AN INVESTIGATION OF CATALYST PREPARATION CONDITIONS AND PROMOTER LOADING (Sn) EFFECTS ON ACTIVITY AND SELECTIVITY OF Pt CATALYSTS IN CITRAL HYDROGENATION

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ABSTRACT

AN INVESTIGATION OF CATALYST PREPARATION CONDITIONS AND PROMOTER LOADING (Sn) EFFECTS ON ACTIVITY AND SELECTIVITY OF Pt CATALYSTS IN CITRAL HYDROGENATION

In this study, citral hydrogenation reaction in liquid phase over silica gel supported Pt and PtSn catalysts were studied. It was desired to hydrogenate carbonyl group (C=O) selectively to produce valuable unsaturated alcohols, namely nerol, geraniol and citronellol. Pt/SiO_2 catalysts were prepared by impregnation method while PtSn/SiO_2 catalysts were prepared by catalytic reduction (CR), co-impregnation (CI) and successive impregnation (SI) methods. Pt loading over silica gel support was 1 % (w/w). For bimetallic catalysts, the (Sn/Pt) loading ratios were varied as 0.3, 0.5 and 0.7.

The effects of parameters investigated in the present study included catalyst activation temperature (350 °C, 450 °C), calcination temperature (400 °C, 500 °C), solvent type (ethanol, 2-pentanol), catalyst activation without calcination, washing of catalyst with 0.1 M NaOH solution, Pt precursor type (hexachloroplatinic acid, platinum II acetylacetonate (PAA)) and Sn loading ratio.

For Pt/SiO_2 catalysts, maximum citral conversion (89 %) was achieved at lower activation (350 °C) and calcination (500 °C) temperatures when PAA was used. Increasing the activation temperature to 450 °C decreased the citral conversion to 52 % but increased the selectivity to unsaturated alcohols (nerol and geraniol) (S_{NE+GE}) from 8 % to 60 %. It was observed that the lower activation temperature provided higher citral conversion but lower selectivity to unsaturated alcohols. Washing of catalyst and using of 2-pentanol prevented the acetal formation. Catalyst activated without calcination step gave lower conversion (20 %) and S_{NE+GE} of 30 %. For bimetallic catalyst (PtSn/SiO_2), maximum citral conversion was observed as 91.1 % when catalyst was prepared by CR method and calcined at 500 °C. Higher citral conversion and selectivity to unsaturated alcohols were achieved at the higher calcination temperature and higher reduction temperature. CR method was the most appropriate preparation method for bimetallic catalysts compared to CI and SI. An optimum of activity (91.1 %) and selectivity (89.7 %) was found at a Sn/Pt ratio 0.5.

ÖZET

KATALİZÖR HAZIRLAMA ŞARTLARININ VE PROMOTER MİKTARININ (Sn) Pt KATALİZÖRLERİN AKTİVİTESİNE VE SEÇİCİLİĞİNE ETKİLERİNİN SİTRAL HİDROJENASYONUNDA İNCELENMESİ

Bu çalışmada, sıvı fazdaki sitral hidrojenasyon reaksiyonunda silika jel destekli Pt ve PtSn katalizörler çalışılmıştır. Değerli doymamış alkollerin, nerol, geraniol ve citronellol, seçicilikle üretilebilmesi için karbonil grubun (C=O) hidrojene edilmesi istenmektedir. Pt/SiO_2 katalizörler emdirme metoduyla hazırlanmıştır. PtSn/SiO_2 katalizörler katalitik indirgeme (CR), birlikte emdirme (CI) ve ardışık empregnasyon (SI) metodlarıyla hazırlanmıştır. Silika jel desteği üzerine Pt yükleme miktarı ağırlıkça % 1'dir. İki metalli katalizörler için (Sn/Pt) yükleme oranları 0.3, 0.5 ve 0.7'dir.

Bu çalışmada, katalizör aktivasyon sıcaklığı (350 °C, 450 °C), kalsinasyon sıcaklığı (400 ^oC, 500 ^oC), çözücü çeşidi (etanol, 2-pentanol), kalsinasyonsuz katalizör aktivasyonu, katalizörün 0.1 M NaOH çözeltisi ile yıkanması, Pt kaynağı çeşidi (hekzakloroplatinik asit, platin II asetilasetonat (PAA)) ve Sn yükleme oranı parametrelerinin etkileri incelenmiştir.

Pt/SiO_2 katalizörü için maksimum sitral dönüşümü (% 89) düşük aktivasyon sıcaklığında (350 ^oC) ve PAA kullanımında elde edilmiştir. Aktivasyon sıcaklığının 450 ^oC'ye yükseltilmesi, sitral dönüşümünü % 52'ye düşürmüş fakat doymamış alkollerin seçiciliğini (S_{NE+GE}) % 8'den % 60' a çıkarmıştır. Düşük aktivasyon sıcaklığının yüksek sitral dönüşümünü sağladığı fakat düşük doymamış alkol seçiciliğine neden olduğu gözlenmiştir. Katalizörün yıkanması veya 2-pentanol kullanılması asetal oluşumunu önlemiştir. Kalsinasyonsuz katalizör aktivasyonu düşük sitral dönüşümüne (% 20) ve S_{NE+GE} (% 30) olmasına neden olmuştur. PtSn/SiO_2' larda, maksimum sitral dönüşümü 500 ^oC'de kalsinasyon ve katalitik indirgeme metoduyla % 91.1 olarak gözlenmiştir. Bimetalik katalizörlerde yüksek sitral dönüşümüne ve doymamış alkollerin yüksek seçiciliğine, yüksek kalsinasyon sıcaklığında ve yüksek indirgeme sıcaklığında ulaşılmıştır. Katalitik indirgeme metodunun en uygun katalizör hazırlama metodu olduğu bulunmuştur. Sn/Pt oranı 0.5 olduğu zaman maksimum sitral dönüşümü (% 91.1) ve doymamış alkollere seçicilik (% 89.7) elde edilmiştir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Table **Page**

CHAPTER 1

INTRODUCTION

Heterogeneous hydrogenation catalysts are most useful for the reduction of various functional groups in chemical synthesis and, thus, widely applied in industrial processes. Usually, hydrogenation reactions are run over metal catalysts and most of them are based on supported Group VIII metals. The selective hydrogenation of unsaturated aldehydes to the corresponding unsaturated alcohols (UA) is of considerable interest due to the numerous applications of those alcohols in Fine Chemistry. However the selective hydrogenation of α-β unsaturated aldehydes is a difficult challenge since the C=C bond is much easily attacked then the C=O bond when a conventional heterogeneous catalysts used. Therefore, many efforts have been made to develop a suitable industrial catalyst that would be able to lead to the hydrogenation of C=O bond to get desired products.

Heterogeneous catalysts may contain nanoparticles which speed up chemical reactions without being consumed by them. The chemical and drug industries spend lots of money for catalysts that are needed to process drugs and other high-value chemicals. In between catalysts, nanoparticles combining platinum and other metals such as tin are prized for reactions including hydrogen because of pairing atoms of hydrogen by platinum and other metals are good at sticking these pairs and leaving the particular hydrogen atoms available for reactions with other molecules.

In the case of supported metal catalysts, applied for the hydrogenation of α,β-unsaturated aldehydes, activity and selectivity can be controlled, for example, by the (i) nature of the individual metal, (ii) presence of a second metal which can form an alloy with the basic metal or operate as cationic promoter (bimetallic catalysts), (iii) metal particle size (dispersion), (iv) electron-donating or -withdrawing ligand effects by the catalyst support material, (v) steric constraints in the metal environment and (vi) strong metal–support interactions (SMSI) (Claus et al., 2006).

Citral is an attractive molecule as unsaturated aldehydes. It has conjugated double bonds, an isolated double bond, furthermore there are possibilities for cis-trans isomerization and for several types of side reactions (cyclisation, acetalyzation and dehydrogenation) (Arvela et al., 2003).

Selectivity to unsaturated alcohols of supported metal catalysts can be improved by introducing of promoters. Os, Ir and Pt based systems provide a significant selectivity in citral selective hydrogenation reactions. In order to achieve good selectivity, Pt-Sn and Pt-Ge based catalysts are used in citral hydrogenation reactions. Pt modified systems fast ageing processes take place while working in flow conditions, thus limiting the working lifetime of catalysts (Recchia et al., 1999; Singh and Vannice, 2001).

In this study, catalysts were prepared to achieve selective hydrogenation of citral to UA. To realize these purposes, monometallic (Pt) and bimetallic (Pt-Sn) catalysts were prepared. Monometallic catalysts were prepared by impregnation method. Bimetallic catalysts were prepared by co-impregnation, catalytic reduction and successive impregnation methods. Effects of catalyst calcination and activation temperatures, Sn/Pt ratio on catalyst activity and selectivity to unsaturated alcohols were investigated.

CHAPTER 2

CITRAL HYDROGENATION

2.1. Hydrogenation

Hydrogenation is the chemical reaction that results from the addition of hydrogen (H_2) to double or trible bonds in hydrocarbons. Important applications of hydrogenation are found in petrochemical industries (e.g. in manufacturing of gasoline), pharmaceutical industries (e.g. in drug processing), food industries (e.g., in the production of edible fats from liquid oils). For the hydrogenation reaction, catalysts are required to run the reaction at low temperatures. Non- catalytic hydrogenation occurs at high temperatures.

2.2. Citral and Citral Hydrogenation

Citral is the most important component of the lemon grass oil which has three hydrogenation sites. These hydrogenation sites are isolated C=C double bond, conjugated C=C double bond and a carbonyl group (C=O). Citral hydrogenation is a complex reaction, including series and parallel reactions as seen in Figure 1 (Yilmaz et al., 2005).

Citral hydrogenation mechanism consists of many steps. Unsaturated alcohols geraniol and nerol are produced through the hydrogenation of the C=O bond. Hydrogenation of conjugated C=C bond leads to the saturated aldehydes citronellal, which can form isopulegol through cyclisation. Finally, the hydrogenation of isolated C=C bond gives 3,7-Dimethyl-octenol and 3,7-Dimethy-l-octanol. In citral hydrogenation, there are possibilities for cis-trans isomerization and for several types of side reactions such as cyclisation, acetalisation, decarbonylation, and dehydrogenation.

Nerol and geraniol are the most important products of citral hydrogenation reaction. These are used in perfumes, fragnances and pharmaceuticals. Although there are many types of hydrogenation reactions, unsaturated alcohols are produced by selective hydrogenation. Citral hydrogenation reaction on metal catalysts provides saving chemicals, reducing wastes and protecting environment (Vilella et al., 2005; Lafaye et al., 2004).

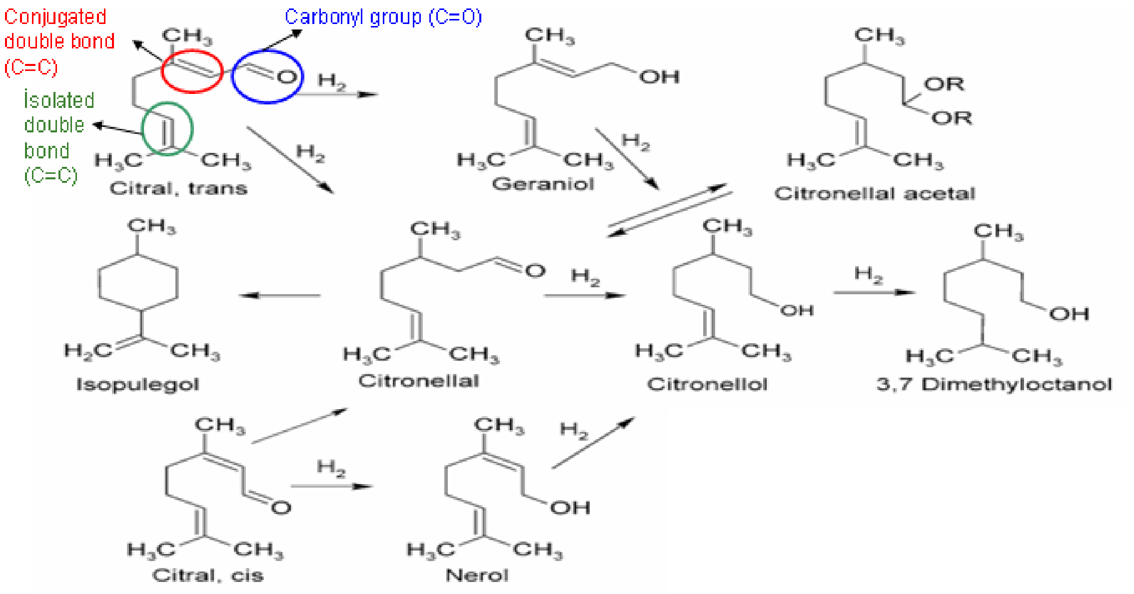

Figure 1. Reaction scheme for citral hydrogenation
(Source: Yilmaz et al., 2005)

2.3. Selective Hydrogenation

Catalytic selective hydrogenation is one of the most useful, versatile, and environmentally acceptable reaction routes available for organic synthesis, and the reaction is usually carried out in a liquid-phase using batch type slurry processes and a supported noble metal (Pd, Pt, or Rh) catalyst. In hydrogenation, citral is realized in multi-phase catalytic reactions using solid catalysts. The advantages of multi-phase catalytic reactions were listed as following such as easy separation of catalysts and products, easy recovery and catalyst recycling and relatively mild operating conditions. (Panpranot et al., 2006; Bhanage and Arai, 2001)

The selective hydrogenation of α-β unsaturated aldehydes (such as citral) to produce unsaturated alcohols (nerol, geraniol, citronellol) is applied in fine chemical manufacturing of fragrances, flavorings and the pharmaceutical industry.

Heterogeneous catalysts act in a different phase than the reactants. Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture.

Heterogeneous catalysts are typically supported, which means that the catalyst is dispersed on a second material that enhances the effectiveness or minimizes their cost. Sometimes the support is merely a surface on which the catalyst is spread to increase the surface area. More often, the support and the catalyst interact, affecting the catalytic reaction. Supports are porous materials with a high surface area, most commonly activated alumina or activated carbon, but special in applications silicon dioxide, titanium dioxide, calcium carbonate or barium sulfate can be found.

2.4. Previous Studies on Citral Hydrogenation

Catalyst activity and selectivity is reported to be influenced by nature of individual metal, presence of second metal which can form an alloy with basic metal or operate as cationic promoter (bimetallic catalysts), electron-donating or –withdrawing ligand effects by the catalyst support material, steric constraints in the metal environment, strong metal-support interaction (SMSI) and catalyst preparation method and activation (Malathi and Viswanath, 2001; Claus et al., 2006; Ruiz et al., 2007).

Literatures on parameters which are in the scope of effecting catalyst activity and selectivity are given below.

2.4.1. Active Component and Promoter Effects

The selectivity to unsaturated alcohol is highly dependant on the nature of the precious metal used as catalyst. Noble metals have been investigated for citral hydrogenation. These metals are Ni, Pd, Pt, Ru and Rh. In general nobel metals are loaded by different methods including impregnation, precipitation and coimpregnation. Supported platinum catalysts are commonly investigated in citral hydrogenation reactions. Using of platinum precursor provided better catalyst activity and selectivity to unsaturated alcohols than other metals. This is related to better influence strong metal-support interaction state in supported platinum catalysts. This interaction also provides selectively producing the unsaturated alcohols rather than the saturated aldehydes (Malathi and Viswanath, 2001)

Vilella et al. (2005) studied Pt and PtSn catalysts supported on an activated carbon felt in the hydrogenation of citral in liquid phase. Pt (5 wt %)/ACF was prepared by impregnation method. The catalyst precursor was dried at 120 °C. PtSn catalysts with the same Pt content (5 wt %) but with different Sn contents (1-3 wt %) were prepared by impregnation of the monometallic catalyst precursor with a hydrochloric solution of $SnCl_2$. They observed that the increasing amount of tin addition did not modify the catalytic activity. Selectivities to unsaturated alcohols were investigated at measured citral conversion of 70 %. For the monometallic catalyst a low formation of unsaturated alcohols (3.7 %) was observed. When the Sn content was increased in the bimetallic catalyst, selectivities to unsaturated alcohols were increased to around 70 % for the catalyst with the highest tin content. This was attributed to low amount of formation of acetals and isopulegol for bimetallic catalysts. Thus, acetals and citronellal formation decreased selectivities to unsaturated alcohols in monometallic catalysts.

Aramendia et al. (1997) studied hydrogenation of citral with Pd catalysts supported on a mixed 80:20 $SiO_2/AlPO_4$ and sepiolite. The metal was deposited by using the method of impregnation to incipient wetness. Temperature, hydrogen pressure and type of solvent effects on the reduction sequence were investigated. Metanol, cyclohexane, dioxane and tetrahidrofurane were used as solvents. Citral hydrogenation reactions were run at hydrogen pressure of 20-60 psi and a temperature in the range 283-323 K. While citral conversion was 25 %, selectivity to unsaturated alcohols was around 40 % in the presence of dioxane solvent at temperature of 303 K. It was obtained that the best solvent was methanol. When methanol was used as solvent, selectivities to citronellal were 99 % and 96 % for citral conversions of 10 % and 25 %, respectively. This was attributed to nonpolar solvents led to greater reduction rates. Using of alcohols gave rise to the formation of acetals between the solvent and citral. They found that $FeCL_2$ addition to the reaction media modified the sequence and increased the selectivity with which the C=O group was reduced. For monometallic Pd catalyst, selectivities to citronellol were around 5 % and 8 for citral conversions of 10 % and 40 %, respectively. They also observed unsaturated alcohol (geraniol+nerol) formation in the presence of bimetallic Pd-Fe catalyst. Selectivities to geraniol and nerol ranged from 30 % to 45 % for citral conversions of 10 % and 40 %, respectively. They explained that increase in selectivity caused by the presence of positively charged ferrous ions on the surface of Pd particles as shown model in Figure 2.

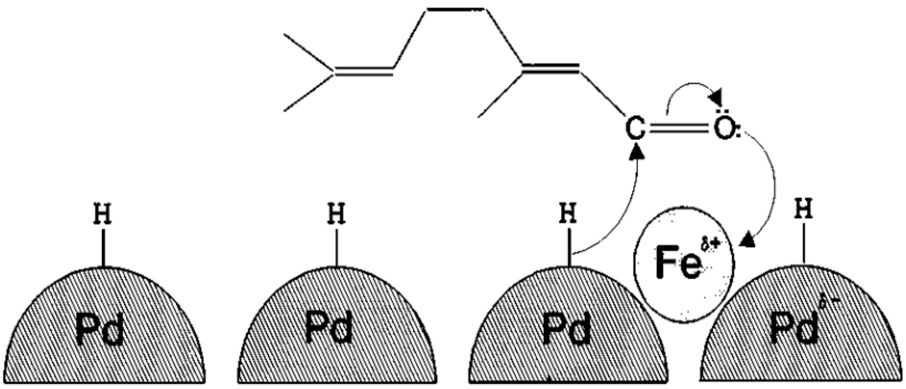

Figure 2. Model for the selective adsorption-reduction of citral on a Pd catalyst doped with $FeCl_2$ (Source: Aramendia et al., 1997)

They reported that unreduced Fe^{2+} ions or electron-deficient Fe^0 atoms were resulted from electronegativity differences between iron and palladium and the remained ferrous ions stayed in solution and did not have any role in the reaction. They also mentioned about how the electron transfer system works between C=O group, Fe and Pd ions. The interaction of positively charged iron with the carbonyl group caused an electron to be transferred from the oxygen atom in the C=O group of citral, which was made electron-deficient. Then, an electron rearrangement took place by which one of the electrons in the pair that formed the double bond was transferred to the oxygen atom while the other was used to form a C–H bond between the carbonyl carbon and a proton bonded to the more electronegative metal (Pd). Finally, the formation of a bond between the second proton and the oxygen caused the alcohol to be released.

In the studies of Ekou et al. (2006) and Coupe et al. (2000) monometallic catalysts of both Rh and Pt supported on alumina or silica generally revealed a poor selectivity to unsaturated alcohols. In addition to this to improve the selective hydrogenation of C=O bond, different promoters (Sn, Ge) were added on these monometallic systems.

Addition of a second metal to the monometallic catalysts improves the selectivity towards the hydrogenation of the carbonyl group. Ekou et al. (2006) investigated the liquid phase hydrogenation of citral over bimetallic Rh-Ge/SiO_2 and Rh-Ge/Al_2O_3 catalysts. Catalysts were prepared by an ion exchange method using the following procedure. Catalysts were dried at 110 °C overnight, followed by calcination for 4 h in flowing air at 300 °C. Finally they were reduced at 300 °C or 500 °C in flowing purge hydrogen for 4 h. It was obtained that Ge addition to Rh catalysts improved the reaction selectivity toward unsaturated alcohols. Selectivity to unsaturated alcohols showed 20 % increment from 70 % to 90 %. In some other studies, Cu addition enhanced the selectivity to unsaturated alcohols in the hydrogenation of α, ß-unsaturated aldehydes in $NiCu/SiO_2$ and $RhCu/SiO_2$ catalysts (Noller and Lin, 1984; Rodriguez et al., 2008).

In the study of Vilella et al. (2005), it was observed that Sn addition to Pt/C or Ru/C catalysts also increased the selectivity to unsaturated alcohols and activity of catalysts. They attributed this to Sn addition to Pt catalysts which enhanced the selectivity to unsaturated alcohols. Also there are some other studies in which other transition elements investigated on selectivity of unsaturated alcohols. The use of Os, Ru and Co favoured the production of nerol and geraniol in the study of Galvagno et al. (1993). The controlled addition of Sn, Pb and Ge made possible the modification of the selectivity to different products according to the Didillon et al. (1993) study. Lastly, Neri et al. (1994, 2002) observed Sn addition to Pt/C enhanced the selectivity to unsaturated alcohols.

2.4.2. Support Effect

In addition to active component and promoter effects, there is also support effect on selectivity to unsaturated alcohols. Many studies have been done on support effect. In the studies of Vannice and Sen (1989), Malathi et al. (2001) and Ekou et al. (2006) reducible support that presents the strong metal support interaction used with monometallic catalysts (Pt based generally) to increase the selectivity to the C=O group hydrogenation of various unsaturated aldehydes. In the study of Silva et al. (1997), a cumulative effect of the titania support with the promoters (Fe, Ge, Sn) was investigated on monometallic (Pt, Ir or Ru) catalysts. Iridium was determined as most selective one. It was observed that presence of ionic species such as promoters (Fe^+, Ge^+) on TiO_2 support led to catalysts highly selective for hydrogenation of the carbonyl group. A monometallic Pt/TiO_2, catalyst gave an excellent selectivity but a rather poor activity. Finally a selectivity to cinnamyl alcohol as high as 97 % and a high activity were reached by using a bimetallic $Pt-Fe/TiO_2$. Addition of Fe increased selectivity from 80 % to 97 %. This good selectivity had been attributed to the metal support interaction, also Ge provided approximately 90 % selectivity to unsaturated alcohols.

