SELECTIVE HYDROGENATION OF CITRAL OVER MESOPOROUS Ru/TiO_2/SiO_2 CATALYSTS

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ABSTRACT

SELECTIVE HYDROGENATION OF CITRAL OVER MESOPOROUS $Ru/TiO_2/SiO_2$ CATALYSTS

The liquid phase citral hydrogenation was investigated over Ru/SiO_2, Ru/TiO_2 and $Ru/TiO_2/SiO_2$ catalysts. TiO_2/SiO_2 supports were prepared by sol-gel deposition, impregnation and absorption methods. The effect of the supports and catalyst reduction temperature, 300 °C (LTR) and 450 °C (HTR) on citral conversion and selectivity to unsaturated alcohols were examined.

A well-defined crystalline anatase phase was only observed on the support prepared by absorption method, TiO_2/SiO_2-ABS. A high dispersion and interaction of Ru were observed over TiO_2 for Ru/TiO_2. $Ru/TiO_2/SiO_2$-ABS also displayed similar properties but to a lower extent.

$Ru/TiO_2/SiO_2$-ABS catalyst showed the highest citral conversion (57.7 %) at LTR among the different $Ru/TiO_2/SiO_2$ catalysts. Its selectivity to UA was also high (70.2 %). This was attributed to a better metal support interaction and dispersion obtained by this method. However, a selectivity of 62.6 % was obtained over Ru/TiO_2.

Activity of the catalysts was mostly observed to decrease as reduction temperature increased from 300 °C to 450 °C. Citral conversion decreased from 57.7 % to 42.3 % over $Ru/TiO_2/SiO_2$-ABS. However, selectivities to unsaturated alcohol (nerol and geraniol) over Ru/TiO_2 and $Ru/TiO_2/SiO_2$ catalysts were increased at HTR, reaching about 80 %. This was suggested to be due to more interaction of TiO_2 with the Ru (strong metal support interaction). There was no significant change in the selectivity to UA obtained at HTR for Ru/SiO_2. This was related to the inert nature of SiO_2.

ÖZET

SİTRAL'İN MEZOGÖZENEKLİ Ru/TiO_2/SiO_2 KATALİZÖRLE SEÇİMLİ HİDROJENASYONU

Sitral'in sıvı fazda hidrojenasyonu, SiO_2, TiO_2 ve TiO_2/SiO_2 destek malzemeleri üzerine yüklenmiş Ru (2 ağ.%) katalizörü kullanarak yarı-kesikli reaktörde gerçekleştirilmiştir. Destek malzemesinin hazırlama methodunun (sol-gel, emdirme ve absorpsiyon) ve katalizör indirgeme sıcaklığının (300 °C (düşük indirgeme sıcaklığı) veya 450 °C (yüksek indirgeme sıcaklığı)) sitral dönüşümü ve doymamış alkollerin seçiciliğine etkisi incelenmiştir.

Anataz kristal fazı absorpsiyon methodu ile hazırlanan destek malzemelerinde (TiO_2/SiO_2-ABS) olduğu görülmüştür. Ru atomunun en iyi dağılım ve etkileşimi Ru/TiO_2 katalizörü üzerinde gözlenmiştir. Ru/TiO_2/SiO_2-ABS katalizörü de daha düşük seviyede de olsa benzer etkileşimler göstermiştir.

Farklı TiO_2/SiO_2 destek malzemeleri arasından en yüksek fruktoz dönüşümü Ru/TiO_2/SiO_2-ABS katalizörü ile elde edilmiştir. Doymamış alkol seçiciliği de yüksek (70.2 %) bulunmuştur. Bunun nedeni de, bu methodun daha iyi metal ve destek malzemesi etkileşimi ve dağılımı sağlamasıdır. Buna karşın, Ru/TiO_2 doymamoş alkollere 62.6 % seçıcilik göstermiştir.

İndirgenme sıcaklığının artmasıyla (300 °C'den 450 °C'ye) katalizör aktivitesin genelde düştüğü gözlenmiştir. İndirgenme sıcaklığı artışı, citral dönüşümünü Ru/TiO_2/SiO_2-ABS üzerinde % 57.7'den % 42.3'e düşürmüştür. Bunun yanında, nerol ve geraniol gibi doymamış alkollere olan seçicilik Ru/TiO_2 ve Ru/TiO_2/SiO_2 katalizörleri üzerinde artarak 80 % çıkmıştır. Bu Ru ve TiO_2 arasındaki etkileşimin artmasına bağlanmıştır (güçlü metal ve destek malzemesi etkileşimi). Ru/SiO_2 katalizörü, doymamış alkollere seçicilikte yüksek indirgenme sıcaklığında önemli bir değişim göstermemiştir. Bu sonuçta SiO_2' nın Ru ile etkileşiminin olmadığını göstermiştir.

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CHAPTER 1

INTRODUCTION

Hydrogenation is the chemical reaction of hydrogen with another substance, especially with an unsaturated organic compound, and usually under the influence of temperature, pressure and catalysts. Important applications of hydrogenation are found in petrochemical, pharmaceutical and food industries. The hydrogenation of α,β-unsaturated aldehydes is an industrially important route to unsaturated alcohols (UA) yielding valuable fine chemicals for producing perfumes, pharmaceuticals, and flavoring materials (Lim et al. 2009). In principle these compounds can be selectively hydrogenated by using homogeneous catalysts, but the use of heterogeneous catalysts in the fine chemistry industry is expanding daily for many advantage reasons, such as its alternative environmentally friendly catalytic processes in which catalysts are separated easily and reused after reaction (Nieto et al. 2006). Selective hydrogenation of α,β-unsaturated aldehydes to UA is great challenge since C=C bond is thermodynamically favored over the hydrogenation of C=O bond. Citral (3,7-dimethyl-2,6-octadienal) has three unsaturated bonds including conjugated C=C and C=O bonds as well as an isolated C=C bond.

Many investigations have been carried out for developing suitable heterogeneous catalyst for selective hydrogenation of citral to unsaturated alcohol (nerol, geraniol). Various catalysts, such as Pt/SiO_2 (Singh et al. 2001), Pt/Na-Y (Aykaç et al. 2008), Rh/TiO_2 (Ekou et al. 2006), Ru/C (Galvagno et al. 199), Ir/TiO_2 (Rojas et al. 2008), Rh/Al_2O_3 (Lafaye et al. 2002) and Pd/Clinoptilolite (Yilmaz et al. 2005) have been tested for this reaction. As active component, Ir and Os are selective to unsaturated alcohol, while Pd, Rh, and Ni are little selective or unselective, whereas Pt, Ru, and Co are moderately selective (Gallezot et al. 1998). Ruthenium, which is one of the most inexpensive noble metals, has shown to be active in hydrogenation of α,β-unsaturated aldehydes, but it has moderate selectivity towards the unsaturated alcohols (Rodríguez et al. 2012). Ru is selected as active component for the catalyst to be developed in this study.

Promoter additions such as Ge and Sn also were found to increase selectivity (Silva et al. 2003 and Ekou et al. 2006). High selectivity to unsaturated alcohols can be arranged by using promoters in bimetallic catalysts. Where, promoters are present as the surface electron-acceptor species acting as adsorption sites coordinating the oxygen atom of the substrate. Furthermore, catalyst preparation methods (Ekou et al. 2011), calcination and reduction temperatures (Silva et al. 2003, Malathi et al. 2001, Rojas et al. 2008, Ekou et al. 2011 and Ekou et al. 2006) were also shown to influence catalyst activity and selectivity.

Metal support interaction has been also shown to effect to increase selectivity to UA, which is associated with reducible oxide supports like TiO_2 (Claus et al. 1997). Titania has attracted much attention during the past 30 years, due to the strong metal-support interaction (SMSI) occurring on the surface of TiO_2. This modifies the catalytic activity and selectivities for different reactions including selective hydrogenation reactions (Rojas et al. 2008 and Ekou et al. 2011). It was found that such effect was primarily due to migration of reduced TiO_x species over the metal surface making special sites at the metal-support interface. These sites would interact with the oxygen atom in the carbonyl group thereby activating the C=O bond. However, TiO_2 has low surface area.

Mesopoure structure of SiO_2 will increase the surface area and minimize diffusion resistances of TiO_2. Creating TiO_2/SiO_2 supported oxides as advanced support materials in which alternative for pure TiO_2, combines the advantage of TiO_2 property; active catalytic support, and SiO_2 properties; good mechanical strength, high surface area and high thermal stability. TiO_2/SiO_2 support by different methods will be prepared for this study. Different catalyst reduction temperatures will be tested to assess the interaction of Ru with different supports.

In this study, it is aimed to develop Ru supported TiO_2/SiO_2 catalysts for selective hydrogenation of citral to unsaturated alcohol. TiO_2/SiO_2 supports are prepared by sol gel deposition, impregnation and absorption methods. Ru (2%) will be loaded by impregnation method. Catalysts will be characterized with different characterization techniques. Effect of TiO_2/SiO_2 supports preparation and catalyst reduction temperature (300 and 450 ^{o}C) on the formation of UA will be examined.

CHAPTER 2

HYDROGENATION

2.1. Hydrogenation Reactions

Hydrogenation is the chemical reaction of hydrogen with another substance, especially with an unsaturated organic compound, and usually under the influence of temperature, pressure and catalysts. Because of the importance of hydrogen, many related reactions have been developed for its use. Important applications of hydrogenation are found in petrochemical, pharmaceutical and food industries. Hydrogenation has three components, the unsaturated substrate, the hydrogen (or hydrogen source) and a catalyst. Pd, Ni, Rh, Ru, Pt, Ir, Os, and Co as pure bulk metals or dispersed on various carriers are the most catalysts for the heterogeneous reduction reactions (Johnstone et al. 1985). The reduction reaction is carried out at different temperatures and pressures depending upon the substrate and the activity of the catalyst.

2.2. Hydrogenation of α-β Unsaturated Aldehydes on Metal Catalysts

The hydrogenation of α,β-unsaturated aldehydes is an industrially important route to unsaturated alcohols (UA) yielding valuable fine chemicals for producing perfumes, pharmaceuticals, and flavoring materials (Lim et al. 2009). Mostly saturated aldehydes are obtained by reduction of the C=C group or to saturated alcohols during the hydrogenation of α,β-unsaturated aldehydes in the presence of most of the conventional group VIII metal hydrogenation catalysts. Therefore, it is necessary to create catalysts which prefer the selectivity of hydrogenation the C=O group while keeping the C=C double bond intact (Figure 2.1. reaction 1 vs. 2). Moreover, successive hydrogenations to the saturated alcohol (reactions 3 and 4) and the isomerization of the allylic alcohol (reaction 5) must be suppressed by the catalyst (Claus et al. 1998).

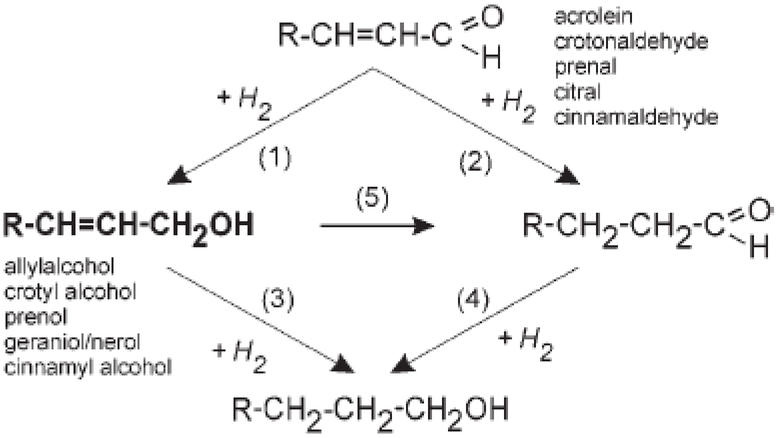
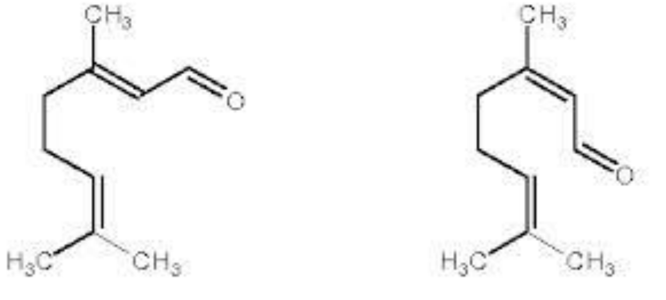


Figure 2.1. Scheme of the reaction pathways in the hydrogenation of α,β-unsaturated aldehydes (Source: Claus et al. 1998).

2.3. Citral and Citral Hydrogenation

Citral ($C_{10}H_{16}O$), is α,β-unsaturated aldehyde, also called 3,7-dimethyl-2,6-octadienal, a pale yellow liquid, with a strong lemon odor, that occurs in the essential oils of plants. It is insoluble in water but soluble in ethanol (ethyl alcohol), diethyl ether, and mineral oil. It is used in perfumes and flavorings and in the manufacture of other chemicals. Chemically, citral is a mixture of two aldehydes (cis (neral) and trans (geranial) isomers) that have the same molecular formula but different structures (see Figure 2.2).



Geranial (trans isomer) Neral (cis isomer)

Figure 2.2. Cis and trans isomers for citral.

Citral has three sites of hydrogenation; the conjugate double C=C bond, the carbonyl group C=O bond and the isolated double C=C bond. Figure 2.3 presents the reaction pathways that can occur to form intermediate compounds during citral hydrogenation.

The hydrogenation of the citral C=O functional group is of great interest to form (cis and trans) unsaturated alcohol (UA) i.e. nerol and geraniol (3,7-dimethyl-6-octen-1-ol), where these unsaturated alcohols are the most valuable products have been employed in the production of flavors, fragrances, insect repellants and in the synthesis of other compounds such as acetate and isobutyrate derivatives. Citronellal (3,7-dimethyl-6-octenal) is obtained by the selective hydrogenation of the conjugated C=C bond and citronellol (3,7-dimethyl-6-octen-1-ol) can be obtained by the selective hydrogenation of the citronellal C=C group or from the C=O bond of nerol and geraniol. These two compounds (citronellal and citronellol) are used in soaps, detergents, perfumes and insect repellants (Kirk-Othmer Encyclopedia of Chemical Technology 4th Edition, 1992). 3,7-dimethyl-octanol is obtained from the hydrogenation of the isolated C=C bond and it is not desirable compound since it give an unpleasant odor to the nerol-geraniol, citronellal and citronellol mixtures. Apart from these main reactions, secondary processes of cyclization where citronellal can cyclized to isopulegol, an intermediary product used in the synthesis of (±)-menthol, or of reaction with the solvent (alcohol) where acetals can be formed (Bertero et al. 2009, Ekou et al. 2012).

The hydrogenation of the carbonyl group C=O is thermodynamically less favored than the hydrogenation of double C=C bonds, since the bond energy of a C=O double bond is about 715 kj/mol, compared with the C=C double bond energy of about 615 kj/mol (Noller et al. 1984). This make conventional hydrogenation catalysts based on noble metals, such as Pt, Ir, Ru, and Rh (which are very active for these reactions), are not able to control the intramolecular selectivity by favoring the hydrogenation of the C=O instead of the C=C bond (Martinez et al. 2008).

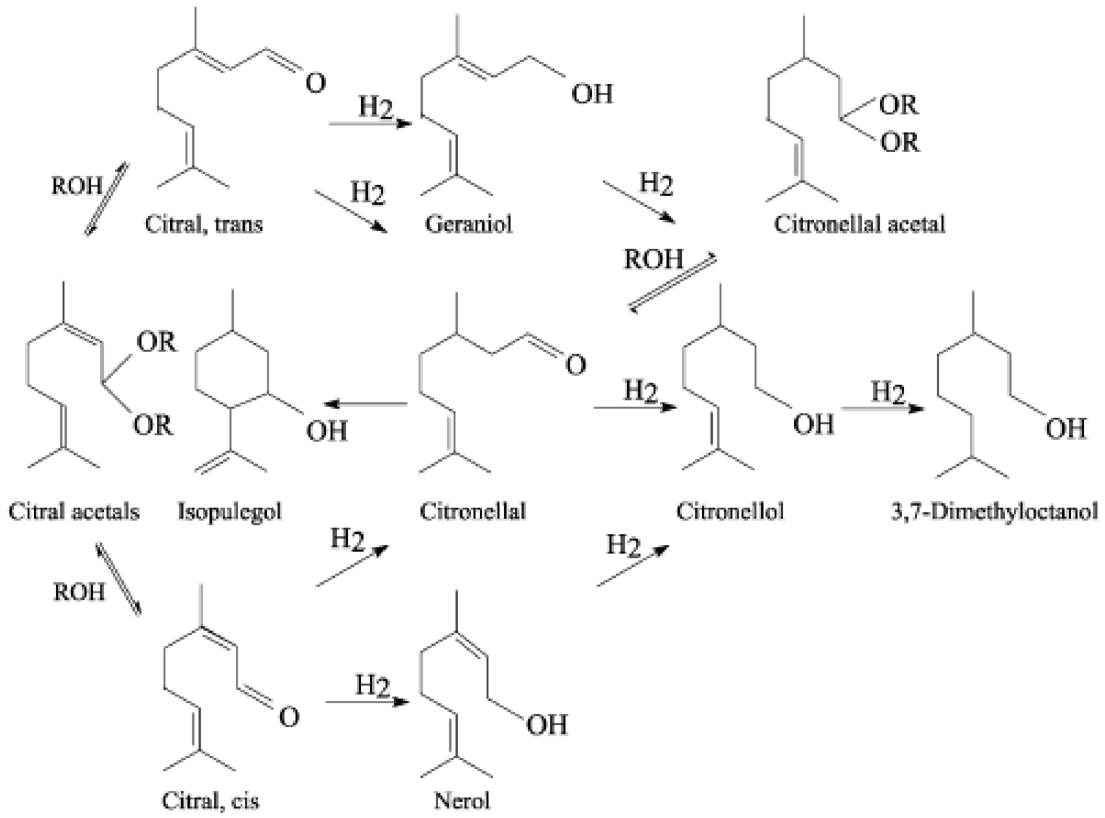


Figure 2.3. Reaction scheme for citral hydrogenation
(Source: Mäki-Arvela et al. 2003).

2.4. Studies on Selective Hydrogenation of α,β-Unsaturated Aldehydes

Many investigations have been pursued and focused for developing the suitable catalytic system based on single and two-metal catalysts supported on different materials. Zeolite, alumina, silica, activated carbon, graphite, and TiO_2 were used as supports to improve the yields and the selectivity of unsaturated alcohol during the hydrogenation of α,β-unsaturated aldehydes; mostly crotonaldehyde, cinnamaldehyde and citral. Many factors that influence the catalytic performance such as the nature of the individual metal, support, electron-donating or withdrawing ligand effects by the catalyst support material, i.e., Strong Metal Support Interactions (SMSI), presence of a second metal which can form an alloy with the basic metal or operate as cationic promoter (bimetallic catalysts), and other parameters like metal particle size catalyst, preparation method and activation. All these factors are studied on α,β-unsaturated aldehydes hydrogenation reactions catalyzed by monometallic and bimetallic catalysts.

2.4.1. Nature of the Active Metal

Hydrogenation activities and selectivities can be affected by the different geometric and electronic properties of metals used. In the conventional monometallic catalysts the metals are selected from the group 10 in the periodic table, for example, Ni, Pd and Pt, or Rh and Ir from group 9 and Ru from group 8 have been used as catalysts, usually supported on silica, alumina, carbon and TiO_2 (Mäki-Arvela et al. 2005).

The catalytic activity of different metal supported catalysts in hydrogenation is determined by ability to activate C=C and C=O bonds as well as the activity of hydrogen to react on the metal surface. These metals have specific selectivities to unsaturated alcohols, where iridium and osmium are selective to unsaturated alcohol, while palladium, rhodium, and nickel are little selective or unselective, whereas platinum, ruthenium, and cobalt are moderately selective (Gallezot et al. 1998).

Deldecq et al. (1995) showed that good selectivity to unsaturated alcohol was achieved with Os, Ru, and Co, while Rh, Ni, and Pd were poor selective. They used theoretical calculations correlated the difference in the selectivity to UA on these metals to their width of the *d*- bands. They suggested larger the band, the stronger the four-electron repulsive interactions with the C=C bond and the lower the probability of its adsorption. *d*- band width increases in the following order Pd < Pt < Ir, Os, in agreement with the UA selectivities classification.

The hydrogenation of citral over Pd (2.42%) supported on clinoptilolite rich natural zeolite was studied by Yilmaz et al. (2005). Pd catalyst (Pd/NZ) was prepared by impregnation of the support with methanol solution of $Pd(NO_3)_2.2H_2O$. The sample was dried overnight at 120 °C, calcined at 430 °C for 2.5 h and reduced in situ under H_2 flow for 2.5 h at 400 °C. Reaction was carried out in ethanol at different temperatures (80, 100, 120°C) under 6 bar H_2 pressure. They found that catalyst mostly hydrogenated the conjugated C=C bond and high selectivity to citronellal (82%) was obtained for an overall citral conversion of 99.5%. While catalyst showed very poor activity for the hydrogenation of the isolated C=C and C=O bonds (Figure 2.4).

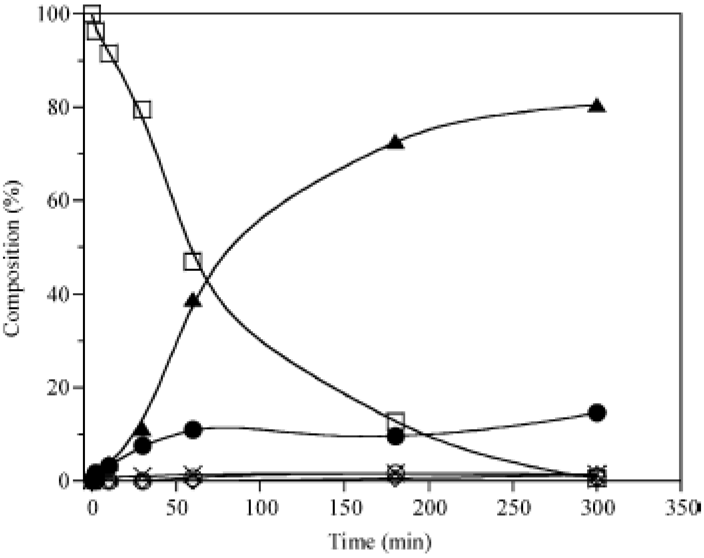


Figure 2.4. Product distribution over Pd/NZ catalyst with 250 mg cat. at 80°C. Citral (☐), citronellal (▲), citronellol (◇), isopulegol (○), nerol + geraniol (×), citronellal acetal (●) (Source: Yilmaz et al. 2005).

In study done by Neri et al. (1994), hydrogenation of citral done over Pt/C catalyst gave selectivity to the isomers geraniol and nerol about 65%, which is significantly higher than that (35%) previously obtained on Ru dispersed on the same carbon support (Galvagno et al. 1993).

2.4.2. Effect of Promoter

The C=O bond is always less easily hydrogenated than the isolated C=C bond. High selectivity to unsaturated alcohols can be arranged by using promoters in bimetallic catalysts. Where promoters are present as the surface electron-acceptor species acting as adsorption sites coordinating the oxygen atom of the substrate. Many studies investigated the effect of promoters, extensively using Ge and Sn, on the activity and selectivity during the hydrogenation of citral.

Vicente et al. (2011) studied the influence of adding Sn to the monometallic Pd/SiO_2 catalyst on the selective hydrogenation of citral to unsaturated alcohol performed at 130°C under 70 bar H_2 pressure and isopropanol was used as solvent. Monometallic catalysts were prepared by wet impregnation using solution of $Pd(acac)_2$ as Pd precursor. Bimetallic catalysts were prepared by successive impregnation where $SnBu_4$ solution was used as Sn precursor. Both monometallic and bimetallic catalysts were dried overnight at 120 °C, calcined in air at 300 °C for 2 h and then reduced under the flow of H_2 at 300 or 500°C for 1 h. They found that monometallic catalyst was very selective for the formation of C=C hydrogenated products, and these results were compatible with the results obtained by Yilmaz et al. (2005). Low addition of Sn content modifies the conversion of the corresponding monometallic catalyst, and for the high Sn contents the conversion drops dramatically to approximately 10% (Figure 2.5.a). Modification of Pd/SiO_2 by Sn favored the formation of nerol and geraniol (UA), >75% selectivity to UA at 30% conversion (Figure 2.5.b). They proposed Pd site modified by the presence of Pd_3Sn alloy providing new sites able to activate C=O bond of citral.

High selectivity to unsaturated alcohol on the bimetallic catalysts was explained the geometric and electronic modification of Pd by Sn. Figure 2.6 presents schematic views of the bimetallic particles of the Pd–Sn/SiO_2 systems reduced at 300°C according to the Sn content. Low Sn content 1 wt% (Figure 2.6a), catalyst showed low selectivity for C=O hydrogenation (S_{UA} = 13% at 30% citral conversion). Characterization techniques revealed that to the presence of some Pd_3Sn entities but rather very limited. Samples with %Sn ≥1.5 wt%, all the Pd atoms are in a Pd_3Sn alloy phase (Figure 2.6b), which maximize the selectivity to UA (S_{UAmax} = 82% at 30% citral conversion for Sn = 1.5 wt%), but inducing a negative effect on the activity. The oxidized form of Sn ($Sn^{\delta+}$) also contribute to activate C=O bond. These oxidized species increase as the Sn content. Increasing the Sn content to 2wt% (Figure 2.6c), a slight decrease in the unsaturated alcohol selectivity (S_{UA} = 77% at 30% citral conversion for Sn=2 wt%). This contributed to the increment of $Sn^{\delta+}$ species which block part of the Pd_3Sn alloy active surface.

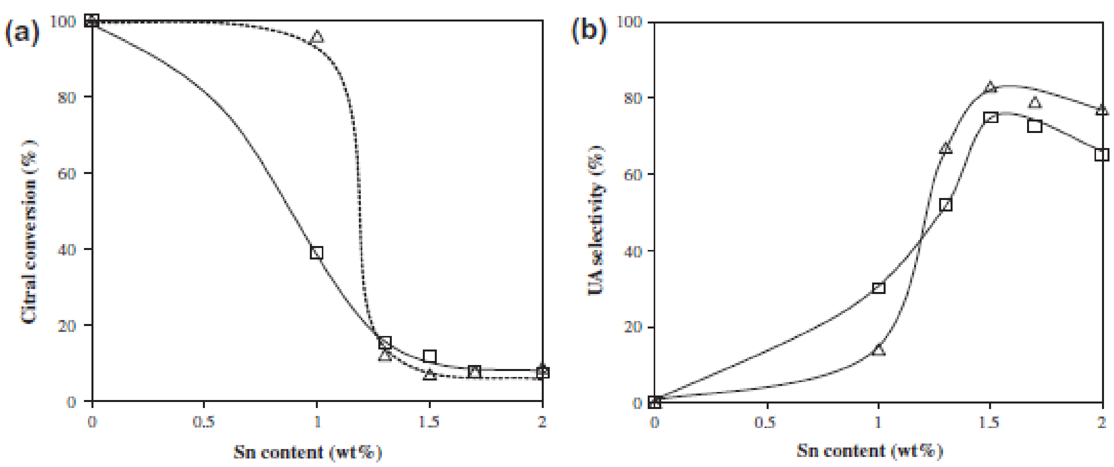


Figure 2.5. (a) Citral conversion after 1 h reaction time and (b) unsaturated alcohols (UA) selectivity at 30% citral conversion as a function of Sn content for 1wt%Pd–*x*wt% Sn/SiO_2 bimetallic catalysts: (△) reduced at 300°C, (☐) reduced at 500°C (Source: Vicente et al. 2011).

