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Effects of Catalyst Precursor Type and Preparation Conditions, and Solvent Type on Activity and Selectivity of Pt/SiO₂ Catalyst in Citral Hydrogenation

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Effects of Catalyst Precursor Type and Preparation Conditions, and Solvent Type on Activity and Selectivity of Pt/SiO₂ Catalyst in Citral Hydrogenation*

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Abstract

In this study, citral hydrogenation reaction in liquid phase over silica gel supported Pt catalysts was investigated. It was desired to hydrogenate carbonyl group selectively to produce valuable unsaturated alcohols, namely geraniol and nerol. Pt/SiO₂ catalysts were prepared by impregnation method. The effects of parameters investigated in the present study included Pt precursor type (hexachloroplatinic acid (HCLPA), platinum II acetylacetonate (PAA)), catalyst activation temperature (350°C and 450°C), catalyst activation without calcination, catalyst washing with 0.1 M NaOH and solvent type (ethanol, 2-pentanol). The catalysts activities and selectivities were affected by the type of precursor and activation temperature. The maximum citral conversion (89.50 percent) was achieved at lower activation temperature (350°C) with PAA precursor based catalyst. It was observed that higher activation temperature provided lower citral conversion but higher selectivity to unsaturated alcohols; increasing the activation temperature to 450°C decreased citral conversion to 26.10 percent. But selectivity to unsaturated alcohols, geraniol and nerol, increased from 7.06 to 54.60 percent. Catalyst washing and 2-pentanol prevented acetal formation. Catalyst activation without calcination gave lower citral conversion (20.84 percent) and selectivity to unsaturated alcohols (30.00 percent).

KEYWORDS: citral, hydrogenation, Pt/SiO₂, unsaturated alcohol, activation temperature

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Introduction

Hydrogenation is the chemical reaction that results from the addition of hydrogen (H_2) to double or triple 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 carry out the reaction at low temperatures. Non-catalytic hydrogenation occurs at high temperatures.

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. Unsaturated alcohols (UA) (geraniol and nerol) are the most important products of the citral hydrogenation reaction. These are used in perfumes, fragrances 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 (Hajek et al., 2003, Vilella et al., 2005).

Recently many works have been reported for developing catalytic systems with improved selectivity to the unsaturated alcohol. The selectivity to unsaturated alcohol is governed by different factors: nature of the active metal (Ru (Galvagno et al., 1993) Pt, Pd, Ru, Rh and Co (Singh et al., 2001) and support (SiO_2 (Singh et al., 2001), Al_2O_3 (Aumo et al., 2002), Clinoptilolite (Yilmaz et al., 2005), Na-Y (Aykaç et al., 2008), carbonaceous materials (activated carbon, activated carbon felt, graphite (Vilella et al., 2005, Bachiller-Beaza et al., 2001), TiO_2 (Silva et al. 1997), ZnO (Consonni et al. 1999)) and presence of promoters (Fe (Aramendia et al., 1997) and Sn (Aykaç et al., 2008) or bimetallic phases (Consonni et al., 1999). Singh et al. (2001) examined activity and selectivity of different metals loaded on to SiO_2 . They reported that Pt was selective to unsaturated alcohols formation. In general it can be stated that oxide supports can provide stronger interactions with the main metal than carbon. Additionally, the full reduction of the metal might be more difficult on an oxide than on carbon (Maki-Arvela et al., 2005).

Catalyst precursor type, activation temperature and solvent type have also been found to affect product distribution obtained in citral hydrogenation. Silvestre-Albero et al. (2006) compared the surface characteristics and catalytic behavior of Pt-Zn/ CeO_2 catalysts prepared from different platinum precursors: H_2PtCl_6 as a chlorinated precursor and $Pt(NH_3)_4(NO_3)_2$ as a chlorine-free precursor. Cl containing catalysts increased hydrogenation of carbonyl group. The

role played by chloride ions on the redox properties of cerium dioxide is well known.

Consonni et al. (1999) found that activities and selectivities of the catalyst differed depending on the Pt precursor used. H_2PtCl_6 precursor was found to form Pt-Zn alloy and its chlorine increased selectivity to unsaturated alcohol. But with $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$, Pt dispersed well over ZnO support and did not form any alloy. Activation temperature was found to effect activity and selectivity. Increasing it from 200 to 400 °C decreased activity and increased selectivity over catalyst prepared from $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ precursor. However, high selectivity observed whatever the reduction temperature for H_2PtCl_6 . Accordingly, in a study by Ammari et al (2005) Pt catalysts prepared from platinum chloride precursor were found to be more selective toward the hydrogenation of C=O than analogous catalysts prepared from tetraammine platinum nitrate.