Aykaç and Yılmaz (2008) investigated the combined effects of support (Na-Y, Clino) and promoter (Sn) on the hydrogenation of citral and aimed to evaluate Na-Y and Clinoptilolite rich natural zeolite as catalyst supports for Pt and Pt-Sn. The monometallic and bimetallic catalysts were prepared by impregnation and coimpregnation. The metal precursor salts of Pt (platinum II acetyl acetonate) and Sn ($SnCl_2.2H_2O$) solved in ethanol was mixed with the supports for some time period. Then ethanol was evaporated, impregnated supports were dried and calcined. They concluded that higher selectivity to unsaturated alcohol was observed over Na-Y support. Among monometallic catalysts, Pt/Na-Y was more selective to citronellol (3.9%) and unsaturated alcohols, geraniol and nerol, (14.1 %). The addition of Sn increased the catalyst activity of monometallic catalysts. It was noted that Pt-Sn/Clino gave the highest yield of unsaturated alcohols (30.8 %). This was attributed to the presence of synergy between Pt-Sn. Metal support interaction and promoter active metal interaction increased the unsaturated alcohol formation.

Albero et al. (2002) studied the effect of reduction temperature on ceria-promoted platinum and platinum-zinc catalysts supported on silica. Catalysts were prepared from chlorine free precursors. Ceria dispersed on silica was prepared by impregnation method. The excess solvent was removed by flowing N_2 through the slurry at 333 K. Then the sample was calcined at 673 K for 4 h. Platinum and zinc were introduced by coimpregnation with acetone solutions of $Pt(NH_3)_4(NO_3)_2$ and $Zn(NO_3)_2.6H_2O$. It was reported that these precursors were chosen in order to avoid the presence of chlorine in the final catalysts, chlorine affect the catalytic behavior. In order to prepare Pt/CeO_2-SiO_2 catalyst, excess solvent was removed and the samples were dried overnight at 383 K and calcined at 673 K for 4 h. Platinum content was 1.1 wt. % where the zinc content in the bimetallic catalyst was 0.6 wt. %. Zn/Pt ratio was 1.6. For Pt/CeO_2 catalyst, they observed that increase in the reduction temperature provided an increase in the intensity of the ceria peaks according to the XRD analysis. They attributed this to sintering of the partially reduced ceria phase. However, they found in a Pt/CeO_2-SiO_2 catalyst, an increase in the reduction temperature caused weak XRD spectra. It was attributed to the presence of silica support. The effect of the reduction temperature on the catalytic activity of Pt/CeO_2–SiO_2 and Pt–Zn/CeO_2–SiO_2 for a structure-insensitive reaction, toluene hydrogenation, was tested at 333K, after treating the catalysts in flowing hydrogen at 473 or 773K. The monometallic Pt/CeO_2–SiO_2 showed the highest activity after reduction at both low and high temperature. The catalytic activity for toluene hydrogenation was greatly decreased after reduction at high temperature (773 K) compared with the results obtained after reduction at low temperature (473 K). In the case of the vapor-phase hydrogenation of crotonaldehyde, the overall catalytic activity increased significantly after reduction at 773 K in the zinc-containing catalyst, and furthermore, the selectivity toward the hydrogenation of the carbonyl bond was improved.

Baeza et al. (2001) studied the influence of the promoter and the effect of an inert active carbon support (C) and of an electron donor support (graphite, H) on the catalysis activity. Bimetallic Ru-Fe catalysts were prepared by coimpregnation method. The liquid phase hydrogenation of citral was done at atmospheric pressure under H_2 flow and at 60 °C, the stirring rate was 850 rpm. Selectivities to geraniol and nerol were obtained for monometallic and bimetallic catalysts as seen in Figure 3. It was reported that for bimetallic Ru-Fe catalysts, selectivities to geraniol and nerol was around 70 % up to complete conversion of citral when H was used as support. When C was used for bimetallic catalysts, selectivity to UA decreased from 70 % to 50 %. For monometallic Ru catalysts, changing support from C to H, did not change selectivity to UA significantly which was around 40 %. It was concluded that addition of Fe (as a promoter) favored the production of geraniol and nerol and iron species in the alloy acted as Lewis sites for the activation of the C=O bond as proposed by Aramendia et al. (1997).

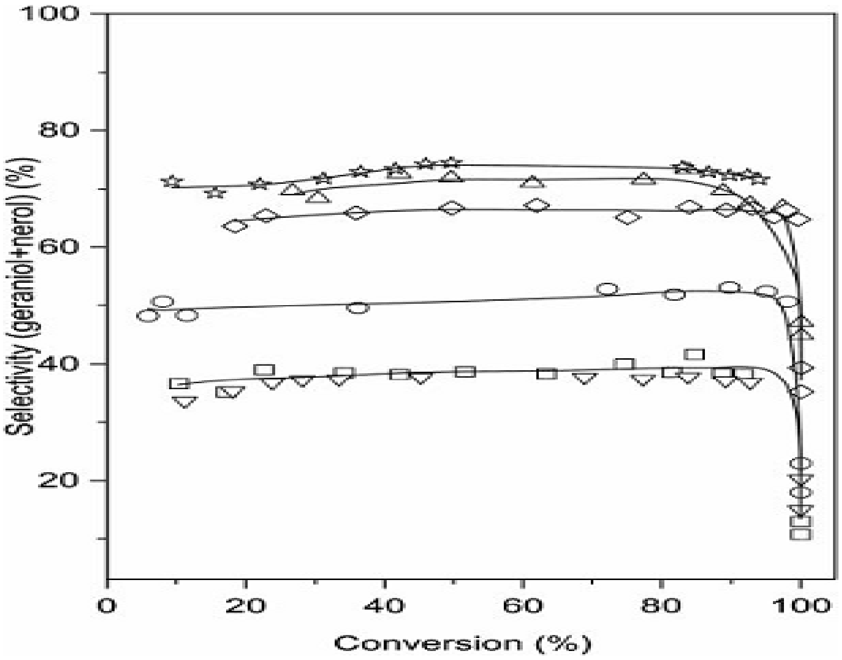

Figure 3. Evolution of selectivity toward geraniol + nerol with conversion in the citral hydrogenation at 333 K for (□) Ru/C, (○) RuFe/C, (△) $RuFe_2/C$, (▽) Ru/H, (◇) RuFe/H, and (☆) $RuFe_2/H$. (C: carbon; H: high-surface-area graphite) (Source: Baeza et al., 2001)

Vilella et al. (2005) studied that the relationship between the characteristics of the metallic surface and the nature of the support and the catalytic behaviour of Pt and PtSn supported on granular activated carbon (C) and activated carbon felt (ACf) in the hydrogenation of citral. Catalysts were prepared by impregnation method. Pt loading was 5 wt %. Citral hydrogenation reaction was performed at 70 °C at atmospheric pressure. 2-propanol was used as a solvent. Catalysts were reduced under flowing H_2 at 350 °C under the stirring rate of 1400 rpm. The selectivities to unsaturated alcohols for monometallic and bimetallic catalysts are reported in Figure 4. Bimetallic catalysts provided higher selectivity to UA than monometallic catalysts at the same citral conversions. For Pt(5wt%)/C-P catalyst, increase in the citral conversion increased selectivity to UA. When citral conversion increased from 35 % to 95 %, selectivity to UA increased from 15 % to 50 %. Tin addition to monometallic catalyst enhanced the selectivity to UA. When Pt(5wt%)Sn(3wt%)/C-P was used, selectivity to UA increased from 70 % to 80 % where citral conversion changed from 35 % to 95 %. High citral conversion and tin addition provided a significant increment in selectivity to UA. For a citral conversion of 95 %, monometallic and bimetallic catalyst selectivities to UA was 50 and 80 %, respectively. They concluded that the modification of the selectivity by the Sn addition to Pt could be related to a change in the structure of the metallic phase. The increase in the selectivity to nerol + geraniol with the addition of Sn could be attributed to a selective increase of the hydrogenation activity of the carbonyl group, since the higher the Sn loading, the higher the percentage of ionic Sn, this favoring the reaction of the chemisorbed hydrogen with the carbonyl group.

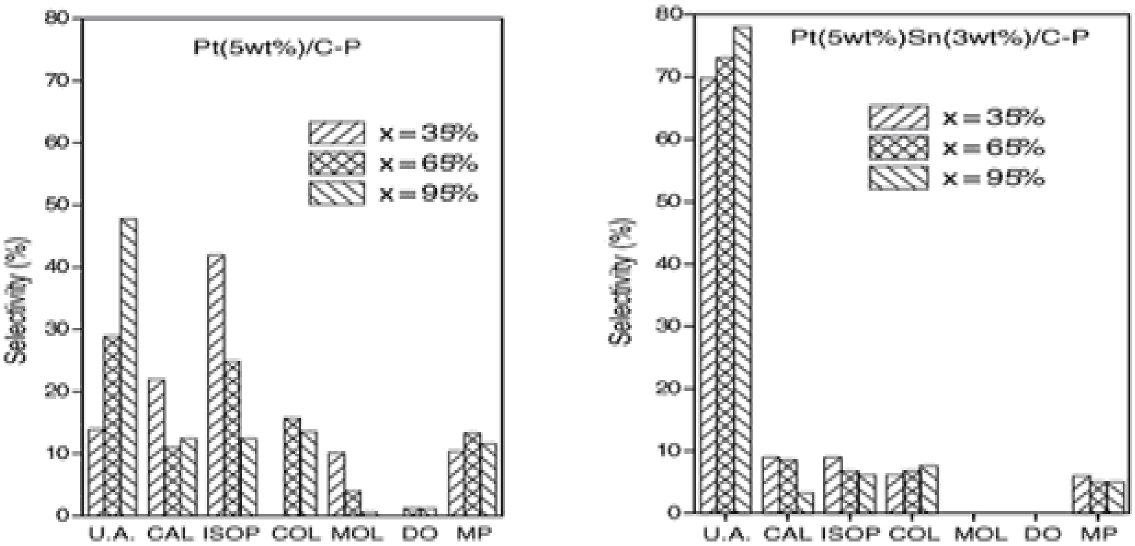

Figure 4. Selectivities to the different products measured at 35, 65, and 95 % conversion levels for C-P-based catalysts. UA: unsaturated alcohols, CAL: citronellal, ISOP: isopulegol, COL: citronellol, MOL: menthol, DO: dimethyloctanol and MP: minor products. (C-P: purified carbon support) (Source: Vilella et al. ,2005)

2.4.3. Catalyst Preparation Method and Activation Effects

Lafaye et al. (2004) prepared bimetallic Rh-Ge catalysts both by catalytic reduction (CR) and successive impregnation methods to examine the influence of several parameters on their catalytic properties for citral hydrogenation. They used $[RhCl(NH_3)_5]Cl_2$ and $GeCl_4$ as precursor salts. In catalytic reduction method, an amount of the pre-reduced monometallic Rh/Al_2O_3 catalyst was activated at 300 °C under hydrogen. Previously degassed (by hydrogen) germanium precursor solution was introduced onto the catalyst at room temperature. The solution was filtered out under hydrogen bubbling then the catalyst was dried. Finally bimetallic catalysts were reduced at different temperatures. In successive impregnation method (SI), $Rh\text{-}Ge/Al_2O_3$ catalysts were prepared by impregnation of the germanium precursor on the monometallic Rh catalysts. After drying they were reduced as for CR method. For the Rh-Ge/Al_2O_3 bimetallic catalysts reduced at 300 °C, a rapid hydrogenation of citral occurred during the first few minutes, and then the catalyst activity decreased. Deactivation decreased as the germanium content of the catalyst increased. They reported that this occurrence could not be explained by a poison effect of chlorine present on the catalysts. Because the sample which had weakest deactivation, had the highest chlorine content. For all the bimetallic catalysts, there was no improvement of the selectivity according to citral conversion, but the selectivity increased with the germanium content. CR method gave 60 % citral conversion where the selectivity to unsaturated alcohols 28 % for 1.0wt.% Rh-1.0wt.% Ge/Al_2O_3 (1Rh-1Ge). For 1.0wt.% Rh-2.5wt.% Ge/Al_2O_3 (1Rh-2.5Ge) catalyst gave 85 % citral conversion where the selectivity to unsaturated alcohols 62 %. For the catalysts prepared by SI method, 1Rh-1Ge gave 50 % citral conversion, where the selectivity to unsaturated alcohols 3 %; 1Rh-2.5Ge gave 38 % citral conversion where the selectivity was 62 %. Thus CR provided higher selectivity to unsaturated alcohols compared to successive impregnation method.

In the study of Ekou et al. (2006), bimetallic TiO_2-supported Rh-Ge and Pt-Ge catalysts were prepared by surface redox reaction between hydrogen activated on a parent monometallic rhodium or platinum catalyst and a germanium salt dissolved in water (catalytic reduction method) for citral hydrogenation. Prepared monometallic Rh/TiO_2 and Pt/ TiO_2 catalysts were dried and calcined. Then they were reduced at high temperature under hydrogen flow. Bimetallic catalysts were prepared by catalytic reduction method. Prereduced monometallic introduced into germanium solution which was previously degassed under hydrogen flow. The bimetallic RhGe/TiO_2 and PtGe/ TiO_2 were dried and finally reduced at high temperature. They concluded that the addition of germanium- to titania-supported 1 wt% Rh or 1 wt% Pt catalysts strongly modified their catalytic properties. For both Rh and Pt based samples, the selectivity in geraniol and nerol had gone through a maximum as function of the Ge content whatever the reduction temperature (300 or 500°C). For Rh-1.6 wt%Ge catalyst (reduced at 300 °C) gave 38 % citral conversion where the selectivity UA was 90 %. For Rh-0.8 wt%Ge (reduced at 500 °C) gave 41 % conversion where the selectivity was 76 %. For Pt-0.4 wt%Ge (reduced at 500 °C) gave 21 % citral conversion where the selectivity was 90 %. At low Ge contents; the higher selectivities were obtained after reduction at 500 °C when the bimetallic and strong metal support interaction effects were combined.

In the study of Rodriguez et al. (2008) bimetallic Ru-Cu catalysts supported on KL zeolite were prepared by coimpregnation with ionic precursors for selective hydrogenation of citral. Monometallic catalysts prepared by incipient-wetness impregnation method were calcined at high temperature (873 K). For bimetallic catalysts, they were impregnated by contacting with second metal promoter solutions of Ru and Cu. Finally the catalysts were dried and then reduced at high temperature. They concluded that RuCu/KL catalysts prepared by coimpregnation method exhibited bimetallic particles with segregated copper species, but without any monometallic ruthenium phase. They suggested formation of alloyed surface at low copper loading (Cu/Ru=0.4). On the contrary, higher Cu/Ru loading ratio provided particularly active and selective catalysts in the hydrogenation of citral to geraniol and nerol. The initial selectivity towards geraniol + nerol (S_{G+N}) was around 15 % and then it increased to 40 % with conversion, for conversions close to 60 %. When RuCuKL was compared with RuKL catalyst, selectivity toward geraniol + nerol strongly decreased for RuCuKL to 9 %. However, for higher copper contents selectivity gradually increased for RuCuKL higher than for Ru/KL. Selectivity to unsaturated alcohols was observed as 20 %.

Ruiz et. al. (2007) studied that the combined effect of two promoters (cerium oxide and tin) on the catalytic properties of Pt in the selective hydrogenation of unsaturated aldehydes. In this study, bimetallic Pt-Sn catalysts supported on C and promoted with highly dispersed ceria on it was prepared. The catalysts were prepared by impregnation (CeO_2/C) and coimpregnation (Pt-Sn/CeO_2/C) method. CeO_2/C was calcined at 200°C and Sn/Pt atomic ratio between 0-0.75 was taken. The liquid phase hydrogenation of citral was carried out at 70 °C at 70 bar. Isopropanol was used as solvent. Effects of Sn/Pt loading ratio and catalyst reduction temperatures (473 K and 773 K) on activity and selectivity were investigated. In Figure 5, temperature programmed reduction (TPR) profiles of the catalysts studied are given. The two overlapped peaks of CeO_2/C were observed at 803 K and 903 K and that was for Pt/CeO_2/C peak at 531 K.

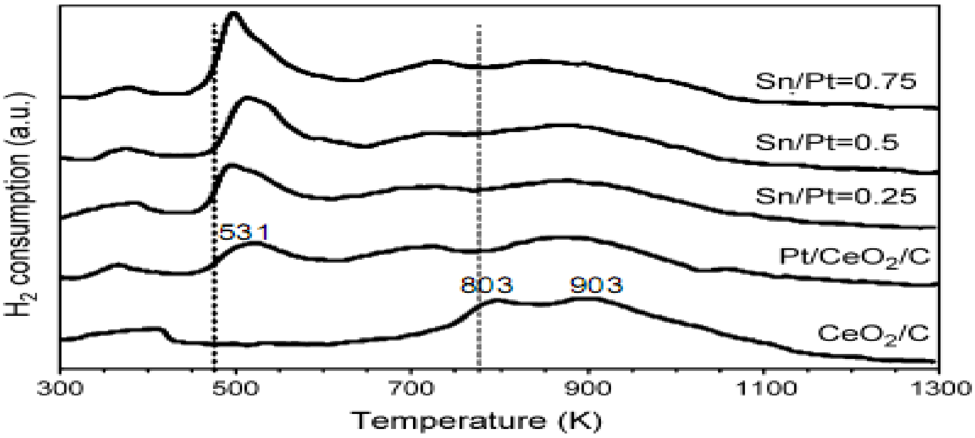

Figure 5. TPR profiles of the Ce/O_2 support and Pt-Sn/CeO_2/C catalysts
(Source: Ruiz et al., 2007)

It was concluded that Pt partially promoted the reduction of ceria, spilled over H_2 from Pt to support, peak area increased with the tin content, tin enhanced the surface ceria reduction process, cerium retards the reduction of tin.

At low catalyst reduction temperature (473 K), a rapid citral hydrogenation was observed during the first 30 min then reaching a stable value where deactivation could be related to citral decomposition or poisoning of active sites (Figure 6 a). It was reported that Pt/CeO_2/C was the most active catalyst (~100% citral conversion). But when Sn content increased, citral conversion decreased.

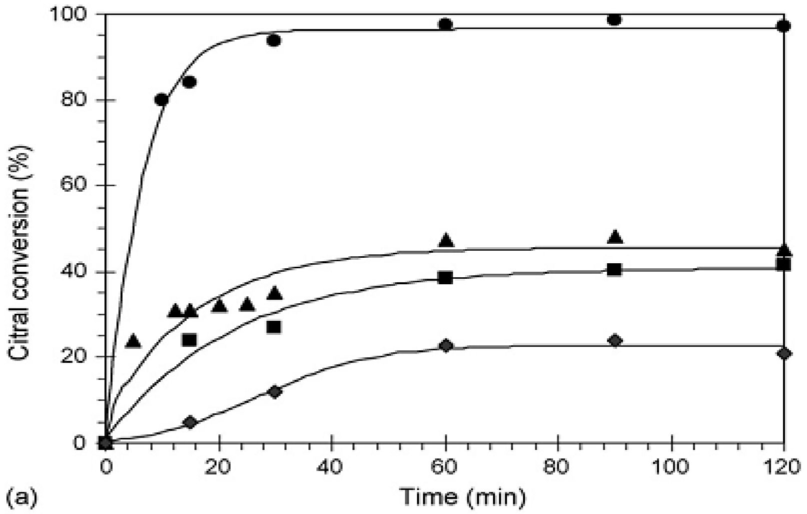

Figure 6. Citral conversion as function of reaction time for (●) Pt/CeO_2/C; (▲) Pt-Sn 0.25 ; (■) Pt-Sn 0.5 ; (♦) Pt-Sn 0.75 after reduction at (a) 473 K and (b) 773 K. (Source: Ruiz et. al., 2007)

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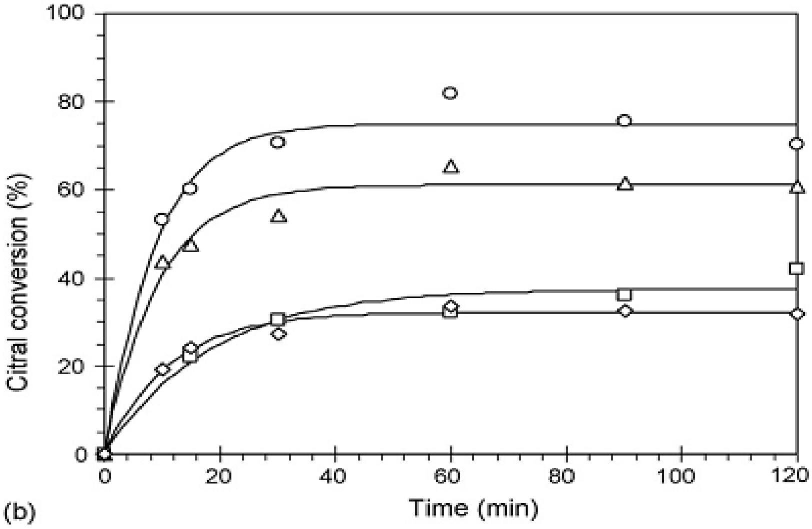

Figure 6. (cont.)

For monometallic Pt/CeO_2/C, citral conversion increased at high reduction temperature**,** for Sn/Pt = 0.25, the citral conversion decreased from 54 % to 35 % at 30 min reaction in Figure 6 b. It was concluded that reduction at high temperature created a new active sites, therefore increased the conversion.

Effect of catalyst reduction temperature on selectivity to unsaturated alcohols is given in Figure 7. It was found that reduction at high temperature (773 K) increased the selectivity to unsaturated alcohols. Bimetallic catalysts showed higher selectivities than monometallic catalysts. Sn addition acted on Lewis acid sites (electron acceptor), causing an increase in selectivity to unsaturated alcohols, which was also proposed by Aramendia et al. (1997). For Sn/Pt ratio of 0.5, the highest selectivity to UA was obtained at 773 K. As Sn/Pt ratio increased volcano type curve was observed.