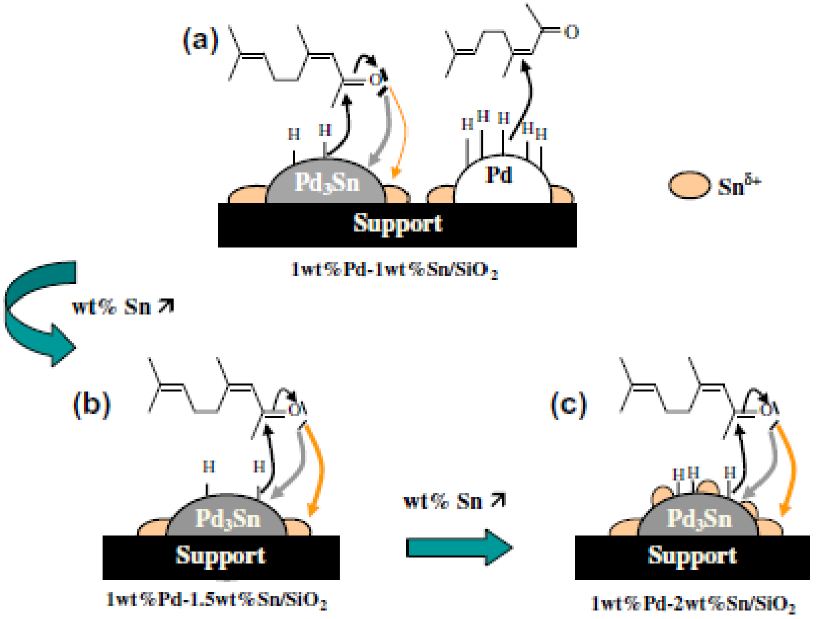


Figure 2.6. Shematic representation of the adsorption modes of citral molecule on Pd–Sn/SiO_2 bimetallic catalysts depending on the Sn content (Source: Vicente et al. 2011).

Also the average particle sizes determined by TEM for the bimetallic catalysts was noted to be lower than that of monometallic one. Thus, the presence of Sn allows to maintain Pd in a more divided state on silica support, because Sn species dispersed on the silica support hinder the mobility of Pd particles, and as a result, lower sintering effect after high temperature reduction on bimetallic catalysts.

Hydrogenation of citral over Ru-Sn supported on activated carbon was studied by Galvagno et al. (1993). Reactions were carried out at 60 °C reaction temperature, 1 atmospheric H_2 pressure and ethanol was used as solvent. Catalyst were prepared by incipient wetness impregnation of activated carbon with aqueous solutions of $RuC1_3$ and $SnC1_2$. Then catalysts were dried at 120 °C and reduced at 300 °C for 1 h under flowing H_2.

They investigated the influence of adding Sn to Ru/C on the selectivity to unsaturated alcohol. Selectivity to geraniol and nerol was increased with the addition of tin from about 35 up to 80 % at a conversion level of 30% (Figure 2.7). They proposed that the presences of tin ions polarize the carbonyl group and facilitating the hydrogen transfer from adjacent Ru site. On the other side, selectivities to products formed by hydrogenation of the conjugated C=C double bound (citronellal and isopulegol) was decreased. In term of conversion, addition of Sn decreased the catalytic activity by poisoning the Ru surface sites.

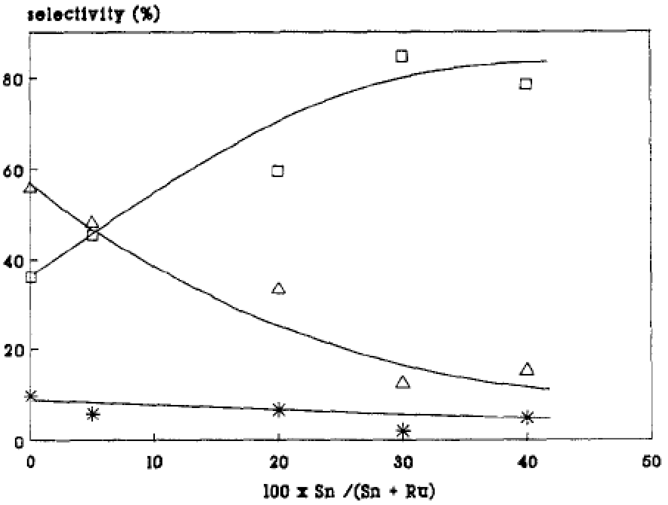


Figure 2.7. Hydrogenation of citral. Influence of the Sn/Ru ratio on the products selectivity. (☐) Geraniol + nerol, (△) citronellal + isopulegol, (✱) citronellol. Selectivity values have been measured at a conversion level of 30% (Source: Galvagno et al. 1993).

Neri et al. (1994) studied the hydrogenation of citral on a Pt-Sn catalyst prepared by incipient wetness impregnation of activated carbon where an aqueous solution of H_2PtCl_6 and $SnCl_2$ were used as precursors. The amount of Pt was kept constant at 2 wt% whereas the Sn content was varied between 0 and 0.82 wt%. Catalysts were dried at 120 °C and then reduced under H_2 at 300 °C. Citral hydrogenation was carried out at 60 °C, atmospheric pressure under H_2 flow in a 100 cm^3 and ethanol was used as solvent. In bimetallic catalysts, they found that the activity increased to about fivefold as the percentage of tin increased from 0% to 20 atomic% Sn/(Sn+Pt) and then decreased at higher Sn content. It was reported that addition of Sn modified the reaction selectivity, shifting the distribution of the products towards the formation of higher amounts of unsaturated alcohols, where the selectivity to unsaturated alcohol (measured at a citral conversion of 50 %) increased with Sn content from 65% to 90% (Figure 2.8). In all investigated catalysts, selectivity to unsaturated alcohols was remained constant within the range of conversion 10-80 % (Figure 2.9). This, the production of unsaturated alcohols was obtained by a parallel pathway which confirms a reaction scheme. Selectivity to citronellal decreased slightly with conversion whereas a parallel increase in the selectivity to citronellol was observed. It suggested that, in the first stage of reaction, citronellol was formed mainly through the reduction of citronellal.

They postulated the mechanism scheme as shown in Figure 2.10 shows. The substrate was adsorbed through the carbonyl on active sites. It was activated by interaction with Sn^{n+} ions, whereas metallic platinum provided the active hydrogen. Hydrogen chemisorbed on noble metal could be considered nucleophilic in nature. Therefore it reacted more easily with the activated carbonyl group to give unsaturated alcohol.

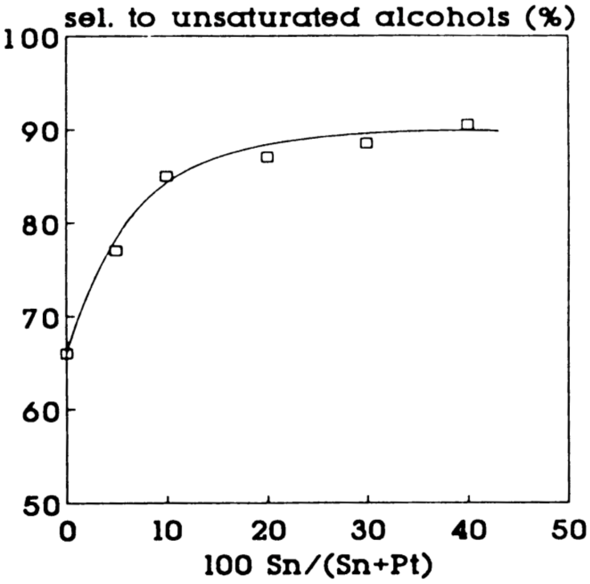


Figure 2.8. Influence of the Sn/Pt ratio on the selectivity to unsaturated alcohols (geraniol + nerol) (Source: Neri et al. 1994).

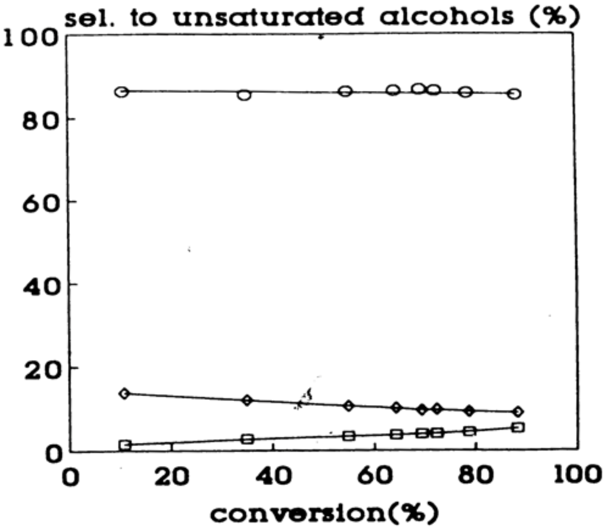


Figure 2.9. Influence of citral conversion on the products selectivity. (○) Geraniol + nerol, (◇) citronellal, (□) citronellol (Source: Neri et al. 1994).

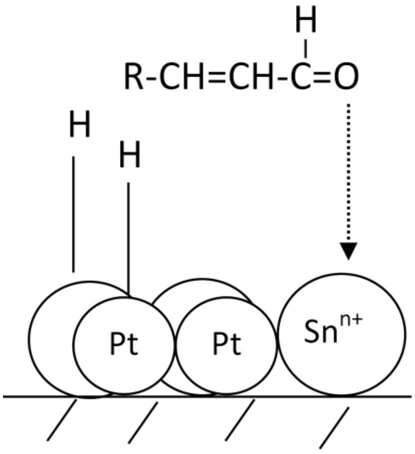


Figure 2.10. Mechanism for adsorption of citral through the carbonyl group on active sites (Source: Neri et al. 1994).

In a study by Zgolicz et al. (2011), Pt and PtSn catalysts supported on commercial Al_2O_3 and $MgAl_2O_4$ (prepared by using co-precipitation method) were used for citral hydrogenation under mild reaction conditions of 70 °C, atmospheric pressure of H_2 and 2-propanol was used as solvent. Monometallic Pt catalysts (5 wt%) were prepared by impregnation with an aqueous solution of H_2PtCl_6. Bimetallic catalysts were produced by successive impregnation of the monometallic ones with a hydrochloric solution of $SnCl_2$. Both monometallic and bimetallic catalysts were dried overnight at 120 °C, calcined at 500 °C for 3 h and reduced under H_2 at 500°C for 3 h. It has been found that selectivity to unsaturated alcohols was enhanced for both catalysts series when the Sn added to the Pt. At 3 wt% of Sn content and 95% conversion, the selectivity to UA for the $PtSn/Al_2O_3$ catalyst reached 88 % while for $PtSn/MgAl_2O_4$ catalyst was lower (65 %). Furthermore, increasing the amounts of Sn (4 wt%) to $Pt/MgAl_2O_4$ did not increase significantly the selectivity to UA (73 %). They suggested that, a fraction of ionic Sn would be deposited near Pt, thus increasing the polarization of the carbonyl group, and a fraction of metallic Sn could form Pt–Sn alloy phases that would hinder the hydrogenation of the olefinic bonds and would be active to the hydrogenation of the carbonyl group. In the terms of activity, different catalytic behaviors when the amounts of Sn increased explained by the presence of different species of Sn (ionic, zerovalent), which could be intercalated among Pt atoms and could be partially blocking them in a different proportion.

Lafaye et al. (2002) investigated the effect of adding Ge on the activity and selectivity of Rh supported on both SiO_2 and Al_2O_3 during the hydrogenation of citral. Bimetallic catalysts were prepared by surface redox reaction (Catalytic Reduction Method, CR) btween hydrogen activated on rhodium, came from the activation of pre-reduced parent catalyst with pure hydrogen, and the solution of Ge precursor ($GeCl_4$) previously degaased under hydrogen flow. The catalysts were dried overnight at 120 °C and reduced at 300 °C for 1 h. Reaction was carried out at 70 bar and 70 °C in isopropanol.

Addition of Ge to Rh improved the selectivity to unsaturated alcohol, and it was more significant on the alumina support, where the selectivity to nerol and geraniol increased from 3 to 78 % while Ge loading changed from 0 to 4.0 wt.% at 50 % citral conversion. This was not only attributed to the colse contact between Ge and Rh (as in silica support), but also to the depositon of Ge on the alumina in the close vicinity of Rh particles, where these Ge species would be partially reduced during the reduction step and would promote the activation of the carbonyl group for hydrogenation.

The effect of Ge addition has been also investigated by Ekou et al. (2012). They studied the selective hydrogenation of citral to unsaturated alcohol over mesoporous Pt/Ti–Al_2O_3 catalysts for two reduction temperatures of 300 °C and 500 °C. The addition of Ge was performed by surface redox reaction. H_2PtCl_6 was used as platinum source. The reaction was carried out at 70 °C, under 70 bar hydrogen in isopropanol. Variation of conversions and selectivities over catalysts containing different Ge amounts is given in the Figure 2.11. Addition of Ge increased the selectivity to unsaturated alcohol (geraniol and nerol) from 5 to 50 % by increasing the Ge content from 0 to 2wt% respectively. It was proposed that the presence of oxidized Ge species onto the platinum or in its close vicinity promotes the activation of the carbonyl function by fixing selectively the oxygen atoms of the C=O group. In addition to the increasing of selectivity to unsaturated alcohol, the Ge addition to the Pt/10%Ti-Al_2O_3 catalyst reduced at 300◦C decreased catalytic activity progressively. This was related to poisoning of Pt by increaseing Ge content where conversion decreased from 60 to 10% by increasing the Ge content from 0 to 2.5wt.% respectively.

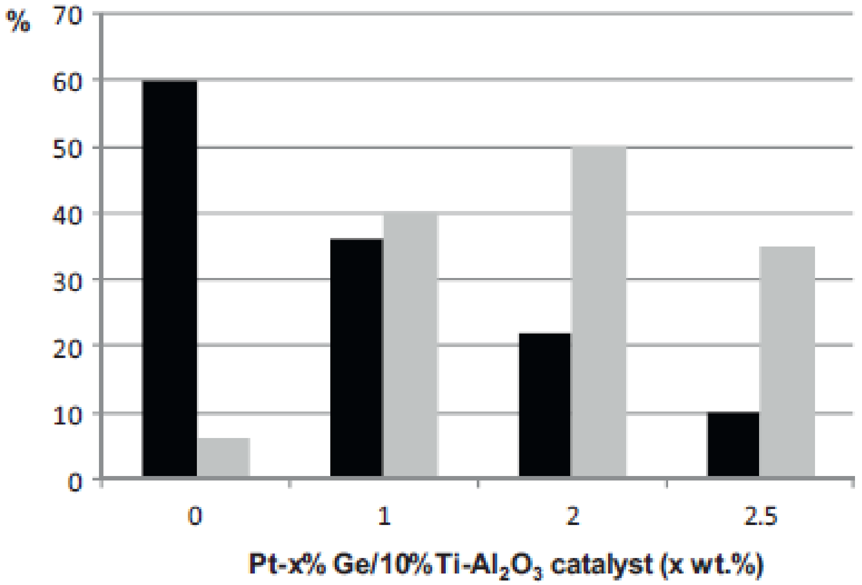


Figure 2.11. Citral conversion after 60 min reaction time (black) and selectivity to unsaturated alcohols at 40% citral conversion (grey) on the 1.0 wt.% Pt–x wt.% Ge/10%Ti–Al_2O_3 bimetallic catalysts reduced at 300 ◦C (Source: Ekou et al. 2012).

2.4.3. Effect of Support

Dispersion of the active metal is the main task for the support, because usually high dispersion produced small metal particles which are more active in activating organic molecules. The most conventional supports are acidic like Al_2O_3 and zeolite or basic oxides like SiO_2 and MgO or reducible oxide like TiO_2 and different types of carbons like activated carbon and graphite. Supports can have very different properties, like specific surface areas ranging from very low 10 to ca. 1200 m^2/gcat or even higher, pore volumes, acidities, electronic and geometrical properties. In terms of their reactivity, supports can be either inert or non-inert. Non-inert ones can form an alloy with the metal or segregate on the metal surface via forming partially reduced groups, like TiO_x (Mäki-Arvela et al. 2005).

G. Neri et al. (1994) studied the hydrogenation of citral over Ru supported catalysts. Where different supports (silica, alumina, and activated carbon), Ru precursors (Ru(acac)$_{3,}$ Ru(NO)$(NO_3)_3$ and $RuC1_3$) and solvents (ethanol and cyclohexane) were used. All the catalysts derived from Ru(NO)$(NO_3)_3$ and $RuC1_3$ were prepared by incipient wetness impregnation of the supports with the appropriate aqueous solution, only catalyst derived from ruthenium acetylacetonate ($Ru(acac)_3$) was prepared by contacting the support with a toluene solution of the precursor. After drying for 2 h at 120 °C in air, the catalysts were reduced for 2 h at 350°C and the reactions were done under 1 atm pressure of H_2 flow and 60°C.

Under the experimental conditions, the products distribution was found to be influenced by the nature of support used (Table 2.1). Ru/SiO_2 catalysts (samples RuC2/S and RuNI2/S prepared from $RuC1_3$ and $Ru(NO)(NO_3)_3$ respectively) showed a behavior similar to Ru/$A1_2O_3$ catalysts prepared from the same precursors (RuC1 and RuNI1). Sample RuC2/S produced mainly the acetals of citronellal, whereas citronellal is the main reaction product on sample RuNI2/S with the production of citronellol by the further hydrogenation of citronellal. On sample RuC2/C (Ru/C prepared from $RuC1_3$) the addition of hydrogen gives a mixture of unsaturated alcohols, citronellal, acetals of citronellal and isopulegol.

They confirmed that the supports did not catalyze the formation of acetals or isopulegol, where acetals were obtained on the acid sites formed by interaction of the chloride ions (derived from the Ru precursor used) with the surface of the support. Furthermore, the large amounts of unsaturated alcohols obtained over RuC2/C catalysts were attributed to the presence of iron impurities (about 1000 ppm) which are known to improve the selectivity to UA.

Table 2.1. Hydrogenation of citral in ethanol solution over Ru supported catalysts (Source: Neri et al. 1994).

Catalyst code	Maximum Yield				
	citronellal	UA	acetals	isopulegol	citronellol
RuC1	< 3	8	70	< 1	5
RuNI1	50	10	< 1	< 1	68
RuC2/S	< 3	12	50	< 1	15
RuNI2/S	58	4	< 1	< 1	55
RuC2/C	9	30	16	9	40

Effect of supports on the products distribution for the hydrogenation of citral was also investigated by Aykaç et al. (2008). Pt and Pt-Sn supported on Na-Y (Zeolyst) and Clino (Clioptilolite rich natural zeolites) were tested. Monometallic and bimetallic catalysts were prepared by impregnation and coimpregnation. Platinum (II) acetyl acetonate and $SnCl_2.2H_2O$ were used as precursors. Catalysts were dried overnight at 120 °C, calcined at 500 °C under dry air flow for 5 h and reduced in situ at 400 °C for 2 h under the flow of H_2 at 4 bars. The reactions were carried out in ethanol at 6 bars hydrogen pressure and 80°C with stirring rate of 600 rpm.

They found that the main products formed over Pt/Na-Y were citronellal (19.2%), citronellol (3.9%), unsaturated alcohol (14.1%), and acetals (6.4%). While the maximum yield of unsaturated alcohol was about 5.1% over Pt/Clino and larger amounts of citronellal and acetal were formed compared to Pt/Na-Y catalyst. The difference in the acetal formation between Pt/Clino and Pt/Na-Y was attributed to the acidity of the catalysts, where acetalization is an acid catalyzed reaction. Clino was much more acidic than Na-Y as confirmed by the NH_3-TPD analysis.

Moreover more metal support interaction was found on Na-Y than on Clino as proved from the TPR analysis, where results showed that Pt was reduced at higher temperature on Clino than on Na-Y. So they suggested that the higher selectivity to unsaturated alcohol obtained with Pt/Na-Y might be resulted from the change in the electron distribution on the active metal caused by the Pt - Na-Y interaction.

Catalytic performance of bimetallic Rh-Ge catalysts on different supports SiO_2 and Al_2O_3 was investigated in the hydrogenation of citral by Lafaye et al. (2002). The monometallic catalysts for different supports were prepared by ion exchange method, calcined for 4 h at 300 °C and reduced for 4 h at 500°C, while the bimetallic catalysts were prepared by surface redox reaction and reduced under hydrogen flow at 300°C for 1h. 800 mg of catalyst was used in the reaction, and the reactions were carried out at 70 °C and under 70 bar H_2 pressure in isopropanol.

For the same Ge content in the solution, the amount of Ge deposited on Rh/Al_2O_3 was greater than Rh/SiO_2 catalyst because Ge deposition occurs on both Rh particles and Al_2O_3 support which was able to adsorb a part of the dissolved Ge salt, contrary to the SiO_2 support, where Ge was deposited only on Rh (Figure 2.12).

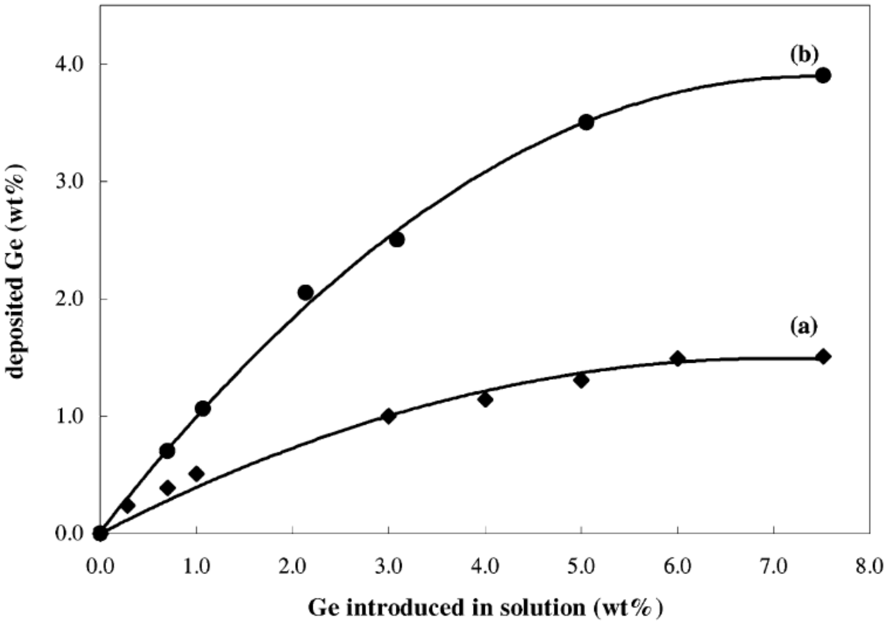


Figure 2.12. Wt.% Ge deposited by catalytic reduction over Rh/SiO_2 (a; ◆) and Rh/Al_2O_3 (b; ●) catalysts as a function of the wt.% Ge introduced in solution (Source: Lafaye et al. 2002).

Sintering of metal particles was observed over Rh/SiO_2 catalyst, where the hydrogen adsorbed on metal particles promote the sintering. This phenomenon was less for Rh/Al_2O_3 catalyst. The same explanation was suggested by Vicente et al. (2011) when SiO_2 was used as support in Pd-Sn/SiO_2 catalyst. The strong mobility of Pd on SiO_2 surface during activation treatments was reported to be due to weak metal-support interactions. Difference in selectivity between the two series of catalysts was explained by higher Ge contents on Al_2O_3 than SiO_2 supported catalyst. For silica-supported catalysts, selectivity reaches a plateau for Ge contents ranging from 1.0 to 1.5 wt.%. The higher selectivity on alumina-supported catalysts would not arise from a higher coverage of Rh particles by Ge but related to Ge deposited on the alumina support in the close vicinity of Rh particles. These Ge species would be partially reduced during the reduction step of the catalyst and would promote the activation of the carbonyl group for hydrogenation.

Reducible support that presents the strong metal–support interaction effect (SMSI effect) has been successfully used with monometallic catalysts to increase the selectivity to the C=O group hydrogenation of unsaturated aldehydes (Silva et al. 2003, Malathi et al. 2001, Rojas et al. 2008). The use of reducible oxide titania (TiO_2) as a support in the selective hydrogenation reaction of citral enhanced the selectivity to UA compare with the inert supports. This behavior was attributed to the presence of partially reduced species (TiO_x) generated upon reduction at high temperature.

Silva et al. (2003) studied the combined effects of support and promoter in the hydrogenation of citral over Ru-Sn catalysts supported over TiO_2 and γ-Al_2O_3 and prepared by impregnation and co-impregnation methods using $RuCl_3$ and $SnCl_2$ as precursors. The catalysts were dried overnight at 120 °C and then further dried under argon at the temperature for 15 h. Alumina-supported samples were calcined at 600 °C, while the titania-supported samples were calcined at 400 °C for 4 h. All samples were reduced at 250 °C (LTR) and 400 °C (HTR). Tests were carried out at 50 bar and 126 °C in n-heptane as a solvent.

They found that Ru/TiO_2 at HTR (400 °C) was more selective to unsaturated alcohol but less active than Ru/Al_2O_3 and Ru/TiO_2 at LTR (250 °C). This was attributed to the presence of strong metal-support interaction (SMSI) effect caused by the high reduction temperature. The migration of TiO_x, due to the high reduction temperature, would block Ru(0) sites and break up larger ensembles of Ru(0) atoms which acts as active site for the hydrogenation of C=C bond and induce special metal-support sites active for the selective hydrogenation of C=O bond. Ru/Al_2O_3 and Ru/TiO_2 catalysts produced both UA (geraniol and nerol) and citronellal, while isopulegol was induced from the cyclisation reaction of citronellal over Ru/Al_2O_3. On the other hand, Ru/TiO_2 found to be less selective to unsaturated alcohol than Ru/Al_2O_3 at LTR. This was attributed to the low reduction temperature which was not enough for the creation of special active sites (the Ru-TiO_2 interaction was not yet effective).

The disadvantage of titania as a support is its low surface area. Studies have been done to increase the surface area of this partially reducible oxide by the using inert oxide material such as silica or alumina as a carrier to deposit titania on it. The high surface area of titania is desirable to increase the selectivity to carbonyl group.

Malathi et al (2001) studied the selective hydrogenation of citral over Pt supported catalysts (5 wt%) was loaded by wet impregnation on different supports; titania (commercial and gel), ceria and mixed oxide support (the percentage of titania and alumina were 22 and 78 % respectively), and reduced at 300 °C (LTR) and 500 °C (HTR). Reaction was carried out at 1 atm and a temperature of 45 °C. For all supported Pt catalysts, selectivity was 100 % towards unsaturated alcohol (geraniol). Thus was attributed to the influence of the SMSI (strong metal-support interaction). The highest conversion of 29 % was found in both titania supported samples (gel at HTR and mixed oxide at LTR) at 300 min. This activity was explained by the strong interaction between the metal and the reduced support. Where, the reduced TiO_2 species was migrated on the surface of the metal and enhancing the preferential hydrogenation of C=O bond. The reason for SMSI state in the gel catalyst was attributed to the increase of reducibility than the commercial sample. While in the case of mixed oxide, it was attributed to the homogeneous distribution of the support.

Ekou et al. (2012), studied the selective hydrogenation of citral to unsaturated alcohol using modified mesoporous support $y\%Ti-Al_2O_3$ (y corresponding to the atomic percent of Ti in alumina, in the range 10-33%) with high surface area. The oxides were synthesized via a sol-gel. The catalysts were reduced at two different temperatures, 300 °C and 500 °C. The use of these materials for further impregnation of Pt metallic precursor and to replace the classical alumina support. The potential of these modified supports to generate improved SMSI effect was investigated.

From the characterization of the catalysts, they suggested that titanium atoms were incorporated in the alumina structure. This result was confirmed by the progressive decrease in γ-Al_2O_3 reflection intensity detected by X-ray diffraction (see Figure 2.13). No crystallized titania phase (anatase, brookite or rutile) was detected by XRD, even at 33% of Ti.

Figure 2.14 displays the citral conversion after 60 min reaction time and the UA selectivity at 40% conversion for each Ti containing catalyst, compared with the Pt samples supported on pure alumina (y = 0%) and pure titania (y = 100%) respectively. In terms of conversion, whatever the titanium content and reduction temperature, the conversion of citral decreased over the $Pt/y\%Ti-Al_2O_3$ catalysts. The decrease in conversion was twice higher than that of Ti-containing catalysts reduced at 500 °C. This was confirmed to be due to SMSI effect, where the reduced titania species ($TiO_{(2-x)}$ ($x < 2$) species) can cover a part of the Pt surface after reduction at 500°C. This decrease in activity was largely lower for Pt/TiO_2 P25 compared by $Pt/y\%Ti-Al_2O_3$ catalysts, suggesting a lower SMSI effect over Pt/TiO_2 P25 compared to the $Pt/y\%Ti-Al_2O_3$ catalyst.