Serrano-Ruiz et al. (2007) studied effect of activation temperature on product distribution using Pt/CeO₂-C catalyst. They used hexachloroplatinic acid (H_2PtCl_6) as Pt precursor, isopropanol as solvent and 200 °C and 500 °C as reduction temperatures. Pt interacted with CeO₂. They concluded that selectivity to UA increased from about 5.5 to 16.0 % as activation temperature increased. But catalyst activity decreased. Even they used hexachloroplatinic acid (HCLPA) as Pt precursor, low acetal formation was reported.

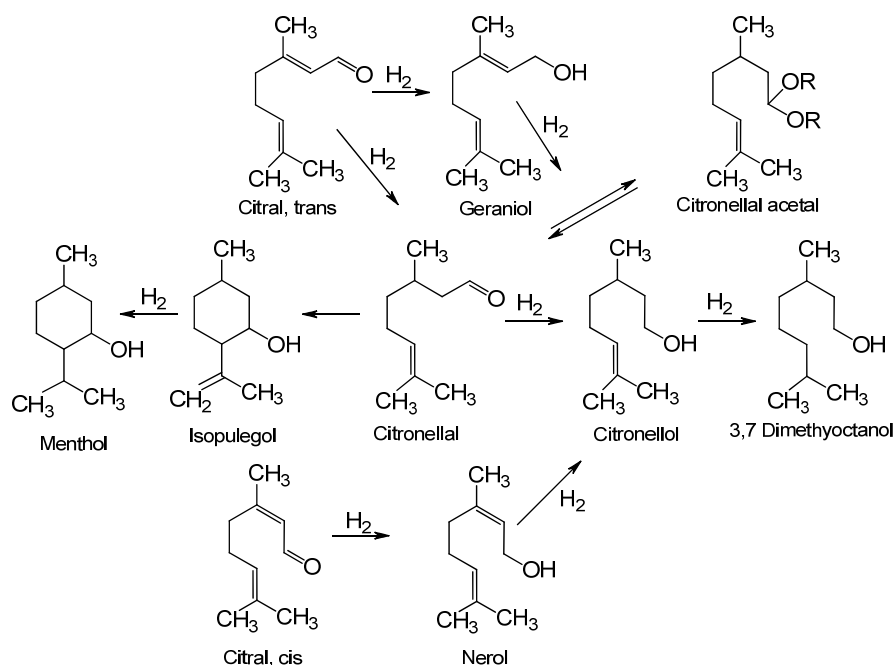


Figure 1. Reaction scheme for citral hydrogenation.

Acetal and isopulegol formation are reported to take place on acid sites on the support (Vilella et al., 2005, Maki-Arvela et al., 2002). In their study on suppression of side reactions, Maki-Arvela et al. (2002) found that acetalization could be suppressed either by using chloride-free catalyst precursors and other supports than active carbon or by using longer chained alcohols, like 2-pentanol and 2-methyl-2-propanol as solvents. Citronellal cyclization increased with the increasing solvent hydrophobicity. The solvent effects include the solubility of hydrogen in the reaction medium, the competitive adsorption of solvent on the catalysts, and the intermolecular interaction between the reactant and the solvent molecules (Chiang et al. (2007)). The role of solvent in citral hydrogenation was studied by Chiang et al. (2007). Non-polar (cyclohexane and hexane) showed higher activities and selectivities to unsaturated alcohols than polar solvents (ethanol and methanol). Aykaç et al. (2008) used platinum (II) acetyl acetonate ($C_{10}H_{14}O_4Pt$, PAA) as Pt precursor type and ethanol as solvent. They reported low amount of acetal formation. Chloride precursor has been shown to favor acetalization (Aumo et al., 2002). No acetals were formed when Pd catalysts prepared from nitrate precursor.

Thus, understanding factors affecting citral hydrogenation is very important. In this study, citral hydrogenation reaction in liquid phase over Pt/SiO_2 was examined. The effects of parameters on catalyst activity and selectivity studied included Pt precursor type (HCLPA and PAA), catalyst activation temperature (350 °C and 450 °C), catalyst activation without calcination, catalyst washing with NaOH solution and solvent type (ethanol, 2-pentanol).