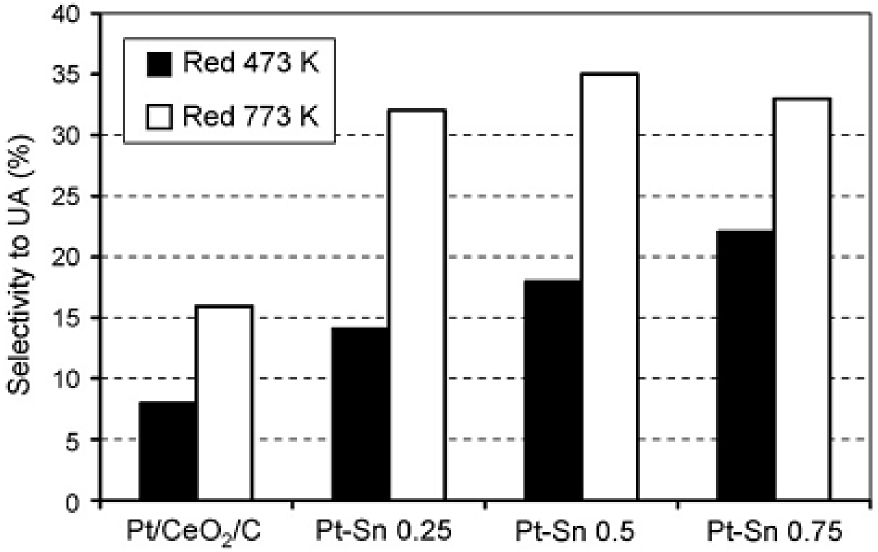

Figure 7. Selectivity to unsaturated alcohols (geraniol + nerol) for the Pt–Sn/CeO_2/C catalysts after reduction at low (200°C) and high (500°C) temperature. (Source: Ruiz et. al., 2007)

Lafaye et al. (2004) prepared bimetallic Rh-Ge catalysts both by catalytic reduction and successive impregnation (SI) methods. The δ-alumina was used as support. For the successive impregnation method germanium precursor was impregnated on the monometallic rhodium catalyst (SI catalysts). SI catalysts were dried and then reduced under hydrogen following the procedure mentioned for catalytic reduction method. They concluded that germanium addition to rhodium improved the reaction selectivity to unsaturated alcohols (nerol and geraniol). Catalysts prepared by CR were more active and selective than SI catalysts. For the same activation temperature (500 °C) citral conversion was increased from 55 % to 75 % for SI. The selectivity to unsaturated alcohols was increased from 20 % to 38 %. When the germanium content was increased (from 1 % to 2.5 %) at lower activation temperature (300°C), citral conversion was increased from 38 % to 85 % while selectivities to unsaturated alcohols remained the same (62 %). They concluded this similarity because of the lower acidity of the SI samples.

CHAPTER 3

EXPERIMENTAL STUDY

Silica Gel support was loaded with Pt and Sn metals to prepare monometallic and bimetallic catalysts. Monometallic catalysts were prepared by impregnation method. Bimetallic catalysts were prepared by catalytic reduction, co-impregnation and successive impregnation methods. After preparation of catalysts, they were characterized and tested in citral hydrogenation.

3.1. Materials

Silica gel (Davisil, grade 643, 200-425 mesh, 150Å, 99+%, Sigma Aldrich, 236810-100G) used as catalyst support. Citral subtrate (cis+trans) (Fluka, 27450, 500ml) had a purity of 97 %. Cyclohexanone (99+%, A.C.S. reagent, Sigma Aldrich (398241-500ml)) was used as an internal standard. Two types of solvent were used to determine the appropriate solvent for citral hydrogenation reaction which were ethanol (J.T. Baker, 8228, 2.5 L) and 2-pentanol (Merck, 8.07501.0500, 500 ml). Pt precursor used were hexachloroplatinic acid hydrate (H_2Cl_6Pt, Fluka, 81080, 5g, purum ~38% Pt) and platinum (II) acetyl acetonate ($Pt(C_5H_7O_2)_2$, Fluka, 81030, 1g, purum). Tin (Sn) was used for bimetallic catalysts preparation. Tetra-n-butyltin (96 %, Acros Organics, 137980050) was used as Sn source.

3.2. Methods

3.2.1. Catalyst Preparation

3.2.1.1. Preparation of Monometallic Catalysts

The monometallic Pt/SiO_2 catalysts were prepared by impregnation method. Pt loading over silica gel support was 1 % (w/w). Silica gel (37-74μm) was calcined at 500

°C for 6 hours under flowing dry air (70 ml/min) in ash oven. Calcined silica gel was added to aqua salt solutions of Pt. Then they were mixed at room temperature for 24 hours. The mixed solution was put into the rotary evaporator and water was evaporated at 60 °C under 200 mbar vacuum pressure for 3 hours at 50 rpm. The resultant material was dried at 110 °C for 12 hours in an oven. After drying, it was calcined at 500 °C for 6 hours under flowing dry air (70 ml/min) to obtain Pt/SiO_2 catalyst.

3.2.1.2. Preparation of Bimetallic Catalysts

Bimetallic catalysts were prepared by catalytic reduction method, coimpregnation method and successive impregnation method. $PtSn/SiO_2$ catalysts with Sn/Pt molar ratio of 0.3, 0.5, and 0.7 were prepared.

In the catalytic reduction method, calcined silica gel was added to platinum (II) acetyl acetonate in ethanol. They were mixed for 24 h at room temperature. The solvent was evaporated by rotary evaporator. The obtained material was dried at 110 °C for 12 hours in an oven and then calcined 500 °C for 6 hours under flowing dry air (70 ml/min) to obtain Pt loaded SiO_2. It was then activated at the activation temperatures of 350 °C or 450 °C under H_2 flow for 4h to obtain Pt/SiO_2. Then it was placed in a glass reactor and tetrabutyl tin dissolved in toluene was added. The slurry was mixed for 1 h under H_2 bubbling. After that it was dried overnight (Lafaye et al., 2004).

In the coimpregnation method, calcined silica gel was added to platinum (II) acetyl acetonate and tetrabutyl tin salt solutions in toluene. They were mixed for 24 h at room temperature. The solvent was evaporated by rotary evaporator. The obtained material was dried at 110 °C for 12 hours in an oven and then calcined at 500 °C for 6 hours under flowing dry air (70 ml/min). The calcined material was then activated at the activation temperatures of 350 °C or 450 °C under H_2 flow for 4h to prepare $PtSn/SiO_2$ catalyst (Coupe et al., 2000; Aykaç and Yılmaz., 2008).

In the successive impregnation method, calcined silica gel was added to platinum (II) acetyl acetonate in ethanol. They were mixed for 24 h at room temperature. The solvent was evaporated by rotary evaporator. The obtained material was dried at 110 °C for 12 hours in an oven under flowing dry air (70 ml/min). Dried monometallic Pt/SiO_2 catalyst was activated at the activation temperatures (350 °C or 450 °C) under H_2 flow for 4h. Then it was placed in a glass reactor and tetrabutyl tin dissolved in toluene was added. The slurry was mixed for 1 h under H_2 bubbling. After that it was dried overnight. Before citral hydrogenation reaction, all of the catalysts were activated either at 350 °C or 450 °C under 4 bar H_2 gas pressure (Coupe et al., 2000; Lafaye et al., 2004; Rodriguez et al., 2006).

3.2.2. Catalyst Characterization

Prepared catalysts were characterized using different instrumental techniques namely scanning electron microscopy (Philips SFEG 30S SEM), X-ray diffraction (Philips X'Pert Pro with Cu Kα radiation), and nitrogen adsorption (Micromeritics ASAP 2010).

The acidity of the samples was determined by Temperature-Programmed Desorption of Ammonia (NH_3-TPD) method using Micromeritics AutoChem II Chemisorption Analyzer instrument. The sample was heated up to 500 °C by increasing the temperature at a rate of 5 °C/min and kept at this temperature for 1 h under He gas flow of 70 ml/min. Then the sample was cooled under He flow of 30 ml/min to 90 °C at a rate of 5 °C/min. This was followed by switching the flow to NH_3-He gas mixture at the rate of 30 ml/min for 30 min. Physically adsorbed NH_3 was removed by degassing the sample at 90 °C under He flow of 70 ml/min for 120 min and then at the rate of 30 ml/min for 150 min. NH_3 desorption of the sample was analyzed by heating the sample at the rate of 10 °C/min from 90 °C to 600 °C. TCD signal was recorded during the NH3-TPD.

Temperature-programmed reduction (TPR) was carried out using the apparatus used for NH_3-TPD measurements. The catalyst samples (Pt/SiO_2 and $PtSn/SiO_2$) were outgassed at 150 °C for 1 h and then cooled to 50 °C under 70 ml/min He flow. TPR profiles were registered while heating the samples from 50 °C to 800 °C by 5 °C/min heating rate under flow of 5 % H_2/He mixture (50 ml/min). The flow was then switched to He and the samples were cooled to 40 °C.

Fourier transform infrared spectroscopy (FTIR) was carried out using FTIR Excalibur Series (FTS 3000MX) for silica gel and calcined silica gel. FTIR analyses were between 400-4000 cm^{-1} wavenumber. Silica gel and calcined silica gel powders were mixed with KBr at weight content of 2 %. They were formed as pellets. After that, they were dried at 150 °C for 4 hours. Finally, FTIR analysis was done for these samples. Moreover, another FTIR analysis was applied for calcined silica gel which was in powder form by using drift method. In this method, FTIR spectrums were taken at 30 °C and 100 °C. Then, this analysis was carried out under 0.075 mbar vacuum pressure at 150 °C for 1 hour.

3.2.3. Catalyst Testing

A stirred, semibatch reactor (500 ml, 4574 model, Parr Instrument Co.) equipped with an electrical heater and temperature controller (4842 model, Parr Instrument Co.) was used in the citral hydrogenation reactions. The system had a high-pressure Oxytrap (Altech) and a bubbling unit, in which the dissolved oxygen was removed. The reaction temperature was controlled with a thermocouple probe inside the reactor. Figure 8 shows the experimental set-up.

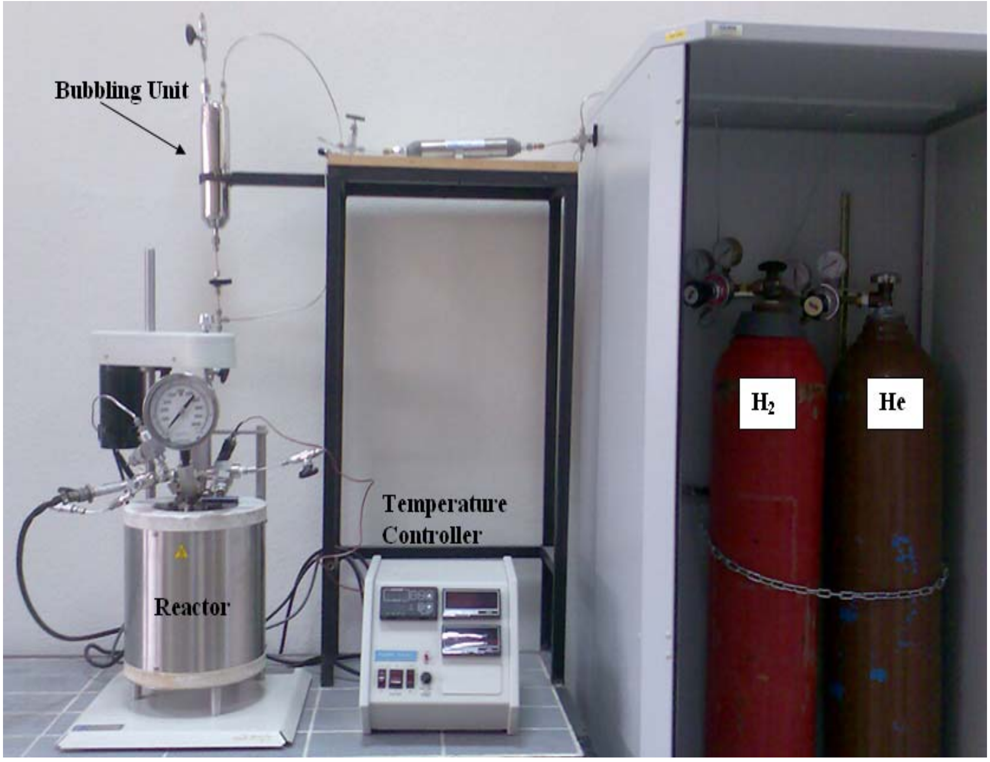

Figure 8. The experimental set-up

Before the reaction, the catalysts were reduced in situ. For this purpose, the reactor was loaded with 0.25 g of catalyst, sealed and leak tested at 6 bar with Helium. Temperature was set to 100 °C and He was filled to the reactor up to 6 bar and released five times. Then the temperature was set to 200 °C. After the temperature reached to 200 °C, He was fed to the reactor with a flow rate of 70 ml/min for 1 h at 4 bar to purge air content from the reactor. After 1 h, gas flow was switched to H_2, temperature was set to 350 °C or 450 °C depending on activation temperature. The reactor was filled up to 4 bar of H_2 (70 ml/min) and discharged for five times. Finally catalyst was activated at 350 °C or 450 °C for 4 h under flow of 4 bar H_2. Then the reactor was cooled to reaction temperature of 80 °C and kept overnight under 4 bar of H_2.

Reactant mixture was prepared as 0.1 M citral and 0.025 M cyclohexanone in ethanol with a total reaction volume of 200 ml. Firstly, 100 ml of ethanol was injected to the bubbling unit to remove the dissolved oxygen. Ethanol was then injected into the reactor and contacted with the catalysts. After 30 minutes of mixing the catalysts and ethanol, reactants were injected into the bubbling unit and then into the reactor. Citral was hydrogenated at 80 °C under 6 bar H_2 with a stirring rate of 1000 rpm. The liquid samples were withdrawn from the reactor at the 0.5, 2, 5, 10, 20, 60, 90, 120, 150, 180 and 300 minutes of reaction durations. Samples were prepared as follows: 0.25 ml of sample and 1 ml ethanol were mixed in vials. 1 μl samples were taken from vials and they were sent to the Gas Chromatograph.

Samples taken from the reactor were analyzed with a Gas Chromatograph (Agilent Technologies 6890N Network GC System Gas Chromatograph) equipped with a flame ionization detector (FID) and a capillary column DB-225 (J&W, 30m, 0.53mm 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.

Hydrogenation products of citral were also identified by GC-MS technique. A capillary column HP-5MS (19091S-433, 30m, 0.25 mm i.d.) was used. The temperature program was as follows: heating from 50°C to 250°C with a heating rate 8 °C/min, heating from 250°C to 300°C with a heating rate 35°C/min and holding 5 minutes at 300°C. The compositions of components in the reaction mixture were determined by internal standardization method. For the retention time determination of citral hydrogenation products, commercially available citral hydrogenation products were used which were citronellal (Fluka, ≥80 %), citronellol (Fluka, 90-95 %), nerol (Fluka, 90 %), geraniol (Fluka, 99.5 %), isopulegol (Fluka, 99 %), menthol (Fluka, 95 %), 3, 7-Dimethyl-1-octanol (Aldrich, 99 %).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Catalyst Characterization

4.1.1. Silica Gel (SiO_2) and Pt/SiO_2 Catalysts

The X-ray diffraction (XRD) analysis of silica gel, calcined silica gel and Pt/SiO_2 catalysts were carried out at 2θ degree of from 5 to 90. This analysis showed that silica gel, calcined silica gel and Pt/SiO_2 catalyst had an amorphous structure as shown in Figure 9. Similar results were found in the study of Chiang et al. (2007). Moreover, Pt characteristic peak couldn't be observed because of the lower loading amount (1 % (w/w)) and also could be due to the good distribution.

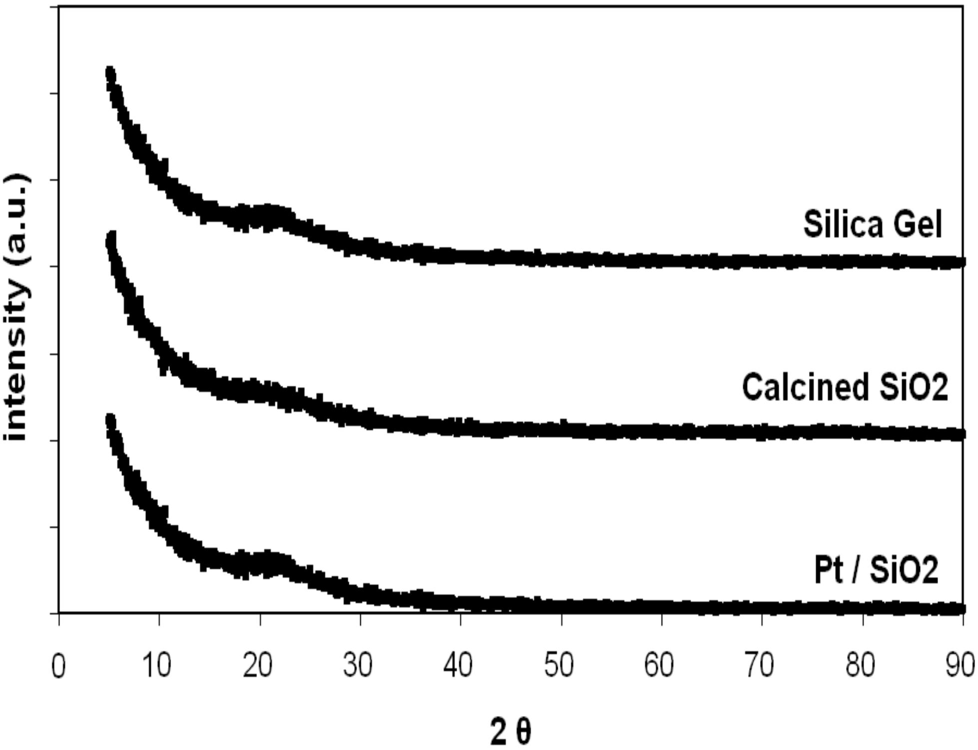

Figure 9. XRD patterns of Silica Gel, Calcined Silica Gel and Pt/SiO_2 catalyst.

Scanning Electron Microscopy (SEM) analysis was also applied to the same samples. SiO_2 gel has particles in the size range of 37-74 μm. SEM analysis showed that SiO_2 gel had approximately 50 μm particulate sizes (average of 30 particle size) as shown in Figure 10 a. In the Pt/SiO_2 catalyst SEM image detailed investigation showed Pt distribution on the surface of particles (Figure 10 b).

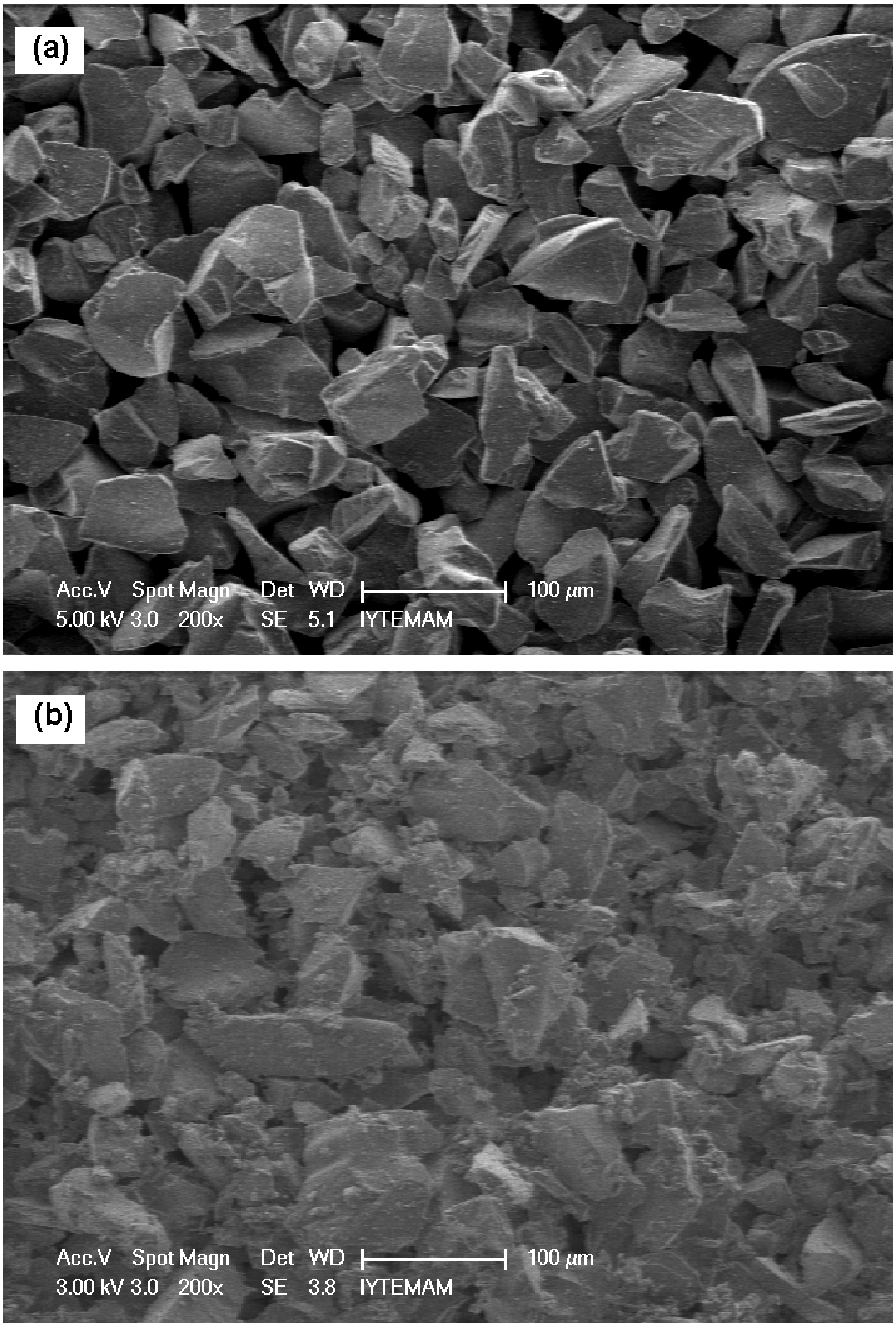

Figure 10. SEM images of (a) Calcined SiO_2 gel, (b) Pt/ SiO_2 catalyst

The reported surface area for SiO_2 gel was 300 m^2/g surface area by the producer. Textural properties of silica gel, calcined silica gel, Pt/SiO_2 and $PtSn/SiO_2$ catalysts are given in Table 1. In micropore area determination of these samples, Herkins-Jura method was used. The investigated sample thickness was between 3.5-5 Å for silica gel, calcined silica gel and Pt/SiO_2. It was between 5.5-8 Å for $PtSn/SiO_2$ catalyst. Calcination at 500 °C decreased micropore area of silica gel from 30.9 to 7.4 m^2/g. This was due to the calcination at high temperature caused micropore blockage so decreasing in micropore area observed. Addition of metal particles to silica gel increased micropore area. Preparing Pt/SiO_2 catalyst increased it to 18.3 m^2/g. To prepare bimetallic catalyst second metal addition also increased micropore area to 28.0 m^2/g. Thus addition of metal particles both for Pt/SiO_2 and $PtSn/SiO_2$ to silica gel formed new micropores. Calcination of silica gel at high temperature decreased BET area from 338.0 to 320.7 m^2/g. Monometallic and bimetallic catalyst preparation increased BET area. For Pt/SiO_2 and $PtSn/SiO_2$ catalysts, they were 359.0 and 373.6 m^2/g, respectively. That was caused by increasing of both micropore area and external surface area for monometallic and bimetallic catalysts. External surface area was calculated by subtraction of micropore area from BET area. Single point total pore volume of pores less than 204 Å diameter at approximately 0.9 relative pressure was investigated for silica gel gel, calcined silica gel and Pt/SiO_2 catalyst. For $PtSn/SiO_2$ catalyst single point total pore volume of pores less than 210 Å diameter at 0.9 relative pressure was investigated. For all samples single point total pore volume did not show significant change and it ranged between 0.96 to 1.06 cm^3/g. Calcination of silica gel at high temperature and addition of metal to support silica gel did not change BJH adsorption average pore diameter significantly. But addition of second metal to monometallic catalyst decreased it from 101.01 to 96.79 Å.