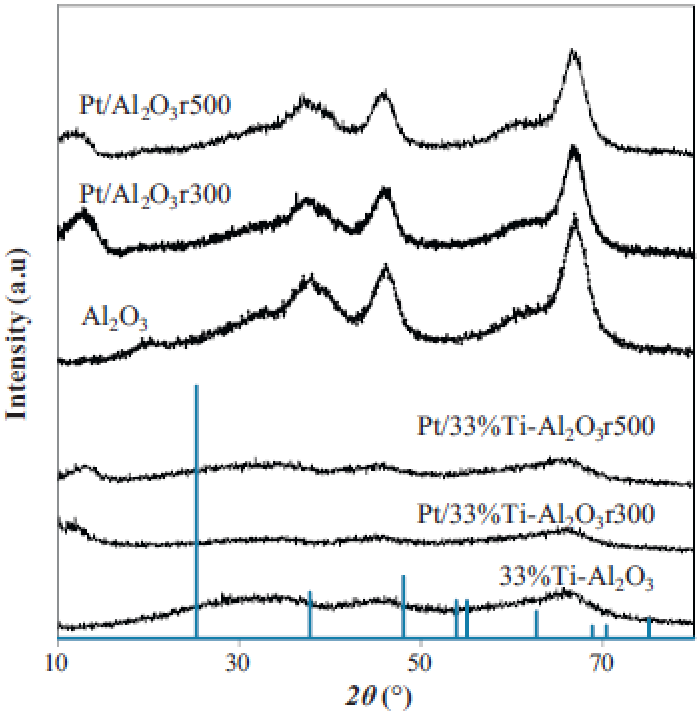


Figure 2.13. X-ray diffraction patterns obtained for the y%Ti‑Al_2O_3 supports and respective 1.0 wt.% Pt/y%Ti‑Al_2O_3 (y = 0 and 33) catalysts reduced at 300°C and 500°C. Vertical bars: TiO_2 anatase phase (JCPDS file no.: 089-4920) (Source: Ekou et al. 2012).

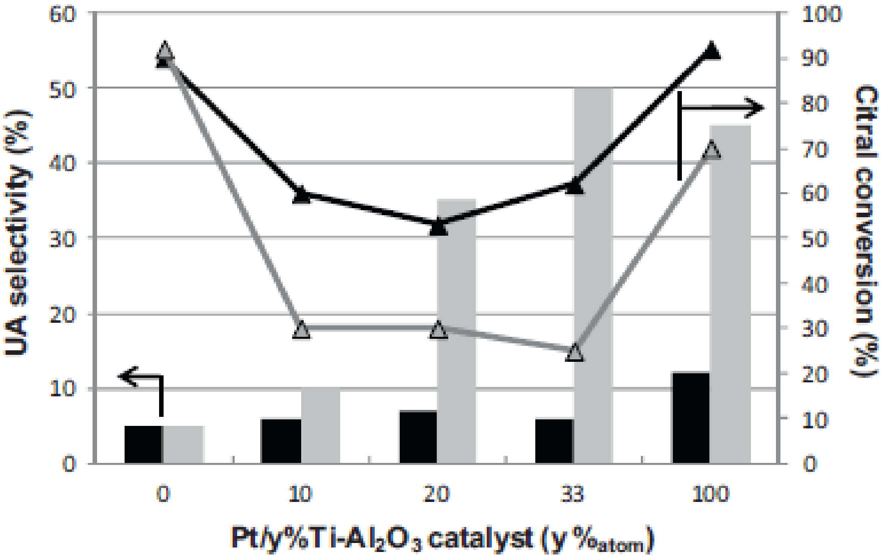


Figure 2.14. Citral conversion after 60 min reaction time and selectivity to unsaturated alcohols at 40% citral conversion on the 1.0 wt.% Pt/y%Ti‑Al_2O_3 monometallic catalysts reduced at 300°C (black) and at 500°C (grey) (Source: Ekou et al. 2012).

Pt/y%Ti-Al_2O_3 catalysts (y = 0 to 100%) reduced at 300°C present very low selectivity to unsaturated alcohol compared with the catalysts reduced at 500°C. Modified alumina with titanium catalysts promoted the selective hydrogenation of the C=O bond compared to Pt sample deposited on pure alumina. The selectivity to unsaturated alcohol over Pt/y%Ti-Al_2O_3 catalysts can be similar or even higher compared to the Pt/TiO_2 P25 (S_{UA} = 45 % after reduction at 500°C). This was related to the existence of a SMSI effect, where the formed $TiO_{(2-x)}$ ($x < 2$) species can participate to the activation of the C=O bond. Such metal-support interaction can then be maximized through the titanium content in the support.

Recently TiO_2 loaded on mesoporous silica by different methods has been investigated as a catalyst support. Mesopore structure of SiO_2 will minimize diffusion resistances and increase TiO_2 surface area. Studies in literature shows that thermal stability, surface area and mechanical strength of TiO_2 can be improved by creating TiO_2/SiO_2 supported oxides as advanced support materials as alternative for pure TiO_2. TiO_2/SiO_2 as a catalyst support combines the advantage of TiO_2 property (active catalytic support) and SiO_2 properties (good mechanical strength, high surface area and high thermal stability).

Catalytic hydrogenation of citral over iridium supported on TiO_2, SiO_2 and supported oxides TiO_2/SiO_2 has been studied by Rojas et al. (2008). The effect of the successive enrichment of TiO_2 on SiO_2 and the reduction temperatures (473 or 773 K) were investigated. All the catalysts were prepared by impregnation using an aqueous solution of H_2IrCl_6 as Ir precursor to give loading of 1 wt.% Ir. Reactions were carried out at 6.2 bar hydrogen and 90°C reaction temperature, using 200 mg of catalyst and n-heptan as a solvent. TiO_2 was loaded on SiO_2 at different wt%, G1=7.3, G2=13.6, G3=19.2, and G4=24, by successive enrichment. Titanium isopropoxide was dispersed in toluene and added to activated an Aerosil silica. The resultant mixture was stirred for 16 h under inert atmosphere at the solvent reflux temperature. Modified silica was filtered, washed with toluene, ethyl ether and deionized water. The resulting solid (G1) was dried for 5 h under vacuum at 150 °C. Similar procedure of reflux, dried, and calcination was used for samples with higher Ti loading.

The evolution of the conversion level with time on both LTR and HTR catalysts are given in Figures 2.15 and 2.16. Lower conversions were displayed by the LTR series compared with the HTR counterpart. Whereas Ir/SiO_2 catalyst showed the lowest activity among both LTR and HTR series, Ir/TiO_2 and Ir/G1 catalysts possess activities slightly higher at LTR. Conversion was enhanced by increasing the TiO_2 loading in the mixed oxides catalysts. For HTR catalysts, they related this to the SMSI effect, where the crystals of Ir metal may be decorated by partially reduced TiO_x species, producing electron deficient iridium species ($Ir^{\delta+}$), which confirmed by characterization results (H_2 chemisorption, XPS, XRD and FT-IR). These species are especially active to polarize the carbonyl group favoring the conversion and selectivity reaction toward the unsaturated alcohol.

Geraniol and nerol were the main products, while citronellal and citronellol were produced in small amounts (Table 2.2). This was attributed to the presence of $Ir^{\delta+}$ species by the ability to polarize the carbonyl bond of the citral molecule to produce mainly geraniol and nerol as hydrogenation products.

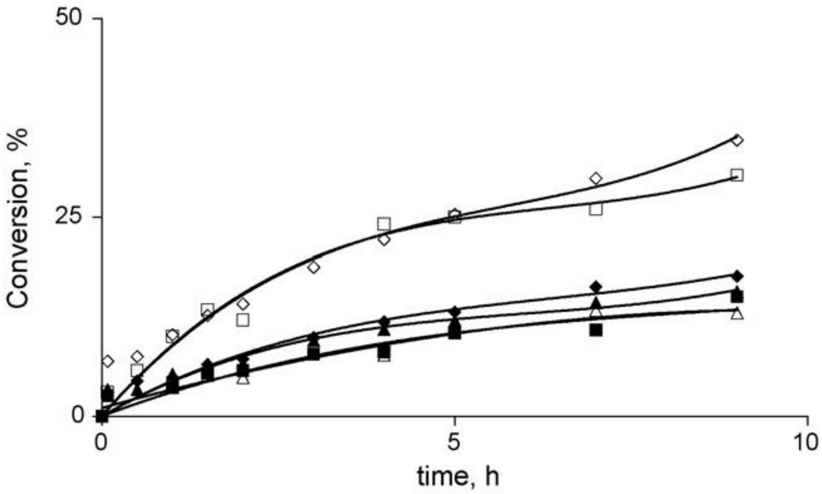


Figure 2.15. Citral hydrogenation at 90°C and 6.2 bar. Conversion level as function of time for Ir catalysts at LRT: (△) Ir/SiO_2; (◇) Ir/TiO_2; (☐) Ir/G1; (▲) Ir/G2; (◆) Ir/G3; (■) Ir/G4 (Source: Rojas et al. 2008).

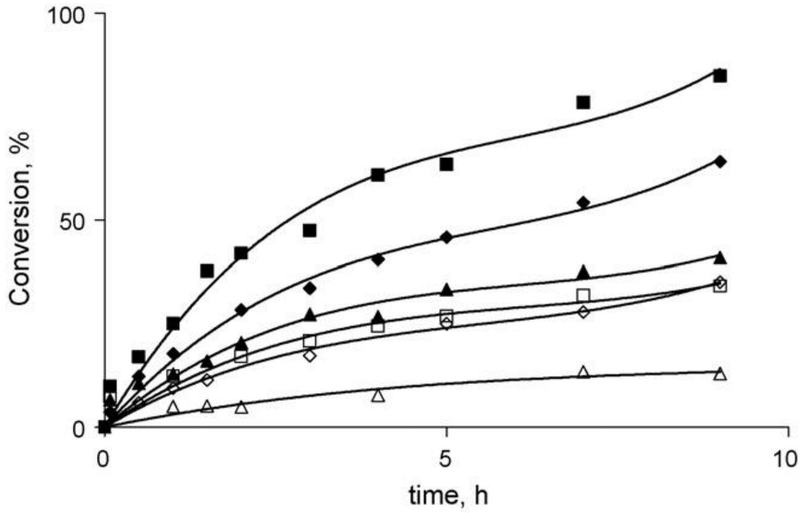


Figure 2.16. Citral hydrogenation at 90°C and 6.2 bar. Conversion level as function of time for Ir catalysts at HRT: (△) Ir/SiO_2; (◇) Ir/TiO_2; (☐) Ir/G1; (▲) Ir/G2; (◆) Ir/G3; (■) Ir/G4 (Source: Rojas et al. 2008).

Table 2.2. Hydrogenation of citral at 90°C and 6.2 bar on Ir catalysts (Source: Rojas et al. 2008).

Catalysts	Selectivity (%)			
	Citronellal	Citronellol	Nerol	Geraniol
Ir/SiO_2 LT	16	16	30	38
Ir/SiO_2 HT	24	29	38	9
Ir/G1 LT	1	4	30	65
Ir/G1 HT	5	5	27	63
Ir/G2 LT	6	5	24	65
Ir/G2 HT	2	5	26	67
Ir/G3 LT	3	4	25	68
Ir/G3 HT	4	5	28	63
Ir/G4 LT	12	7	18	63
Ir/G4 HT	0	7	33	60
Ir/TiO_2 LT	5	4	24	67
Ir/TiO_2 HT	9	0	21	70

Selectivity at 10% conversion.

In another study performed by Ekou et al. (2011), they investigated the liquid phase hydrogenation of citral using 1.5 wt% Pt catalysts supported on TiO_2 grafted on mesoporous silica (SBA-15). Two mesoporous Pt/Ti-SBA catalyst series were synthesized with 8 nm and 20 nm initial pore diameter, at various titanium loadings, 25 wt.%, 40 wt.% or 60 wt.% of TiO_2 in the final material after calcination at 400°C. By using slow impregnation method, titania was loaded on silica using dilute solution of

$Ti(OiPr)_4$ in dry ethanol (volume ratio $V_{(Ti(OiPr)_4)}/V_{(EtOH)}=0.05$). Pt was impregnated on the supported oxides using hexachloroplatinic acid solution (H_2PtCl_6) as precursor. After calcination catalysts were reduced under hydrogen at 300°C. Reactions were carried out in a stirred autoclave at 70 °C under 76 bar H_2 pressure using 400 mg of catalysts.

XRD was used to assess the structural ordering of the parent silica SBA, and of the Ti-SBA and Pt/Ti-SBA materials (see Figure 2.17). At low loading of titanium (25 wt.%) no peak associated with the formation of a crystallized TiO_2 phase (anatase structure) was detected. While at high loading of titanium (40 and 60wt.%), TiO_2 anatase structure was observed on the XRD pattern. They reported that small amounts of Ti species would be easily grafted on the silica surface, and the probability to aggregate remained low. In contrast, higher Ti concentration caused the formation of larger TiO_2 clusters, due to the limited silica sites for grafting. On the other hand, the anatase crystalline phase was detected easily by XRD whatever the support (8 nm or 20 nm) or the titania loading when Pt deposited on the mixed oxide materials. This was because the platinum deposition and reduction steps also result in important modifications of the material structural properties.

The effect of Ti loading on the hydrogenating properties of the Pt/SBA catalysts is presented in Figure 2.18. The results showed that citral conversion was decreased as the Ti loading increased in the Pt/x%Ti-SBA catalysts. While dispersion of TiO_2 in the SBA8 nm or SBA20 nm supports lead to an improvement of the UA selectivity. Selectivity to UA reached to about 26 % for the Pt/40%Ti-SBA8 nm and 28% for Pt/60%Ti-SBA20 nm at 80% citral conversion.

They explained these results by specific role of the reducible TiO_2 species, which can generate a strong metal-support interaction (SMSI effect) with platinum. The decrease of the conversion by increase of TiO_2 was related to the higher covering of Pt atoms with the reducible TiO_2 species. However, the increase in selectivity to UA was related to the SMSI effect involved the formation of partially reduced $TiO_{(2-x)}$ species ($x < 2$) on the support, which favored the activation of the carbonyl function. Similar explanations were proposed by Rojas et al. (2008).

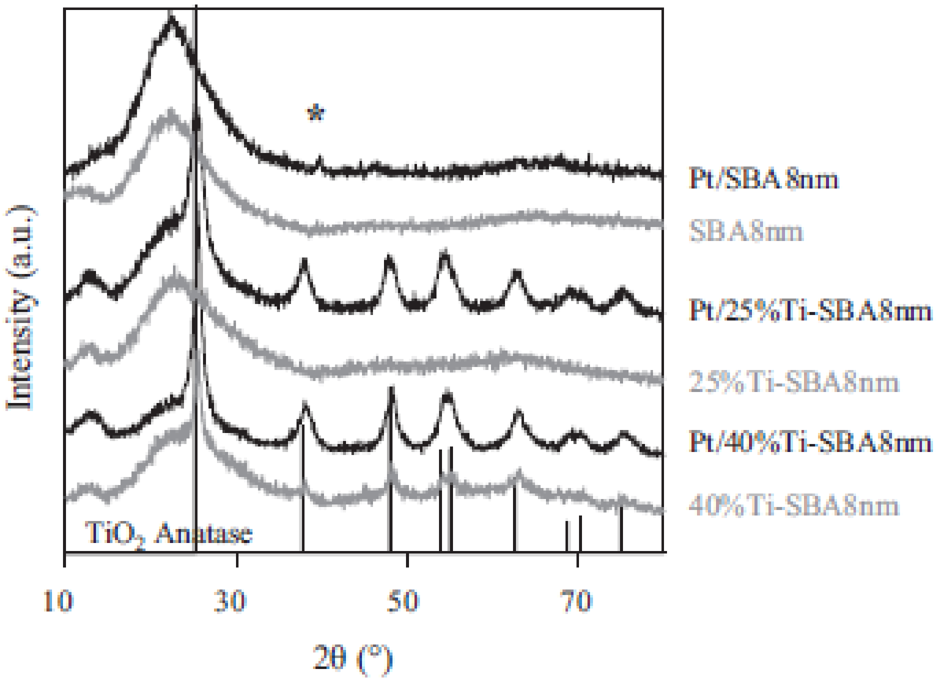


Figure 2.17. X-ray diffraction patterns obtained on the Ti-SBA8 nm supports and respective Pt/Ti-SBA8 nm catalysts. (*) Platinum phase detected (Source: Ekou et al. 2011).

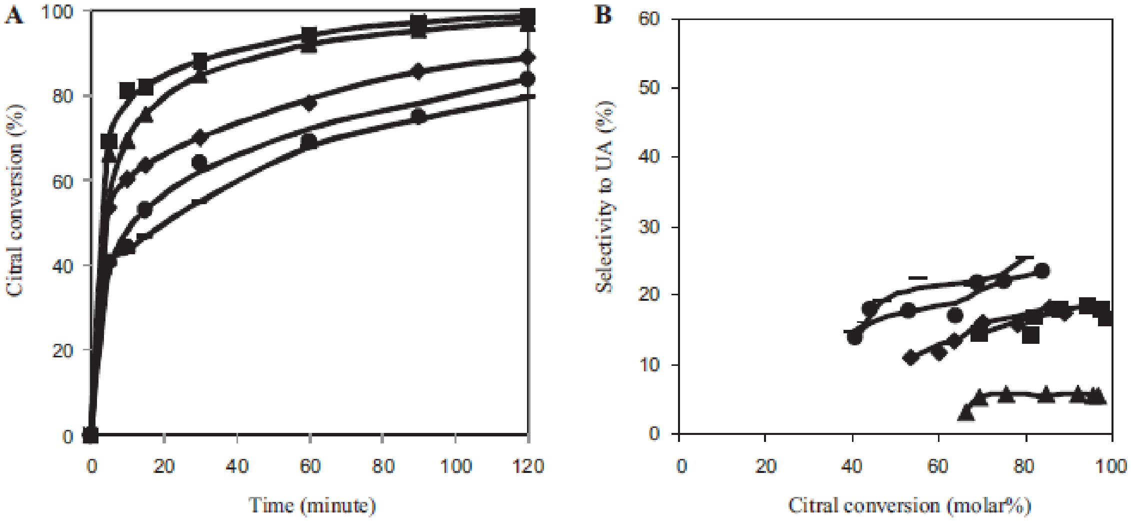


Figure 2.18. Citral conversion as function of time (A) and selectivity to unsaturated alcohols (UA) as function of citral conversion (B) over the nanocomposites catalysts: Pt/TiO2 P25 (■); Pt/SBA20 nm (▲); Pt/25%Ti-SBA20nm (◆); Pt/40%Ti-SBA20 nm (●) (Source: Ekou et al. 2011).

As results from the previous literature reviews, active metal plays an important role in the selective hydrogenation of citral, and Pt, Ir and Ru are the most compounds used for this type of reaction. Furthermore, catalyst preparation methods and reduction temperature were also shown to influence catalyst activity and selectivity. Metal support interaction plays a major role in increasing the selectivity to UA, which is associated with reducible oxide supports, like TiO_2. In this view, we suggest to use Ru as active component, which is one of the most inexpensive noble metals, to be supported on the mesoporous TiO_2/SiO_2 support.

CHAPTER 3

EXPERIMENTAL STUDY

Ru was loaded by impregnation onto silica gel (SiO_2), titanium dioxide (TiO_2) and TiO_2/SiO_2 supports. The prepared catalysts were characterized and tested for liquid phase hydrogenation of citral in a semi batch reactor.

3.1. Materials

Silica gel (SiO_2) (200-425 mesh, 236810 Sigma-Aldrich, 99+%) and TiO_2 (Degussa P25) (BET=50±15 AEROXIDE/Evonik) were used as supports. Titanium (IV) Isopropoxide ($Ti(OiPr)_4$) (205273 Aldrich, 97%) was used as titanium precursor. Ruthenium (III) Acetylacetonate (282766 Aldrich, 97%) was used as ruthenium precursor. Citral (C83007 Aldrich 95%) was the reactant compound. Cyclohexanone (398241 Sigma-Aldrich, ≥99%) was used as internal standard compound. 2-Propanol (24137 Sigma-Aldrich, ≥99.5%), Ethanol (1.11727 Merck, ≥99.9%), Toluene (24529 Sigma-Aldrich, ≥99.5%) and Diethyl Ether (31700 Fluka, 99%) were used as solvents during the preparation of catalysts and in the citral hydrogenation reaction.

3.2. Preliminary Study

In the preliminary study, Ru/SiO_2, Ru/TiO_2, $Ru\text{-}Sn/TiO_2$ and $Ru/TiO_2/SiO_2$ catalysts were prepared and tested in ethanol and isopropanol at 80 and 100 °C. Effect of catalyst calcination also examined. Acetal formation was prevented in isopropanol. Catalyst calcination did not affect the product distribution for Ru/SiO_2. Titania support increased conversion and selectivity to UA. Results and their detailed discussions are given in appendix A.

From these studies it was decided to investigate TiO_2/SiO_2 supports prepared by different methods on activity and selectivity of Ru catalysts in citral hydrogenation.

3.3. Catalyst Preparation

3.3.1. Preparation of Catalyst Supports

Commercial SiO_2 and TiO_2 were heat treated at 500 °C in flowing dry air for 4 h before being used. Other supported oxides TiO_2/SiO_2 were prepared by different methods given below.

3.3.1.1. Preparation of TiO_2/SiO_2 by Sol Gel Deposition Method

Method developed by Grzechowiak et al. (2003) applied to prepare TiO_2/SiO_2 as a support with 25 wt% of TiO_2 loading, where SiO_2 was added to titanium (IV) isopropoxide ($Ti(OiPr)_4$) dissolved in isopropyl alcohol. During continuous mixing at room temperature, water was added to obtain a molar ratio of $H_2O:Ti(OiPr)_4 = 4:1$. The sol was gelated at room temperature. The next step, the sample was placed in a dryer and heated up stepwise: sample was kept at 30 °C for 30 min and then increased from 20 °C to 50 °C and kept for 30 min. Then the temperature increased to 70 °C and kept for 30 min. The drying continuous in the same way until the temperature reached 110 °C and kept at this temperature for 12 h. Then, sample was calcined at 400 °C in flowing dry air for 4 h. This support was called TiO_2/SiO_2-SGD.

3.3.1.2. Preparation of TiO_2/SiO_2 by Slow Impregnation Method

Silica was slowly impregnated by a dilute solution of $Ti(OiPr)_4$ in dry ethanol (volume ratio $V_{(Ti(OiPr)_4)}/V_{(EtOH)}=0.05$, impregnation at room temperature). Titania loading was adjusted to 25 wt.%. Titanium loaded silica was dried at 110 °C and calcined at 400 °C with a heating rate of 1 °C/min. This support was called TiO_2/SiO_2-IMP.

3.3.1.3. Preparation of TiO_2/SiO_2 by Absorption Method

Titanium isopropoxide (1 mmol g^{-1} of silica) dispersed in toluene (150 ml) was added to the calcined silica. The resultant mixture was stirred for 16 h at 100 °C. Then, the modified silica was filtered, washed with toluene, diethyl ether and ultra-pure water. The resulting solid with 8 wt% TiO_2 loading was dried for 1 h at 110 °C and then for 12 h at 150 °C. After drying, the sample was calcined at 400 °C for 4 h. The 8 wt% titanium supported oxide was further koaded by $Ti(OiPr)_4$ to obtain 16 wt% TiO_2 loading, following the same procedure. Same steps were followed to obtain higher TiO_2 loading (25 wt%) (Rojas et al. 2008, Hoffmann et al. 2001). This support was called TiO_2/SiO_2-ABS.

3.3.2. Preparation of Ru Supported Catalysts

Ruthenium (2 wt.%) was loaded on to the various supports, SiO_2, TiO_2 and TiO_2/SiO_2, by impregnation method. For this, calcined supports were placed in to ethanolic solution of Ru(III) acetyl acetonate (150 ml) and mixed at room temperature for 24 h with a magnetic stirrer. Then, the ethanol was evaporated in a rotary evaporator at 46 °C under 200 mbar vacuum pressure for 3 h at 50 rpm. The impregnated catalysts were dried at 110 °C overnight. Then all the catalysts were calcined at 400°C with a heating rate of 2.5 °C/min under flowing dry air (70-80 ml/min) for 4 h to obtain the desired catalysts.

3.4. Characterization of Catalysts

Characterizations of catalysts were carried out by different instrumental techniques. Powder X-ray diffraction (XRD) patterns were collected on Philips X’Pert Diffractometer with CuKα radiation to determine the crystalline structures of catalysts. The scattering angle 2θ was varied from 5° to 80° with a step length of 0.033.

The surface area and adsorption isotherms of the samples were determined by using the nitrogen adsorption technique over a Micromeritics Gemini V model static 30 volumetric adsorption instrument. Degassing was performed at 300°C for 24 h under 5µmHg vacuum.

Morphology of the catalysts was investigated by Philips SFEG 30S scanning electron microscopy (SEM).

Temperature-programmed reduction (TPR) was carried out using Micromeritics AutoChem II Chemisorption Analyzer instrument. The catalyst samples were outgassed at 150°C for 2h and then cooled to 45°C under 70 ml/min Ar flow. TPR profiles were registered while heating the samples from 45°C to 800°C by 10°C/min heating rate under flow of 10% H_2/Ar mixture (50 ml/min). The flow was then switched to Ar and the samples were cooled to 40°C.

Chemical composition of catalysts was determined by X-Ray Fluorescence Spectrometer (XRF) using Spectro IQ II apparatus.

3.5. Catalytic Activity

Citral hydrogenation experiments were carried out in a stirred, semi batch reactor (500 ml, 4575 model, Parr Instrument Co.) with an electrical heater and a temperature controller (4842 model, Parr Instrument Co.). The reaction temperature was measured and controlled by a thermocouple probe placed inside the reactor. The system was equipped also with a bubbling unit. Figure 3.1 illustrate the reactor set-up. Swagelok valves (needle, three-way and shut off valves), fittings and connectors were used.

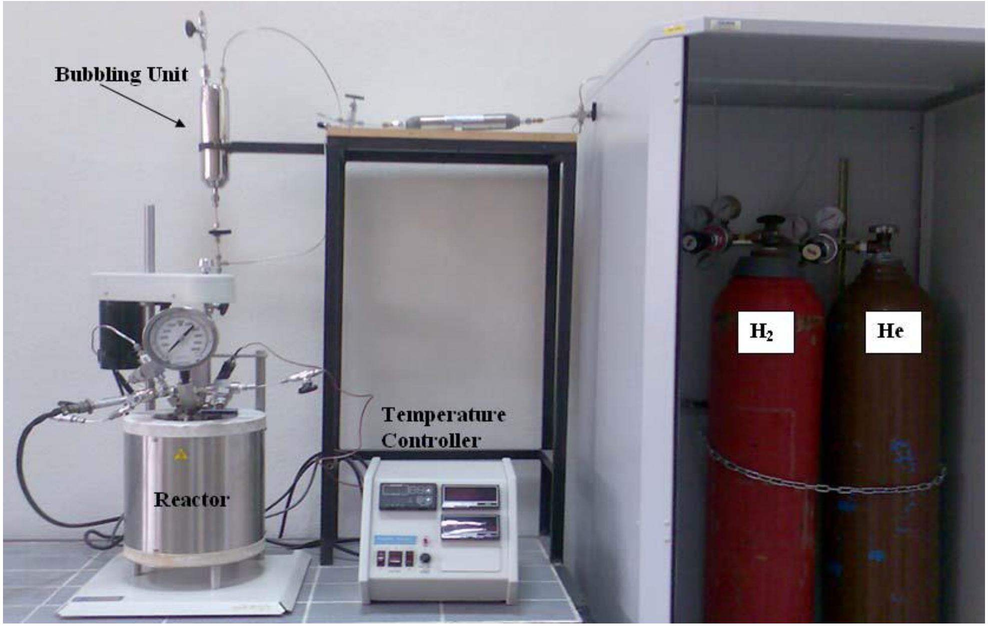


Figure 3.1. Reactor set-up.