2. Experimental

2.1. Preparation of catalysts

Silica gel (Davisil, grade 643, 200-425 mesh, 150 Å, purity $\geq 99\%$, Sigma Aldrich, 236810) was used as a support. Citral (Fluka, 27450, purity $\sim 97\%$ (cis 37%, trans 60%)) was used as a reactant. Cyclohexanone (purity 99%, A.C.S. reagent, Sigma Aldrich (398241)) was used as an internal standard. Pt precursor sources were hexachloroplatinic acid hydrate (Fluka, 81080, purity $\sim 38\%$ Pt) and platinum (II) acetyl acetonate (Fluka, 81030)). Two types of solvent were used to determine the appropriate solvent for citral hydrogenation reaction: ethanol (J.T. Baker, 8228) and 2-pentanol (Merck, 8.07501.0500).

Pt/SiO_2 catalysts were prepared by impregnation method. Prior to impregnation, silica gel (37-74 μm) was calcined at 500 °C for 6 h under dry air flow of 70 ml/min. Calcined silica gel was added to 100 ml of aqueous Pt solution and then mixed at room temperature for 24 h. Pt loading over silica gel support

was 1 % (w/w). The mixed solution was put into the rotary evaporator and the excess water was evaporated at 60 °C under 200 mbar vacuum for 3 h at 50 rpm. The obtained material was dried at 110 °C for 12 h in an oven. Finally, it was calcined at 500 °C for 6 h under flowing dry air (70 ml/min).

2.2. Characterization of catalysts

Prepared catalysts were characterized using different instrumental techniques. X-ray diffraction (Philips X'Pert Pro with Cu K α radiation) was used to determine crystallinity of the catalysts. Textural properties were determined by nitrogen adsorption (Micromeritics ASAP 2010). Elemental analysis was determined by Varian-96 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) with fusion dissolution method. The morphology of the catalysts was determined by scanning electron microscopy (Philips SFEG 30S SEM).

The acidity of the catalysts was determined by Temperature-Programmed Desorption of Ammonia (NH₃-TPD) method using Micromeritics AutoChem II Chemisorption Analyzer instrument.

Temperature-programmed reduction (TPR) was carried out using the apparatus used for NH₃-TPD measurements. The catalyst samples were outgassed at 150 °C for 1 h and then cooled to 40 °C under Ar flow of 70 ml/min. TPR profiles were registered while heating the samples from 40 °C to 800 °C by 10 °C/min heating rate under 50 ml/min flow of 10 % H₂-Ar mixture.

H₂ chemisorption was performed using the same apparatus for acidity determination. The catalysts were heated under Ar flow of 50 ml/min to 150 °C where it was kept for 150 min. And then flow was changed to H₂ and temperature was raised to 200 °C with a heating rate of 3 °C/min and kept there for 30 min. After that they were heated with the same heating rate to 450 °C where it was kept for 2 h. This was followed by Ar flow of 50 ml/min at the same temperature for 90 min. The catalysts were then cooled to 40 °C and waited for 60 min. After that pulses of 0.250 ml H₂-Ar (10 % H₂ in Ar) were injected until consecutive pulses of equal areas of peaks were obtained from the TCD detector.

2.3. Catalyst Testing

Citral hydrogenation reaction was carried out in a semi-batch reactor (500 ml, 4574 model, Parr Instrument Co.) equipped with an electrical heater and temperature controller. Before the reaction, 250 mg of catalysts were placed in the reactor and reduced (activated) in situ at 350 or 450 °C for 4 h under flow of H₂ at 4 bar. Then the reactor was cooled to reaction temperature and stored overnight under H₂ at 2 bar. The reactions were carried out at constant hydrogen pressure of

6 bar at 80 °C with a stirring rate of 1000 rpm. The reaction was started by the injection of 0.1 M citral (250 ml ethanol) in to the reactor. Samples taken from the reactor were analyzed with an Agilent Technologies 6890N Network GC System Gas Chromatograph equipped with a flame ionization detector (FID) and a capillary column DB-225. Hydrogenation products of citral were identified by GC-MS technique (Agilent 6890N/5973N Network GC/MSD System). The compositions of components in the reaction mixture were determined by the internal standardization method.