Table 1. Textural properties of supports and catalysts

	Micropore Area (m^2/g)	**External Surface Area (m^2/g)**	**BET Area (m^2/g)**	**Single Point Total Pore Volume (cm^3/g)**	**BJH Adsorption Average Pore Diameter (Å)**
Silica Gel	30.9	307.1	338.0	1.02	106.26
Calcined Silica Gel	7.4	313.3	320.7	0.96	104.67
Pt/SiO_2	18.3	340.7	359.0	0.99	101.01
$PtSn/SiO_2$	28.0	345.6	373.6	1.06	96.79

The adsorption isotherms of silica gel, calcined silica gel, Pt/SiO_2 and PtSn/SiO_2 catalysts are given in Figure 11. Adsorption isotherms of given support and catalysts were obtained almost the same. Calcination of silica gel did not change significantly the isotherm of silica gel. Preparing monometallic and bimetallic catalysts also did not change the isotherms. This also indicated that the structure of the silica gel was preserved during preparation steps. The isotherms showed that silica gel had an mesoporous structure.

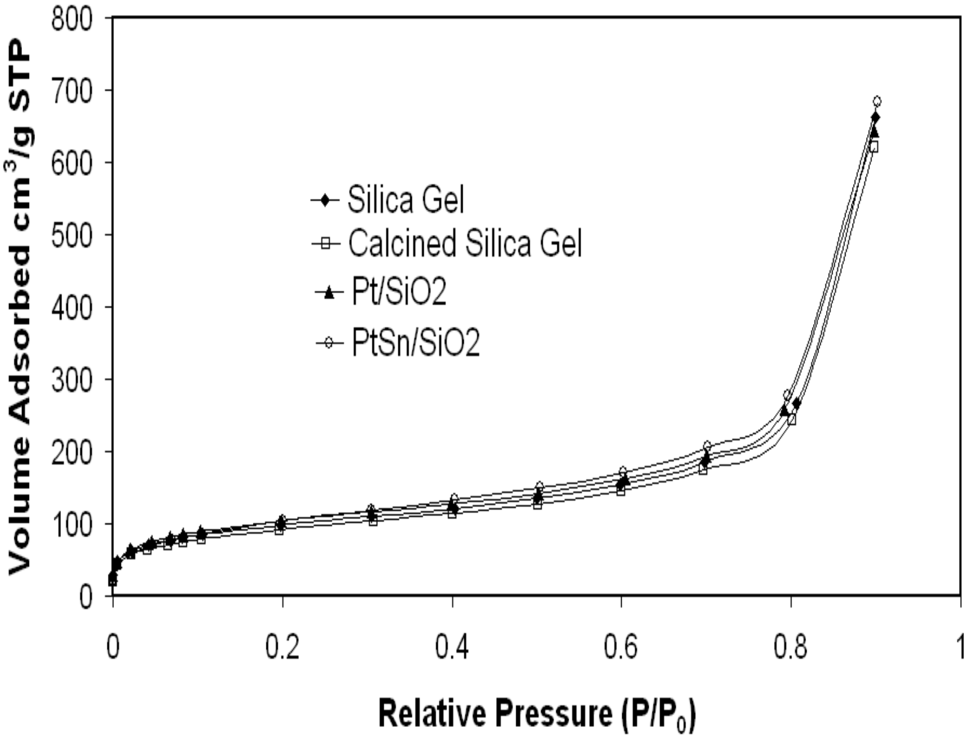

Figure 11. Adsorption isotherms of silica gel, calcined silica gel, Pt/SiO_2 and PtSn/SiO_2 catalysts

Adsorption and desorption isotherms of silica gel, calcined silica gel, Pt/SiO_2 and PtSn/SiO_2 catalysts are shown in Figures 12-15, respectively. For all of the samples, adsorption and desorption isotherms did not show any significant hysteresis loop.

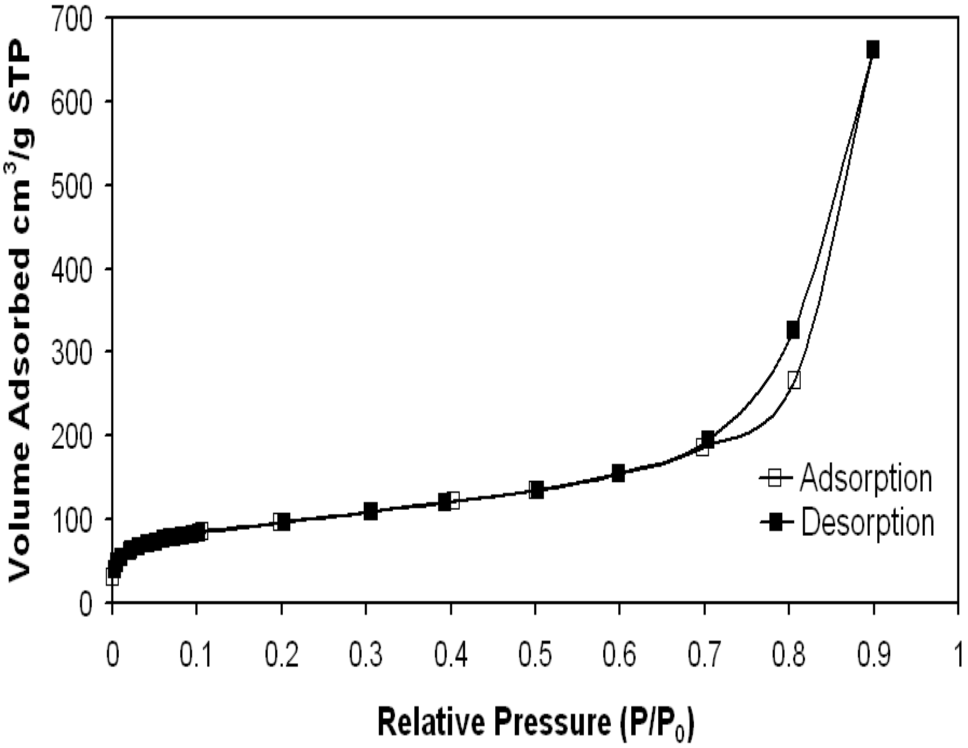

Figure 12. Adsorption and desorption isotherms of Silica Gel

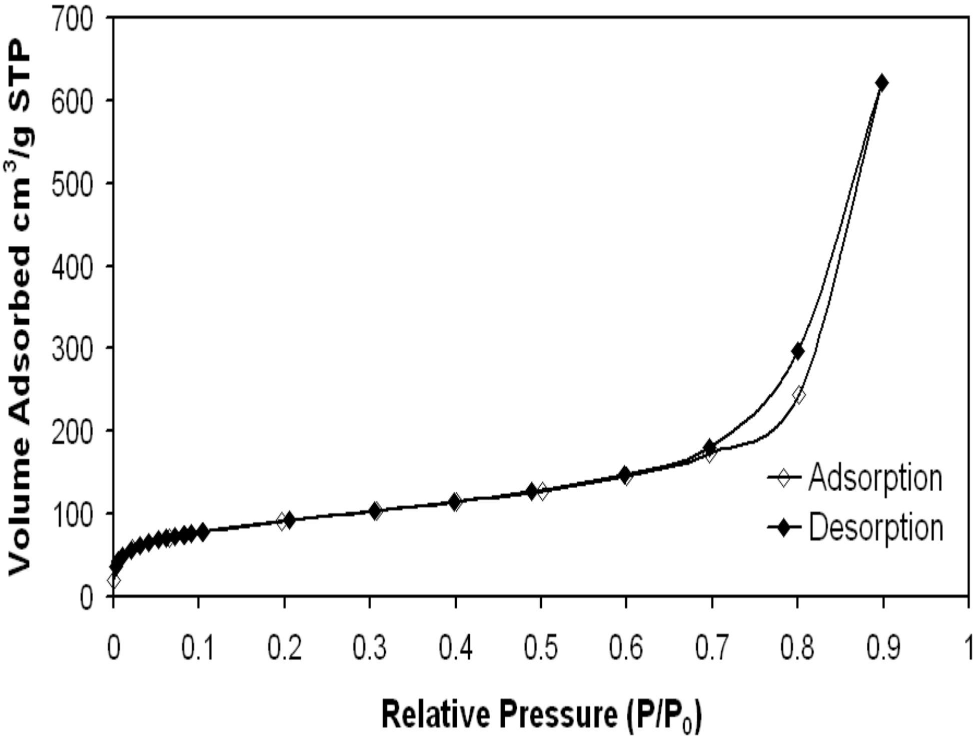

Figure 13. Adsorption and desorption isotherms of Calcined Silica Gel

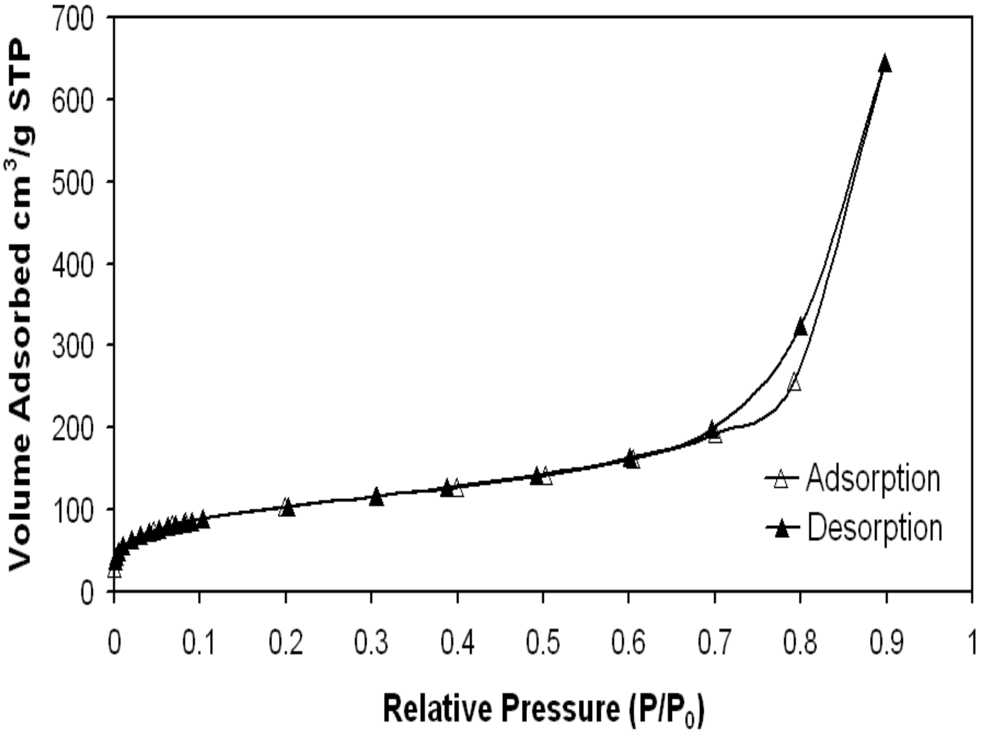

Figure 14. Adsorption and desorption isotherms of Pt/SiO_2 catalyst

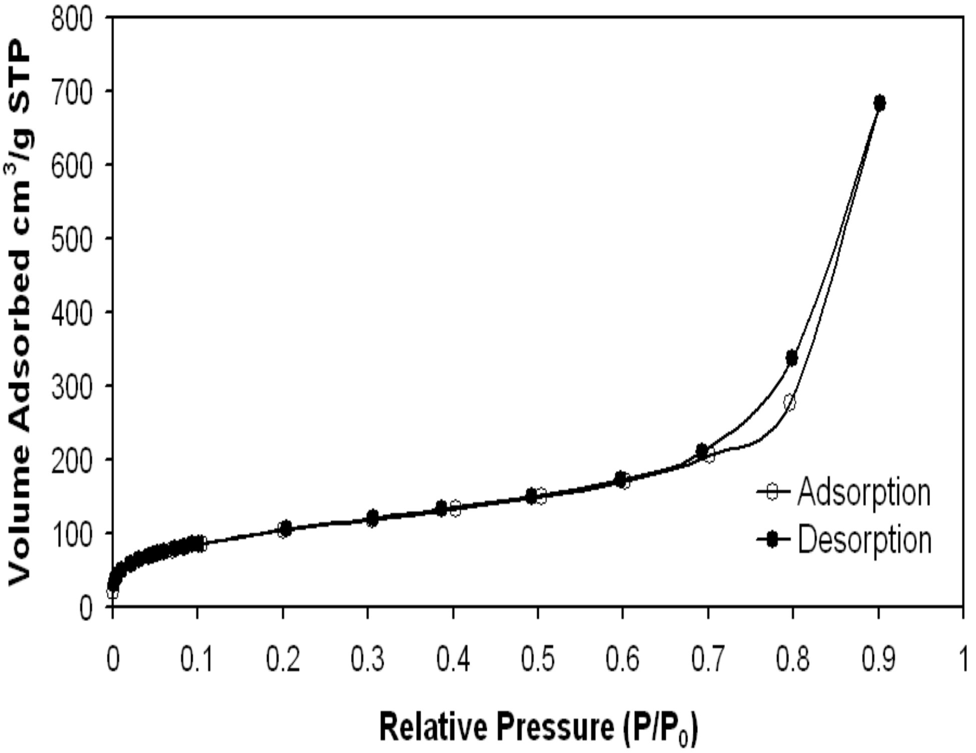

Figure 15. Adsorption and desorption isotherms of PtSn/SiO_2 catalyst

Acidities of Silica Gel, Calcined Silica Gel, Pt/SiO_2 catalysts prepared by using PAA and HCLPA precursors measured are given in Figure 16. It was observed SiO_2 gel had low acidity. At 200 °C weak acid sites and at approximately 350 °C strong acid sites were observed over silica gel. Calcinations and metal loading from different precursors reduced even its acidity. So increase in acidity was not observed due to Cl containing precursor of HCLPA. Reduction of acidity could be due to interaction of acid sites with Pt particles

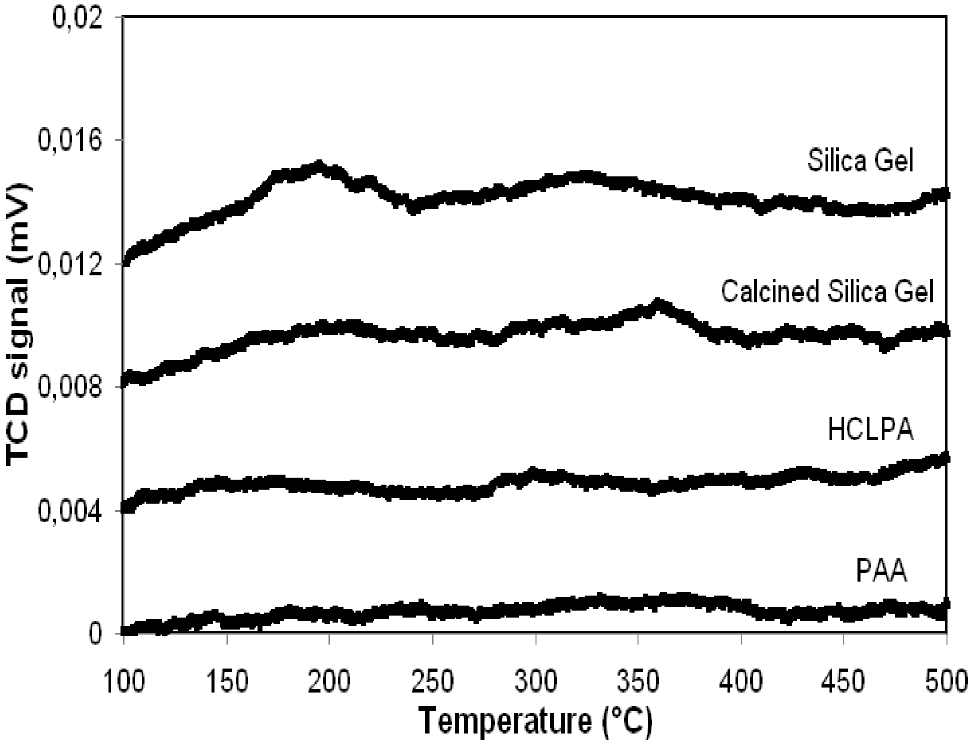

Figure 16. NH_3-TPD diagram of silica gel, Calcined silica gel and Pt/SiO_2 catalysts

Temperature-programmed reduction (TPR) profiles of Pt/SiO_2 and PtSn/SiO_2 catalysts are shown in Figure 17. For this analysis Pt/SiO_2 catalyst was prepared by impregnation method in which PAA used as Pt precursor type. It was calcined and activated at 500 °C and 350 °C, respectively. PtSn/SiO_2 catalyst was prepared by catalytic reduction method. It was calcined and activated at 500 °C and 450 °C, respectively. H_2-TPR analysis showed that the reduction peak of Pt/SiO_2 catalyst was obtained between the temperatures of 325 °C-390 °C. This meant that monometallic catalysts were reduced before the reaction by activation temperatures used in our study. For PtSn/SiO_2 catalyst, the reduction peak was observed between the temperatures of 400 °C-590 °C. Higher reduction temperatures were needed for reduction of bimetallic catalysts. According to H_2-TPR analysis, reduction amount of PtSn/SiO_2 catalyst was more than Pt/SiO_2 catalyst. This showed that more metals were reduced.

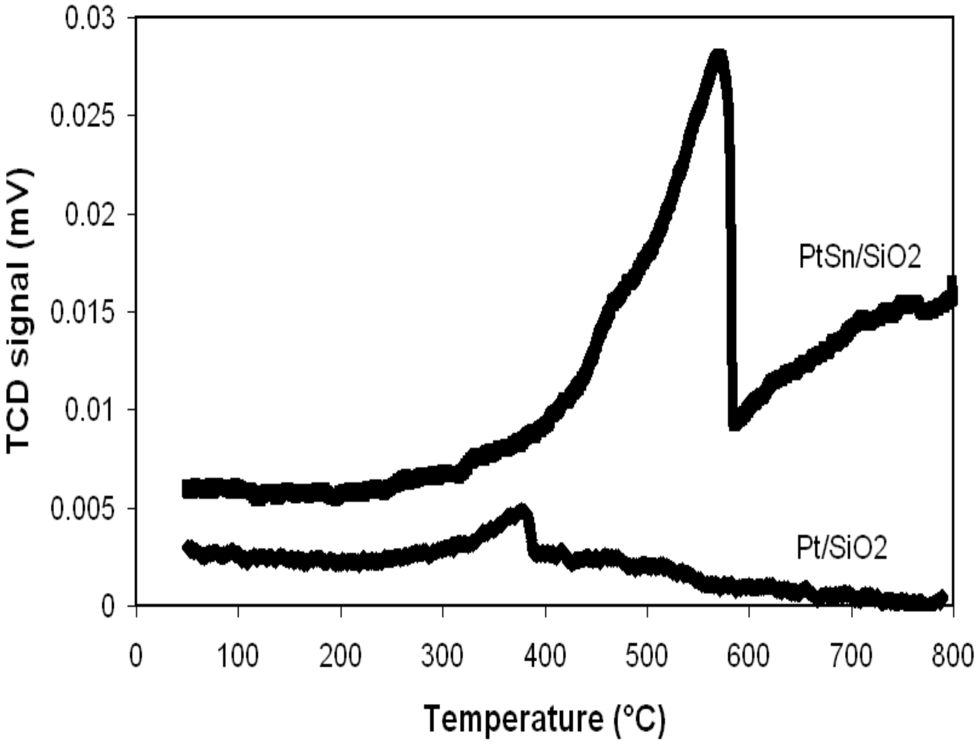

Figure 17. TPR profiles of Pt/SiO_2 and PtSn/SiO_2 catalysts

The infrared absorption spectra of silica gel and calcined silica gel dried at 150 °C for 4 hours in pellet form in a spectral range 400-4000 cm^{-1} are shown in Figure 18. The adsorption band 450 cm^{-1} for both samples were due to Si-O-Si bending vibration. The band observed at 820 cm^{-1} for both samples were the characteristic frequency for the Si-O-Si symmetric stretching vibration. The band at 983 cm^{-1} due to Si-H bending vibration. It decreased with calcination of silica gel at 500 °C. The band at 1114 cm^{-1} was due to the Si-O stretching vibration for both samples. The adsorption band at 3458 cm^{-1} for calcined silica gel due to symmetric Si-OH (hydroxyl groups of the silica gel) stretching vibration, decreases by calcination at 500 °C when compared with the adsorption band at 3510 cm^{-1} for silica gel. This was attributed to the $Si(OH)_4$ which is not converted into the SiO_2. Similar results were found in the studies of Battisha et al. (2007) and Khosravan and Salijooghi (2009).

The infrared absorption spectra of calcined silica gel were also observed in powder form by using drift method at 150 °C under 0.075 mbar vacuum pressure as in

Figure 19. No significant change was observed by drift method when compared with previous FTIR analyses.

