hydrazine, or reduction-deposition *in situ* of Ni precursor with hydrazine. The hydrogenation of citral was performed operating at 50 °C, a H<sub>2</sub> pressure of 5 MPa, under 500 rpm of stirring, and using around 0.4–0.5 g catalyst and 0.4–0.5 mL of citral in 100 mL of 2-propanol. The catalytic results indicated that the determining factor in the activity data was the reduction method employed independently of the Ni precursor. While the treatment of reduction in hydrogen flow Ni<sup>0</sup> was obtained, the reduction with hydrazine provided low proportions of Ni<sup>0</sup> sites and mainly oxidised Ni<sup>2+</sup> and/or Ni<sup>3+</sup> species. These oxidised Ni species can activate the unsaturated aldehyde hydrogenation via the C=O bond. In fact, when only Ni<sup>0</sup> was present the hydrogenation activity was the highest; several orders of magnitude higher than those observed for catalysts prepared by reduction with hydrazine, however, these catalysts were not selective to the unsaturated alcohol formation. On the contrary, catalysts

pre-treated with hydrazine were much more selective to unsaturated alcohols than the hydrogen pre-treated ones, but with very poor activities.

Zhao *et al.* [109] prepared catalysts for the selective hydrogenation of citral towards citronellal, instead to the unsaturated alcohols, using Pd catalysts supported on a graphite oxide (GO) pre-treated with 1,1,3,3-tetramethylguanidine (TMG). It is known that the use of palladium-supported catalysts in citral hydrogenations together with basic promoters, such as NaOH or NaCO<sub>3</sub>, leads to higher selectivity toward citronellal [110,111]. In this case, the above mentioned procedure was the basis to modify the GO surface for immobilizing Pd nanoparticles and using Pd(CH<sub>3</sub>COO)<sub>2</sub> in ethanol solution. In a last step, the catalyst was reduced in a NaBH<sub>4</sub> aqueous solution, obtaining the GO supported Pd nanocatalysts. This type of catalyst had small Pd particle sizes, in a narrow size distribution, which produced a selectivity to citronellal of 89.6% with a high activity.

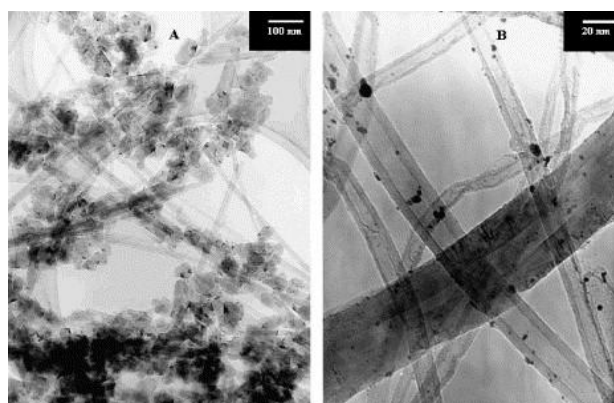
#### 4.3. Carbon Nanotubes

Recently [32], carbon nanotube (CNT) structures have been found to produce remarkable catalytic effects when they are used as a support for selective hydrogenation reactions due to their unique properties such as excellent electrical and thermal conductivity, uniform pore size distribution, development of meso and macropore bodies [112], and high length-to-diameter aspect ratio, the latter providing them a high external surface area [113]. These special properties could influence the metallic particle size distribution, dispersion, metal oxidation state, but also can reduce problems as mass transfer rates obtaining high catalytic performances in comparison with other conventional supports [114]. Besides, due to their three-dimensional nanoscale structure of rolled up graphene layers, a transfer of electronic density from the support to the deposited metallic particles [115,116] could take place affecting the properties of the metallic phase and their catalytic behaviour [117]. For these reasons, they have been recently used as supports in the hydrogenation selective of citral, because they can improve the selectivity to the unsaturated alcohol due to a transfer of the p-electrons from the graphene layer to the metal particles. Moreover, the curvature of the CNT channel could also induce an extra modification on the molecular adsorption on the metallic phase, which also would modify the catalytic activity and/or selectivity of the hydrogenation reaction. However, during the CNT synthesis other carbon forms and amorphous carbon are formed as well. Therefore, it is necessary to have a good knowledge of the purity of CNT when using them for catalytic applications.