3. Results and Discussion

3.1. Catalyst Characterization

The X-ray diffraction analysis of calcined silica gel and Pt/SiO₂ catalysts were performed at 2θ degree of 5 to 90. This analysis showed that Pt/SiO₂ catalyst had an amorphous structure. Moreover, Pt characteristic peaks were not observed which was attributed to low active metal loading (1 % w/w).

SiO₂ gel having particle size ranging from 37 to 74 μm were taken for catalyst preparation. SEM analysis showed that SiO₂ gel after being calcined had approximately 50 μm average particle size and they were like pieces of particles.

Textural properties of the support and the catalysts are given in Table 1. Calcined SiO₂ gel was found to have a BET surface area of 320.7 m²/g. Pt loading from PAA precursor increased the surface area to 359.1 m²/g. However, HCLPA use increased surface area significantly. This was mostly due to increase in the external surface area. Catalysts had mesopore pore structure.

HCPLA based catalyst was found to have 0.30 % Cl, which was determined by ion chromatography. NH₃-TPD findings showed that the catalysts did not have any significant acidity; they were very very low compared to H-FER.

Figure 2 shows the temperature-programmed reduction profiles of the catalysts. The hydrogen consumption peak was consequence of a reduction process of the metallic oxides on the support obtained after calcination. Both catalysts showed reduction peaks centered at around 100 °C and 280 °C. But there were Pt reduction at higher temperature with the HCLPA based catalyst. This showed that active sites of both catalysts differ from each other. The peaks at 100 and 280 °C could be assigned to reduction of oxidised Pt species to metallic Pt (Reyes et al., 2006, Barias et al., 1996). These results showed that the activation temperature of 350 °C was not high enough to reduce both catalysts. And activation temperature of 450 °C was only high enough to reduce active sites of PAA.

Table 1. Textural and physicochemical properties of calcined silica gel and Pt/SiO₂ catalysts.

Sample	Micropore Area (m ² /g)	External Surface Area (m ² /g)	BET Area (m ² /g)	Pt (wt %)	Mean Pt dia. (nm)	Pt dispersion (%)
Calcined Silica Gel	7.4	313.3	320.7	-	-	-
Pt/SiO ₂ (PAA)	18.3	340.7	359.1	0.89	1.30	52.85
Pt/SiO ₂ (HCLPA)	16.0	404.1	420.1	0.83	1.00	68.54

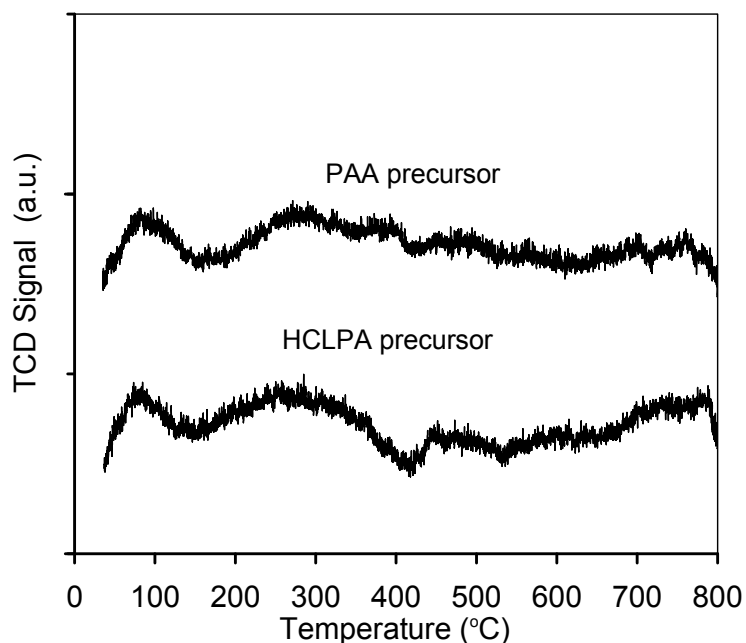


Figure 2. Temperature reduction profiles of Pt/SiO₂ catalysts prepared from two different Pt precursors.

Mean Pt crystallite size and their dispersion determined by H₂ chemisorption are given in Table 1. HCLPA based catalyst had higher dispersion than PAA based catalyst. Mean Pt crystallite size was determined as 1.00 nm for HCLPA and 1.30 nm for PAA based catalyst. Although crystallite size differs slightly for different Pt precursors, crystallite size effects are not expected to have a significant influence on the differences observed in product distribution. This

reaction is reported to be structure insensitive (Singh et al. 2001, Mercadante et al., 1996, Galvagno et al., 1993).