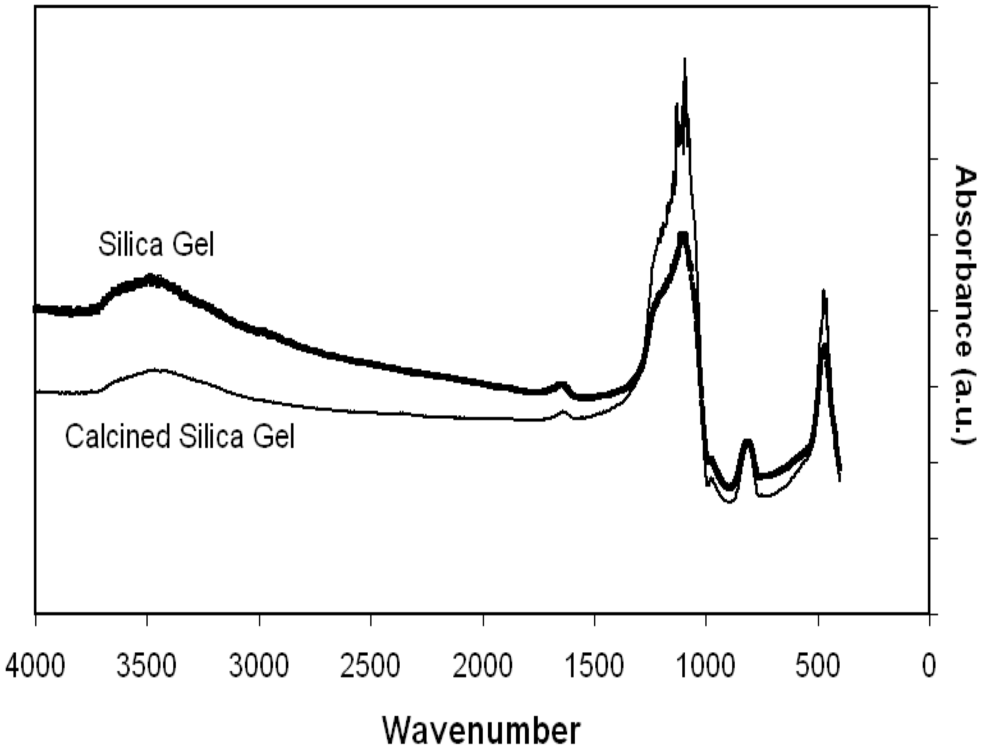

Figure 18. Infrared spectra of silica gel and calcined silica gel

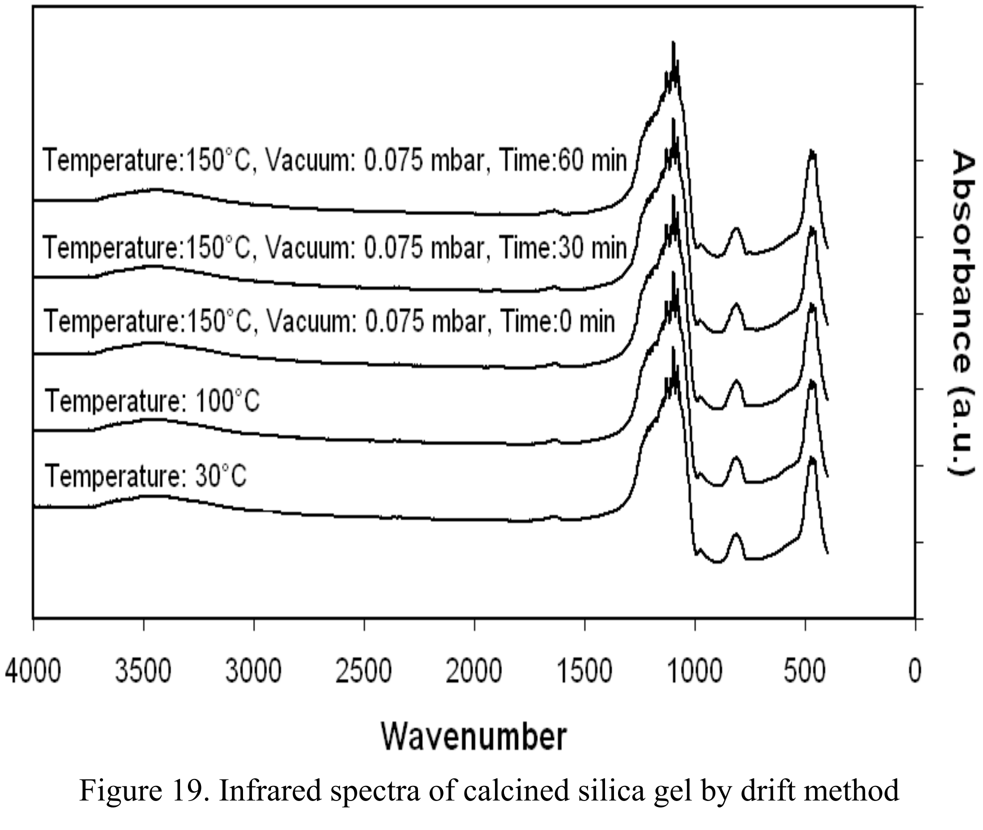

Figure 19. Infrared spectra of calcined silica gel by drift method

4.1.2. PtSn/SiO$_2$ Catalysts

XRD diagrams of bimetallic PtSn/SiO$_2$ catalysts which prepared by catalytic reduction (CR400, CR500) and coimpregnation methods (CI400, CI500) at calcination temperatures of 400 °C and 500 °C are shown in Figure 20. The XRD analyses of these catalysts were done between 2θ degrees of from 5 to 80. The Pt loading amount kept constant for all of the bimetallic catalysts. Sn/Pt ratios were 0.5 for all the catalysts. It was observed that the structures of the catalysts were amorphous as in Pt/SiO$_2$ catalysts. Also, Pt and Sn characteristic peaks could not be observed, because of the lower loading and good dispersion. When calcination temperature increased, the structure remained stable.

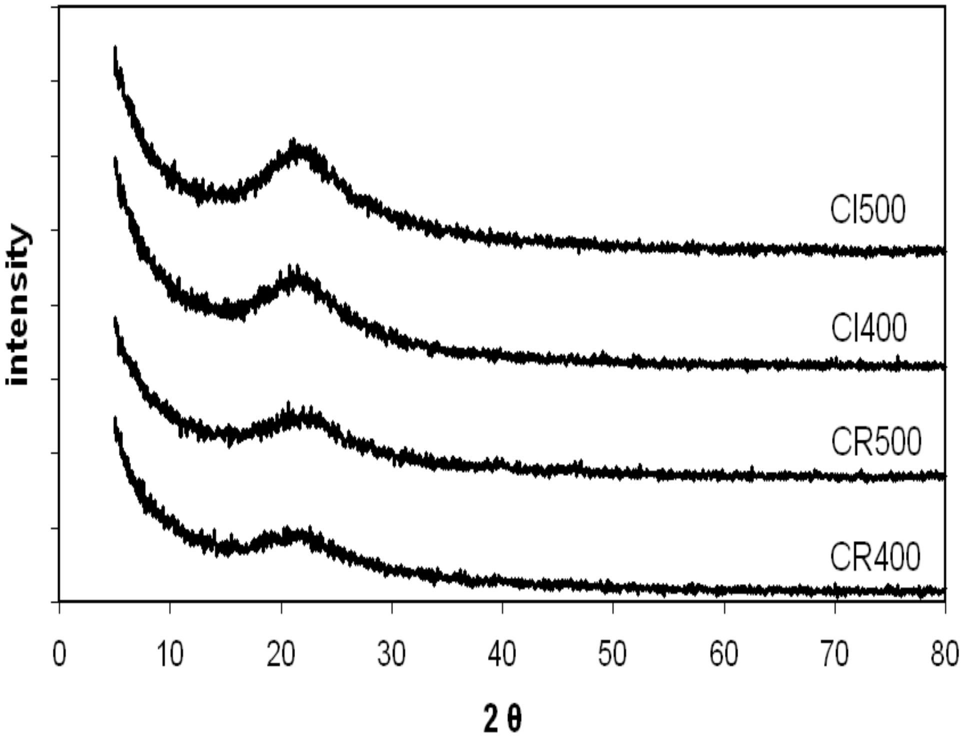

Figure 20. XRD patterns of PtSn/SiO$_2$ catalysts (CI500, CI400, CR500 and CR400)

The SEM images of the catalysts which prepared by catalytic reduction method (calcined at 500 °C, CR500), co-impregnation (calcined at 500 °C, CI500) and successive impregnation (calcined at 500 °C, SI500) are shown in Figures 21-23. It was observed that the some deposites were observed on the surface of the catalysts. Calcination of silica gel at 500 °C and application of other heat treatments for all bimetallic catalyst preparations caused breaking of larger particles into smaller particles as shown in Figure 21 a, Figure 22 a and Figure 23 a when compared with Figure 10 a.

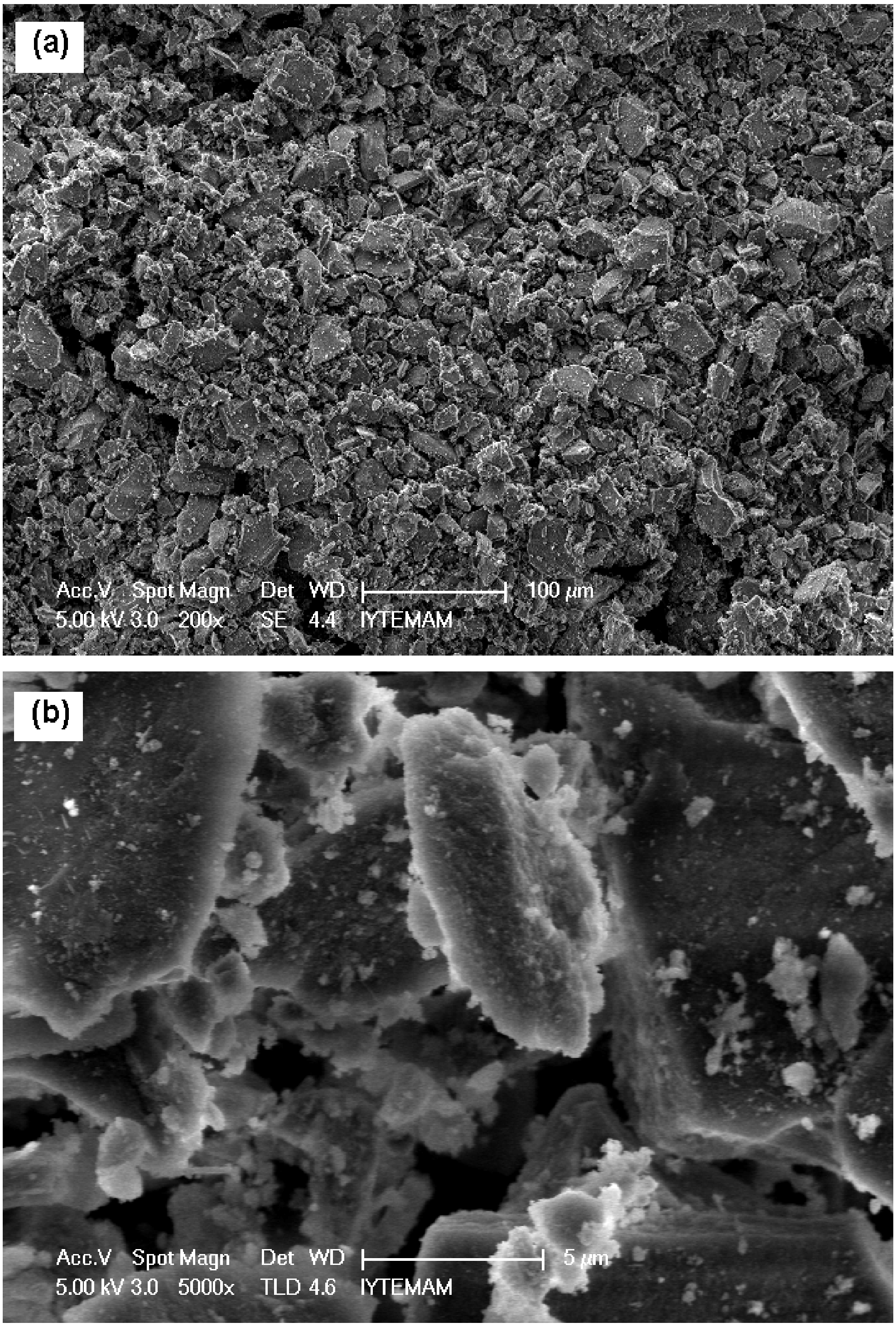

Figure 21. SEM images of CR500 at (a) 200X, (b) 5000X magnification

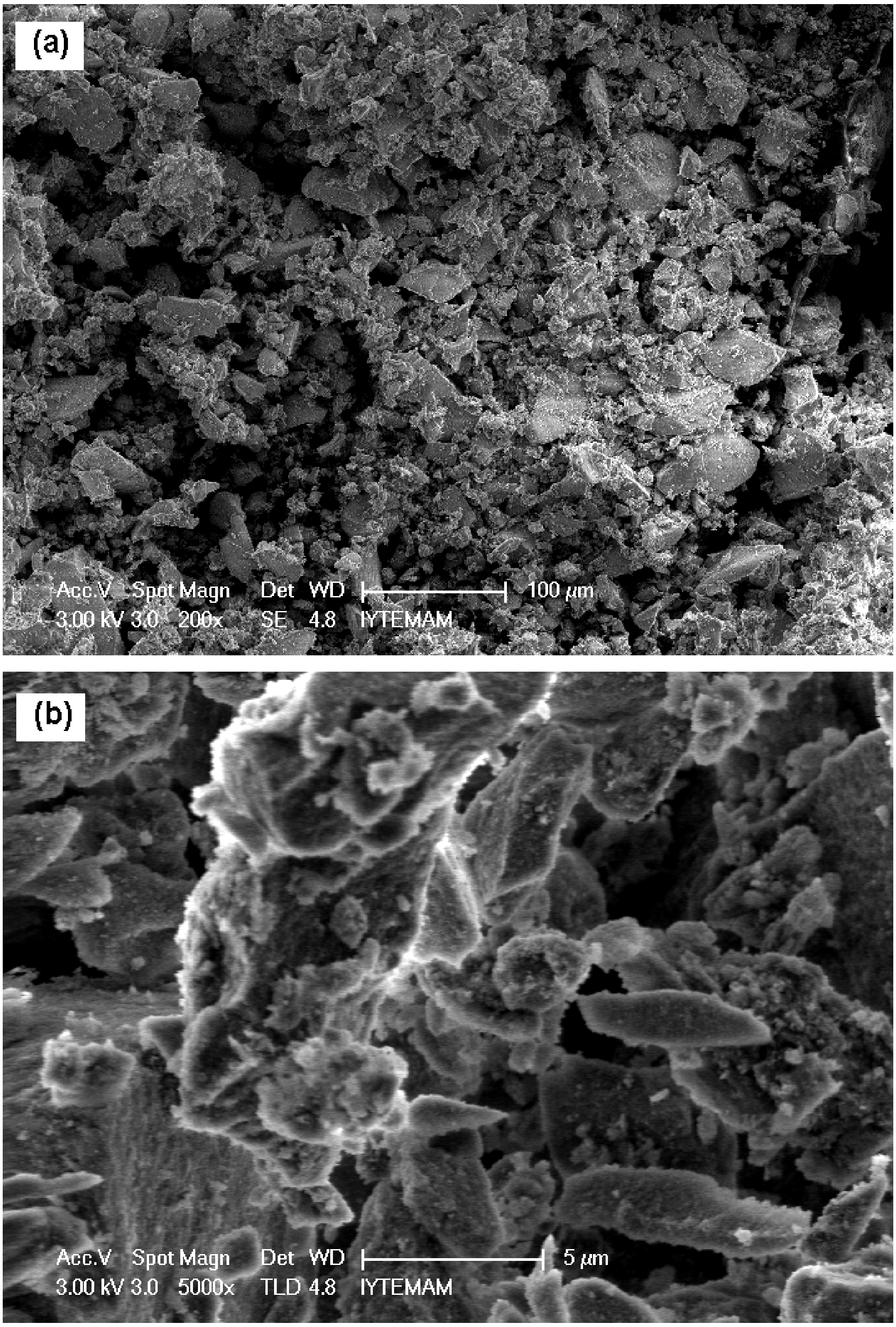

Figure 22. SEM images of CI500 at (a) 200X, (b) 5000X magnification

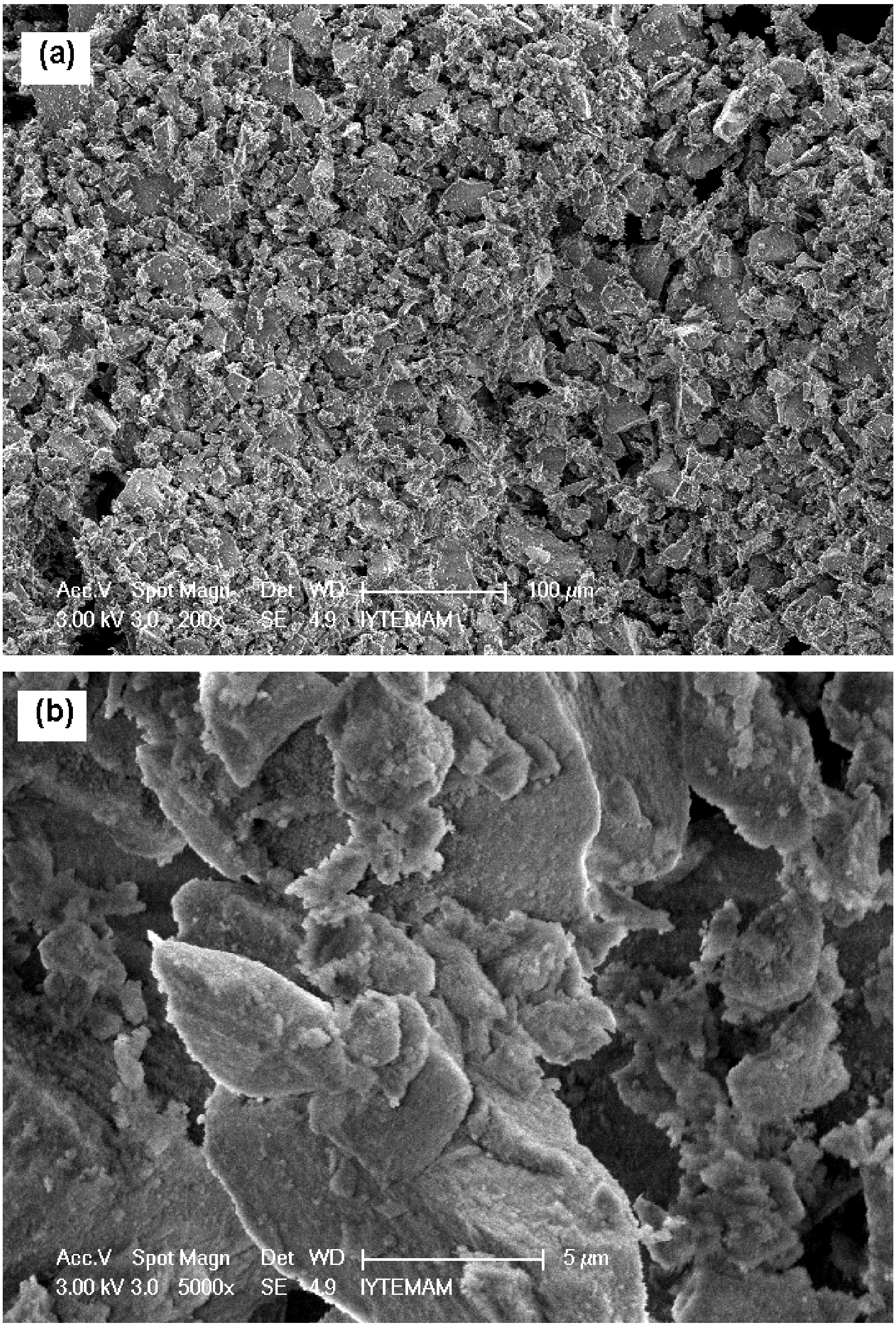

Figure 23. SEM images of SI500 at (a) 200X, (b) 5000X magnification

4.2. Catalyst Testing

The prepared catalysts were tested in citral hydrogenation reaction. Reactions were carried out at 80 °C temperature, 6 bar H_2 pressure and 1000 rpm stirring speed with 250 mg of catalysts.

The citral conversion was calculated as the molar percent of reactant consumed as follows:

$$\text{Conversion (molar \%)} = \frac{(citral)_{in} - (citral)_{out}}{(citral)_{in}} x100 \qquad (4.1)$$

The selectivities to desired products were defined as the ratio of the number of moles of desired product to the number of total moles of products.

$$\text{Selectivity (mole \%)} = \frac{(Desired\ \mathrm{Pr}oduct)_{out}}{(Total\ Moles\ Of\ \mathrm{Pr}oducts)_{out}} x100 \qquad (4.2)$$

The citral hydrogenation reaction gives variety of products that are citronellal, citronellol, nerol, geraniol, 3,7-Dimethyl-1-octanol. These products were obtained during the citral hydrogenation during this study. The GC-MS chromatograms of each product were given in Appendix A section.

4.2.1. Activity and Selectivity Tests for Monometallic Catalysts

Figure 24 shows the product distribution observed over Pt/SiO_2 catalyst reduced at 350 °C prepared from platinum (II) acetyl acetonate (PAA). Citral reacted fastly in the first 20 minutes of the reaction then slowly decreased up to the end of the reaction. The main products formed were citronellal (82.4 %), nerol + geraniol (6.3 %). Moreover undesired products were also formed which were 3,7 Dimethyl 1- Octanol (0.7 %) and citral acetals (0.8 %) in very low amounts. It can be said that this catalyst had some selectivity toward the hydrogenation of conjugated double bond.

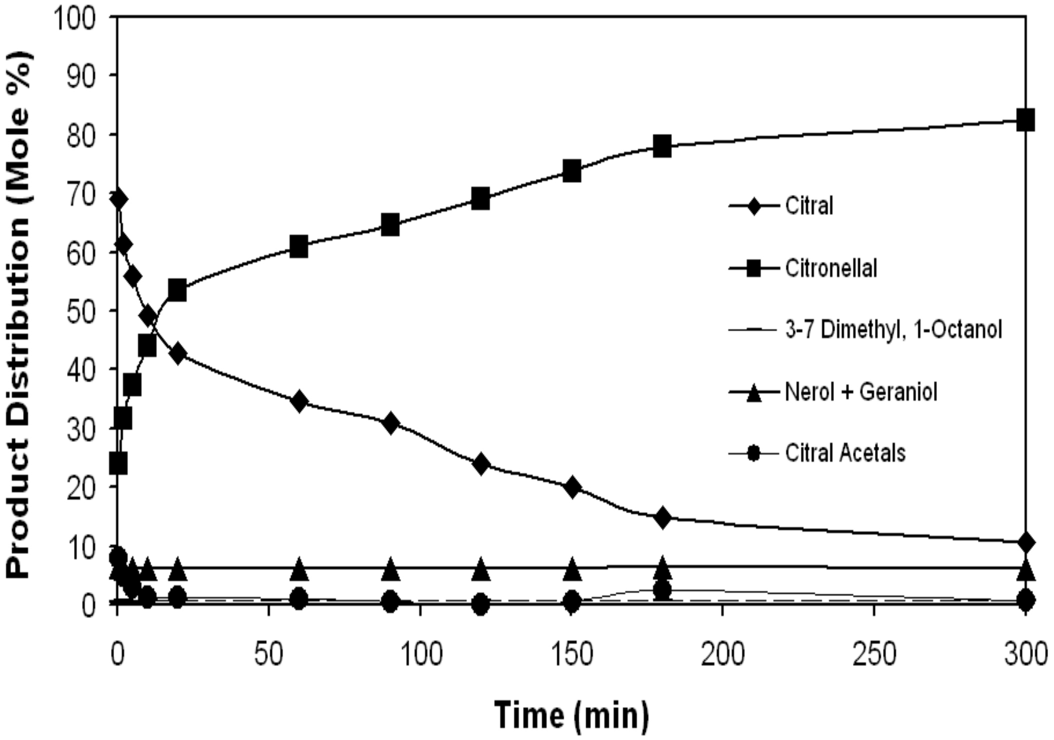

Figure 24. Product distribution obtained over Pt/SiO_2 catalyst activated at 350 °C and calcined at 500 °C including platinum (II) acetyl acetonate (PAA)

Figure 25 shows the product distribution observed over Pt/SiO_2 catalyst (reduced at 350 °C) using hexachloroplatinic acid (HCLPA) as precursor. Citral reacted fastly in the first 20 minutes of the reaction then slowly decreased and deactivated. Deactivation could be due to inhibition by adsorbed CO produced by the decomposition of either citral or unsaturated alcohol (Singh and Vannice, 2001). The main products formed were nerol + geraniol (35.6 %), citronellal (29.9 %). Moreover undesired products were also formed which were 3-7 Dimethyl 1- Octanol (2.8 %) and citral acetals (16.3 %). It can be said that this catalyst had some selectivity toward the hydrogenation of carbonyl bond.