Before the reaction, 400 mg of catalysts were placed in the reactor and reduced (activated) in situ at low reduction temperature 300°C (LTR) or high reduction temperature 450 °C (HTR). Leak test is done with He gas. Temperature is set to 100 °C. After the temperature reached to 100°C, He was filled to the reactor up to 6 bar and released five times to flush the contents in the reactor. Then the temperature was set to 200 °C. When the temperature reached to 200 °C, He was filled to the reactor and released five times. Gas flow was then switched to H_2, temperature was set to 300 °C or 450 °C gradually depending on activation temperature. During the heating, the reactor was filled and emptied for 5 times. When the temperature reached to the desired reduction temperature, H_2 flow through the reactor at 6 bar with flow rate of 100-120 ml/min was sent for 4 h. Reactor was cooled to reaction temperature and kept overnight under 2 bar hydrogen pressure.

After activation of the catalyst, 100 ml of solvent (isopropanol) was injected into the bubbling unit from the upper valve of the bubbling unit. The gas pressure of He was adjusted to 1 atmosphere and the He gas was sent from the bottom of the bubbling unit for 10 minutes for deoxygenation. After that, flowing gas was switched to H_2 and it was sent through the top of the bubbling unit. Solvent was sent into the reactor by opening the valves under the bubbling unit. At that time the pressure was increased slowly to 3 bars. 5 minutes later, the two valves under the bubbling unit were closed. The stirrer was switched on, and the catalyst was stirred for 60 minutes (catalyst preconditioned) at 500 rpm. The pressure was set to 2 bars.

After following the steps above reactor was ready for reactant solution addition, which was prepared and fed to the reactor as follows; 0.02 mole of citral and 0.005 mole of cyclohexanone (internal standard) were added to 100 ml of isopropanol and they were stirred in a closed bottle for 20 min. Since there was 100 ml of isopropanol already in the reactor, this gave 0.1 M citral and 0.025 M cyclohexanone. The reactant solution was injected into the bubbling unit and He was fed from the bottom to the bubbling unit to remove dissolved O_2 if there is any for about 3 min. Then the gas was switched to H_2 and H_2 was fed to the bubbling unit, so the He gas was removed. The stirrer was stopped and the reactant solution was injected into the reactor by passing the H_2 gas from the top valve of the bubbling unit, so H_2 pushes the solution in to the reactor. H_2 pressure was adjusted to 4 bar. After 30 sec, the stirrer was turned on at 1000 rpm. The reactor pressure was increased to 6 bar.

Samples were taken within specified intervals, after starting the stirring, at 2.5, 5, 10, 20, 60, 120, 180, 240, 300 and 360 min. The stirrer was stopped before taking the samples. The samples should be taken as in little amounts as possible. Each sample should not be over 1 ml.

Samples taken from the reactor were filtered, diluted with isopropanol (0.2 ml of sample was diluted with 0.8 ml of isopropanol. Then it was further diluted where 0.1 ml of the previous diluted sample was mixed with 0.9 ml of isopropanol to obtain 50X dilution. Reaction samples were analyzed with Agilent Technologies 6890N Network GC System Gas Chromatograph equipped with a flame ionization detector (FID) and a capillary column DB-225 (J&W, 30 m, 0.25 mm i.d.). The temperature program of analysis was as follows: Heating from 80 °C to 100 °C at 2 °C/min, heating from 100 °C to 180 °C at 3 °C/min and holding at 180 °C for 1 min. Injector and detector temperatures were 190 °C and 200 °C, respectively while the velocity of carrier gas He was 21 cm/s.

Hydrogenation products of citral were identified by GC-MS technique (Varian Saturn 2000). The compositions of components in the reaction mixture were determined by internal standardization method as shown in appendix B. The commercially available citral hydrogenation products were Nerol (Cis-3,7-Dimethyl-2,6-Octadien, 268909 Aldrich, 97 %), Geraniol (48798 Fluka, analytical standard), (±)-Citronellal (72638 Fluka, analytical standard), (±)-β-Citronellol (51381 Fluka, analytical standard), 3,7-Dimethyl-1-Octanol (305774 Aldrich, ≥98 %), (+)-Isopulegol (59765 Fluka, analytical standard), (+)-Menthol (63658 Fluka, ≥99 %).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Catalysts Characterization

4.1.1. X-Ray Diffraction (XRD) Analysis

The XRD patterns of SiO_2 and Ru/SiO_2 catalyst are shown in Figure 4.1. These results showed that silica had an amorphous structure, and it was compatible with the results by Ekou et al. (2011), while RuO_2 was observed by peaks at 28°, 35° and 54° of the Ru/SiO_2 catalyst [JCPDS 40-1290]. This indicated that there were well-crystallized RuO_2 particles on SiO_2 support as observed in literature (Ma et al. 2009, Lanza et al. 2007).

Figure 4.2 shows the XRD analysis for TiO_2 and Ru/TiO_2. Typical diffraction peaks corresponding to anatase (JCPDS 21-1272) and rutile (JCPDS 21-1276) phase were observed for TiO_2. Ru characteristic peaks were not observed on the Ru/TiO_2 catalyst. This could be related to the good distribution of Ru on TiO_2 support. Also the intensity of the main peaks of TiO_2 support were significantly decreased by loading Ru. This was related to the coverage of the TiO_2 crystals by the loaded metal.

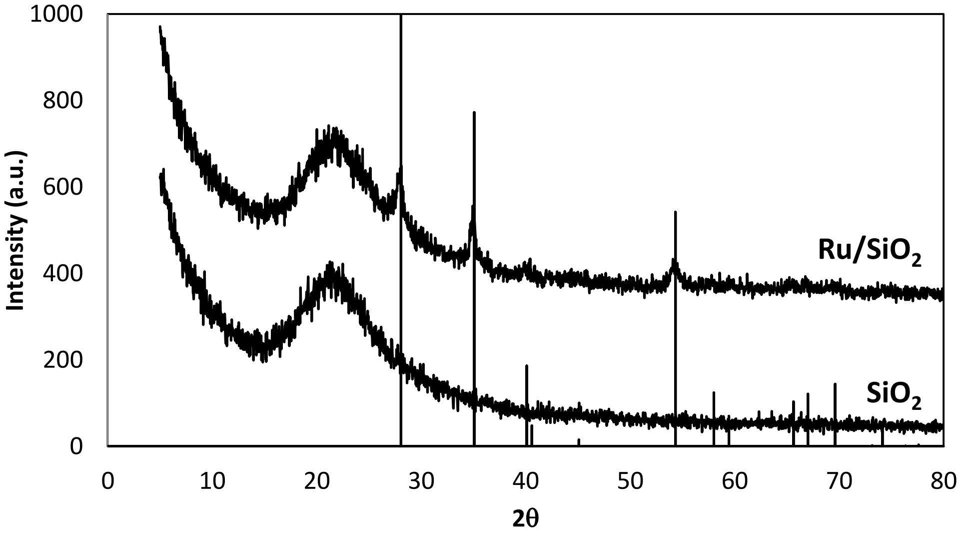


Figure 4.1. X-Ray diffraction of SiO_2 and Ru/SiO_2.

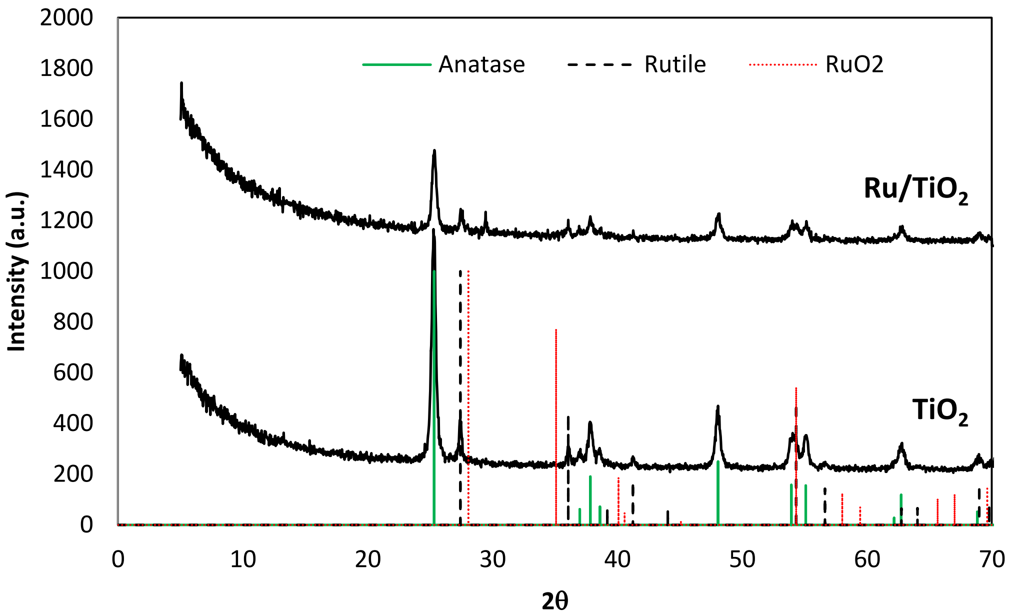


Figure 4.2. X-Ray diffraction of TiO_2 and Ru/TiO_2.

Catalyst support (TiO_2/SiO_2) and Ru supported on the TiO_2/SiO_2 prepared by different methods also were analyzed by X-Ray diffraction (Figure 4.3). The results showed no significant peaks could be detected for anatase phase for TiO_2/SiO_2-SGD and TiO_2/SiO_2-IMP. This could be related to the low titanium loading (25wt.%), indicating that the grafting of titanium results in the formation of small TiO_2 particles (Ekou et al. 2011). Some investigators reported that XRD cannot detect the presence of TiO_2 crystallites (anatase) below 30% TiO_2 loading, suggesting that the TiO_2 crystalline particles on SiO_2 are very small and below the detection sensitivity of the XRD technique (< 40 Å) (Gao et al. 1998). While for TiO_2/SiO_2-ABS, sharp peak was observed at 2θ of 25.1° which was related to the anatase phase. Also for the same TiO_2/SiO_2-ABS, small and wide peaks appeared at 2θ values 37.7°, 48° and 54° which also showed presence of anatase phase. Ru characteristic peaks were obsorved on $Ru/TiO_2/SiO_2$-SGD, $Ru/TiO_2/SiO_2$-IMP and $Ru/TiO_2/SiO_2$-ABS catalysts at 28°, 35° and 54°. These peaks were small and wide in $Ru/TiO_2/SiO_2$-ABS. This might be related to the dispersion of Ru on TiO_2 in the supported oxide material, which was confirmed by SEM and TPR analysis.

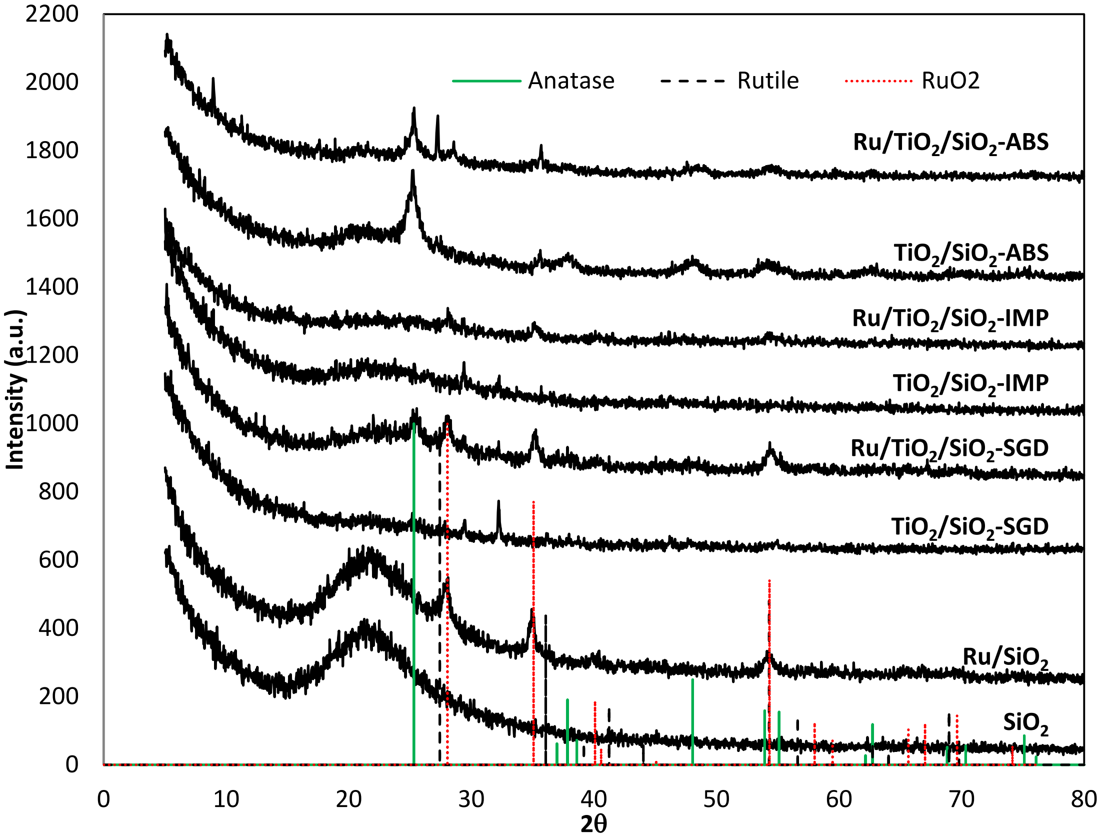


Figure 4.3. X-Ray diffraction of the supports and the catalysts.

4.1.2. Scanning Electron Microscopy (SEM) Analysis

Morphology of SiO_2, Ru/SiO_2, TiO_2 and Ru/TiO_2 are shown in the Figure 4.4. SiO_2 reported to have particles in the size range of 37-74 μm. For SEM analysis (image A) showed that SiO_2 had approximately 50 μm particulate sizes (average of 30 particles size). For Ru/SiO_2 catalyst (image B) revealed that Ru were presented in ensembles and not fine dispersed on the SiO_2. SEM for TiO_2 support is shown in image C, and small white spots can be seen on the image D were related to Ru dispersed on the TiO_2 support. On the other hand, grafted TiO_2 on the surface of SiO_2 could be observed for the supported oxides (TiO_2/SiO_2) (Figure 4.5. E, G and I images). Agglomerations of Ru particles were observed on TiO_2/SiO_2-SDG supported oxide (Figure 4.5. F image). This agglomeration was less on the support prepared by the impregnation and absorption method; image H and J respectively.

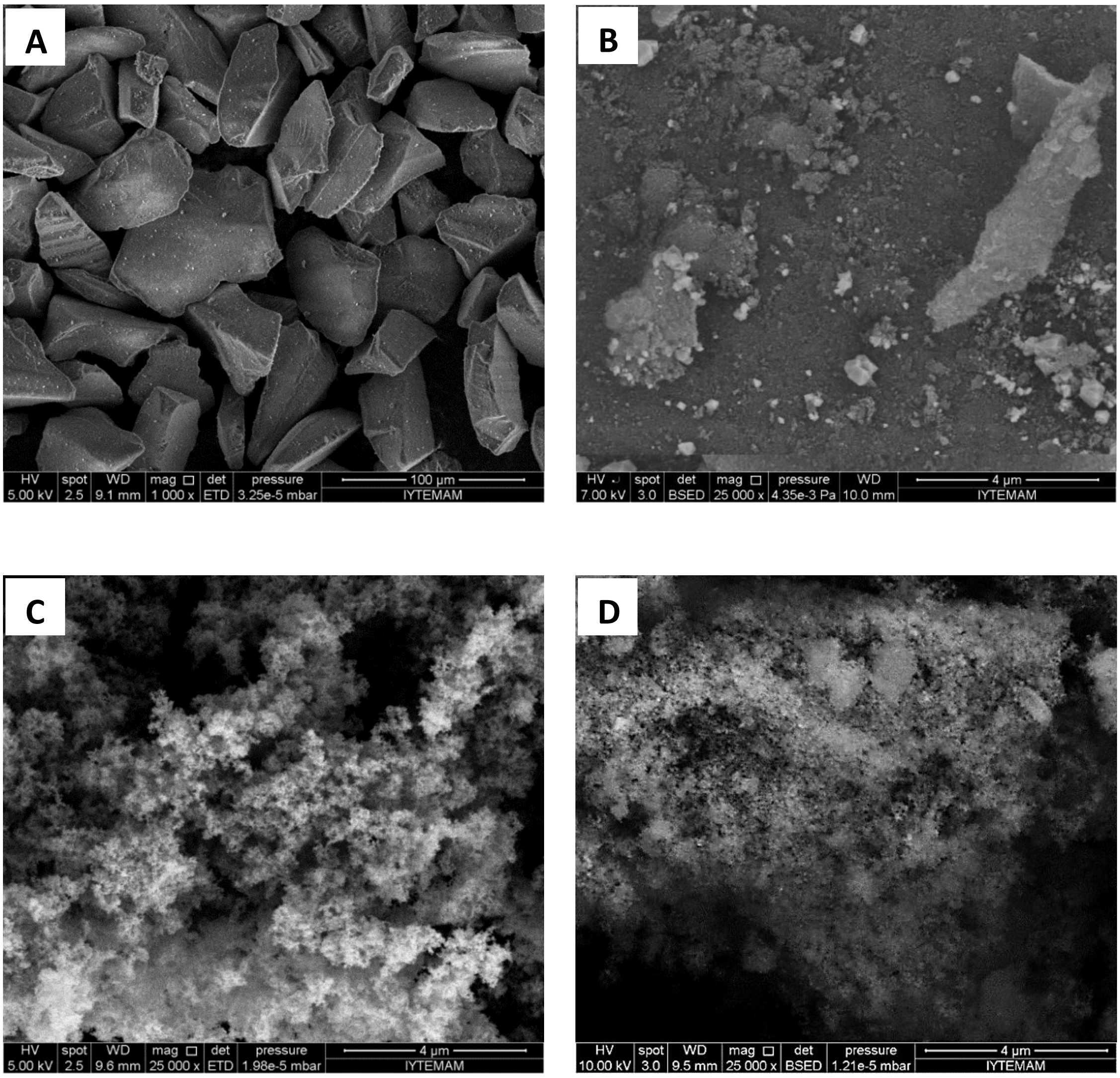


Figure 4.4. SEM images of SiO_2 (A), Ru/SiO_2 (B), TiO_2 (C), Ru/TiO_2 (D).

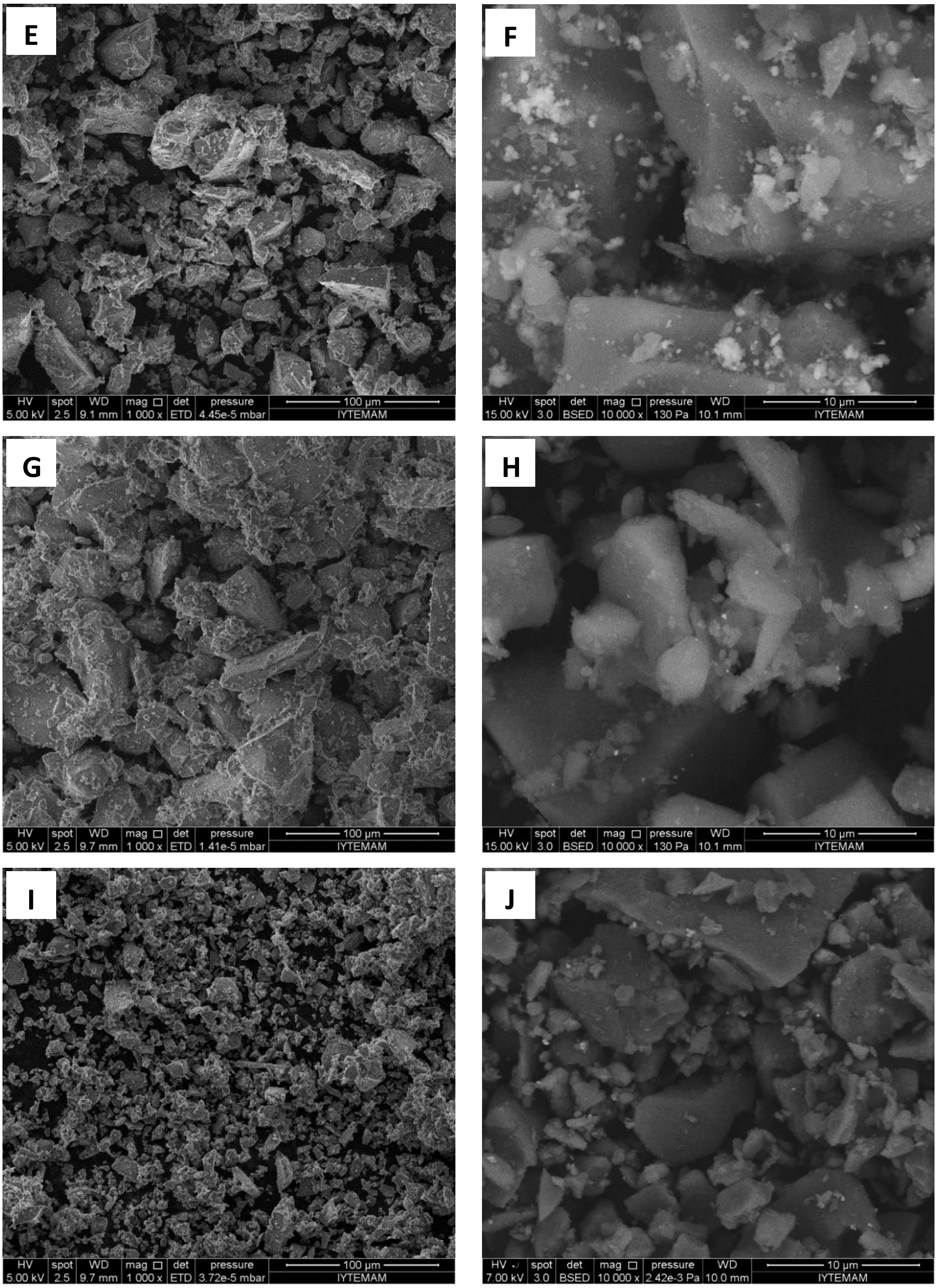


Figure 4.5. SEM images of TiO_2/SiO_2-SGD (E), $Ru/TiO_2/SiO_2$-SGD (F), TiO_2/SiO_2-IMP (G), $Ru/TiO_2/SiO_2$-IMP (H), TiO_2/SiO_2-ABS (I) and $Ru/TiO_2/SiO_2$-ABS (J).

4.1.3. X-Ray Fluorescence Spectrometer (XRF) Analysis

Chemical composition of catalysts was determined by X-Ray Fluorescence Spectrometer (XRF). Table 4.1 shows the composition of the supported-oxide produced by the different methods. Although the samples were loaded to 25% TiO_2, by absorption method less TiO_2 (20.12%) was loaded. This might be caused by the sequenced steps of washing and filtering which was followed by this method to eliminate unreacted titanium isopropoxide.

Table 4.1. Composition of the TiO_2/SiO_2 prepared by different methods.

	TiO_2/SiO_2-SGD	TiO_2/SiO_2-IMP	TiO_2/SiO_2-ABS
% SiO_2	73.60	75.08	79.21
% TiO_2	25.57	24.11	20.12

4.1.4. Surface Area and Pore Volume Measurements

The texture properties (specific surface area, cumulative pore volume and average pore diameter) of the supports and catalysts are listed in Table 4.2. The support SiO_2 showed high specific surface area (S_{BET}), while the S_{BET} of TiO_2 was considerably low. S_{BET} were decreased when TiO_2 were loaded on SiO_2 in different supported oxides except TiO_2/SiO_2-ABS, where S_{BET} was increased. This might be related to the creation of new areas during the loading of TiO_2 using absorption method.

BJH adsorption cumulative pore volume of pores between 17.000000 Å and 3000.000000 Å diameter and BJH adsorption average pore diameter (Å) were obtained for all types of supports and catalysts. SiO_2 had larger cumulative pore volume and average pore diameter than other supports (TiO_2/SiO_2). When TiO_2 was loaded on SiO_2, cumulative pore volume was decreased. The drop in the pore volume was very low with TiO_2/SiO_2-ABS support. This might be revealed that most of the TiO_2 were dispersed on the surface of SiO_2 and not inside the pore structures. From the values of average pore diameter, all the samples can be classified as mesoporous materials. The average pore diameter for TiO_2/SiO_2-ABS was 100.49 Å, while they were 92.18 Å and 86.01 Å for TiO_2/SiO_2-SGD and TiO_2/SiO_2-IMP respectively

The adsorption isotherms of SiO_2, TiO_2 and modified supported oxide (TiO_2/SiO_2) are shown in the Figure 4.6. SiO_2 and TiO_2/SiO_2 supports adsorption isotherms referred to type IV isotherms which are typical for mesoporous materials. The loading of TiO_2 on the SiO_2 did not change the shape of silica adsorption isotherm. The shape of the isotherm was preserved. This indicated that the structure of SiO_2 remained same. But pore size and pore volume changed upon loading. This might be resulted from pores blocking during the preparation of the TiO_2/SiO_2 supports. This blocking was low with TiO_2/SiO_2-ABS support. The same results have been observed when Ru was loaded on the different supports, That is, Ru loading did not influence the adsorption isotherms.

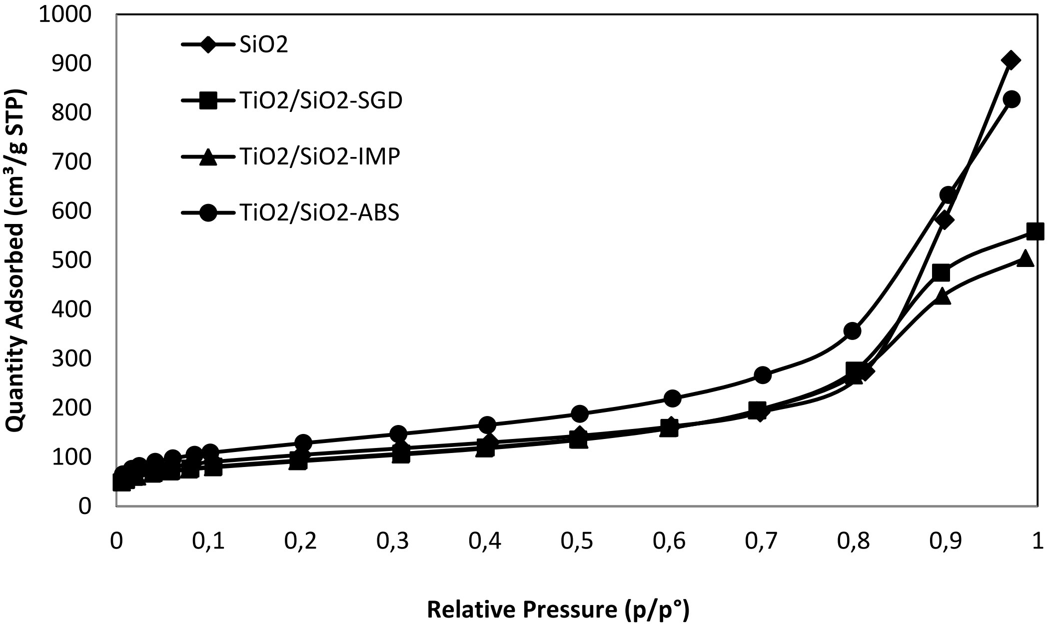


Figure 4.6. Adsorption isotherms of SiO_2 and modified supported oxide (TiO_2/SiO_2).

Table 4.2. Textural properties of supports and catalysts.