3.2. Catalyst Testing

Figure 3 shows product distribution observed over Pt/SiO₂ catalyst prepared from PAA which was activated at 350 °C. Citral reacted fastly in the first 20 min of the reaction then slowly decreased up to the end of the reaction. The main products formed were citronellal (82.36 %) and geraniol+nerol (6.31 %). Moreover, undesired products in low amounts were also formed which were 3,7-dimethyloctanol (0.73 %) and citral acetals (0.82 %). These results showed that the catalyst had high selectivity for the hydrogenation of conjugated double bond.

The product distribution observed over Pt/SiO₂ catalyst using HCLPA as precursor which was activated at 350 °C is given in Figure 4. Citral reacted very fast in the first 20 min of the reaction then slowly decreased and then remained constant (catalyst deactivated). The main products formed were geraniol+nerol (35.55 %) and citronellal (29.90 %). Moreover, undesired products were also formed which were 3,7- dimethyloctanol (2.76 %) and citral acetals (16.33 %). Thus, this catalyst had some selectivity toward the hydrogenation of carbonyl bond, which was different from that of PAA precursor.

Pt from two different precursors showed different activities and selectivities. Use of PAA to prepare Pt/SiO₂ catalyst prevented acetal formation significantly as reported in literature (Aykaç et al., 2008; Serrano Ruiz et al., 2007). When PAA was used as precursor, catalyst did not deactivate as fast as HCLPA and it reached 89.50 % conversion. However, catalyst deactivated after 20 min and conversion reached was 72.67 % with HCLPA. Geraniol+nerol amount was higher with HCLPA based catalyst. Similar findings are reported in literature (Silvestre-Albero et al., 2006, Ammari et al., 2005, Bachiller-Baeza et al., 2000). However, Cl content is related to acetal formation as well (Aumo et al., 2002). This might explain high amount of acetal formation over HCLPA catalyst which was found to contain 0.30 % Cl. The undesired product (3,7-dimethyloctanol) amount also increased significantly when HCLPA was used.

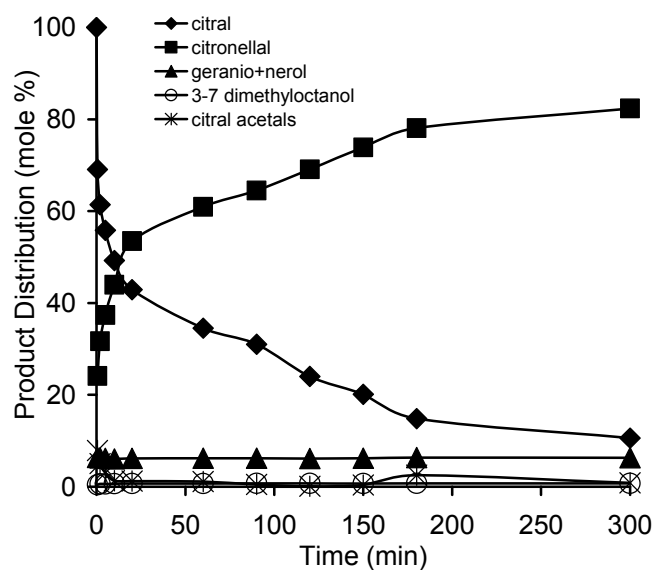


Figure 3. Product distribution obtained over Pt/SiO₂ catalyst prepared from PAA precursor which was activated at 350 °C.