Using of PAA to prepare Pt/SiO_2 catalyst prevented significantly the acetal formation as mentioned in literature (Aykaç and Yılmaz, 2008; Ruiz et al., 2007; Vilella et al., 2005). When PAA was used as precursor, catalyst did not deactivate and reached 89.5 % conversion. However, catalyst deactivated after 20 minute and conversion reached was 72.7 % with HCLPA. Nerol + geraniol amount increased when the HCLPA was used. The undesired product (3-7 Dimethyl 1- Octanol) amount increased when HCLPA was used. Citronellal formation increased in the presence of PAA. So Pt from two different precursors showed different activities and selectivities.

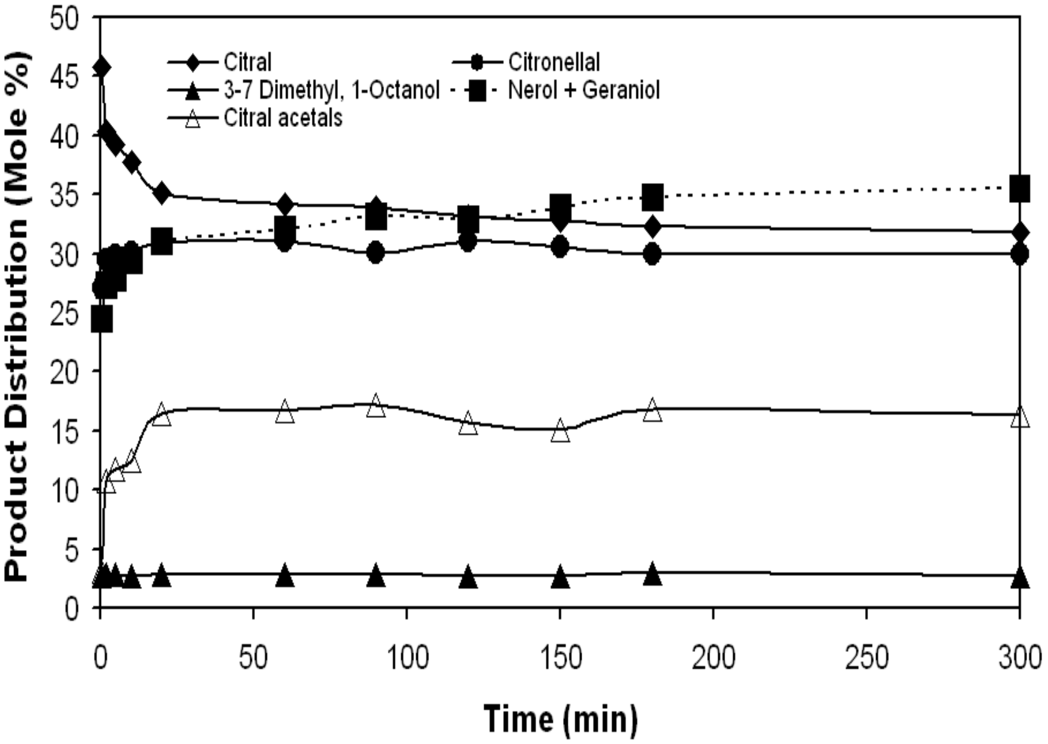

Figure 25. Product distribution observed over Pt/SiO_2 catalyst activated at 350 °C and calcined at 500 °C including hexachloroplatinic acid (HCLPA)

Activation temperature affected activity significantly as shown in Figure 26. Increasing activation temperature from 350 to 450 °C decreased citral conversion from 72.7 to 46.5 % for HCLPA precursor. The maximum citral conversion achieved was 89.5 % at activation temperature of 350 °C when PAA was used. This showed that lower activation temperature was appropriate to achieve higher citral conversion for the monometallic Pt/SiO_2 catalysts as reported in the previous studies (Ruiz et al., 2007; Vilella et al., 2005). Selectivity to different products obtained are given in Figure 25. Changing activation temperature from 350 to 450 °C decreased $S(_{NE+GE})$ from 39.1 % to 22.9 % for the catalyst prepared from HCLPA. Use of PAA decreased acetal formation during reaction and increased the $S(_{NE+GE})$ 7.1 from to 56.4 % for higher activation temperature. In the study of Vilella et al. (2005), they observed that acetals were produced by reaction between citral and citronellal with the alcohol used as a solvent. On the contrary, when PAA was used, citronellal formation was observed at low amounts in the present study. By this, acetal formation was at lower amount. This provided an increase in $S(_{NE+GE})$. PAA gave higher selectivities to $S(_{NE+GE})$ compared to HCLPA.

Changing solvent from ethanol to 2-pentanol decreased activity of catalyst prepared from HCLPA precursor (Figure 26); conversion obtained in ethanol was 72.7 % while it was 30.0 % in 2-pentanol. Also $S_{(NE+GE)}$ was decreased from 39.1 to 31.7 % to as solvent changed from ethanol to 2–pentanol (Figure 27). Using of 2-pentanol decreased acetal formation. Thus use of higher carbon alcohol did not improve $S_{(NE+GE)}$. When catalyst used without calcinations in 2-pentanol, catalyst activity decreased significantly as $S_{(NE+GE)}$ almost remained constant. This showed that generation of active sites during calcinations was important.

To minimize acetal formation over the catalyst prepared by HCLPA, catalyst was washed. Washing catalyst increased conversion from 46.5 to 55.7 % (Figure 26) and reduced acetal formation from 32.0 to 15.0 %. Higher $S_{(NE+GE)}$ was observed with washed catalyst which was 62.4 % compared to original unwashed catalyst, 22.9 %. This showed washing was successful in removing acid sites. Similar findings are reported in literature (Aumo et al., 2002).

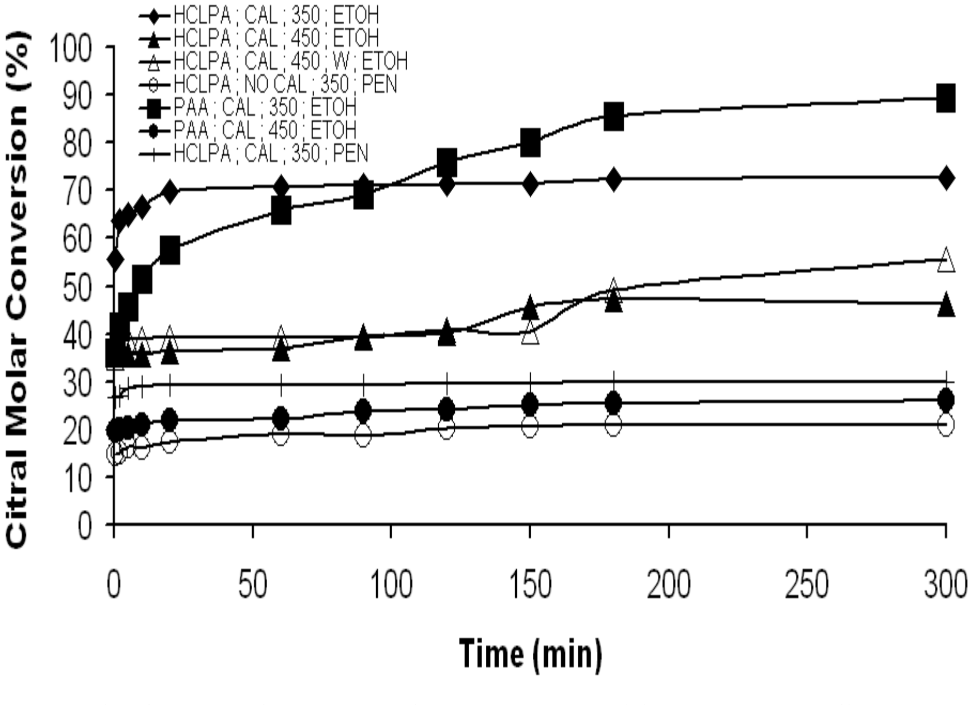

Figure 26. Citral % molar conversion amounts with respect to different applied parameters. (**HCLPA:** Hexachloro platinic acid, **PAA:** Platinum II acetyl acetonate, **CAL:** Calcination at 500 °C, **NO CAL:** Without Calcination, **350;450:** Reduction temperatures (°C), **W:** Washed catalyst, **ETOH:** Ethanol, **PEN:** 2-pentanol)

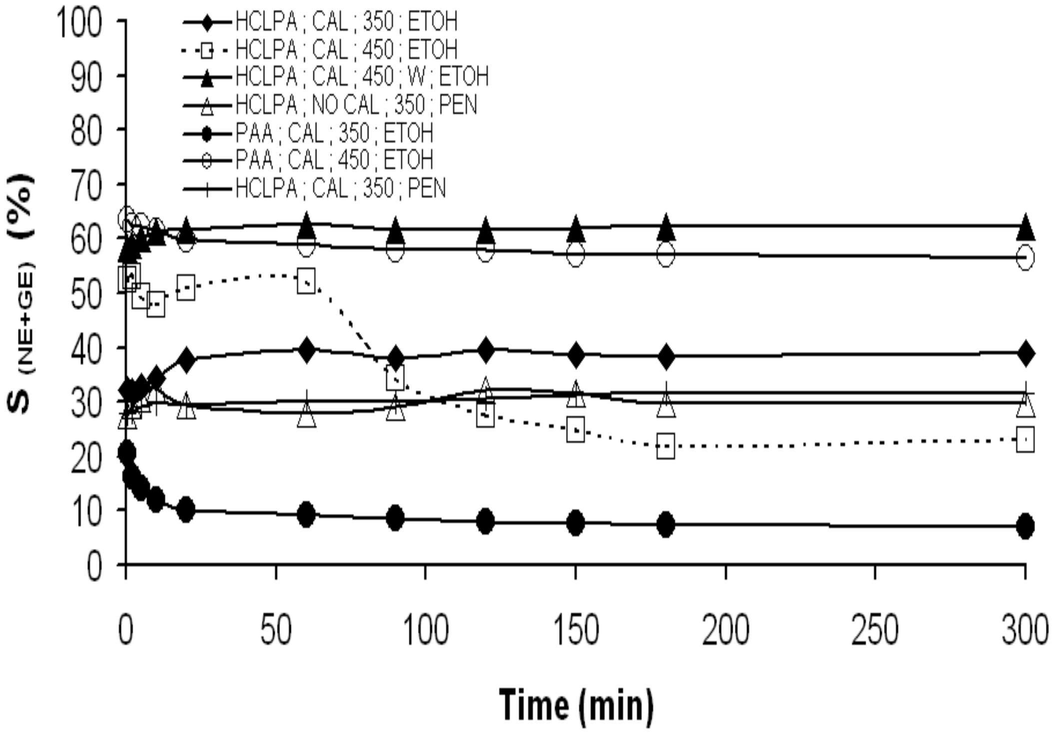

Figure 27. Selectivity % to unsaturated alcohols with respect to different applied parameters.(**HCLPA:** Hexachloro platinic acid, **PAA:** Platinum II acetyl acetonate, **CAL:** Calcination at 500 °C, **NO CAL:** Without Calcination, **350;450:** Reduction temperatures (°C), **W:** Washed catalyst, **ETOH:** Ethanol, **PEN:** 2-pentanol)

4.2.2. Activity and Selectivity Tests for Bimetallic Catalysts

Product distribution observed over PtSn/SiO_2 catalyst is shown in Figure 28. The bimetallic catalyst was prepared by catalytic reduction method. Used Pt precursor was platinum (II) acetyl acetonate. This catalyst was calcined at 500 °C and activated at 450 °C before the citral hydrogenation reaction. Sn/Pt ratio was 0.5. Citronellal, 3-7 Dimethyl 1-octanol, geraniol and citronellol were observed as products. Geraniol and citronellol was observed at higher amounts. Undesired products (citronellal and 3-7 Dimethyl 1-octanol) formed at lower amounts. Acetilisation was not observed during the reaction since used precursor did not contain any Cl ions. Formation of total geraniol+citronellol (unsaturated alcohols for bimetallic catalysts in the present study) was 83.5 % while the consumption of citral 91.0 %. No acetal formation improved the selectivity to unsaturated alcohols, 89.7 % (Figure 30). Thus in the present study, the best product distribution was achieved for bimetallic catalyst when catalyst prepared by catalytic reduction method, calcined at 500 °C and activated at 450 °C.

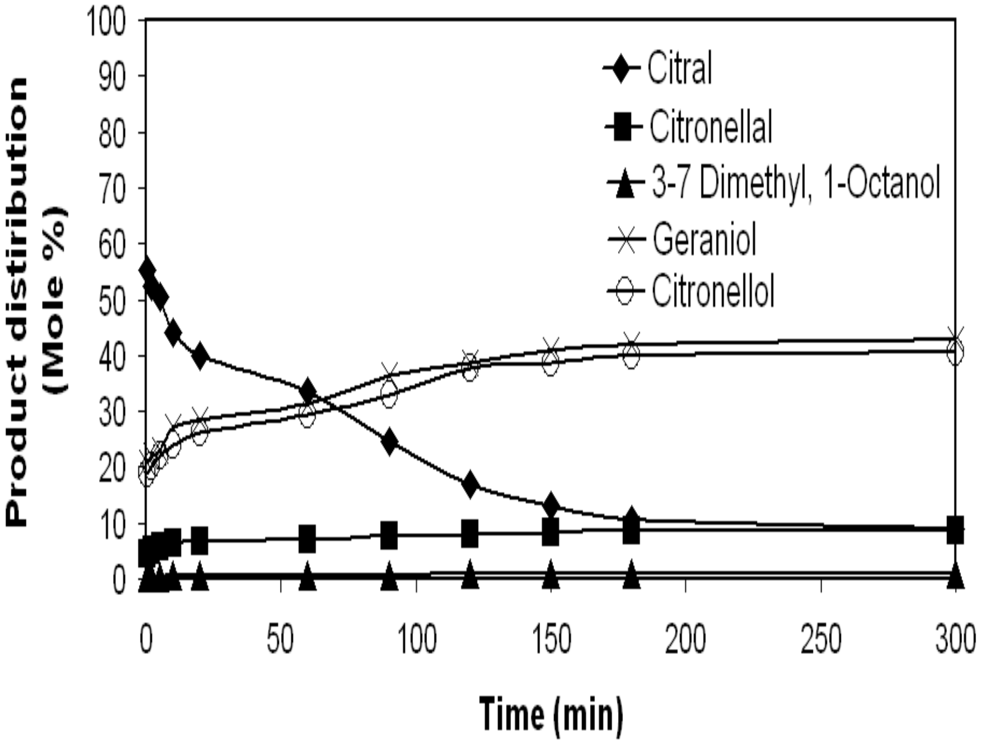

Figure 28. Product distribution observed over $PtSn/SiO_2$ catalyst (prepared by catalytic reduction method; calcined at 500 °C; activated at 450 °C; Sn/Pt = 0.5)

For bimetallic $PtSn/SiO_2$ catalysts different preparation methods (catalytic reduction (CR), co-impregnation (CI) and successive impregnation (SI)), calcination temperatures (400 °C and 500 °C), reduction temperatures (350 °C and 450 °C) and (Sn/Pt) loading ratios (0.3, 0.5 and 0.7) were investigated. For all of the catalysts the Pt loading ratio was constant (1 % (w/w)). Geraniol (GE) and citronellol (COL) were obtained as the major citral hydrogenation products for $PtSn/SiO_2$ catalysts. The results are given below.

4.2.2.1. Effect of Promoter (Sn) Addition: Pt/SiO_2 and $PtSn/SiO_2$ Catalysts

The monometallic Pt/SiO_2 catalyst prepared by impregnation and the bimetallic $PtSn/SiO_2$ catalyst prepared by catalytic reduction method were compared. Both of the catalysts were calcined at 500 °C and activated at 450 °C. For $PtSn/SiO_2$ catalyst Sn/Pt ratio was 0.5. The citral % molar conversion with respect to Sn addition is shown in Figure 29. Also, the selectivity to unsaturated alcohols is shown Figure 30. Preparing $PtSn/SiO_2$ catalyst with catalytic reduction method provided favorable results. At the same calcinations and activation temperature, Sn addition to Pt/SiO$_2$ catalyst increased both conversion and selectivity to unsaturated alcohols. Sn addition increased conversion from 26.1 % to 91.1 %. Pt interaction with Sn increased unsaturated alcohol formation from 56.4 % to 89.7 %. Second metal promoter (Sn) addition to Pt/SiO$_2$ catalysts affected the citral % molar conversion and selectivity to unsaturated alcohols significantly. According to the study of Vilella et al. (2005), addition of Sn to Pt catalysts enhanced citral conversion. In the study of Ruiz et al. (2007), low reduction temperature gave high citral conversion. On the contrary, for bimetallic catalysts, high reduction temperature gave high citral conversion. Similarly, Sn addition provided high catalyst activity for CR method.

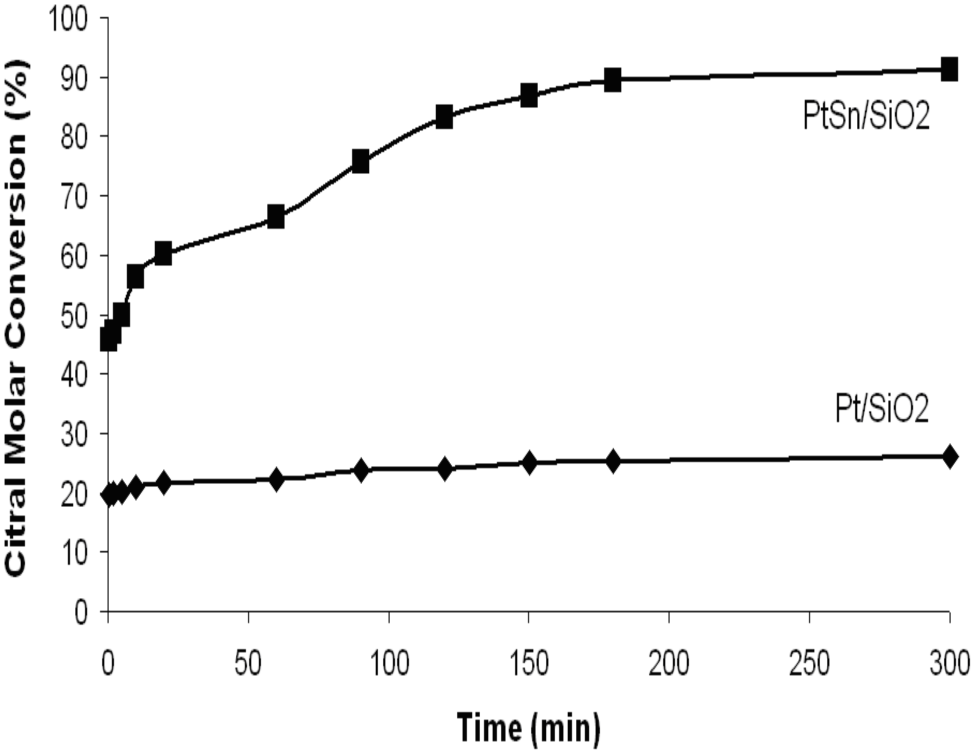

Figure 29. Citral % molar conversion with respect to Sn addition to Pt/SiO$_2$ catalyst. (Catalysts calcined at 500 °C and activated at 450°C.)

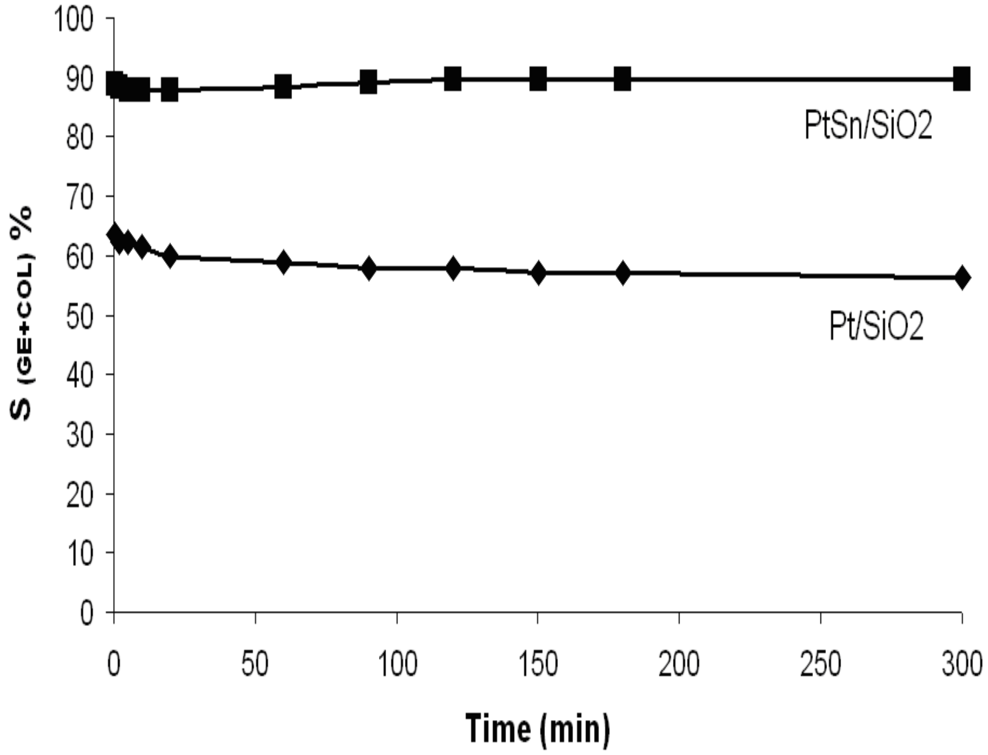

Figure 30. Selectivity to unsaturated alcohols with respect to Sn addition to Pt/SiO$_2$ catalyst. (Catalysts calcined at 500 °C and activated at 450°C.)