	Micropore Area (m^2/g)	External Surface Area (m^2/g)	BET Surface Area (m^2/g)	BJH Adsorption Cumulative Volume of Pores (cm^3/g)	BJH Adsorption Average Pore Diameter (Å)
SiO_2	19.9	341.5	361.4	1.36	143.11
Ru/SiO_2	46.4	366.8	413.2	1.52	143.07
TiO_2/SiO_2-SGD	18.3	309.0	327.3	0.84	92.18
$Ru/TiO_2/SiO_2$-SGD	36.0	365.5	401.5	1.01	93.88
TiO_2/SiO_2-IMP	19.5	302.1	321.6	0.75	86.01
$Ru/TiO_2/SiO_2$-IMP	32.3	319.5	351.8	0.84	88.42
TiO_2/SiO_2-ABS	12.6	440.6	453.2	1.23	100.49
$Ru/TiO_2/SiO_2$-ABS	21.0	299.1	320.1	0.84	99.19
TiO_2	0.2	52.4	52.6	0.24	-
Ru/TiO_2	1.8	50.6	52.4	0.31	-

4.1.5. Temperature-Programmed Reduction (TPR) Analysis

TPR profiles in Figure 4.7 show that all the catalysts were reduced below 300°C. This showed that activation temperatures studied (i.e. LTR and HTR) were sufficient to reduce the active metal (i.e. Ru). Catalysts prepared by different preparation methods showed different reduction behaviors. Reduction of the Ru/SiO_2 catalyst was observed in the temperature range between 130 °C and 250 °C and was characterized by one sharp peak with a maximum temperature around 210 °C. This reduction peak might be attributed to the reduction of RuO_2, and this sample was used as a basis for comparison. These results were compatible with the results obtained in other studies (Hu et al. 2001, Ma et al. 2009). On the other hand, the reduction of Ru/TiO_2 catalyst occurred in the temperature range between 100 °C and 295 °C where four peaks can be observed. The reduction peak at 125 °C is attributed to the reduction of poorly crystallized or so-called amorphous bulk RuO_x. While, the other wide reduction peaks are attributed to the reduction of amorphous RuO_x with Ru-support interaction (Le et al. 2009). For the Ru supported on TiO_2/SiO_2 prepared by sol gel deposition, reduction peak can be observed at ~198 °C which can be assigned to the reduction of RuO_2. For the Ru supported on

TiO_2/SiO_2 prepared by slow impregnation, sharp reduction peak can be observed at 209 °C which can be assigned to the reduction of RuO_2. While a shoulder at 175 °C could be attributed to the reduction of dispersed RuO_x. On the other hand, three peaks could be observed for the Ru supported on TiO_2/SiO_2 prepared by absorption at 170 °C and 182 °C which assigned to the reduction of dispersed RuO_x, and at 230 °C assigned to the reduction of RuO_2 (Lanza et al. 2007). Such results could be agreed with explanations that well dispersion and high interaction of Ru were observed on TiO_2 support, while Ru is probably slightly less dispersed when supported on SiO_2. On the other hand, for $Ru/TiO_2/SiO_2$ catalysts prepared by different methods, catalyst prepared with absorption method showed high dispersion and interaction with the titanium containing materials than the other catalysts, which was confirmed by the characteristic peaks of Ru appeared at low temperatures.

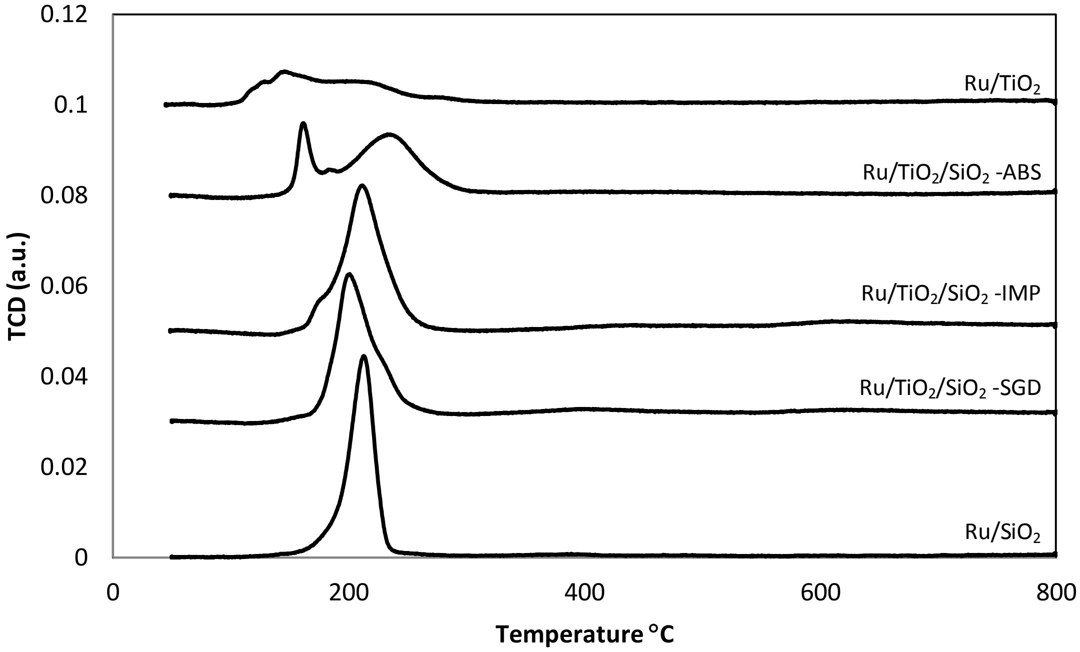


Figure 4.7. TPR profiles of Ru supported catalysts.

4.2. Catalysts Testing

The performances of the $Ru/TiO_2/SiO_2$ catalysts, as well as of the Ru/SiO_2 and Ru/TiO_2 catalysts were evaluated in liquid phase hydrogenation of citral carried out at 100 °C, 6 bar hydrogen pressure and 1000 rpm stirring speed using isopropanol as a solvent. For each run, 400 mg for each catalysts were reduced in situ at 300 °C (LTR) or 450 °C (HTR) before the test.

The conversion was calculated as the mole percent of citral (the reactant material) consumed, as follows:

$$\text{Conversion (mole \%)} = \frac{(\text{citral})_{\text{in}} - (\text{citral})_{\text{out}}}{(\text{citral})_{\text{in}}} \times 100$$

The selectivities of the desired products were defined as the ratio of the number of moles of desired product to the total number of moles of products, as follows:

$$\text{Selectivity (mole \%)} = \frac{(\text{desired product})_{\text{out}}}{\sum (\text{products})_{\text{out}}} \times 100$$

The main products for the citral hydrogenation are: citronellal, citronellol, geraniol and nerol (α,β-unsaturated alcohols, noted UA), and 3,7-dimethyl-1-octanol. The GC-MS chromatograms of each product are given in appendix C.

4.2.1. Activity and Selectivity of Ru/SiO_2 and Ru/TiO_2 catalysts

The compositions change of citral and main products over Ru/SiO_2 catalyst at 300 °C (LTR) reduction temperatures is shown in Figures 4.8. Low amounts of products were observed. Nerol and geraniol amounts increased steadily with the reaction time. The production did not exceed 10 % for nerol and geraniol (UA), 2.85 % for citronellal and 1.8 % for citronellol after 360 min reaction time. Moreover, very low amounts of undesired products; 3,7-dimethyl-1-octanol (0.6 %) and acetals (0.1 %) were produced at the same reaction time.

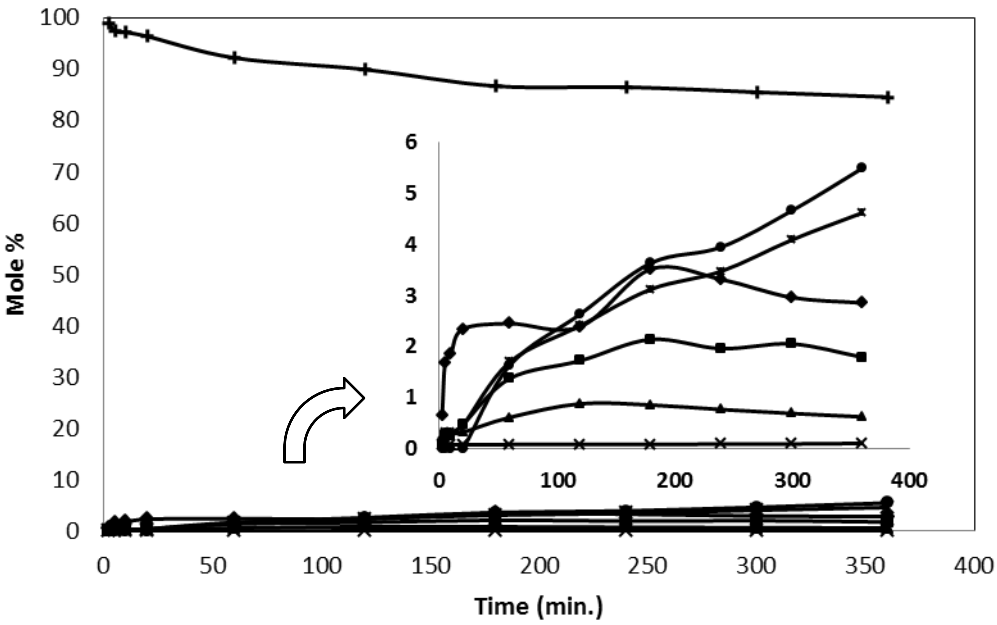


Figure 4.8. Composition of different species in citral hydrogenation over Ru/SiO_2 reduced at 300 °C: citral (+); nerol (✱); geraniol (●); citronellal (◆);citronellol (■); 3,7-dimethyl-1-octanol (▲); acetals (✕).

Figure 4.9 shows citral conversion and selectivity to UA as function of time for Ru/SiO_2 catalyst at 300 °C (LTR). In terms of conversion, Ru/SiO_2 showed slight increase in the conversion of citral through the reaction time reaching a maximum value of 15.5% at 360 min of reaction time. Deactivation of catalyst represented by the low value of conversion might be attributed to the blocking of Ru active sites by adsorbed CO yielded from the decomposition of either citral or unsaturated alcohol (Singh et al. 2001, Ekou et al. 2011). Moreover, Ru/SiO_2 showed good selectivity to UA increasing with reaction time up to 65% at 360 min. It can be deduced that this catalyst was more favored toward the hydrogenation of carbonyl bond.

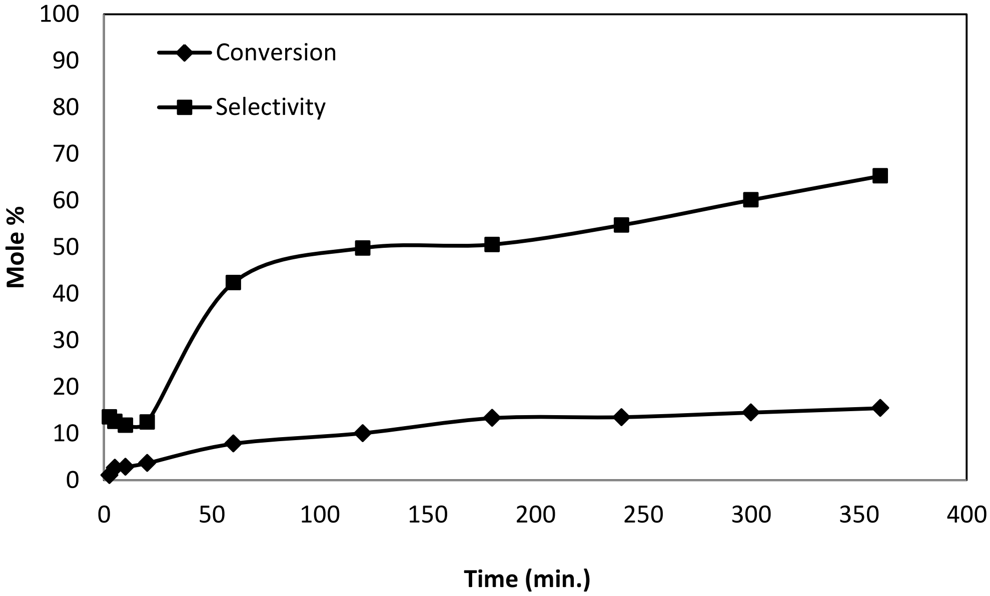


Figure 4.9. Citral conversion and selectivity to UA as function of time over Ru/SiO_2 catalyst at 300 °C.

On the other hand, Ru/TiO_2 catalyst showed higher activity than Ru/SiO_2 catalyst (Figure 4.10). This could be observed from the amount of the products produced. At the first 20 min citronellal was the main product then the reaction progressed towards the production of nerol and geraniol. The amount of UA was 51 %, 13 % citronellal, 17 % citronellol and little amount of 0.6 % 3,7-dimethyl-1-octanol and acetals. The results clearly showed that on Ru/TiO_2 catalyst, the C=C/C=O adsorption competition of the citral molecules is mainly in favor of the C=O bond, leading to a very high UA formation.

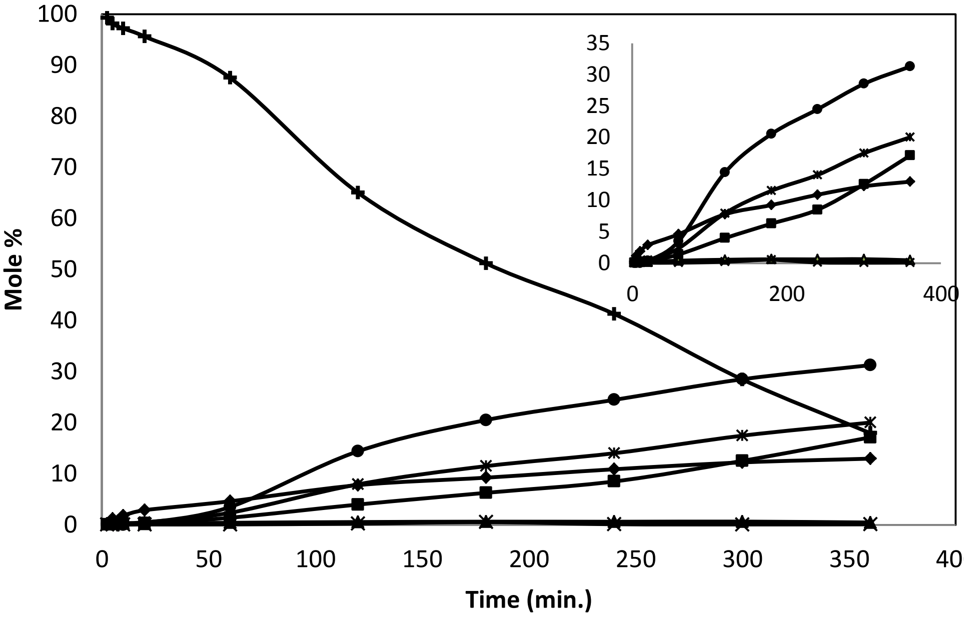


Figure 4.10. Composition of different species in citral hydrogenation over Ru/TiO_2 reduced at 300 °C: citral (+); nerol (✱); geraniol (●); citronellal (◆);citronellol (■); 3,7-dimethyl-1-octanol (▲); acetals (✕).

Conversion and selectivity to UA obtained over Ru/TiO_2 is given in Figure 4.11. Ru/TiO_2 catalyst showed higher activity, where maximum citral conversion achieved was 82% at 360 min reaction time. This could be related to the well dispersion and interaction of Ru on TiO_2 support, which was confirmed by XRD, SEM and TPR results. While maximum value for selectivity to UA was 65.7% at 48.8% citral conversion. However, selectivity to UA was found to be scarcely influenced by conversion in the range of 35-82 %. This indicates that consecutive reactions leading to citronellol and 3,7-dimethyl-1-octanol become important only when almost all citral has consumed (Galvagno et al. 1993).

The conversion and selectivity to the different products at LTR over Ru/SiO_2 and Ru/TiO_2 are shown in Table 4.3. In spite of the low surface area of TiO_2 compared with SiO_2, but this variation in the conversion values could be explained by the well dispersion of Ru over TiO_2 support.

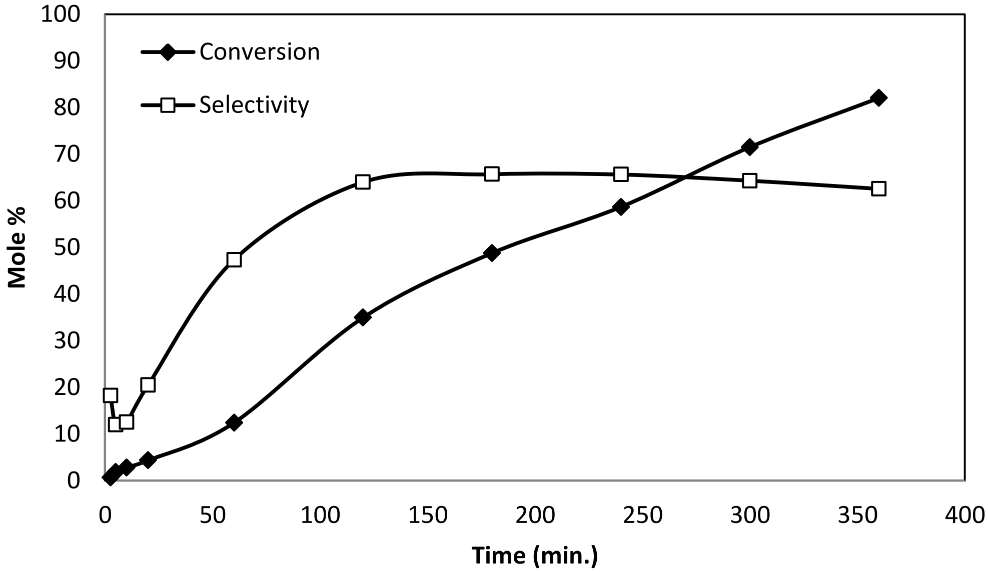


Figure 4.11. Citral conversion and selectivity to UA as function of time over Ru/TiO_2 catalyst at 300 °C.

Table 4.3. Conversion and selectivity to the different products at LTR over Ru/SiO_2 and Ru/TiO_2 at 360 min of reaction time.

Catalysts	**Conversion (%)**	**Selectivity (%)**				
		Citronellal	**Citronellol**	**UA (nerol & geraniol)**	**3,7-dimethyl-1-octanol**	**Acetals**
Ru/SiO_2 LTR	15.5	18.4	11.6	65.3	4.0	0.7
Ru/TiO_2 LTR	82.0	15.8	20.9	62.6	0.6	0.1

4.2.2. Activity and Selectivity of Ru/TiO_2/SiO_2 Catalyst

4.2.2.1. Ru/TiO_2/SiO_2 -SGD Catalyst

Figure 4.12 displays the products distribution for the hydrogenation of citral over Ru/TiO_2/SiO_2-SGD catalyst. The catalyst showed an increase in the major products amounts compared to the amounts produced by Ru/SiO_2 catalyst. No significant amount of UA were produced during the first hour of reaction, where the main product was citronellal and very small amount of citronellol and undesired compounds (3,7-dimethyl-1-octanol and acetals). After 60 min, the amount of UA increased within the reaction time to 19.5% after 360 min. This amount was double the amount that was obtained by Ru/SiO_2 catalyst (10%).

Figure 4.13 displays citral conversion and selectivity to UA as a function of time. The curves corresponding to the Ru/SiO_2 catalyst were also given for comparison. In terms of conversion, the modified catalyst showed increase in conversion (27.8%) compared with the non-modified one (15.5%) at 360 min reaction time. However, the increase in the selectivity to UA was low. The dispersion of TiO_2 on the SiO_2 support let to an improvement in the conversion and selectivity to UA which could be explained by the specific role of the reducible TiO_x species which can generate a strong metal-support interaction (SMSI effect) with Ru after reduction at 300 °C when the anatase nanocrystals were formed (Bonne et al. 2010, Li et al. 2004). These results were compatible with the results obtained by Ekou et al. (2011) and Rojas et al. (2008).

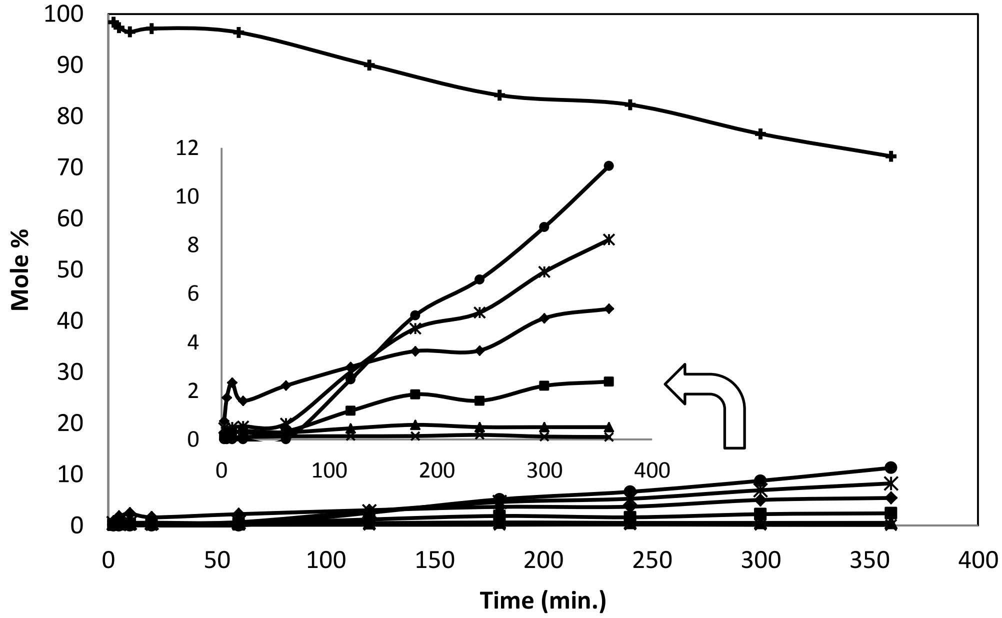


Figure 4.12. Composition of different species in citral hydrogenation over Ru/TiO_2/SiO_2 -SGD reduced at 300 °C: citral (+); nerol (✱); geraniol (●); citronellal (◆);citronellol (■); 3,7-dimethyl-1-octanol (▲); acetals (✕).

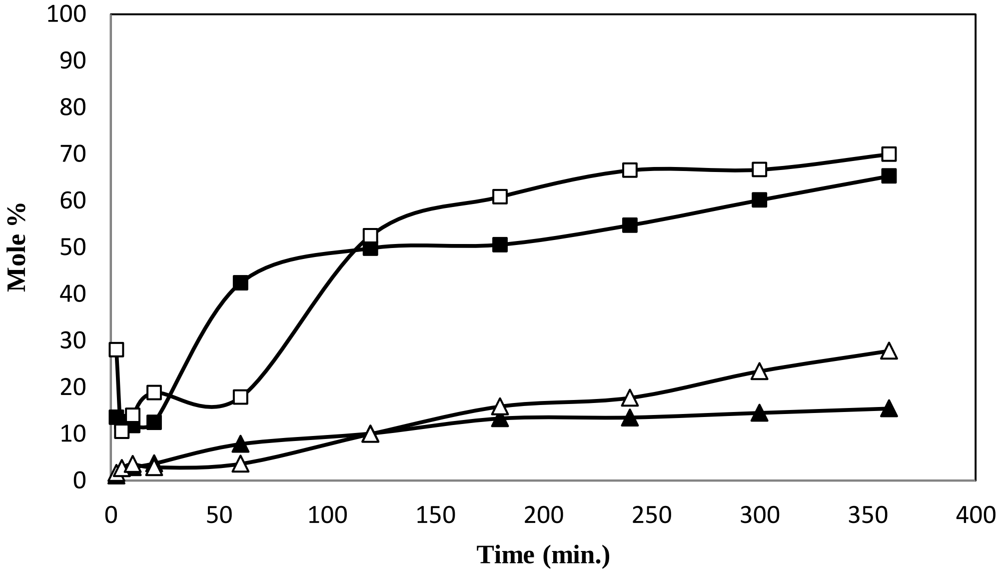


Figure 4.13. Citral conversion and selectivity to UA as function of time at LTR. (△) conversion and (☐) selectivity to UA for $Ru/TiO_2/SiO_2$ -SGD and (▲) conversion and (■) selectivity to UA for Ru/SiO_2.

4.2.2.2. $Ru/TiO_2/SiO_2$-IMP Catalyst

Figure 4.14 displays the product distribution for the hydrogenation of citral over $Ru/TiO_2/SiO_2$-IMP catalyst. The results revealed that the concentration of UA (nerol and geraniol), citronellal and citronellol formed was low in the first 120 min, after that a significant increase was observed, especially for UA.

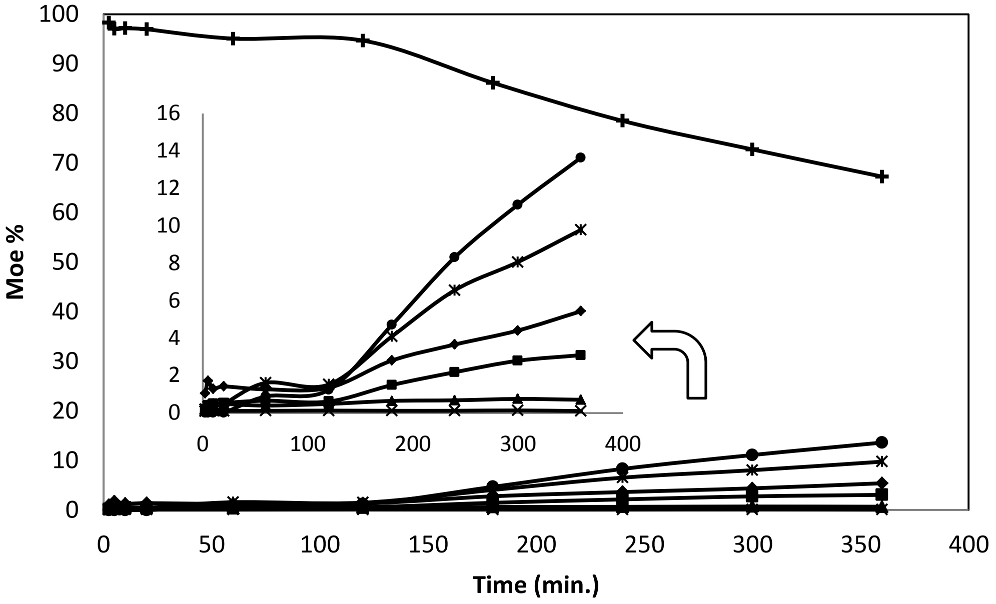


Figure 4.14. Composition of different species in citral hydrogenation over Ru/TiO$_2$/SiO$_2$ -IMP reduced at 300 °C: citral (+); nerol (✱); geraniol (●); citronellal (◆); citronellol (■); 3,7-dimethyl-1-octanol (▲); acetals (✕).

The results of conversion and selectivity to UA are shown in Figure 4.15. Conversion of citral was increased from 15.5% to 32.7% compared to Ru/SiO$_2$. However, this increment can be explained by the SMSI effect (Rojas et al. 2008, Ekou et al. 2011), while selectivity to UA was increased by 5%. On the other hand, the differences in activity and selectivity to UA for both catalysts can be related to the differences in dispersion of Ru on the surface of support for both catalysts. Dispersion and interaction of the Ru on the titanium containing materials for Ru/TiO$_2$/SiO$_2$-IMP catalyst was confirmed by TPR results. This was suggested that the interaction between Ru and TiO$_2$ could be preventing the active metals to aggregate and make big crystal during the reduction. XRD results were confirmed this suggestion from decreasing the intensity of Ru characteristic peaks Ru/TiO$_2$/SiO$_2$-IMP catalyst compared with Ru/SiO$_2$ catalyst.