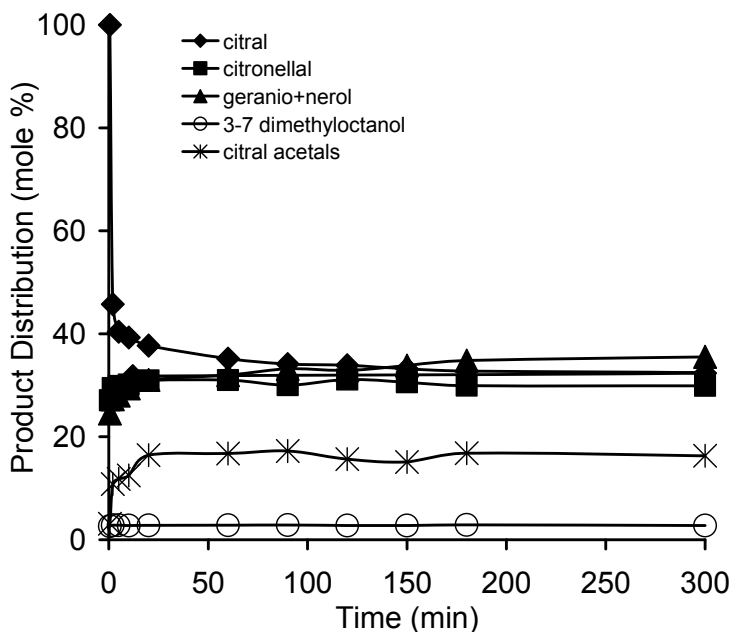


Figure 4. Product distribution observed over Pt/SiO₂ catalyst from HCLPA precursor which was activated at 350 °C.

Activation temperature affected activity significantly as shown in Figure 5. Increasing activation temperature from 350 to 450 °C decreased citral conversion from 72.67 to 46.46 % for HCLPA precursor and from 89.50 to 26.10 % for PAA precursor. This showed that lower activation temperature was appropriate to achieve higher citral conversion as reported in the previous studies (Serrano-Ruiz et al., 2007, Vilella et al., 2005). The selectivity to geraniol+nerol obtained for these conditions are given in Figure 6. Changing activation temperature from 350 to 450 °C decreased selectivity to geraniol and nerol ($S_{(GE+NE)}$) from 39.05 % to 22.88 % for the catalyst prepared from HCLPA. However, the use of PAA decreased acetal formation during reaction and increased the $S_{(GE+NE)}$ from 7.06 to 56.4 % for higher activation temperature. PAA gave higher selectivities to $S_{(GE+NE)}$ compared to HCLPA. The change in product distribution between the catalysts could be attributed to degree of metal reduction and to the type of metal precursor. Chloride precursor was more difficult to reduce than acetylacetonate source as discussed in the characterisation section. This showed that there was different support and metal interaction, which could have also played a role in the product distribution obtained for the catalysts prepared from different precursors.

Changing solvent from ethanol to 2-pentanol decreased activity of catalyst prepared from HCLPA precursor (Figure 5); conversion obtained in ethanol was 72.67 % while it was 30.00 % in 2-pentanol. Also $S_{(GE+NE)}$ was decreased from 39.05 to 31.72% (Figure 6). Use of 2-pentanol decreased acetal formation as reported by Maki-Arvela et al. (2002). But it did not increase selectivity to geraniol and nerol. Thus, use of higher carbon alcohol did not improve $S_{(GE+NE)}$. When the catalyst without calcination was used in 2-pentanol, catalyst activity decreased significantly as $S_{(GE+NE)}$ almost remained constant. This showed that generation of active sites during calcinations was important.

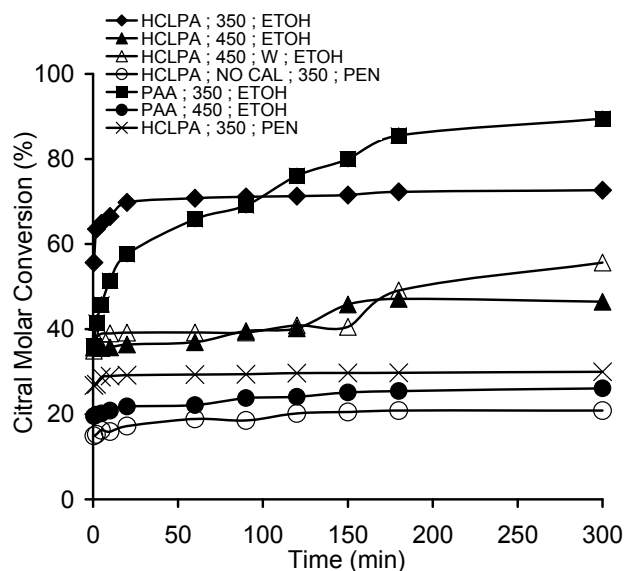


Figure 5. Citral conversion for different investigated parameters, where HCLPA: Hexachloroplatonic acid, PAA: Platinum acetylacetonate, NO CAL: Without calcination, 350 or 450 : Reduction temperature, W: Washed catalyst, ETOH: Ethanol, PEN: 2-Pentanol.