4.2.2.2. Effect of Different Calcination Temperatures on Activity and Selectivity

Five different catalysts were prepared by CR, CI and SI methods and calcined at 400 °C and 500 °C. The activation temperature was 450 °C. As calcination temperature increased, conversion increased similarly for both catalysts prepared by CR and CI methods. Higher activities were observed at higher calcination temperatures which are needed for better S$_{(GE+COL)}$. This could be due to increase in Pt-Sn interaction as calcination temperature increased.

In Figure 31, the effect of calcination temperatures on citral conversion is given. Maximum citral conversion was achieved as 91.1 % when catalysts were prepared by CR method and calcined at 500 °C. Lowering the calcination temperature to 400 °C, decreased the citral conversion to 83.3 % for CR method. Preparing the catalysts by CI method showed lower activity than CR. The catalyst calcined at 500 °C for CI method gave 70.4 % citral conversion. The lowest citral conversion was obtained as 55 % when CI was used at calcination temperature of 400 °C. Tests with catalysts prepared by successive impregnation gave 63.2 % conversion and selectivity to unsaturated alcohols of 47.6 %. Thus, it was determined that the convenient catalyst preparation method was CR and the appropriate calcination temperature was 500 °C.

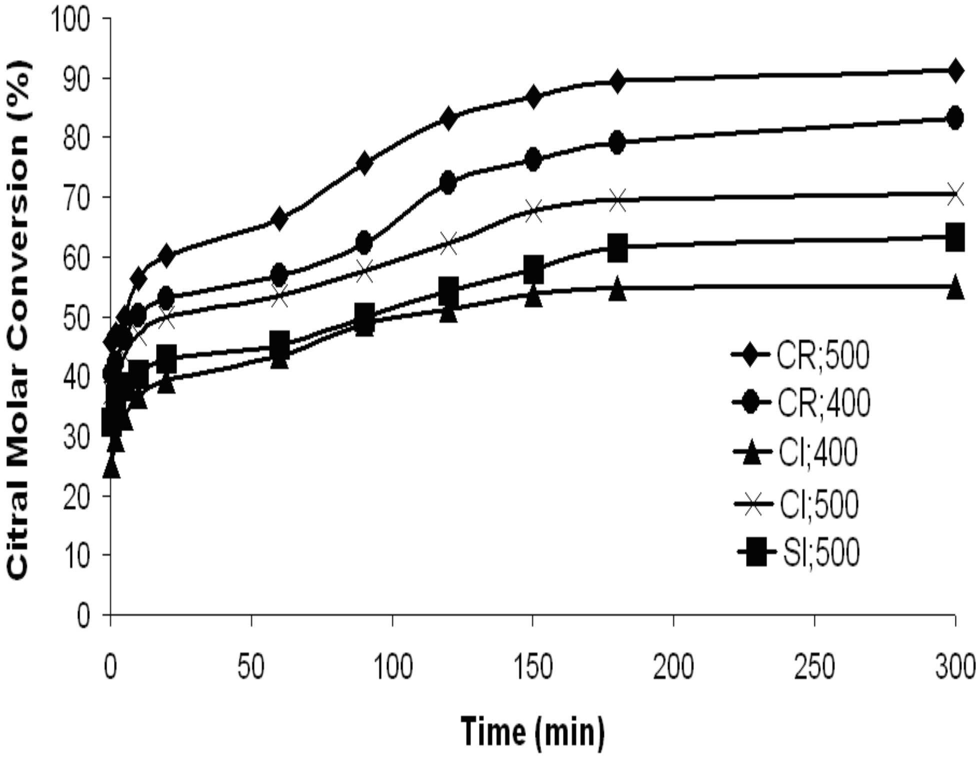

Figure 31. Citral % molar conversion for different calcination temperatures and different preparation methods at activation temperature of 450 °C.

In Figure 32, the selectivities of different catalysts to unsaturated alcohols ($S_{(GE+COL)}$) with respect to reaction time are given. Maximum $S_{(GE+COL)}$ % was achieved as 89.7 % when the bimetallic catalyst prepared by CR method and calcined at 500 °C. Decreasing the calcination temperature to 400 °C decreased the $S_{(GE+COL)}$ % as 85.8 %. This showed that selectivity was not affected much with calcinations temperature when CR was used. When the $PtSn/SiO_2$ catalyst was prepared by CI method, it was observed that there was sharp decrease in $S_{(GE+COL)}$ %. At 400 °C and 500 °C calcination temperatures, the $S_{(GE+COL)}$ % were obtained as 16.9 % and 7.4 %, respectively. Decrease in $S_{(GE+COL)}$ % may be caused by not a good interaction between Pt and Sn. The active sites of the catalyst were blocked with deposites and thus the activity of the catalyst decreased. Thus, catalytic reduction method was superior to coimpregnation and successive impregnation methods.

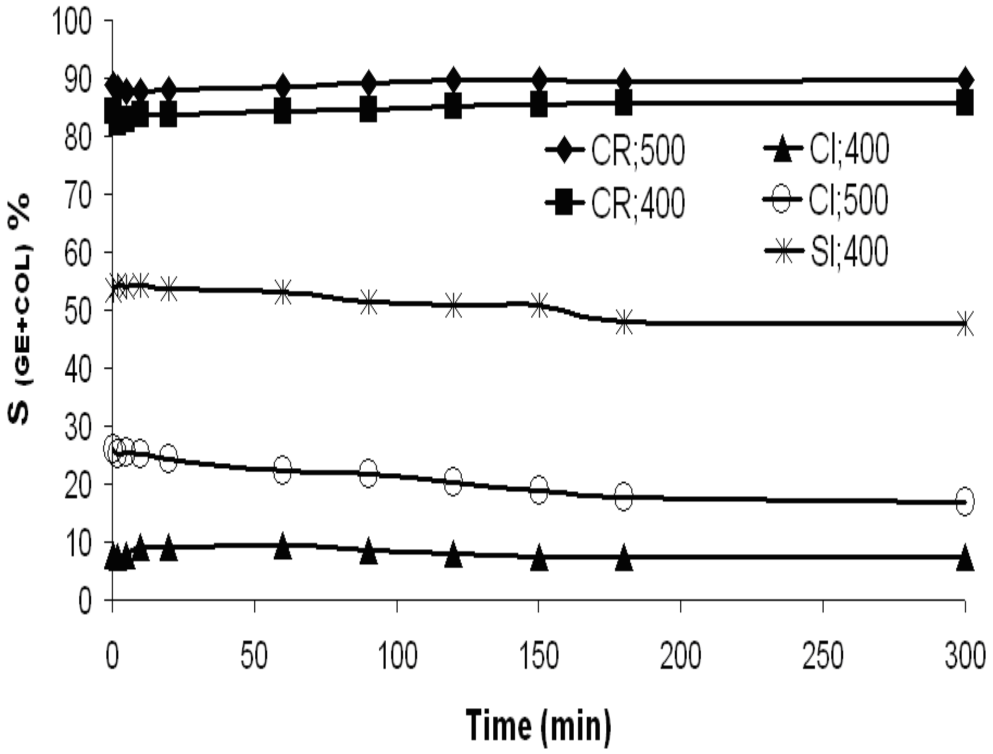

Figure 32. Selectivity to unsaturated alcohols (geraniol and citronellol) for different calcination temperatures and different preparation methods at activation temperature of 450°C.

4.2.2.3. Effect of Different Catalyst Activation Temperatures on Activity and Selectivity

In this case, different catalyst activation temperatures (350 °C and 450 °C) effect was investigated on citral conversion and selectivity to unsaturated alcohols ($S_{(GE+COL)}$). The calcination temperature was kept constant at 500 °C and $PtSn/SiO_2$ catalysts prepared by CR, CI and SI methods were tested.

In Figure 33, citral molar conversion for different activation temperatures and different preparation methods at calcinations temperature 500 °C is given. The highest citral conversions were obtained by CR method. The maximum citral conversion was achieved as 91.1 % at activation temperature of 450 °C by CR method. Decreasing the activation temperature didn’t change the conversion significantly. It was 89.8 % when the activation temperature was 350 °C. When the catalyst was prepared by CI method, lower conversions were observed. The conversions were 78.7 % and 70.4 % when the activaiton temperatures were 350°C and 450°C, respectively. The lowest activity was observed with catalyst prepared by SI method, which gave 63.2 % conversion.

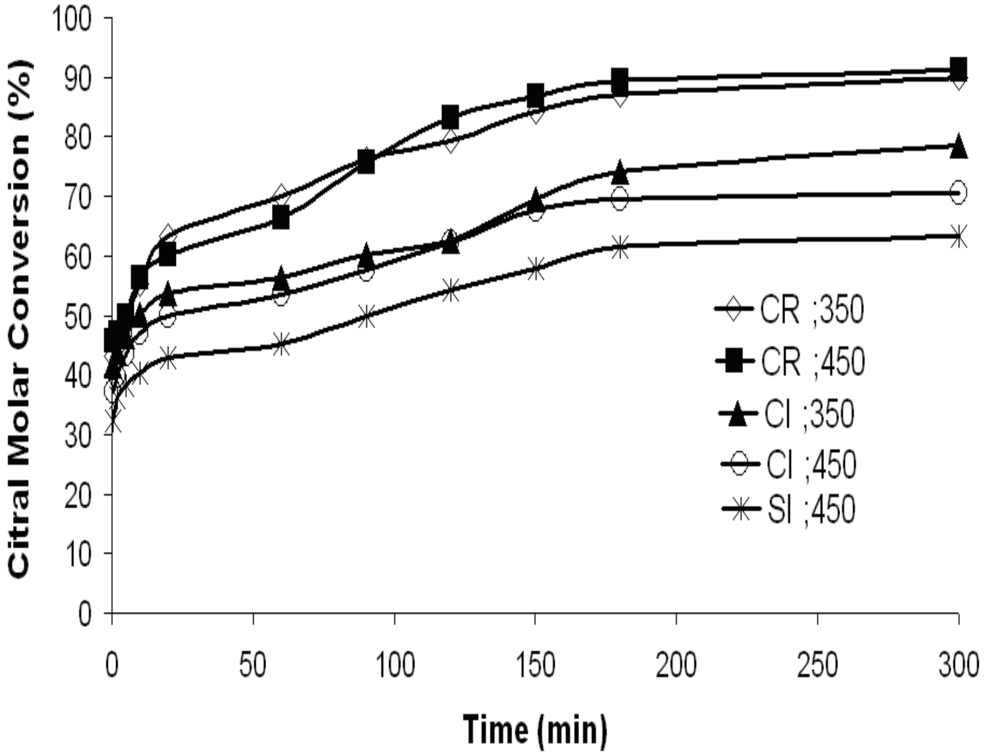

Figure 33. Citral % molar conversion for different activation temperatures and different preparation methods at calcination temperature 500 °C.

In Figure 34, the selectivity to unsaturated alcohols for different activation temperatures (350 °C and 450 °C) is shown. Higher $S_{(GE+COL)}$ were achieved by CR method. The $S_{(GE+COL)}$ were close to each other. They were 89.7 % and 88.5 % for activation temperatures of 450 °C and 350 °C, respectively. When the catalyst was prepared by CI method, the $S_{(GE+COL)}$ decreased significantly. They decreased to around 17 % for each of both activation temperatures. Thus CR method at low activation temperature was an appropriate to reach high conversion and selectivity.

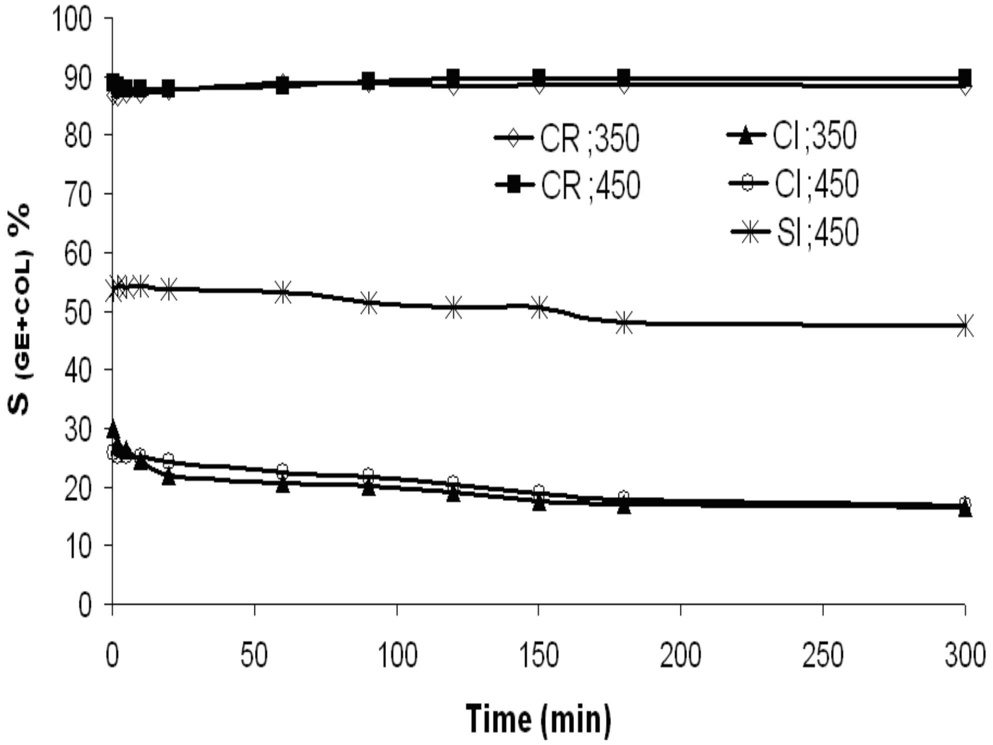

Figure 34. Selectivity to unsaturated alcohols (geraniol and citronellol) for different activation temperatures and different preparation methods at calcination temperature 500°C.

4.2.2.4. Effect of Promoter (Sn) Loading on Activity and Selectivity

The effect of (Sn/Pt) ratio was investigated for catalytic reduction and successive impregnation methods. It was varied as 0.3, 0.5 and 0.7 for CR and 0.5 for SI catalyst preparation method to determine the optimum Sn loading. Calcination and activation temperatures were kept constant at 500 °C and 450 °C, respectively.

In Figure 35, the effect of (Sn/Pt) on citral molar conversion with respect to reaction time is given. When the (Sn/Pt) was 0.5 for CR method, the highest citral conversion was achieved as 91.1 %. But it was the lowest value for SI method as 63.2 %. Citral conversion was similar when Sn/Pt ratio was 0.3 and 0.7 for CR method. They gave lower conversion compared to Sn/Pt of 0.5. It was decreased to 75.0 % when compared to (Sn/Pt) 0.5. Thus, the optimum (Sn/Pt) loading ratio was determined as 0.5 as shown in Figure 35. In Figure 36, conversion and $S_{(GE+COL)}$ with respect to various (Sn/Pt) loading ratios are shown. Sn/Pt ratio affected conversion and selectivity. They both showed an optimum at Sn/Pt ratio of 0.5. At Sn/Pt ratio 0.5, conversion was 91.1 %, $S_{(GE+COL)}$ was 89.7 %. Changing Sn/Pt ratio from 0.5 to 0.3 gave conversion of 74.4

% and S $_{(GE+COL)}$ of 72.4 %. When Sn/Pt ratio was 0.7, conversion was 75.7 % and S $_{(GE+COL)}$ was 69.3 %.

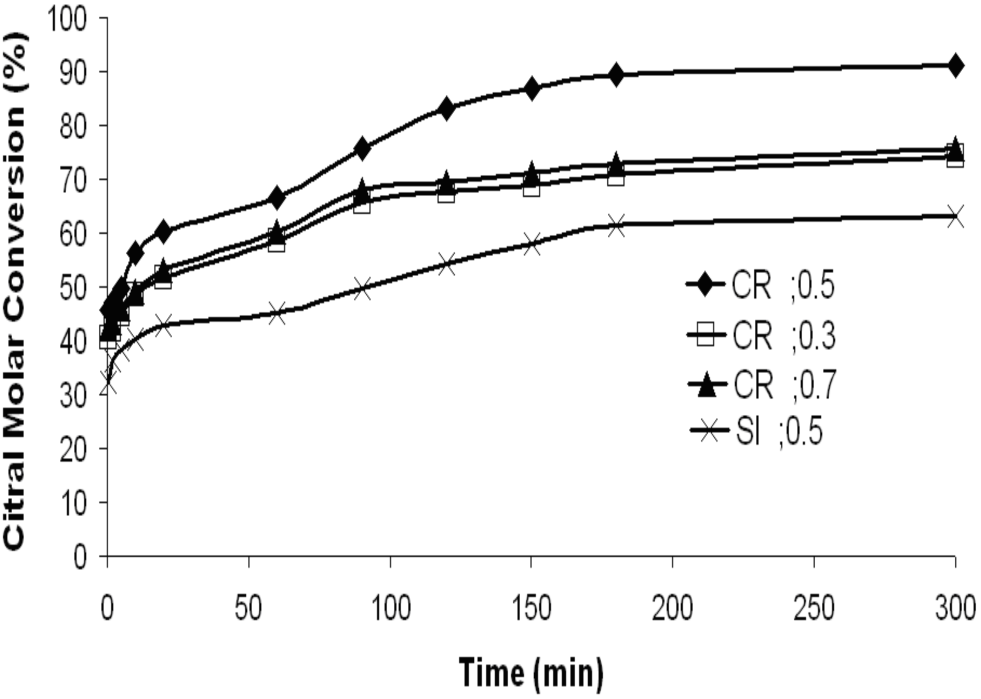

Figure 35. Citral % molar conversion for different (Sn/Pt) ratios at different preparation methods for calcinations temperature 500 °C and activation temperature 450 °C.

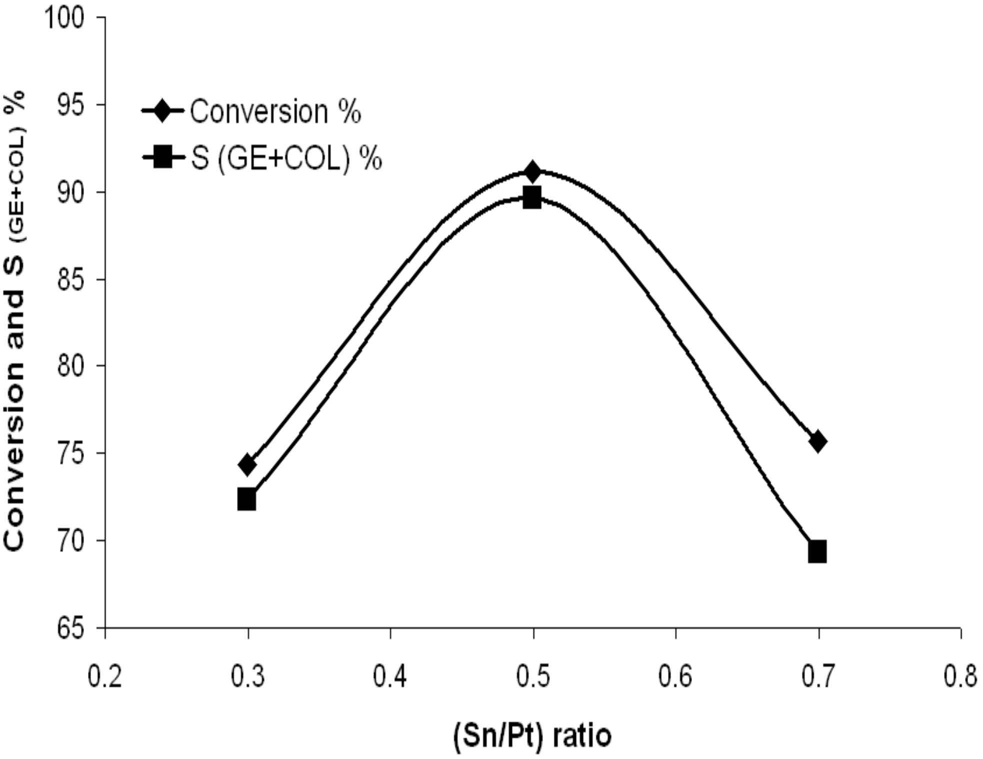

Figure 36. Conversion and S $_{(GE+COL)}$ % with respect to various (Sn/Pt) loading ratios.

In Figure 37, the effect of (Sn/Pt) on the selectivity to unsaturated alcohols with respect to reaction time is given. The highest selectivity was achieved as 89.7 % when the (Sn/Pt) loading ratio was 0.5 for CR method. Both (Sn/Pt) loading ratio increasing to 0.7 or decreasing to 0.3, decreased S $_{(GE+COL)}$ % to around 70.0 %. The lowest value was obtained by SI method which was 47.6 %.

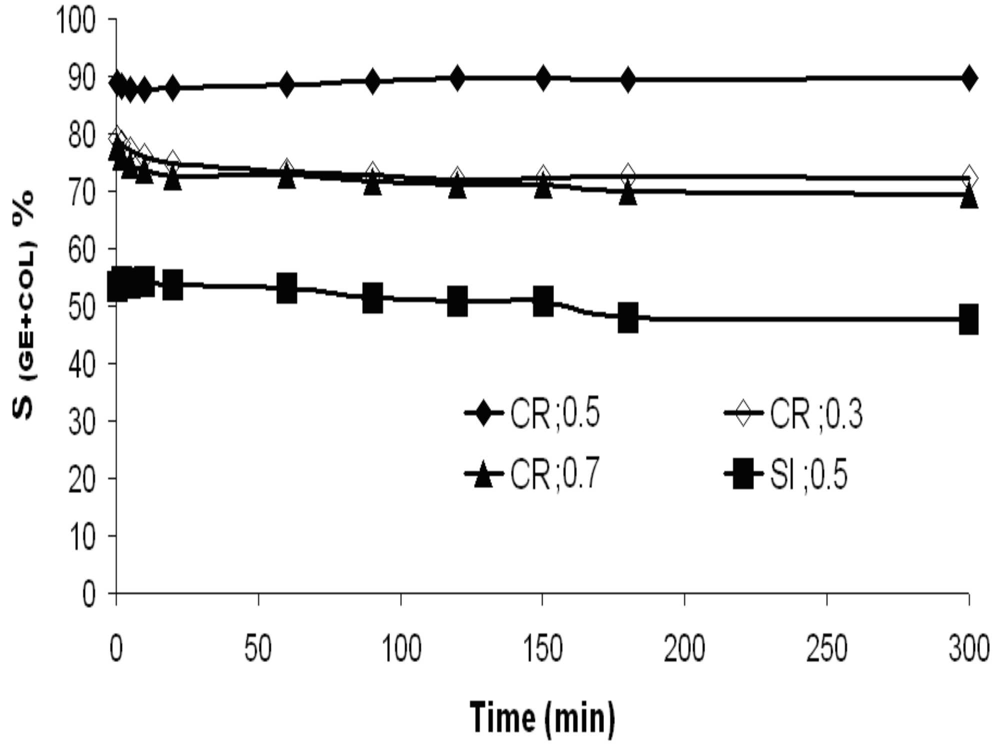

Figure 37. Selectivity to unsaturated alcohols (geraniol and citronellol) with respect to reaction time for different (Sn/Pt) ratios at different preparation methods.