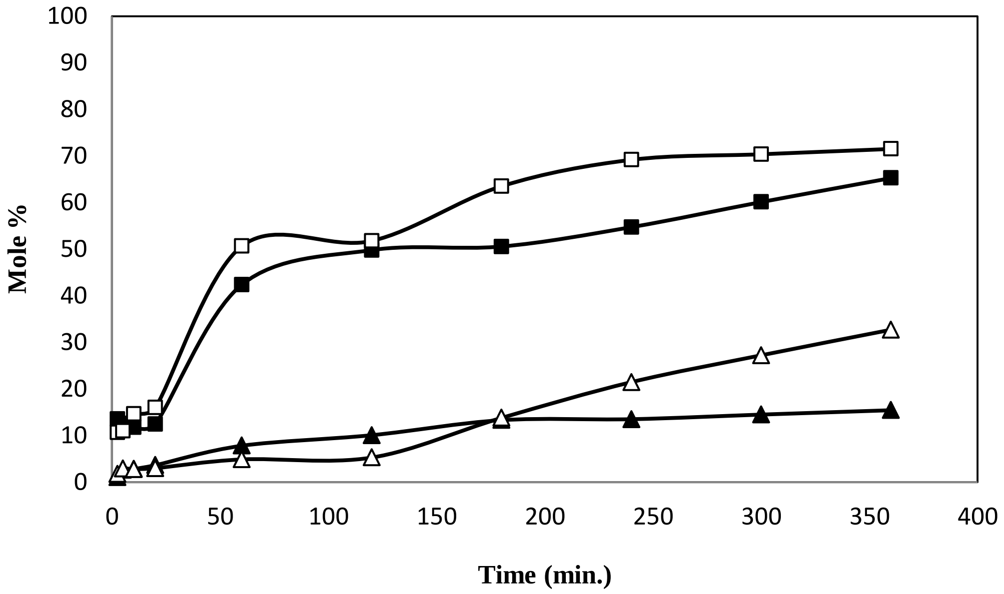


Figure 4.15. Citral conversion and selectivity to UA as function of time at LTR. (△) conversion and (☐) selectivity to UA for Ru/TiO_2/SiO_2-IMP and (▲) conversion and (■) selectivity to UA for Ru/SiO_2.

4.2.2.3. Ru/TiO_2/SiO_2 Catalyst-ABS

Product distribution observed over Ru/TiO_2/SiO_2-ABS catalyst is shown in Figure 4.16. Citral was consumed steadily with the reaction time. Geraniol and nerol were the main products reaching composition of 24 % and 16.4 % respectively after 360 min. Hydrogenation of conjugated C=C bond also occurred to produce citronellal. Formation of some amount of citronellol was also observed from consecutive hydrogenation of citronellal and UA. From further hydrogenation of citronellol, small amount of 3,7-dimethyl-1-octanol was produced. Negligible amount of acetals was observed over this modified catalyst. Acetals might be formed from the reaction between citral and citronellal with the solvent (Vilella et al. 2005).

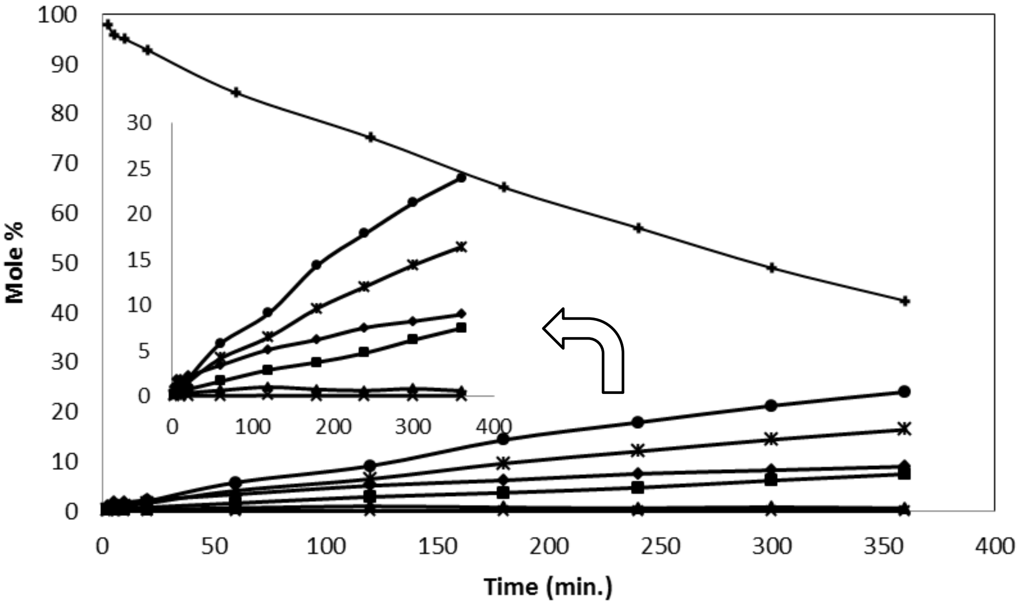


Figure 4.16. Composition of different species in citral hydrogenation over Ru/TiO_2/SiO_2 -ABS reduced at 300 °C: citral (+); nerol (✱); geraniol (●); citronellal (◆);citronellol (■); 3,7-dimethyl-1-octanol (▲); acetals (✕).

Large enhancement occurred in the conversion by using Ru/TiO_2/SiO_2-ABS catalyst compared to Ru/SiO_2 catalyst (Figure 4.17). The conversion obtained by the modified catalyst reached to 57.7 % while it was 15.5 % for Ru/SiO_2 catalyst. The change in conversion could be related to the good dispersion of Ru on the modified support which was proved by the TPR results. Furthermore, selectivity to UA reached to about 70 % after 180 min of reaction time and remained constant at this value. Results obtained were compatible with the other studies (Rojas et al. 2008, Ekou et al. 2011). This improvement could be explained by the SMSI effect generated from the formation of partially reduced $TiO_{(2-x)}$ species ($x < 2$) on the support, which participate to the activation of carbonyl function (Silva et al. 2003, Ekou et al. 2011).

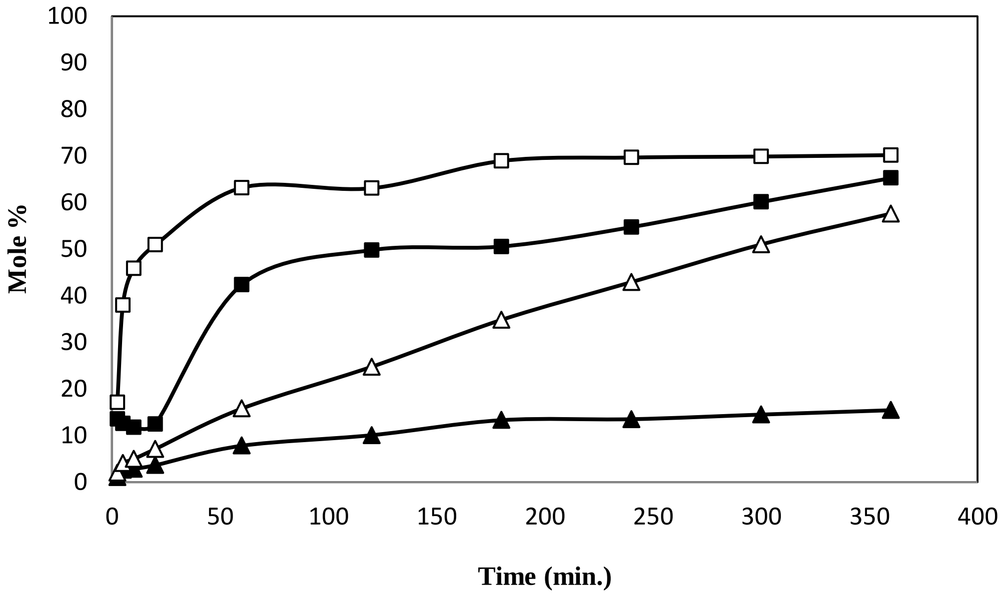


Figure 4.17. Citral conversion and selectivity to UA as function of time at LTR. (△) conversion and (☐) selectivity to UA for Ru/TiO_2/SiO_2 -ABS and (▲) conversion and (■) selectivity to UA for Ru/SiO_2.

4.2.3. Comparison Activity and Selectivity for Ru/TiO_2/SiO_2 Catalysts

Conversions of citral over Ru/TiO_2/SiO_2 catalysts prepared by different methods, namely sol gel deposition, slow impregnation and absorption, are shown in Figure 4.18. Catalyst prepared by absorption showed much higher conversion than other catalysts. This could be explained by the method used to create TiO_2/SiO_2 support. TiO_2/SiO_2 support using absorption method was prepared by loading TiO_2 on SiO_2 in multiple steps (three steps to reach the desired loading of TiO_2). This provided a better TiO_2 dispersion on SiO_2, this was confirmed by the SEM results. As a result good interaction for Ru was obtained and proved by TPR. Also active sites were different as noted by and XRD (anatase phase). However, single step loading was used to load TiO_2 on the surface of SiO_2 to create other supports (TiO_2/SiO_2-SGD and TiO_2/SiO_2-IMP). On these supported oxides, SEM showed that agglomeration of TiO_2 on the surface of SiO_2, which might be revealed to the poor dispersion of TiO_2 on SiO_2.

In terms of selectivity, there was no significant difference in overall selectivities for all the catalysts after 240 min of reaction (Figure 4.19). When reaction time was less than 240 min. there was a clear difference in the selectivities, where Ru/TiO_2/SiO_2-ABS catalysts showed higher selectivity to UA than other catalysts. This might be related to the good dispersion of TiO_2 on the surface of SiO_2 and good interaction of Ru on TiO_2/SiO_2 prepared by absorption method.

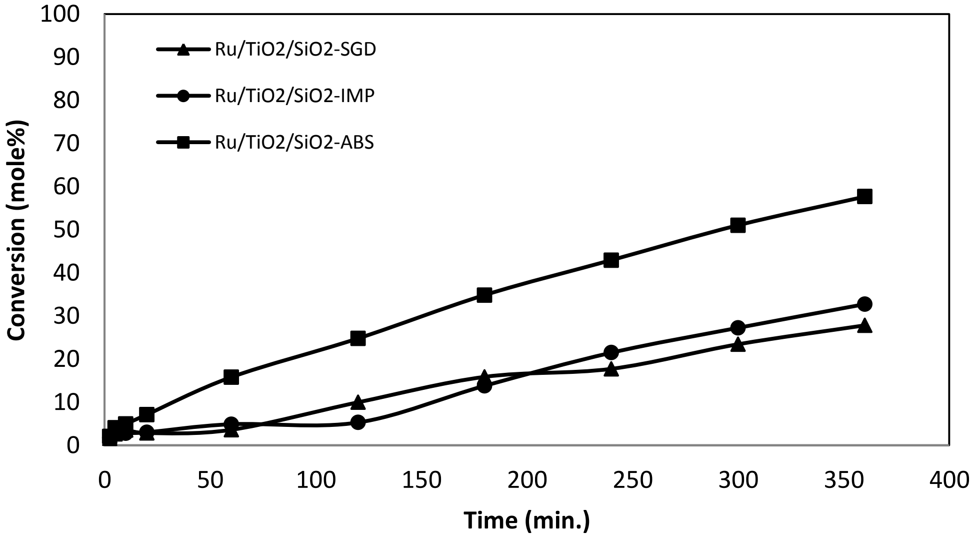


Figure 4.18. Comparison of citral conversions for different $Ru/TiO_2/SiO_2$ catalysts as a function of time.

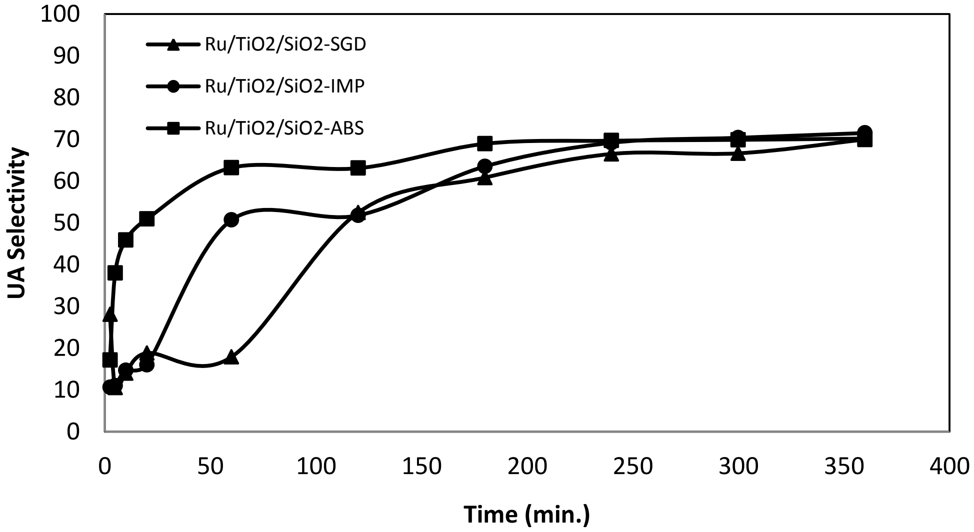


Figure 4.19. Comparison of selectivities to UA for different $Ru/TiO_2/SiO_2$ catalysts as a function of time.

4.2.4. Effect of Different Reduction Temperatures

The influence of catalyst reduction temperature on the activity and selectivity of Ru/SiO_2, Ru/TiO_2 and $Ru/TiO_2/SiO_2$ catalysts was investigated. For this purpose, citral hydrogenations were carried out over catalysts activated at 450 °C (HTR).

4.2.4.1. Ru/SiO_2 Catalyst

Figure 4.20 shows products distribution for Ru/SiO_2 catalyst activated at HTR. At the first 60 min citronellal, citronellol and UA were produced steadily with the reaction time. After that, amount of citronellal and citronellol did not change noticeably. Only there was formation of nerol and geraniol (UA). Moreover, very low amounts of 3,7-dimethyl-1-octanol and acetals were produced.

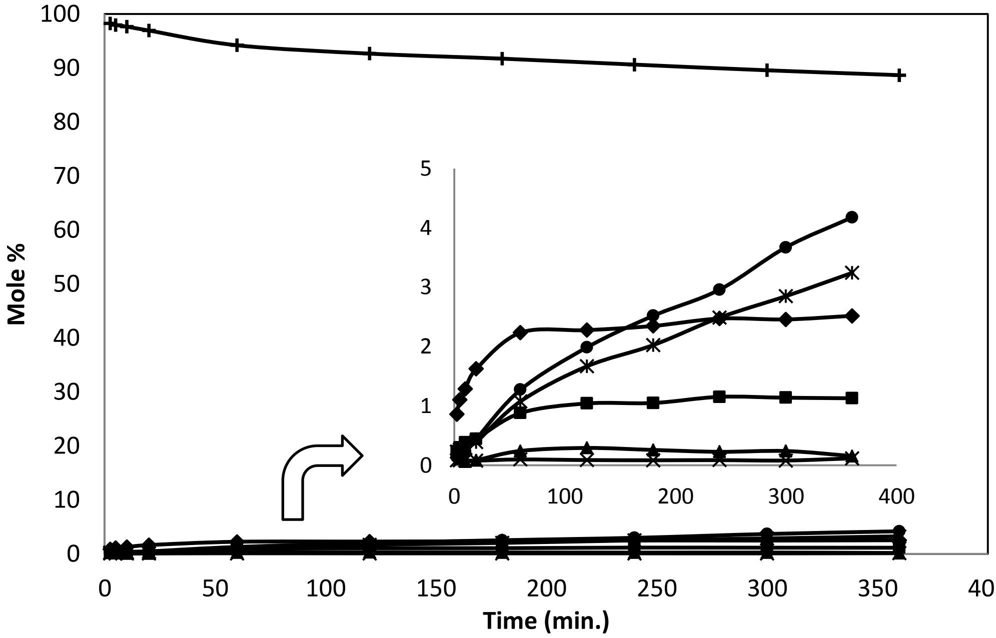


Figure 4.20. Composition of different species in citral hydrogenation over Ru/SiO_2 reduced at 450 °C: citral (+); nerol (✱); geraniol (●); citronellal (◆);citronellol (■); 3,7-dimethyl-1-octanol (▲); acetals (✕).

On the other hand, at high reduction temperature, the conversion was 11.3 %, while it was 15.5 % at LTR. This might be explained by the low interaction of Ru with SiO_2 which could be caused by the sintering of active sites during the activation at high temperature (Vicente et al. 2011). Furthermore, there was no change observed in the selectivity to UA at HTR compared to LTR during the reaction time (Figure 4.21). This phenomenon could be related to the nature of SiO_2 which act as inert support and did not affect the catalyst very much.

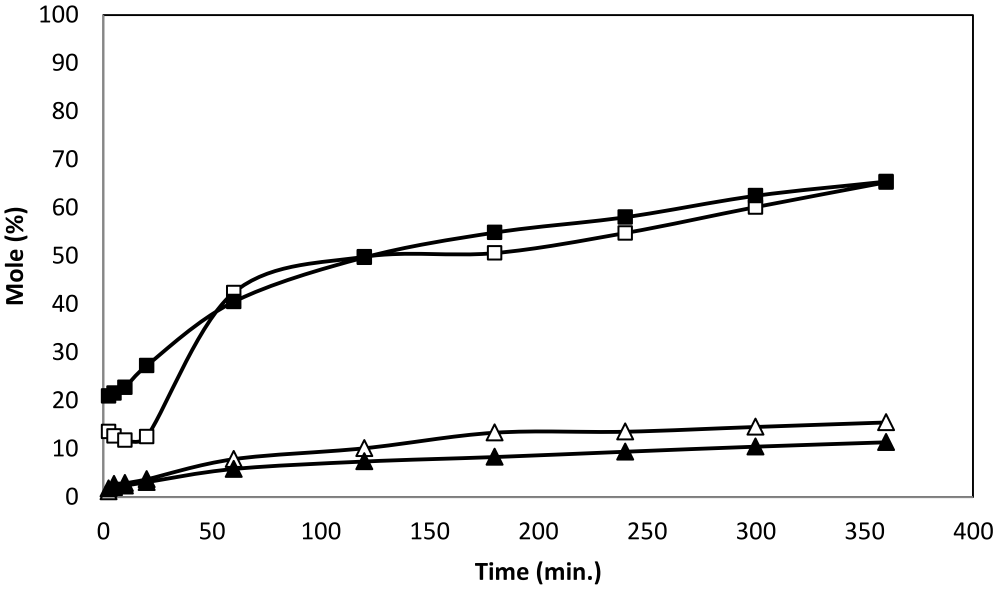


Figure 4.21. Comparison of citral conversion and selectivity to UA as function of time over Ru/SiO_2 catalyst at LTR (△) conversion and (☐) selectivity to UA, and HRT (▲) conversion and (■) selectivity to UA.

4.2.4.2. Ru/TiO_2 Catalyst

Citronellal was the main product in the first 20 min. After that, amounts of nerol and geraniol were increased progressively and reached to 15.9 % and 27.9 %, respectively at 360 min. Production of 3,7-dimethyl-1-octanol and acetals were low; i.e. not significant (Figure 4.22). Figure 4.23 shows the comparison of citral conversion and selectivity to UA at low and high reduction temperature. For the same reaction time, the conversion was decreased from 82 % at LTR to 62.5 % at HTR. The decrease in conversion might be due to the coverage part of active metal by TiO_x reduced species. However, selectivity to UA was larger at HTR than that at LTR. This was in agreements with the results obtained by other studies (Silva et al. 2003, Rojas et al. 2008, Ekou et al. 2011), in which this was explained by role of SMSI effect. The promoting effect on selectivity could be resulted from the creation of $TiO_{(2-x)}$ (x < 2) partially reduced species of TiO_2 support, which would participate in the hydrogenation of C=O bond.

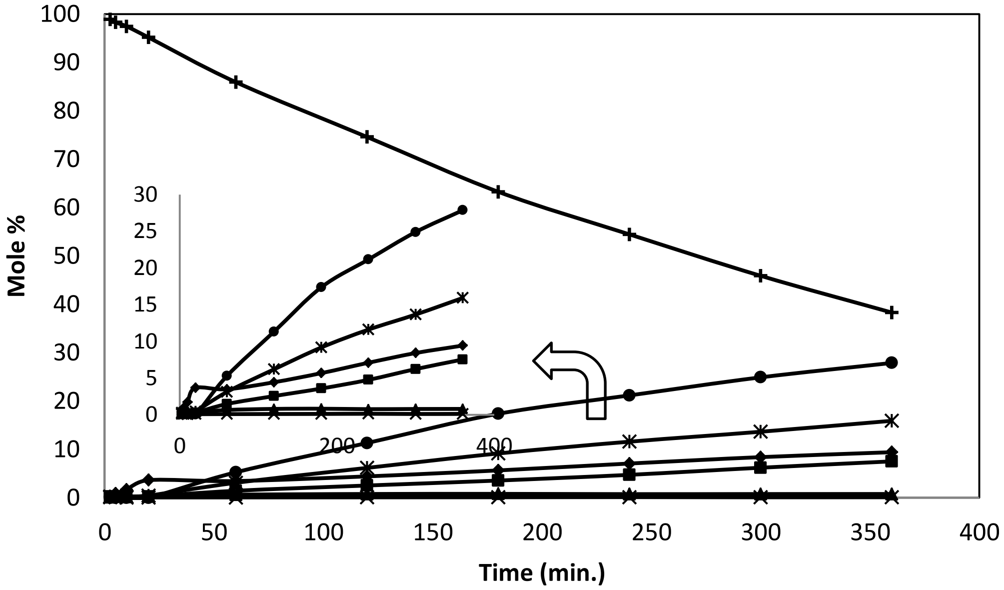


Figure 4.22. Composition of different species in citral hydrogenation over Ru/TiO_2 reduced at 450 °C: citral (+); nerol (✱); geraniol (●); citronellal (◆);citronellol (■); 3,7-dimethyl-1-octanol (▲); acetals (✕).

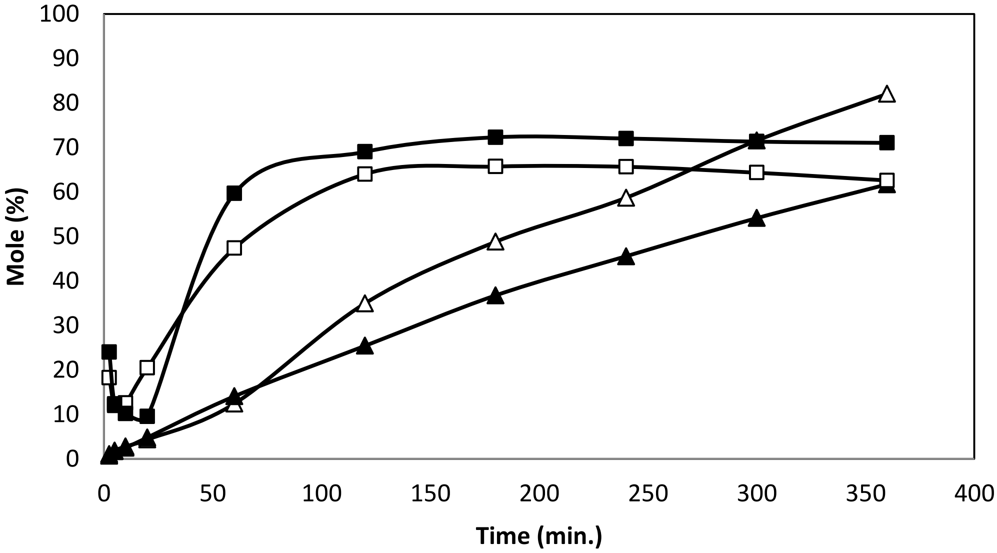


Figure 4.23. Comparison of citral conversion and selectivity to UA as function of time over Ru/TiO_2 catalyst at LTR (△) conversion and (□) selectivity to UA, and HRT (▲) conversion and (■) selectivity to UA.

4.2.4.3. Ru/TiO$_2$/SiO$_2$-SGD Catalyst

Figure 4.24 displays the product distribution of citral hydrogenation over Ru/TiO$_2$/SiO$_2$-SGD catalyst at HTR. The major product observed was citronellal in the first 10 min of reaction and then nerol and geraniol was started to increase gradually. Production of citronellol was observed to be associated with the production of citronellal. Its amounts were increased and decreased with citronellal. However, 3,7-dimethyl-1-octanol was produced from further hydrogenation of citronellol.

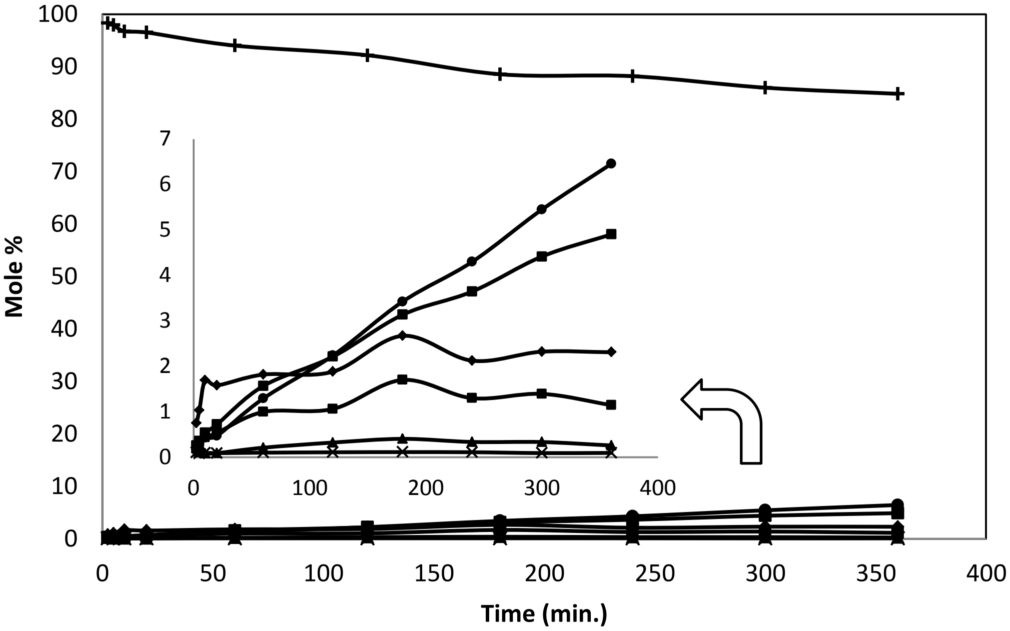


Figure 4.24. Composition of different species in citral hydrogenation over Ru/TiO$_2$/SiO$_2$-SGD catalyst reduced at 450 °C: citral (+); nerol (✱); geraniol (●); citronellal (◆);citronellol (■); 3,7-dimethyl-1-octanol (▲); acetals (✕).

Conversion and selectivity to UA over Ru/TiO$_2$/SiO$_2$-SGD catalyst at LTR and HTR are shown in Figure 4.25. There was no significant change in conversion during the reaction time after 180 min of reaction. Lower conversion was observed for HTR. This could be explained by the sintering of active sites and/or poisoning the active site by the reduced TiO$_x$ species. The change in selectivity to UA at different reduction temperatures was little. This might be related to the few modified site created from the SMSI between the TiO$_x$ species and the metals. This could be due to the low dispersion of Ru on TiO_2 areas which in turn was resulted from the poor distribution of TiO_2 on SiO_2 surface (SEM and TPR results).

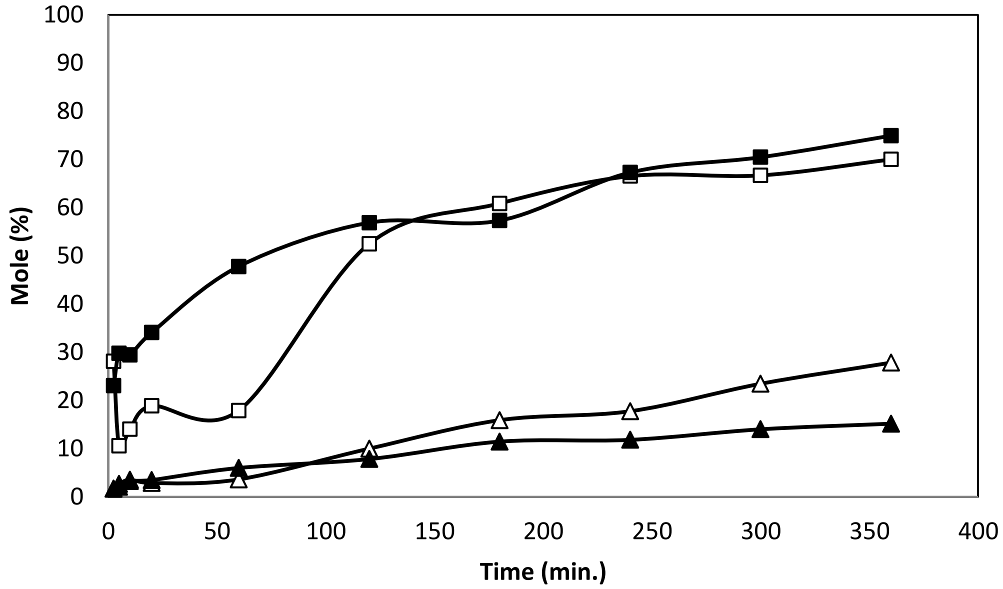


Figure 4.25. Comparison of citral conversion and selectivity to UA as function of time over $Ru/TiO_2/SiO_2$ -SGD catalyst at LTR (△) conversion and (□) selectivity to UA, and HRT (▲) conversion and (■) selectivity to UA.