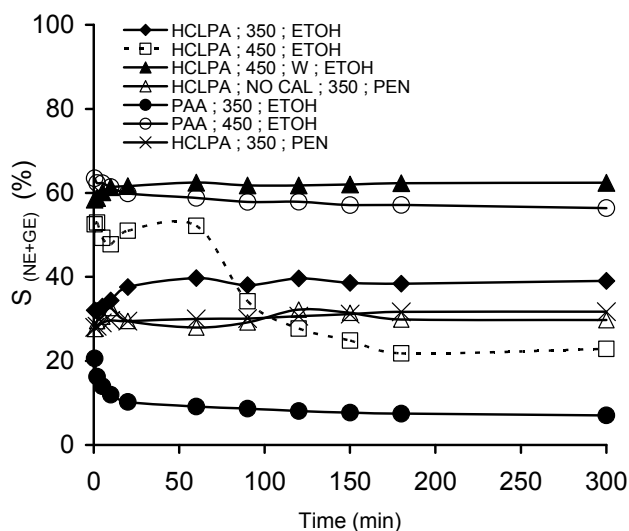


Figure 6. Selectivity to geraniol+nerol for different applied parameters, where HCLPA: Hexachloroplatonic acid, PAA: Platinum acetylacetonate, NO CAL: Without calcination, 350 or 450 : Reduction temperature, W: Washed catalyst, ETOH: Ethanol, PEN: 2-Pentanol.

To minimize acetal formation over the catalyst prepared with HCLPA, catalyst was washed with 0.1 M NaOH. Washing catalyst increased conversion from 46.46 to 55.66 % (Figure 5) and reduced acetal formation from 32.00 to 15.00 %. It also improved $S_{(GE+NE)}$, which was 62.4 % for washed catalyst compared to original unwashed catalyst, 22.88 % (Figure 6). This indicated that washing was successful in chloride removal, which caused acetal formation. Similar findings are reported in literature (Aumo et al., 2002).

4. Conclusions

Catalysts prepared from different precursors were found to have different active sites. Reduction of chloride precursor based catalysts was more difficult than acetylacetonate. Acetal formation was much higher for the catalyst based on HCLPA. Acetal formation was attributed to the presence of chloride in the catalyst. Washing of catalyst, using 2-pentanol or PAA decreased acetal formation. Pt/SiO₂ catalysts activities decreased when activation temperature increased. However, selectivity to geraniol+nerol was affected differently with the activation temperature depending on the precursor type. With PAA based catalyst, selectivity increased with temperature while it decreased for HCLPA based catalyst. This was attributed to presence of different active sites and presence of Cl. Catalyst washing also improved activity and selectivity. Catalyst calcination before activation improved activity and selectivity of the catalysts.

References

- Ammari F., Milone C., Raymonde T., Selective Hydrogenation of Crotonaldehyde on Pt/ZnCl₂/SiO₂ Catalysts, *Journal of Catalysis*, 2005, 235, 1–9.
- Aramendia, M. A. Borau V., Jimenez C., Marinas J. M., Porras A., Urbano F. J., Selective Liquid-Phase Hydrogenation of Citral over Supported Palladium, *Journal of Catalysis*, 1997, 172, 46–54
- Aumo J., Lilja J., Maki-Arvela P., Salmi T., Sundell M., Vainio H., Murzin D. Yu., Hydrogenation of Citral over a Polymer Fibre Catalyst, *Catalysis Letters*, 2002, 84, Nos. 3-4.
- Aykac H., Yilmaz S., Hydrogenation of Citral over Pt and Pt-Sn Catalysts, *Turkish Journal of Chemistry*, 2008, 32, 653 – 662.