Asedegbega-Nieto *et al.* [118], studied the catalytic behaviour of four different carbon materials, including two types of carbon nanotubes with very similar sizes, as supports of Pt catalysts: commercial carbon nanotubes obtained by arc discharge (CNT1) with a 30–40 wt.% of nanotube content, carbon nanotubes obtained by CVD (CNT2), carbon black and a high surface area graphite, pretreated at 900 °C in He flow in order to remove surface groups. The Pt catalysts were prepared by impregnation of the supports with hexachloroplatinic acid obtaining the smallest particle sizes on graphite and carbon black probably due to their highest surface area in comparison with CNTs. Figure 6 shows some pictures of Pt supported on carbon nanotubes. Citral hydrogenation reactions were carried out at 50 °C and H<sub>2</sub> pressure of 50 bar, with 500 rpm of stirring, employing isopropanol as solvent. Regarding the catalytic results, Pt supported on carbon, graphite and CNT1 showed similar selectivity to unsaturated alcohols, around 30%, but using CNT2 which had much fewer carbon impurities, a

selectivity of 62% was achieved. The presence of graphitized carbon in CNT1 conferred to this catalyst a behaviour similar to the graphite-supported one, probably because the Pt particles were localized mainly on the carbon impurities, which have a flat-like morphology and not the round-shaped structure of CNTs; consequently, the carbon impurities did not produce the effect of electronic transfer of the CNTs. In this line, Qin *et al.* [119] also obtained higher selectivity using carbon nanotubes produced by CVD than using activated carbon as supports of Pt catalysts: 59% vs. 26%, respectively.

**Figure 6.** Pt catalysts supported on carbon nanotubes [118].



Functionalized carbon nanotubes have also been studied as catalyst supports similar to graphite. So, Qin *et al.* [119,120] modified carbon nanotubes by functionalization with polyacrylic acid (PAA). In this work Pt was introduced into pure and PAA grafting multi-walled carbon nanotubes (MWNTs) by electroless metal deposition method as used as catalysts for hydrogenation of citral. These catalysts exhibited higher activity when compared with Pt impregnated activated carbon catalyst, similar to previous discussed results [118]. However, a decrease in the selectivity to unsaturated alcohols from 59% for MWNTs without functionalization, to 7% for PAA grafted MWNTs, was observed. This result is related to the large amount of carboxylic groups that PAA treatment fixed on the outside of the MWNTs, which decreased the electronic effect of the support. Moreover, PAA prevented the formation of Pt {111} affecting the various product distributions obtained. The PAA treatment in the nanotube leads to better dispersion of Pt nanoparticles and, therefore, better activities, but worse selectivity towards unsaturated alcohols.

Zgolicz *et al.* [121] also functionalized carbon nanotubes by thermal and oxidative treatments. Pt and Pt-Fe catalysts supported by multi-wall carbon nanotubes were developed to study the influence of the support surface composition on the catalytic performance for the unsaturated alcohols. The citral hydrogenation was performed at 70 °C and atmospheric pressure in a discontinuous reactor using 0.3 mL of citral, 0.300 g of catalyst in 30 mL of 2-propanol. Low numbers of oxygen groups on the support surface produced an optimized Pt size. The Pt loading of the catalysts was 5 wt.% which together with the presence of Fe, yields a very high selectivity (96%) to unsaturated alcohols.

Bimetallic catalysts have also been prepared using CNT as supports. Ananthan *et al.* [122] prepared Pt, Ru and Pt-Ru catalysts over carbon nanotubes to study the effect of these bimetallic particles. They also studied the effect on the catalysts of the carbon nanotube surface chemistry by a previous functionalization of the support with nitric acid followed by two different heat treatments (375 °C and

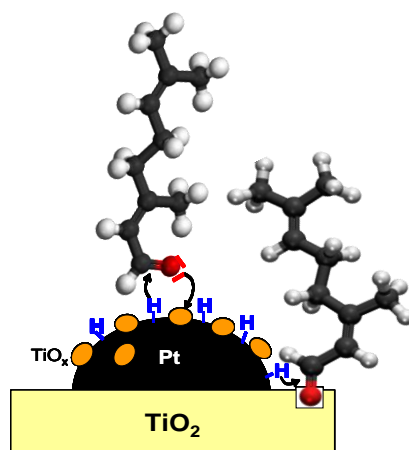
675 °C in N<sub>2</sub> flow), in order to partially remove the oxygen-containing groups from the CNT surface. The catalytic results showed that as expected the removal of oxygen-containing groups increased both activity and selectivity. In fact, the selectivity to the unsaturated alcohols reached 95% by using bimetallic catalysts, due to a close contact between Pt and Ru nanoparticles where a charge transfer could be developed from Ru to Pt atoms. Recently [123], these authors have developed Pt-Au bimetallic catalysts supported on CNT confirming the above mentioned effect of the oxygen groups on CNT, however the Pt-Ru system was more selective to unsaturated alcohols than the Pt-Au; 95% vs. 70%, respectively.