4.2.4.4. $Ru/TiO_2/SiO_2$-IMP Catalyst

Figure 4.26 displays the product distribution of citral hydrogenation over $Ru/TiO_2/SiO_2$-IMP catalyst at HTR. Production of nerol, geraniol and citronellal were almost produced in the same rate at the first 60 min. After that, amount of citronellal decreased and then increased slightly during the reaction time. While the amount of nerol and geraniol increased significantly during the reaction. Also the production of citronellol was associated with the production and hydrogenation of citronellal. The amounts of undesired products (3,7-dimethyl-1-octanol and acetals) were very low.

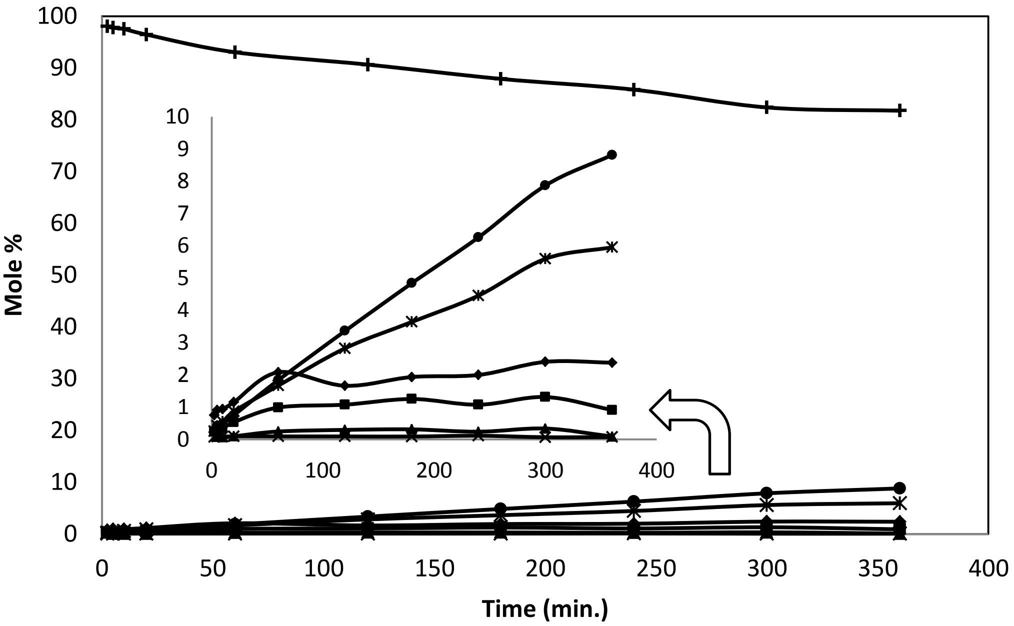


Figure 4.26. Composition of different species in citral hydrogenation over $Ru/TiO_2/SiO_2$-IMP catalyst reduced at 450 °C: citral (+); nerol (✱); geraniol (●); citronellal (◆);citronellol (■); 3,7-dimethyl-1-octanol (▲); acetals (✕).

The differences in the conversion and selectivity to UA at different reduction temperatures are shown in the Figure 4.27. At HTR, the value of conversion was decreased to the half (about 18 %) at 360 min, while it was ~36 % at LTR. This also could be explained by the poisoning of active sites through the SMSI effect and/or by the sintering of Ru species. Moreover, selectivity to UA was increased during the reaction time at HTR where reached 81 % at 360 min compared to the value of 71.5 % at LTR. These results were revealed to the effect of SMSI and were compatible to the results obtained by many studies (Malathi et al. 2001, Silva et al. 2003, Rojas et al. 2008 and Ekou et al. 2011).

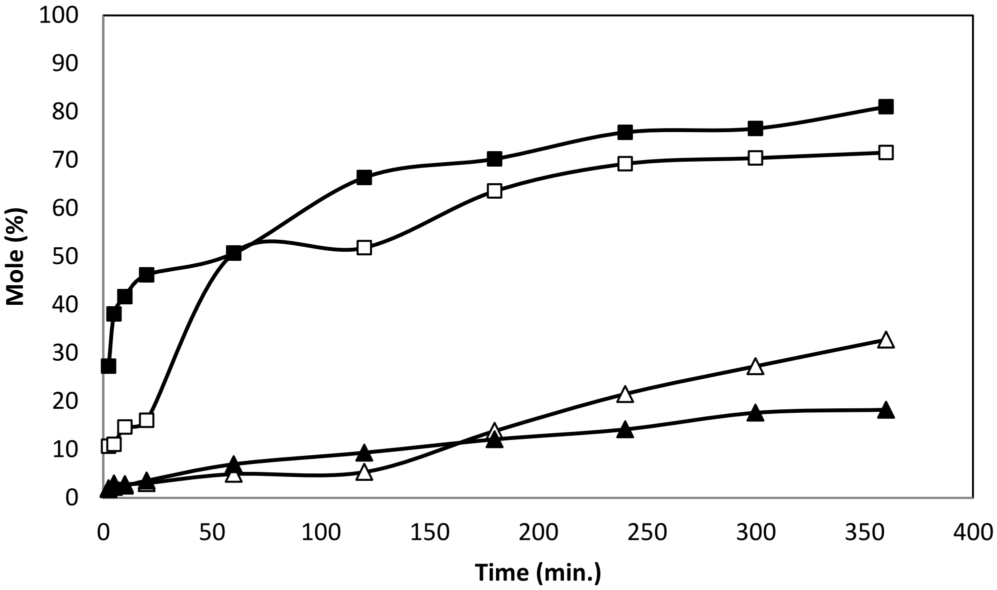


Figure 4.27. Comparison of citral conversion and selectivity to UA as function of time over $Ru/TiO_2/SiO_2$-IMP catalyst at LTR (△) conversion and (☐) selectivity to UA, and HRT (▲) conversion and (■) selectivity to UA.

4.2.4.5. $Ru/TiO_2/SiO_2$-ABS Catalyst

Figure 4.28 displays the product distribution of citral hydrogenation over $Ru/TiO_2/SiO_2$-ABS catalyst activated at HTR. Concentrations of major products (nerol, geraniol and citronellal) were increased with the reaction time. Figure 4.29 are shown the comparison of citral conversion and selectivity to UA as function of time over $Ru/TiO_2/SiO_2$-ABS catalyst at LTR and HTR. The conversion of citral decreased during the reaction time to 42.2 % at 360 min for HTR, while it was 57.6 % at LTR. This was due to SMSI effect as discussed in the previous section. In terms of selectivity to UA, there was no significant change occurred for the selectivity to UA for both reduction temperatures. These results indicated that probably metal support interaction was not affected very much by temperature change as it was already obtained at LTR.

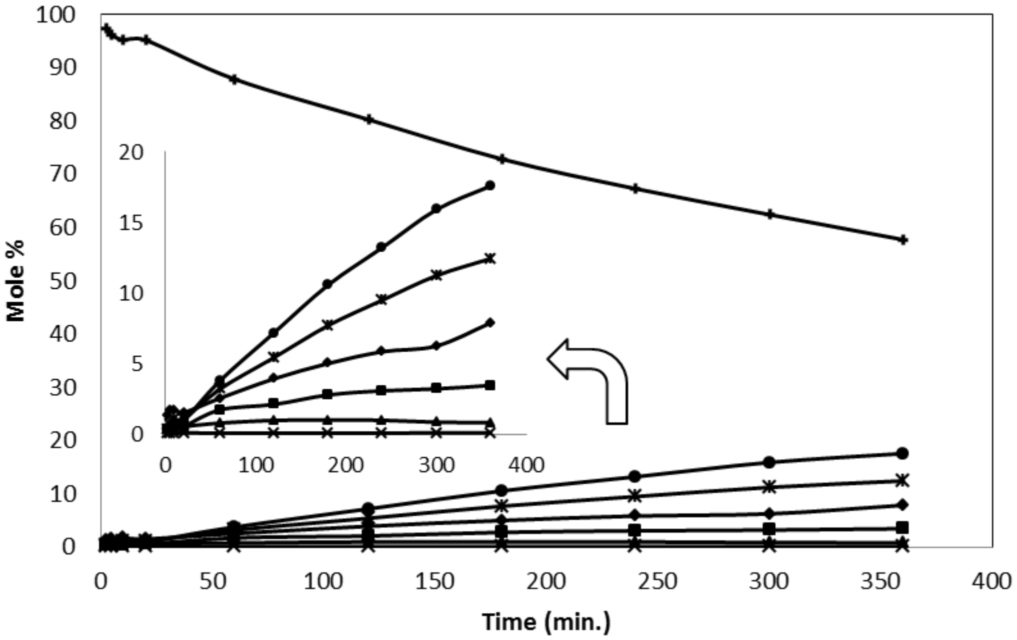


Figure 4.28. Composition of different species in citral hydrogenation over $Ru/TiO_2/SiO_2$-ABS catalyst reduced at 450 °C: citral (+); nerol (✱); geraniol (●); citronellal (◆);citronellol (■); 3,7-dimethyl-1-octanol (▲); acetals (✕).

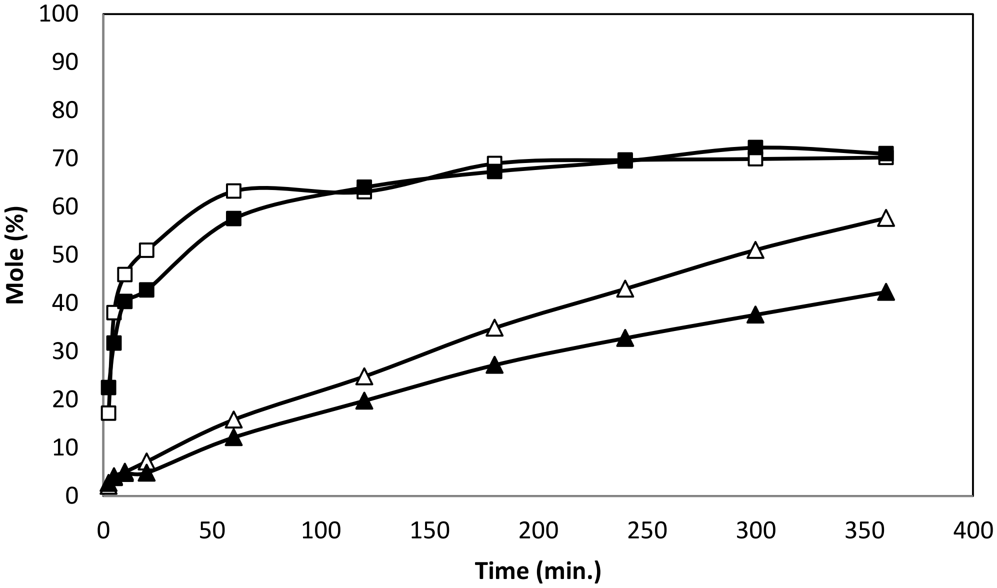


Figure 4.29. Comparison of citral conversion and selectivity to UA as function of time over $Ru/TiO_2/SiO_2$-ABS catalyst at LTR (△) conversion and (□) selectivity to UA, and HRT (▲) conversion and (■) selectivity to UA.

4.2.4.6. Comparison of Citral Conversion and Selectivity to UA at LTR and HTR for All Catalysts

In Figure 4.30, citral conversion for different catalysts at different reduction temperature (LTR and HTR) is given. For a given reaction time, all the catalysts reduced at 300 °C were found to be more active for the hydrogenation of citral than their counterparts reduced at 450 °C. For Ru/TiO_2 and different types of Ru/TiO_2/SiO_2 catalysts, this behavior could be explained by the presence of partially reduced species ($TiO_{(2-x)}$ ($x < 2$)) generated after reduction at high temperature, which can cover part of the metallic surface (Silva et al. 2003, Ekou et al. 2011) and/or might be due to the sintering of active compounds at high reduction temperature. In the case of Ru/SiO_2 the decrease in the activity at HTR could be related to the decrease the number of active sites by sintering at high temperature.

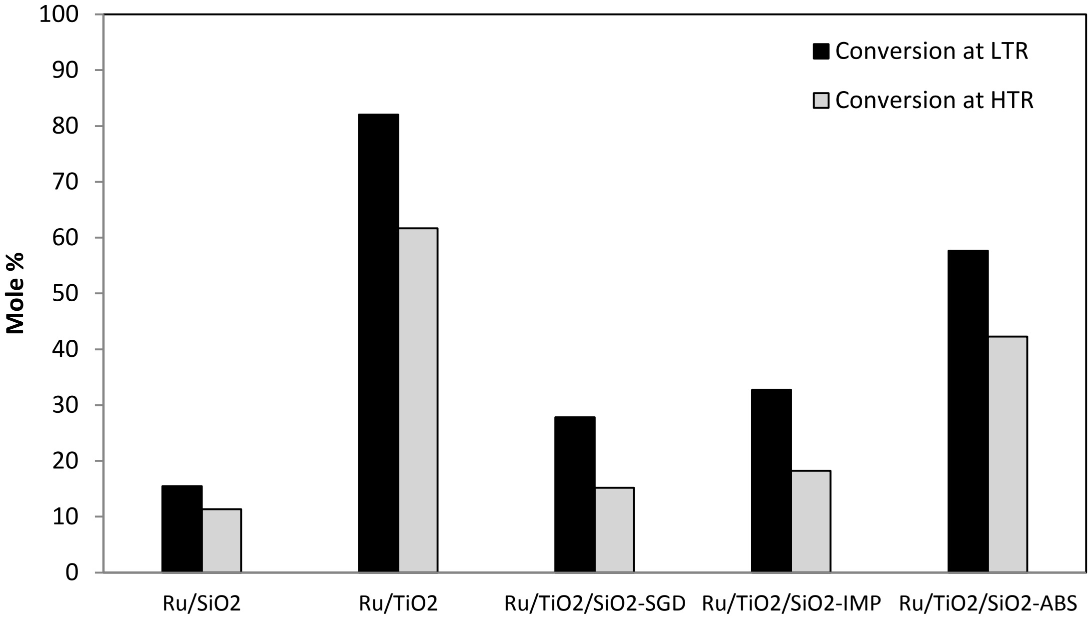


Figure 4.30. Conversion of citral at 360 min for different catalysts at LTR and HTR.

On the other hand, the overall selectivities to unsaturated alcohol for different catalysts at HTR were found to be greater than that obtained from their counterparts at LTR except Ru/SiO_2 catalyst (Figure 4.31). Increment of selectivity to UA at HTR explained by the SMSI effect, where the reduction at high temperature leads to a surface decoration of the Ru metal crystallites by TiO_x species, contributing to the polarization of the carbonyl group, C=O, and they make easier the hydrogenation of citral to produce corresponding UA (nerol and geraniol) (Silva et al. 2003, Ekou et al. 2011, Rojas et al. 2008). However, no significant change in the selectivity to UA was obtained at HTR for Ru/SiO_2. This might be attributed to the nature of SiO_2 which act as inert material.

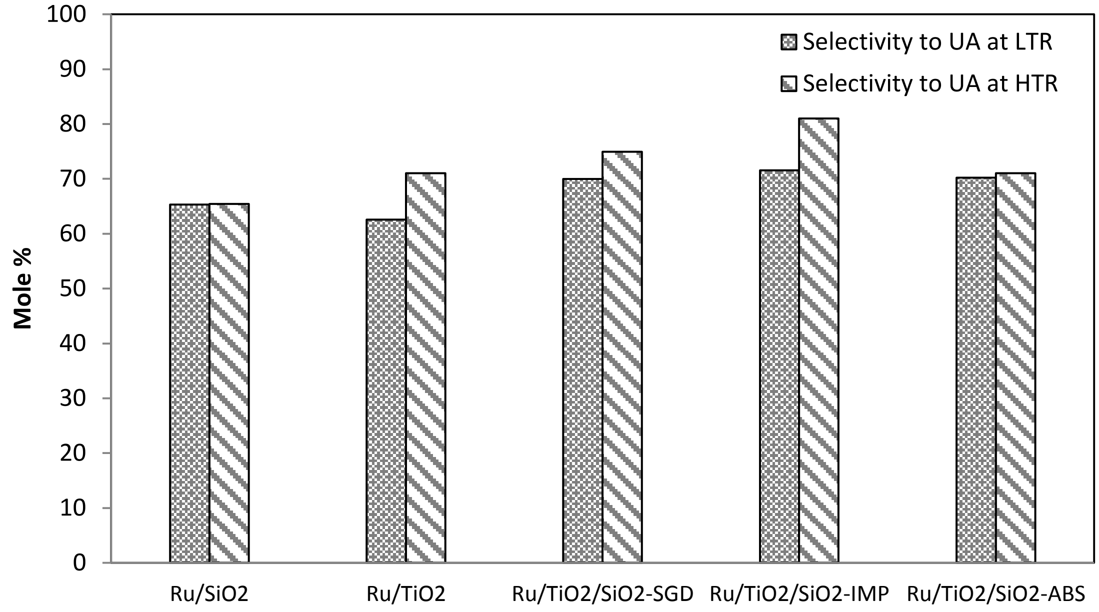


Figure 4.31. Selectivity to UA at 360 min for different catalysts at LTR and HTR.

4.2.5. Comparison of Catalysts Activities and Selectivities

Conversions, selectivities to different products at low and high reduction temperatures are reported in Table 4.4. From the results below, Ru/TiO_2 catalyst showed the highest activity in term of conversion among the other catalysts at LTR. Ru/TiO_2/SiO_2-IMP catalyst showed the highest selectivity to UA among the other catalysts at HTR. Furthermore, Ru/TiO_2/SiO_2-ABS catalyst showed the highest conversion among the Ru/TiO_2/SiO_2 modified catalysts, also with high selectivity to UA reached to 71% at HTR. Citronellal was produced with all type of catalysts, and maximum selectivity of 22.2 % was observed over Ru/SiO_2 catalyst at HTR with respect to other catalysts. Maximum selectivity to citronellol was obtained over Ru/TiO_2. These results were similar to what observed by Ekou et al. (2011) over Pt catalysts supported on SBA and TiO_2 (P25). Moreover, Ru/TiO_2/SiO_2-ABS catalyst seems to be more selective to citronellol and less selective to citronellal compared with other modified catalysts.

Table 4.4. Conversion and selectivity to the different products at LTR and HTR over different type of catalysts at 360 min of reaction time.

Catalysts	**Conversion (%)**	**Selectivity (%)**				
		Citronellal	**Citronellol**	**UA (nerol & geraniol)**	**3,7-dimethyl-1-octanol**	**Acetals**
Ru/SiO_2 LTR	15.5	18.4	11.6	65.3	4	0.7
Ru/SiO_2 HTR	11.3	22.2	10	65.4	1.4	1
Ru/TiO_2/SiO_2-SGD LTR	27.8	19.3	8.5	70.0	1.8	0.4
Ru/TiO_2/SiO_2-SGD HTR	15.2	15.2	7.5	75.0	1.7	0.6
Ru/TiO_2/SiO_2-IMP LTR	32.7	16.6	9.4	71.5	2.1	0.3
Ru/TiO_2/SiO_2-IMP HTR	18.2	13.1	5.0	81.0	0.5	0.4
Ru/TiO_2/SiO_2-ABS LTR	57.7	15.6	13.0	70.2	1.1	0.1
Ru/TiO_2/SiO_2-ABS HTR	42.3	18.6	8.2	71.0	2.0	0.2
Ru/TiO_2 LTR	82.0	15.8	20.9	62.6	0.6	0.1
Ru/TiO_2 HTR	61.7	15.3	12.2	71.0	1.3	0.2

CHAPTER 5

CONCLUSIONS

TiO_2 dispersion on SiO_2 showed differences among different preparation methods used, sol-gel deposition, impregnation and absorption. Well defined crystalline anatase phase was only observed by absorption method (TiO_2/SiO_2-ABS). Ru characteristic peaks were observed over all the catalysts except Ru/TiO_2.

TiO_2 loading decreased the pores sizes. Surface area also decreased during the loading of TiO_2 in different supported oxides except the one prepared by absorption method, where new areas might be created. All catalysts were mesoporous materials.

TPR results revealed that high dispersion and interaction of Ru with TiO_2 support. Ru interaction was the highest with TiO_2/SiO_2-ABS among other supported oxide. Over SiO_2, interaction was weaker.

Ru supported catalysts favoured the hydrogenation of carbonyl bond, leading to high unsaturated alcohol (UA) formation. Activities and selectivities were affected by the support used. Ru titania interaction increased activity and selectivity. The highest activity and selectivity was obtained over Ru/TiO_2. Among the different supported oxides, Ru/TiO_2/SiO_2-ABS catalyst gave the highest conversion at lower reduction temperature. Its selectivity to UA was also high. Anatase phase presence might have also contributed to the catalytic activities obtained.

All the catalysts showed a decrease in the conversion level at higher reduction temperature. This was explained by the poisoning of active sites with the reduced TiO_x species which covered part of active compounds. In case of Ru/SiO_2, this was related to the sintering of the active sites.

Selectivity to unsaturated alcohol (nerol and geraniol) was higher than other products. Selectivities were increased at HTR compared to LTR over titania containing catalysts. The promoting effect on selectivity resulted from more interaction between Ru with TiO_2. However, no significant change in the selectivity to UA was obtained at HTR for Ru/SiO_2. This was related to the inert nature of SiO_2.

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APPENDIX A

RESULTS AND DISCUSSIONS OF PRELIMINARY STUDY

In the preliminary study, selective hydrogenation of citral was studied over many types of catalysts using different conditions. Table A.1 presents the catalysts, condition and the selectivities of products for citral hydrogenation and Figure A.1 shows the composition of different species in citral hydrogenation over different catalysts and conditions.

All the catalysts were prepared by impregnation method. The procedure for this method was described in the experimental study section of this thesis. In all the runs, 250 mg of catalyst was reduced in-situ in flow of H_2 to the desired reduction temperature.

In run 1 (Figure A.1 a), the main product was acetals, where the selectivity reached about 71 %. The selectivity to UA (nerol and geraniol) was 18.5 %. Increasing the reduction temperature to 450 °C in run 2 (Figure A.1 b), the conversion was decreased from 41.6 % to 35.7 %. This could be resulted from the decreasing the numbers of active sites caused by the sintering of these sites during the activation at high temperature (Vicente et al. 2011). Again there was a lot of acetal formation. The production of acetals might be formed from the reaction between citral and citronellal with the solvent (Vilella et al. 2005). For this reason reaction was carried out in isopropanol (run 3, Figure A.1 c). No detectable amount of acetals was formed. This confirmed the role of the solvent.

To asses influence of calcination on catalyst activity and selectivity, catalysts were activated without calcination run 4 (Figure A.1 d) and 5 (Figure A.1 e). Similar results to runs 1 and 2 were obtained. Showing that calcination was not the reason for the activities obtained. The difference in the production of acetals might be resulted from the acidity of ethanol which might be sufficient to promote acetalization. When the catalyst was reduced to Ru^0, part of Ru could be positively charged giving $Ru^{\delta+}$, the latter possesses a weak Lewis acidity promoting acetalization (Mäki-Arvela et al. 2002).

To examine influence of the support, Ru was loaded onto TiO_2 (run 6, Figure A.1 f). Higher activities and selectivitivies were obtained compared to SiO_2 support.

Conversion of 42.6 % and the selectivity to UA of 72.7 % was achieved at 420 min. This could be related to the good interaction of Ru with TiO_2 as confirmed in characteristic analysis of this study. Although the reaction was carried out in ethanol, selectivity to acetals was low (4.1 %). This also showed the role of the active species in acetal formation.

The effect of bimetallic catalyst on the activity was investigated by preparing Ru-Sn/TiO_2 using catalytic reduction method (run 7, Figure A.1 g). The details of this method are as follows. A known amount of Ru/TiO_2 catalyst was activated at the activation temperatures of 350 °C under H_2 flow for 4 h. Then it was placed in a glass reactor with tetrabutyl tin dissolved in toluene. The slurry was mixed for 1 h under H_2 bubbling. After that it was filtered out and dried at 120 °C overnight (Lafaye et al., 2004). This catalyst gave 65.4 % conversion and 69.2 % selectivity. Increase in the activity of catalysts compared to the monometallic catalysts in run 6 could be related to the increment of reaction temperature. However selectivity dropped slightly. This showed that bimetallic catalyst did not give much benefit for the selectivity.

To increase conversion and selectivity, higher temperature could be pursued and TiO_2 could be dispersed on high surface area support. This will improve the mechanical strength, thermal stability, and surface area of TiO_2. Two different methods were applied, incipient wetness impregnation and sol-gel deposition for TiO_2/SiO_2 preparation.

In incipient wetness impregnation, SiO_2 support was initially preheated to remove the physisorbed water before impregnation. A 2-propanol solution of titanium isopropoxide (5 g 2-propanol and 0.597 g $Ti(OiPr)_4$) was prepared. The preparation was performed inside a glove box in an inert atmosphere of N_2. SiO_2 (3 g) was impregnated with the 2-propanol solution at room temperature. The samples were kept inside the glove box with flowing N_2 for overnight. The samples were subsequently dried at 120 °C in flowing N_2 for 1 h and calcined at 500 °C in flowing air for 4 h. Ru (2wt %) catalyst supported on 8wt%TiO_2/SiO_2 used in run 8 (Figure A.1 h) was reduced at 300 °C. The conversion of citral was about 31 %, but the product distributions and selectivities were almost the same as in run 4 when SiO_2 support was used. This might be related to low loading of TiO_2 and/or to the not well distribution of TiO_2 on the surface of SiO_2. A significant amount of acetal formation was observed.

In sol-gel deposition method, mixture of tetraethylorthosilicate (TEOS), H_2O and ethanol were prepared and HCl was added by drop wise until the solution pH reaches to 3. This mixture was allowed to stir for 2 h. After 2 h, specified amount of titanium isopropoxide ($Ti(OiPr)_4$) dissolved in ethanol ($Ti(OiPr)_4$/ethanol=1:10) and was added to the TEOS solution. The mixture temperature was kept around 20 ^oC during $Ti(OiPr)_4$ addition in order to prevent the precipitation of Ti particles. Then, solution temperature was increased to 80 ^oC to complete the gelation. Formed gel was dried at 80 ^oC for 24 h. The dried catalysts were grinded and calcined at 550 ^oC for 6 h. After Ru was loaded with 2 wt%, catalyst was used in run 9 (Figure A.1 i). Although good selectivity to UA was obtained, the activity of catalyst was low (9.7 % conversion). Less acetal was formed compared to Ru/8wt%TiO_2/SiO_2. This could be related to the method of mixed-oxide preparation, where Ti atoms are shown to substitute Si in the silica framework or matrix (Gao et al. 1998).

From the above studies it was decided to investigate TiO_2/SiO_2 supports prepared by different methods on activity and selectivity of Ru catalysts in citral hydrogenation.

Table A.1. Products selectivities for citral hydrogenation carried out over different catalysts and conditions.

Run	Catalyst	Calcination Temp. of Catalyst,°C	Reduction Temp. °C	Solvent	Reaction Temp. °C	Conversion %	Selectivity %				
							Citronellal	Citronellol	Nerol & Geraniol (UA)	3,7-dimethyl-1-octanol	Acetals
1	1wt%Ru/SiO_2	500	350	Ethanol	80	41.6	2.1	2.2	18.5[a]	6.1	71.2
2	1wt%Ru/SiO_2	500	450	Ethanol	80	35.7	1.6	3.1	19.5	4.8	71.0
3	1wt%Ru/SiO_2	500	450	2-propanol	80	0.9	39.7	0	60.3	0	0
4	2wt%Ru/SiO_2	N.C[b]	350	Ethanol	80	46.6	8.6	2.6	17.1	1.1	70.6
5	2wt%Ru/SiO_2	N.C	450	Ethanol	80	31.5	9.1	3.1	18.5	0.9	68.4
6	2wt%Ru/TiO_2[c]	400	300	Ethanol	80	42.6	15.0	7.8	72.7	0.5	4.1
7	2wt%Ru-Sn/TiO_2[d]	400	300	Ethanol	100	65.4	14.1	9.1	69.2	0.7	6.8
8	2wt%Ru/8wt%TiO_2/SiO_2[e]	400	300	Ethanol	100	30.8	5.2	2.8	19.0	3.2	69.8
9	2wt%Ru/6wt%TiO_2-SiO_2(SG)[f]	400	300	2-propanol	100	9.7	16.8	10.8	60.9	2.1	9.4

a) Geraniol not produced.