- Bachiller-Baeza B., Guerrero-Ruiz A., Wang, P., Rodriguez-Ramos I., Hydrogenation of Citral on Activated Carbon and High-Surface-Area Graphite-Supported Ruthenium Catalysts Modified with Iron, *Journal of Catalysis*, 2001, 204, 450–459.
- Bachiller-Baeza B., Guerrero-Ruiz A., Rodríguez-Ramos I., Role of the Residual Chlorides in Platinum and Ruthenium Catalysts for the Hydrogenation of α,β -unsaturated Aldehydes, *Applied Catalysis A: General*, 2000, 192, 289–297.
- Barias O.A., Holmen A., and Blekkan E.A., Propane Dehydrogenation over Supported Pt and Pt–Sn Catalysts: Catalyst Preparation, Characterization, and Activity Measurements, *Journal of Catalysis*, 1996, 158, 1-12.
- Chiang S.J., Yang C.H., Chen Y.Z., Liawa B.-J., High-active Nickel Catalyst of NiB/SiO₂ for Citral Hydrogenation at Low Temperature, *Applied Catalysis A: General* 2007, 326, 180–188.
- Consonni M., Jokic D., Murzin D. Yu, Touroude R., High Performances of Pt/ZnO Catalysts in Selective Hydrogenation of Crotonaldehyde, *Journal of Catalysis*, 1999, 188, 165–175.
- Galvagno S., Milone C., Donato A., Neri G., Pietropaolo R., Influence of Metal Particle Size in the Hydrogenation of Citral over Ru/C, *Catalysis Letters*, 1993, 18, 349-355.
- Hájek J., Kumar N., Mäki-Arvela P., Salmi T., Murzin D.Yu., Paseka I., Heikkilä T., Laine E., Laukkanen P., Väyrynen J., Ruthenium-modified MCM-41 Mesoporous Molecular Sieve and Y Zeolite Catalysts for Selective Hydrogenation of Cinnamaldehyde, *Applied Catalysis A: General*, 2003, 251, 385–396.
- Mäki-Arvela P., Tiainen L.P., Neyestanaki A. K., Sjöholm R., Rantakylä T.K., Laine E., Salmi T., Murzin D. Yu, Liquid Phase Hydrogenation of Citral: Suppression of Side Reactions, *Applied Catalysis A: General*, 2002, 237, 181–200.
- Maki-Arvela P., Hajek J., Salmi T., Murzin D.Yu., Review: Chemoselective Hydrogenation of Carbonyl Compounds over Heterogeneous Catalysts, *Applied Catalysis A: General*, 2005, 292, 1–49.

- Mercadante, L., Neri, G., Donato, A., and Galvagno, S., Hydrogenation of α,β -Unsaturated Aldehydes over Ru/Al₂O₃ Catalysts, *Journal of Molecular Catalysis*, 1996, 105, 93-101.
- Ramos-Fernandez E.V., Ferreira A.F.P., Sepulveda-Escribano A., Kapteijn F., Rodriguez-Reinoso F., Enhancing the Catalytic Performance of Pt/ZnO in the Selective Hydrogenation of Cinnamaldehyde by Cr Addition to the Support, *Journal of Catalysis*, 2008, 258, 52–60.
- Reyes P., Rojas H., Hydrogenation of Citral Over Pt and Pt-Fe SiO₂ Catalysts, *Reaction Kinetics and Catalysis Letter*, 2006, 88, 363-369.
- Serrano-Ruiz J. C., Sepulveda-Escribano A., Rodriguez-Reinoso F., Duprez, D., Pt-Sn Catalysts Supported on Highly-Dispersed Ceria on Carbon Application to Citral Hydrogenation, *Journal of Molecular Catalysis A: Chem.*, 2007, 268, 227–234.
- Silva A. B., Jordao E., Mendes M. J., Fouilloux P., Effect of Metal-support Interaction During Selective Hydrogenation of Cinnamaldehyde to Cinnamyl Alcohol on Platinum Based Bimetallic Catalysts, *Applied Catalysis A: General*, 1997, 148, 253-264.
- Silvestre-Albero J., Coloma F., Sepulveda-Escribano A., Rodriguez-Reinoso F., Effect of the Presence of Chlorine in Bimetallic PtZn/CeO₂ Catalysts for the Vapor-phase Hydrogenation of Crotonaldehyde, *Applied Catalysis A: General*, 2006, 304, 159–167.
- Singh U.K., Vannice M. A., Liquid-Phase Citral Hydrogenation over SiO₂-Supported Group VIII Metals, *Journal of Catalysis*, 2001, 199, 73–84.
- Vilella I.M.J., Miguel S.R., Scelza O.A., Hydrogenation of Citral on Pt and PtSn Supported on Activated Carbon Felts (ACF), *Latin American Applied Research*, 2005, 35, 51-57.
- Yilmaz S., Ucar S., Artok L., Gulec H., The Kinetics of Citral Hydrogenation over Pd Supported on Clinoptilolite Rich Natural Zeolite, *Applied Catalysis A: General*, 2005, 287, 261-266.