#### 4.4. Composite Materials

By attempting to combine the carbon materials and partially reducible oxide properties, new composite materials have been developed as supports for the selective hydrogenation of citral. In this line, the influence of the supports carbon-TiO<sub>2</sub> and carbon-CeO<sub>2</sub> on the deposited metal phase have been mainly studied [96,124–127].

Partilly Pt catalyst supported by reducible oxides have shown very good selectivity to C=O bond hydrogenation as it was described [78,128]. Figure 7 shows a scheme for the preferred orientation of citral when it is hydrogenated on TiO<sub>2</sub> [75], pretreated at high temperatures.

**Figure 7.** Citral being hydrogenated on Pt supported on TiO<sub>2</sub>. ● Ti<sup>3+</sup> or Ti<sup>4+</sup> species and □ oxygen vacancies and ● C=O bond [75,129].



Zhu *et al.* prepared carbon nanofibers (CNFs)–TiO<sub>2</sub> composites [125–127] as supports for Pd catalysts. In this way, TiO<sub>2</sub> was impregnated with aqueous solutions of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O or mixture of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, and then a reduction treatment at 600 °C in N<sub>2</sub>/H<sub>2</sub> (80:20) was carried out. CNFs were grown by methane decomposition at 873K for 5h, and finally, Ni and Cu particles were removed by means of a treatment with HNO<sub>3</sub> at 120 °C. A TiO<sub>2</sub> coated cordierite monolith was also prepared by a sol-gel method [126] which also was used for CNFs growing. The CNF-TiO<sub>2</sub> support contained 38% of carbon phase, which was composed by CNFs, 95%, and amorphous carbon, 5%. Pd catalyst was prepared by impregnation with an aqueous solution of PdCl<sub>2</sub> and then it was tested in the citral hydrogenation with the aim of obtaining citronellal as the main product. A commercial Pd/activated carbon catalyst (Pd/AC) was also tested for comparison.

Pd/CNF-TiO<sub>2</sub> catalyst had a very low surface area—58.1 m<sup>2</sup>/g *versus* 810 m<sup>2</sup>/g—of Pd/activated carbon. Moreover, the porosity was also very different being that Pd/CNF-TiO<sub>2</sub> is mainly mesoporous with an average pore diameter of 9.7 nm while Pd/AC was microporous with an average pore diameter of 2.1 nm. Regarding the activity and selectivity of these supports, Pd/AC was more active than Pd/CNF-TiO<sub>2</sub> (90% conversion after 4 h and 32 h, respectively) which could be explained by the higher Pd dispersion and narrow Pd particle size distribution in Pd/AC due to its larger surface area; conversely, a poorly dispersed catalyst with larger Pd particles was obtained over Pd/CNF-TiO<sub>2</sub> due to its smaller surface area which would lead to lower catalytic activity than for Pd/AC. In regards to selectivity to citronellal, considering that palladium catalysts are very active in the hydrogenation of the C=C bonds, the selectivity towards citronellal was expected to be very high in both cases, however the selectivity towards citronellal achieved with Pd/CNF-TiO<sub>2</sub> was significantly higher than Pd/AC, and particularly at high conversion (88% *versus* 35% selectivity, respectively, at 90% conversion). This result suggested that the porosity of the supports could play an important role, as explained by the following: on the catalyst external surface citral would be firstly hydrogenated to citronellal and then citronellal can be easily desorbed from Pd crystals to the solution. Inside the porosity, the product distribution should be different. If the reaction took place in the macro- and meso-pore network of the catalyst, the main products would be citronellal as they occur on the external surface because these pore sizes are wide enough to not influence product diffusions, while if the reaction took place inside the micropores, citral would also be hydrogenated to citronellal but it would be confined inside the micropores and, therefore, it would be completely hydrogenated to 3,7-dimethyloctanol. According to this explanation, at low conversions the selectivity to citronellal was similar in both catalysts due to only the external surface being involved in the reaction, however, at higher conversions, the selectivity to citronellal using Pd/AC decreased, increasing the formation of 3,7-dimethyloctanol in the microporosity of the active carbon.