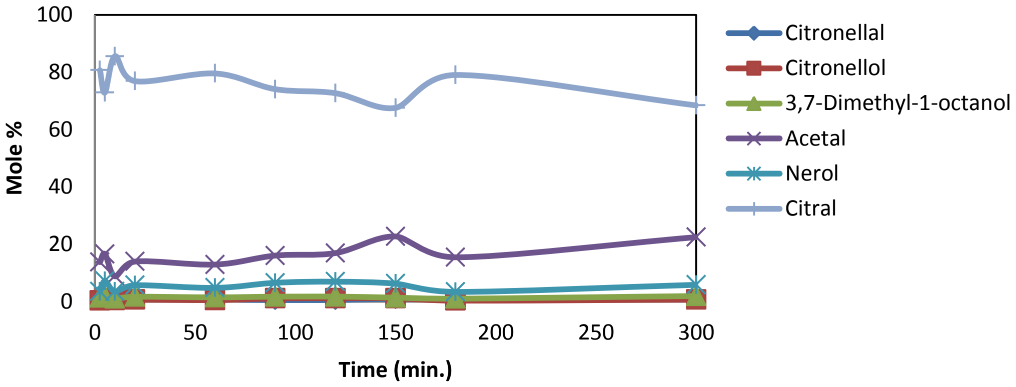
b) Catalyst not calcined.

c) Reaction time was 420 min.

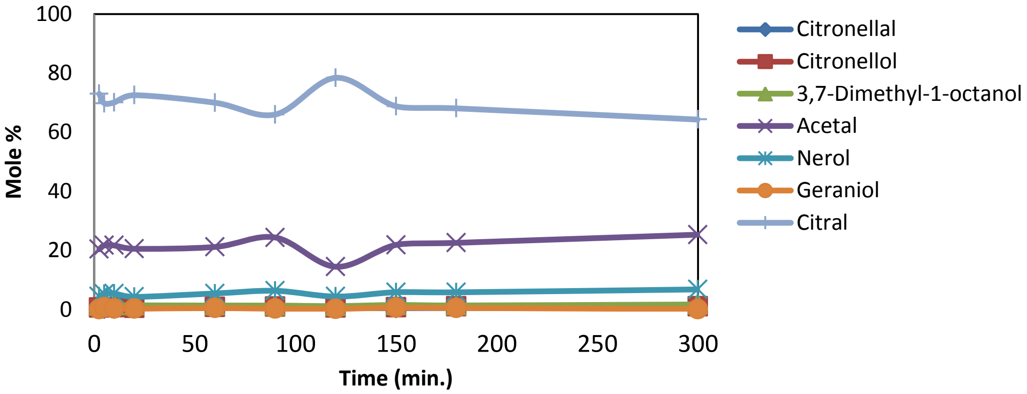
d) Bimetallic catalyst were prepared by catalytic reduction method with (Sn/Ru =0.3) atomic ratio. Reaction time was 420 min.

e) Supported oxide (8wt%TiO_2/SiO_2) was prepared by incipient wetness impregnation. Reaction time was 420 min.

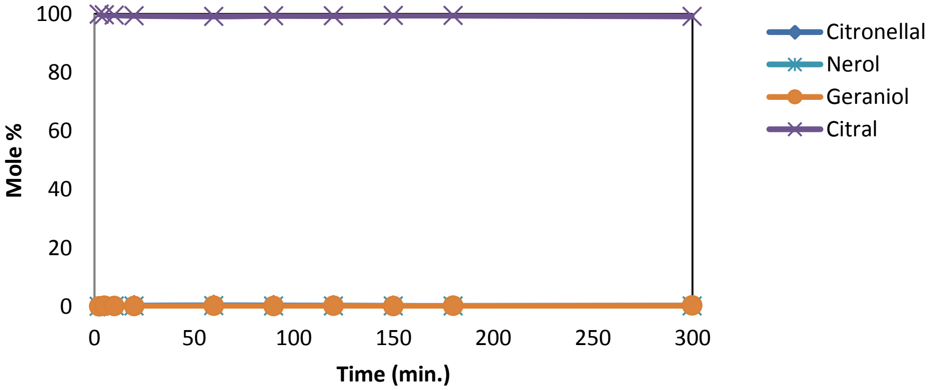
f) Mixed oxide (6wt%TiO_2-SiO_2) was prepared by Sol-Gel method. Reaction time was 180 min.



a) Catalysts used in run 1.



b) Catalysts used in run 2.



c) Catalysts used in run 3.

Figure A.1. Composition of different species in citral hydrogenation over different catalysts and conditions.

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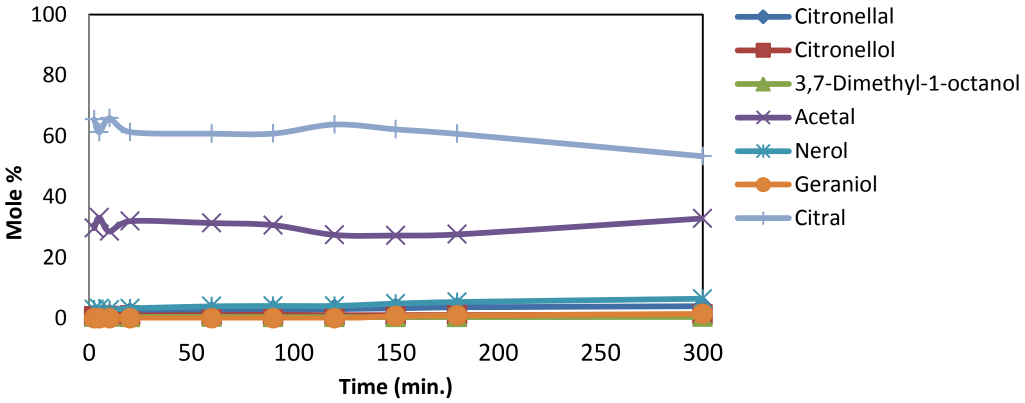
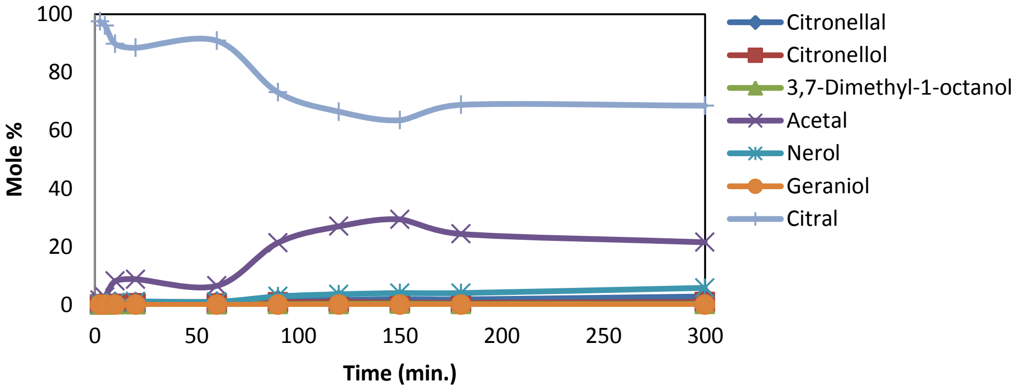
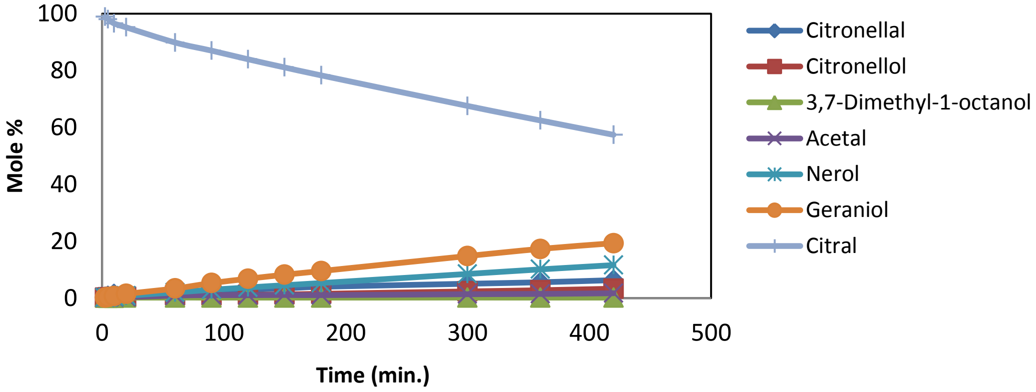


d) Catalysts used in run 4.



e) Catalysts used in run 5.



f) Catalysts used in run 6.

Figure A.1. (cont.)

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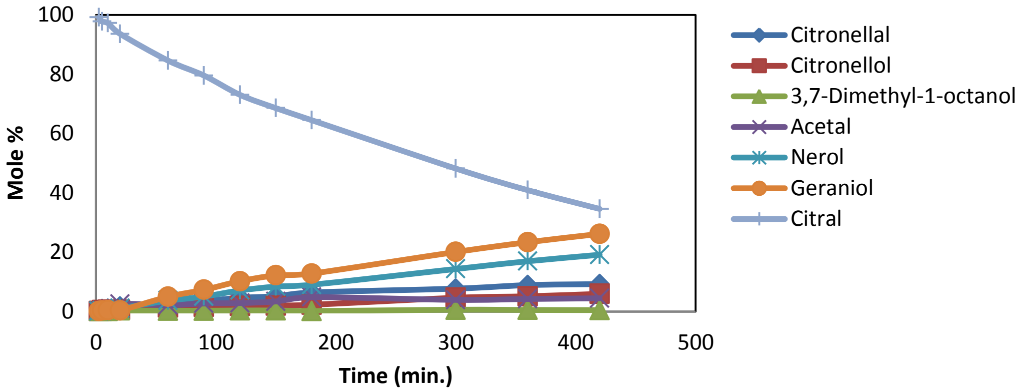
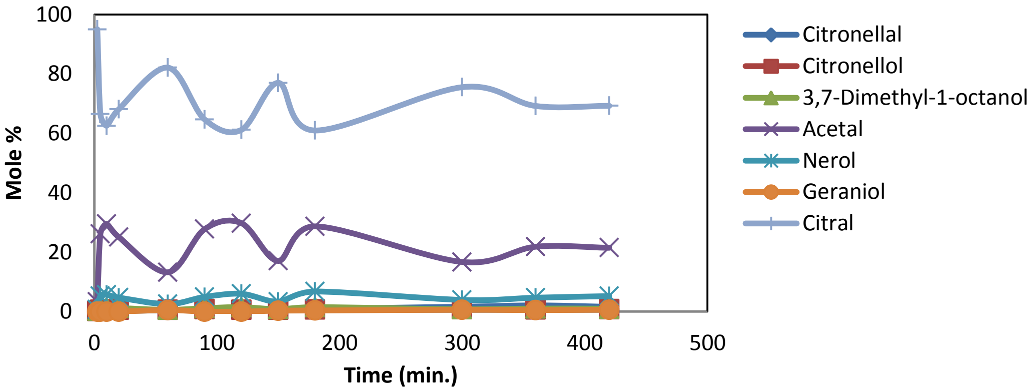
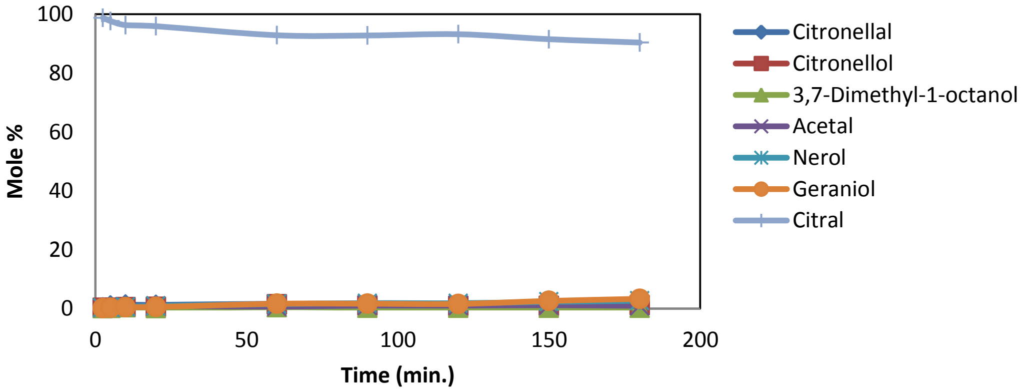


g) Catalysts used in run 7.



h) Catalysts used in run 8.



i) Catalysts used in run 9.

Figure A.1. (cont.)

APPENDIX B

INTERNAL STANDARD METHOD CALCULATIONS

Internal Standard method requires at least two analyses. The first analysis contains a known amount of internal standard and the compounds of interest (standards). Response factor for each compounds of interest (standards) was calculated using the following equation:

$$\text{IRF} = \frac{\text{area}_{\text{IS}} \times \text{concentration}_{\text{SC}}}{\text{concentration}_{\text{IS}} \times \text{area}_{\text{SC}}}$$

IS = Internal Standard (Cyclohexanone)
SC = Specific Compound of Interest (Citral or Products)
IRF = Internal Response Factor

Internal response factors for compounds of interest (citral and products) are given in Table B.1. A known amount of the internal standard was added to all samples taken from the reactor. The amount of the unknown component was calculated using the following equation:

$$\text{Concentration of specific compound} = \frac{\text{concentration}_{\text{IS}} \times \text{area}_{\text{SC}} \times \text{IRF}_{\text{SC}}}{\text{area}_{\text{IS}}}$$

Table B.1. Internal response factors of compounds of interest (standards; citral and products).

Component	IRF
Citral	1.027
Citronellal	1.247
Citronellol	1.293
Nerol	1.029
Geraniol	1.015
Isopulegol	0.680
3,7-dimethyl-1-octanol	1.105

APPENDIX C

GC-MS CHROMATOGRAMS OF PRODUCTS

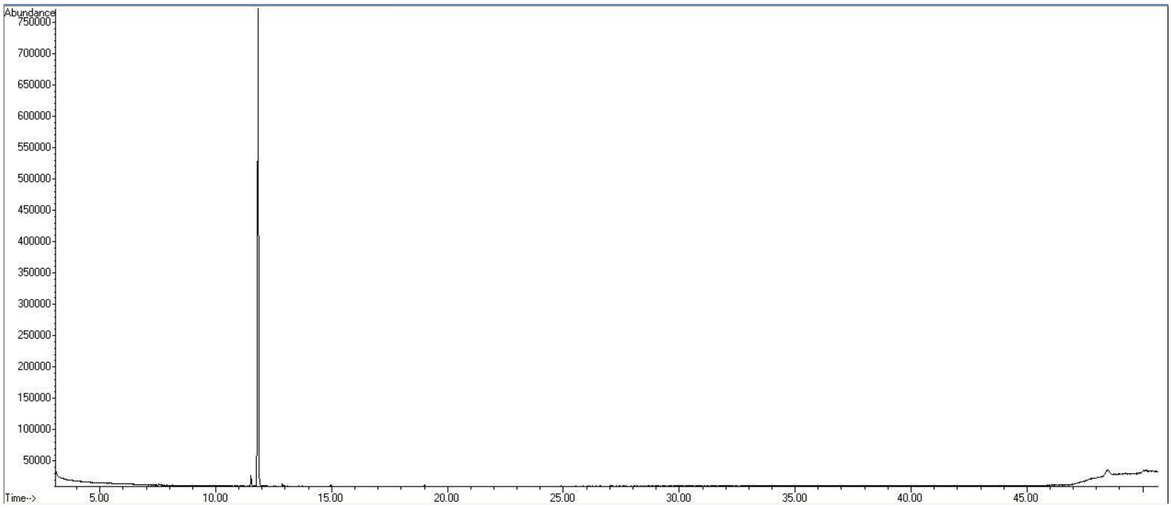


Figure C.1. GC-MS chromatogram of citronellal.

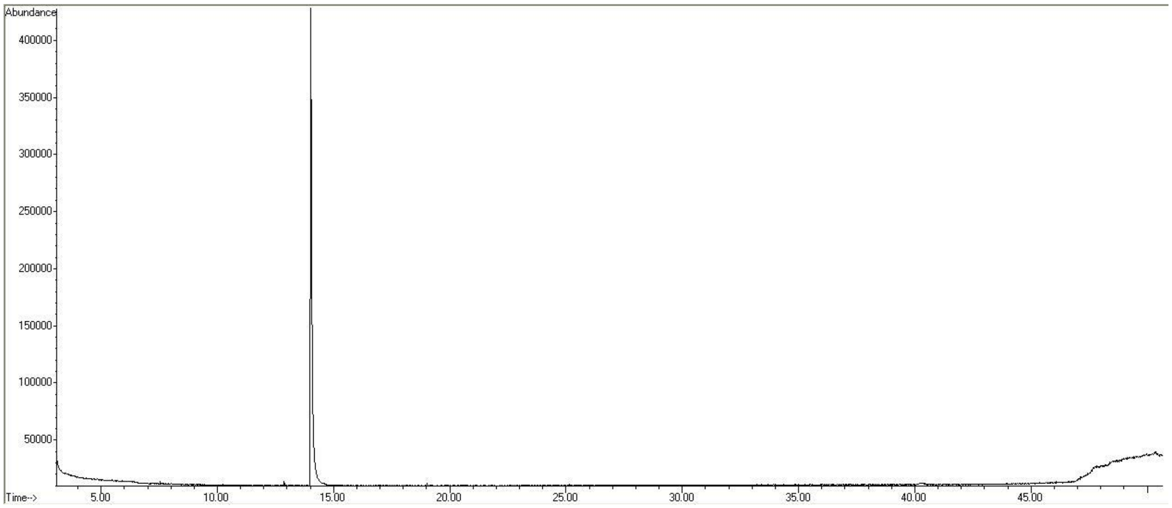


Figure C.2. GC-MS chromatogram of citronellol.

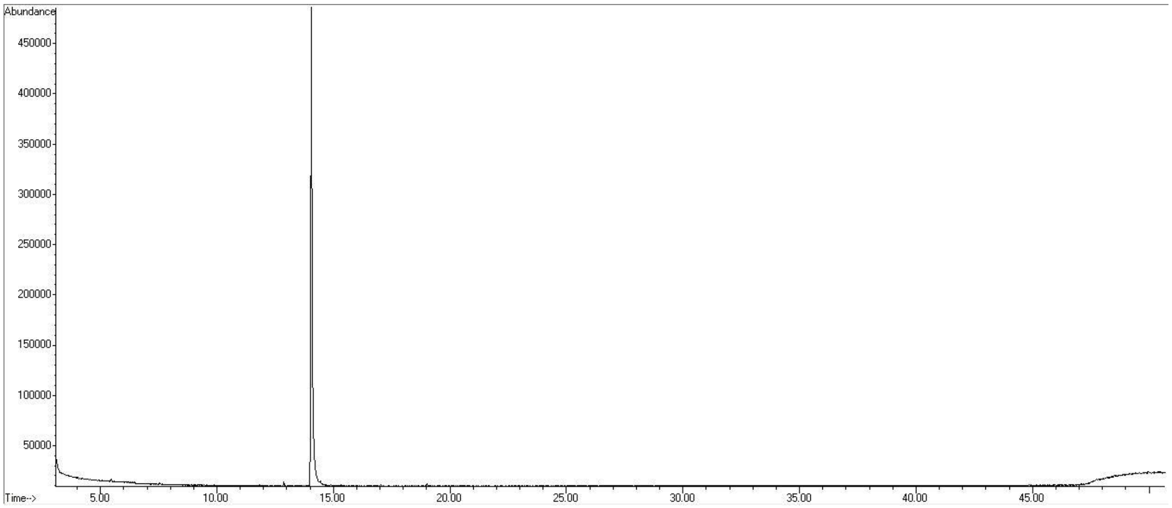


Figure C.3. GC-MS chromatogram of nerol.

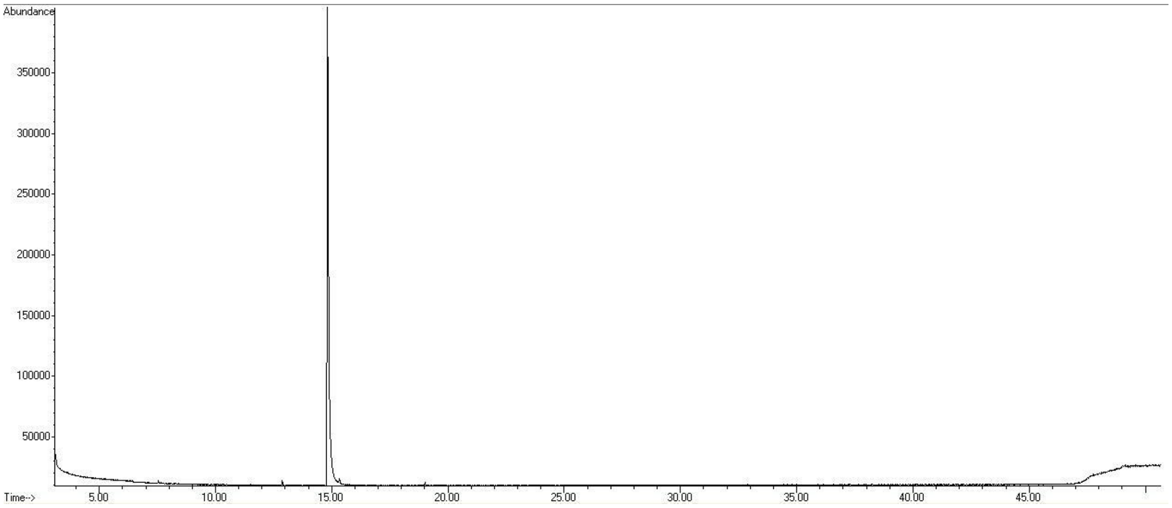


Figure C.4. GC-MS chromatogram of geraniol.

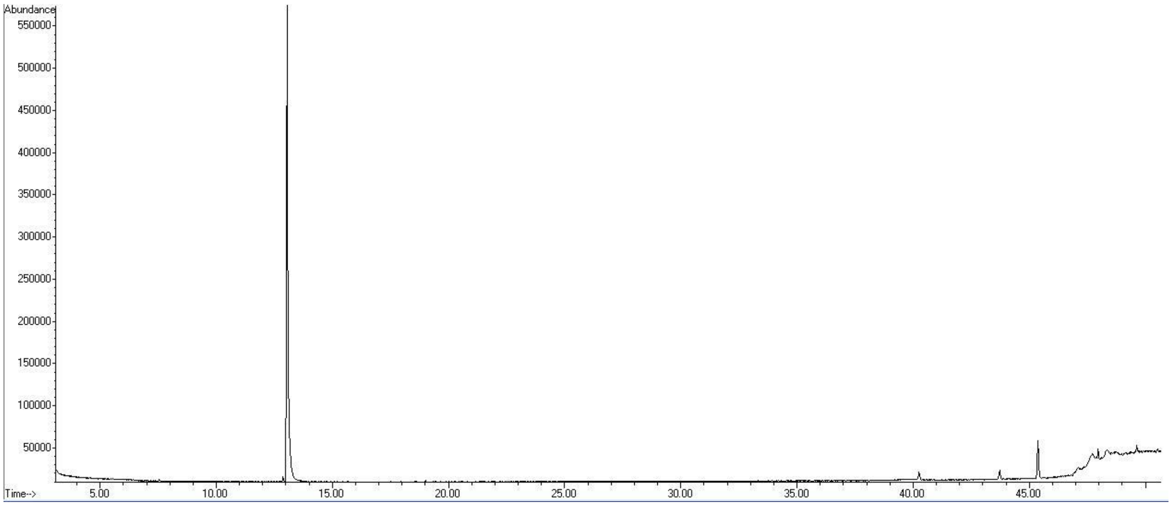


Figure C.5. GC-MS chromatogram of 3,7-Dimethyl-1-octanol.

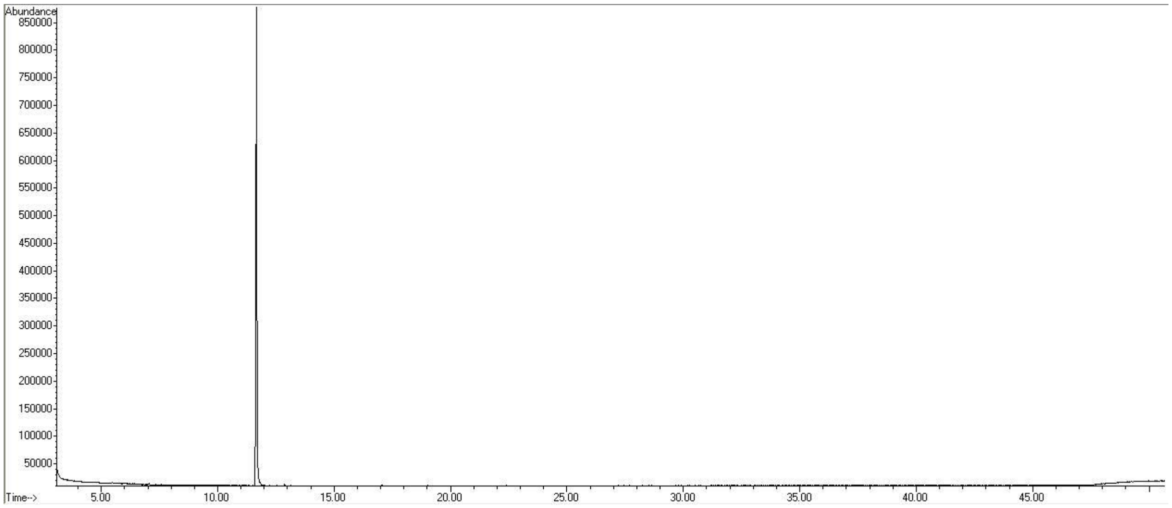


Figure C.6. GC-MS chromatogram of Isopulegol.

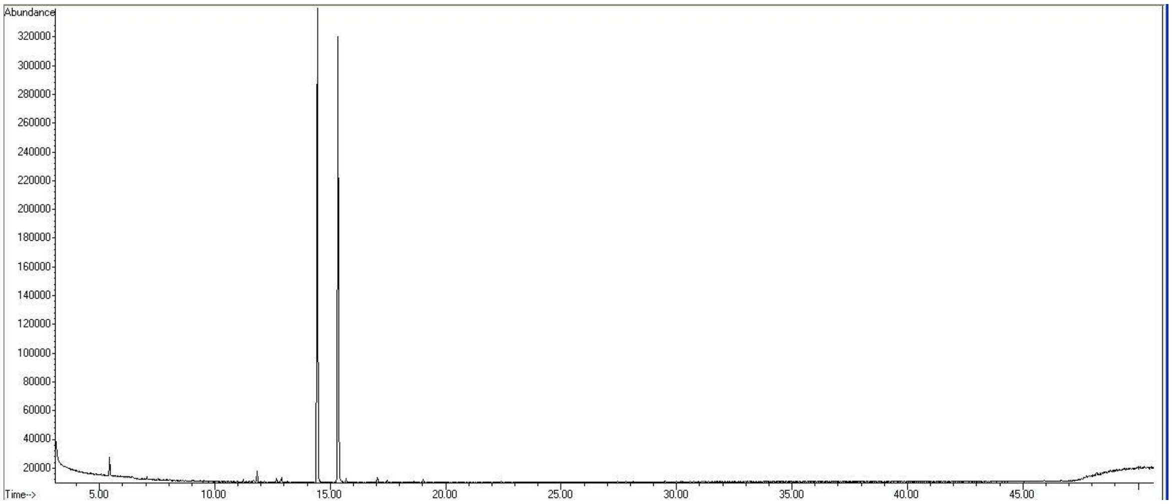


Figure C.7. GC-MS chromatogram of Citral.