CHAPTER 5

CONCLUSIONS

Calcined silica gel and Pt/SiO_2 and PtSn/SiO_2 catalysts had an amorphous structure. The structure of the catalyst was preserved during the catalyst preparation. Increase in acidity was not observed due to use of Cl containing Pt precursor. Pt and Sn characteristic peaks could not be observed for bimetallic catalysts, because of the lower loading and good dispersion.

Activity and selectivity tests for monometallic catalysts, the main products formed were citronellal, nerol + geraniol. Moreover undesired products were also formed which were 3,7 Dimethyl 1- Octanol and citral acetals in very low amounts. Using of PAA to prepare Pt/SiO_2 catalyst prevented significantly the acetal formation. When PAA was used as precursor, catalyst did not deactivate and reached 89.5 % conversion. Activation temperature affected activity significantly. Lower activation temperature was appropriate to achieve higher citral conversion for the monometallic Pt/SiO_2 catalysts. Changing activation temperature from 350 to 450 °C decreased S($_{NE+GE}$) from 39.1 % to 22.9 % for the catalyst prepared from HCLPA. Use of PAA decreased acetal formation during reaction and increased the S($_{NE+GE}$) 7.1 from to 56.4 % for higher activation temperature. PAA gave higher selectivities to unsaturated alcohols ($S_{(NE+GE)}$) compared to HCLPA since preventing the acetal formation. Changing solvent from ethanol to 2-pentanol decreased activity of catalyst prepared from HCLPA precursor. Washing of catalyst minimized acetal formation over the catalyst prepared by HCLPA. Higher S($_{NE+GE}$) was observed with washed catalyst which was 62.4 % compared to original unwashed catalyst, 22.9 %.

In activity and selectivity tests for bimetallic catalysts, acetilisation was not observed during the reaction since used precursor did not contain any Cl ions. The best product distribution was achieved for bimetallic catalyst when catalyst prepared by catalytic reduction method, calcined at 500 °C and activated at 450 °C. At the same calcinations and activation temperature, Sn addition to Pt/SiO_2 catalyst increased both conversion and selectivity to unsaturated alcohols. Sn addition increased conversion from 26.1 % to 91.1 %. As calcination temperature increased, conversion increased similarly for both catalysts prepared by CR and CI methods. Higher calcination temperatures were needed for better S $_{(GE+COL)}$ %. Activation temperature did not change significantly catalyst activity and selectivity for CR method. The maximum citral conversion was achieved as 91.1 % at reduction temperature of 450 °C by CR method. Citral conversion was similar when Sn/Pt ratio was 0.3 and 0.7 for CR method. They gave lower conversion and selectivity to unsaturated alcohols compared to Sn/Pt of 0.5.

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APPENDIX A

GC-MS CHROMATOGRAMS OF PRODUCTS

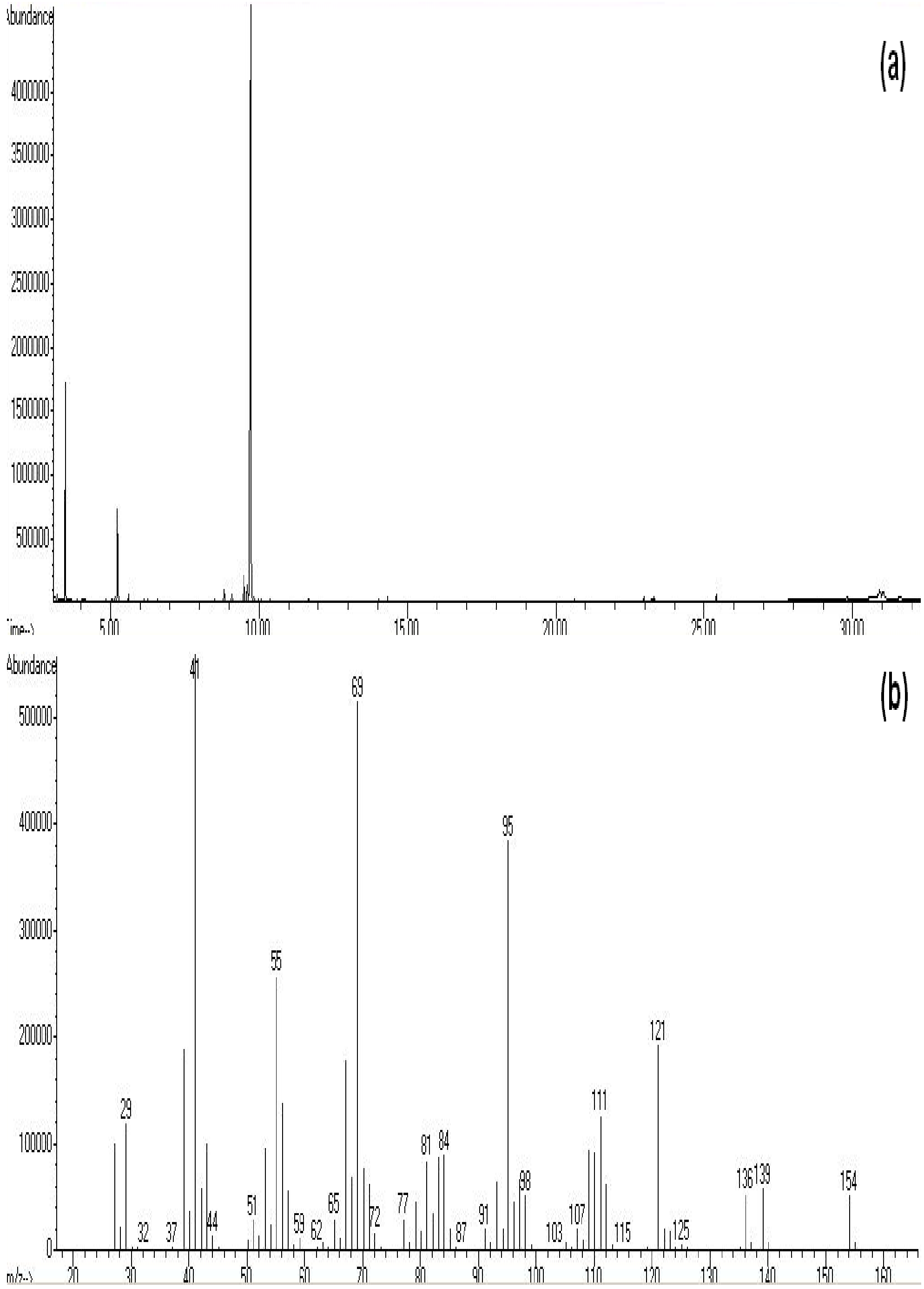

Figure 38. GC-MS chromatogram (a) and spectrum (b) of citronellal (9.72 min)

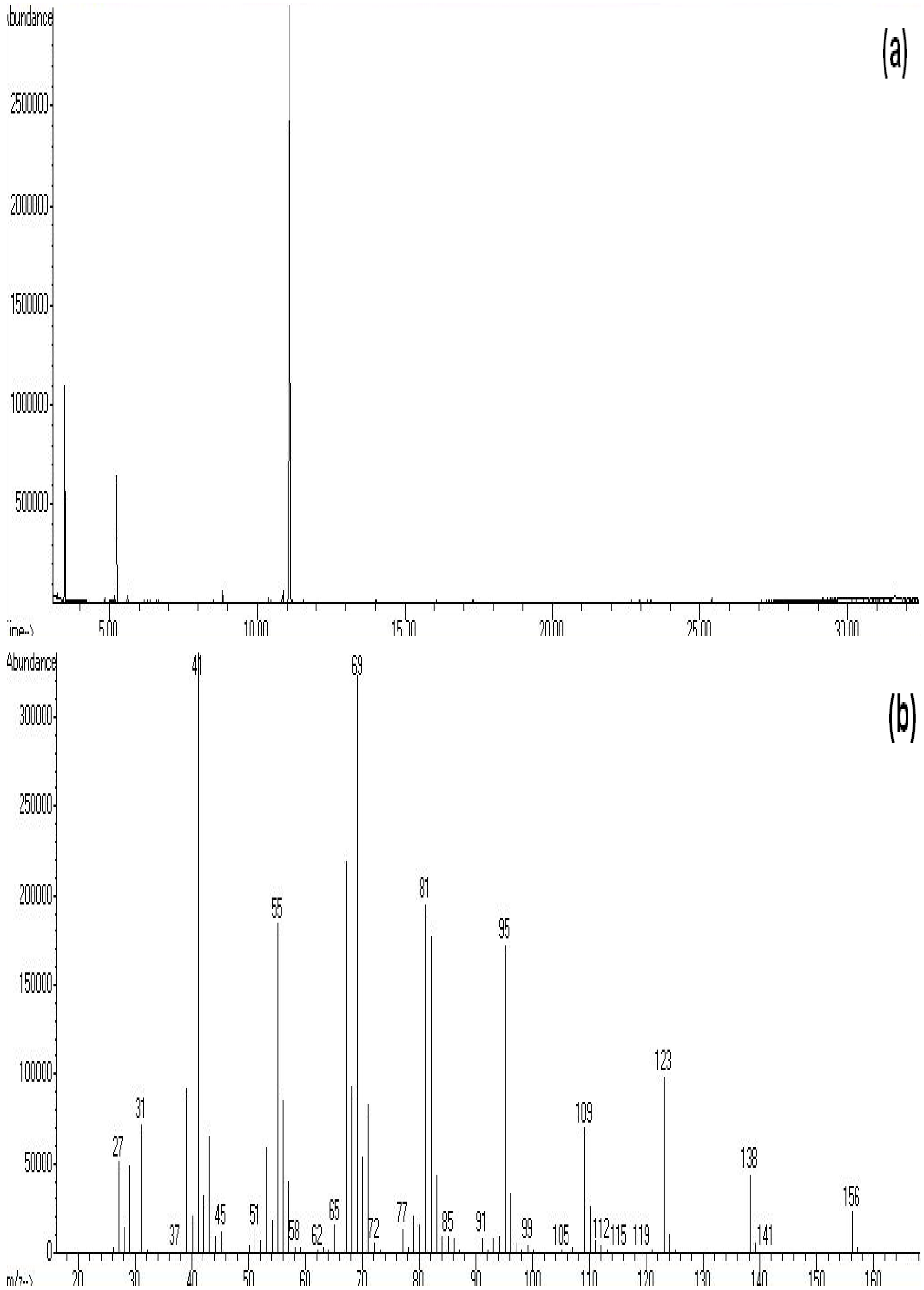

Figure 39. GC-MS chromatogram (a) and spectrum (b) of citronellol (11.10 min)

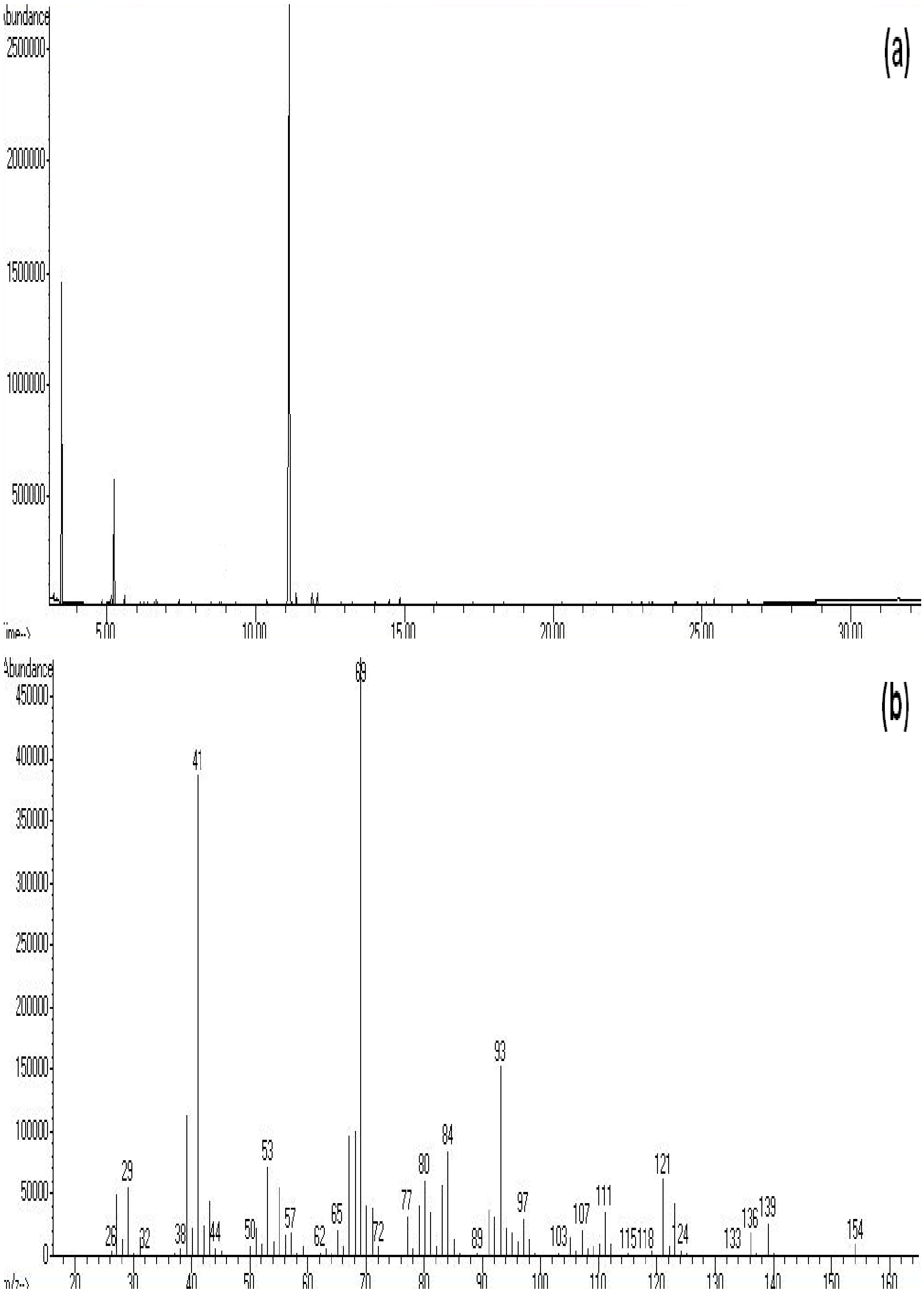

Figure 40. GC-MS chromatogram (a) and spectrum (b) of nerol (11.13 min)

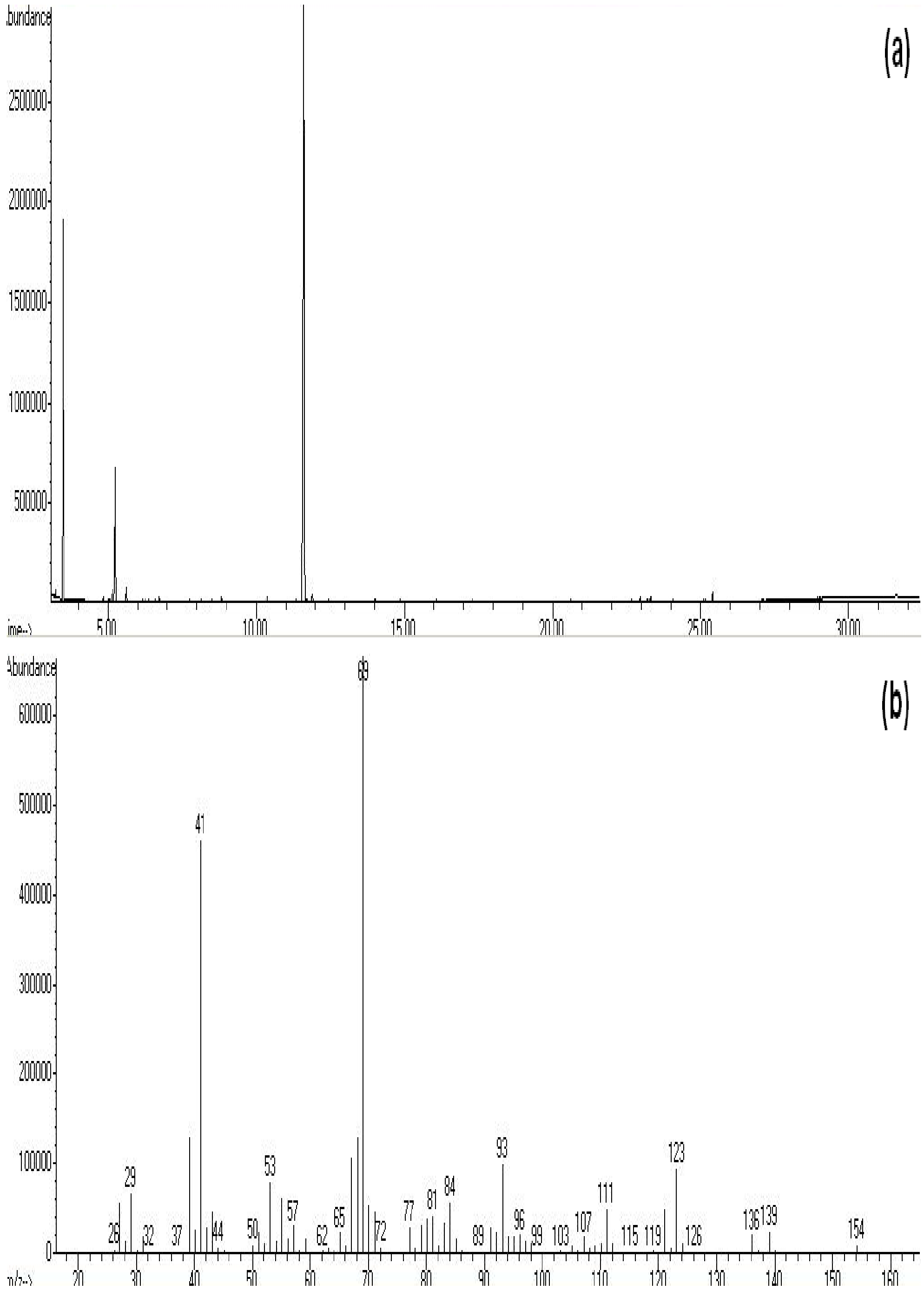

Figure 41. GC-MS chromatogram (a) and spectrum (b) of geraniol (11.61 min)

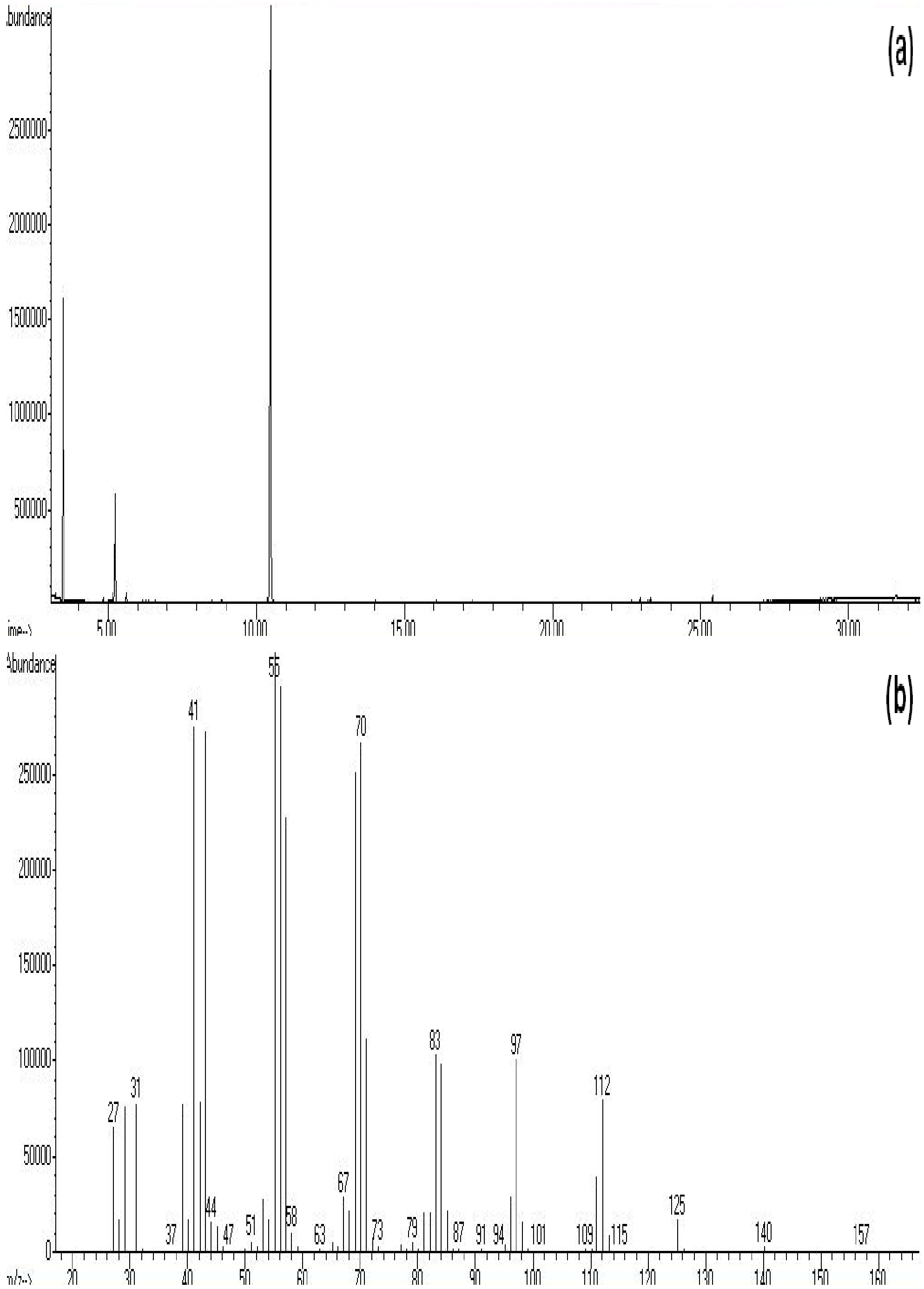

Figure 42. GC-MS chromatogram (a) and spectrum (b) of 3,7 Dimethyl-1- octanol (10.47 min)