Regarding the TiO<sub>2</sub> coated cordierite monolith [126], it was used to grow CNFs in order to be employed as structured supports of Pd catalyst as well. The obtained results showed a very good selectivity to citronellal which was also explained in terms of decreasing internal diffusion limitation.

On the other hand, Serrano-Ruiz *et al.* [96] dispersed ceria on a carbon Norit in order to enhance the amount and surface area of partially reducible CeO<sub>2</sub> sites which acts to improve the selectivity towards unsaturated alcohols. The composite material was prepared by impregnation of carbon (previously outgassed) with an acetic solution of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O obtaining a CeO<sub>2</sub> loading of 20 wt.%. On this support, Pt and Pt-Sn catalysts were deposited, and then, they were pre-treated at both 200 °C, and 500 °C, in order to evaluate the strong metal-support interactions effect. Bimetallic catalyst achieved higher selectivity to unsaturated alcohols than monometallic ones, increasing the selectivity parallel to the amount of Sn; however, regarding the conversion, the trends were the opposite: conversion decreased when the Sn loading increased which was ascribed to some Pt particles being able to be covered by Sn species. On the other hand, reduction treatment at 500 °C increased the selectivity to geraniol and nerol by 50% in both monometallic and bimetallic catalysts, explained by the presence of new Pt-SnO<sub>x</sub> and/or Pt-CeO<sub>x</sub> active sites. It is noteworthy that although bimetallic cluster and partially reducible oxide were used, and being well known that both favour the C=O bond hydrogenation, a selectivity to unsaturated alcohol was achieved that was not too high (35%).



Bachiller-Baeza *et al.* [124] also prepared composite materials, as supports of Ru catalysts, using Ce or Mg as promoter phases in combination with activated carbon (AC) or Al<sub>2</sub>O<sub>3</sub>. Composites were prepared by different impregnations procedures, where RuNO(NO<sub>3</sub>)<sub>3</sub> pre-impregnated supports, Ru/AC or Ru/Al<sub>2</sub>O<sub>3</sub>, were again impregnated with aqueous solutions of Ce(NO<sub>3</sub>)<sub>3</sub> or Mg(NO<sub>3</sub>)<sub>2</sub>. All the composite catalysts and Ru free supports were tested in the selective hydrogenation of citral and crotonaldehyde. Addition of MgO or CeO<sub>2</sub> decreased the hydrogenation activity. However, while MgO did not influence the selectivity, CeO<sub>2</sub> increased the selectivity to unsaturated alcohols, especially on carbon supported catalysts. Finally, the authors suggested that defects on the surface of the promoter were highly selective sites for unsaturated aldehydes hydrogenation due to their influence on the C=O bond activation.

## 5. Conclusions

Three types of carbon materials have been mainly used as catalyst supports in the selective hydrogenation of citral: activated carbons, graphite, and carbon nanotubes. In most cases, Pt was the metal supported, followed by Ru, and only a few works have been found focusing on the use of carbon composite materials in this reaction. It is noteworthy that no work has been found where carbon aerogels or xerogels were used as support, in spite of the extensive uses these materials have for very different catalyzed heterogeneous reactions. Carbon materials have shown very good performance as catalyst support for citral hydrogenation; both characteristic porosity and chemical surface can be used to modify selectivity in different ways. Moreover, very high selectivity to the unsaturated alcohols nerol and geraniol has also been reported in some cases. It should be mentioned that the amount of work discovered for citral hydrogenation is smaller than that of other  $\alpha,\beta$ -unsaturated aldehydes. Thus, we consider that it is still possible to improve the catalyst development for this reaction, which is a challenge that can be addressed with new carbon materials, such as carbon gels, carbon nanotubes or carbon fibers, or new carbon material-oxide composites, though optimizing in all cases the metal particle sizes and their distribution throughout the porosity of the supports.

## Acknowledgments

This work is supported by the MICINN-FEDER, project CTM2010-18889.

## Conflicts of Interest

The authors declare no conflict of interest.

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