Liquid-Phase Hydrogenation of Citral Over Pt/TiO₂ and Pt-Fe/TiO₂ Catalysts

S.A. ANANTHAN[*] and V. NARAYANAN

Department of Inorganic Chemistry, School of Chemical Science, University of Madras, Guindy Campus, Chennai-600 025, India

*Corresponding author: Fax: +91 4422300488; E-mail: saananth2@yahoo.com

The liquid phase hydrogenation of citral to unsaturated alcohol over supported platinum catalysts has been studied. The catalysts were used Pt/TiO₂ reduced at low or high temperature and the bimetallic Pt-Fe/TiO₂ low or high temperature catalysts. As solvent *n*-heptane, an equimolar mixture *n*-heptane-1-propanol and 1-propanol were used. The reactions were carried out at a hydrogen pressure of 8.27 bar at 363 K. In the low temperature catalyst, the catalytic activity increases upon the addition of Fe^{3+}. This positive effect was obtained keeping constant the selectivity to the unsaturated alcohol, being high selective to the products obtained by hydrogenation of the C=O bond. In the high temperature catalysts, both the addition of Fe and the presence of TiO₂ moieties generated by the strong metal support interaction (SMSI) effect, lead to an increase of surface acidity. In low or high temperature catalysts, an increase in the polarity of the solvent increases the catalytic activity. However the reaction pathway is modified by the presence of acid sites which in polar solvents allow the formation of acetals, mainly in the high temperature catalysts.

Key Words: Citral hydrogenation, Solvent, Bimetallic catalyst, Strong metal-support interaction.

INTRODUCTION

The selective reduction of α, β unsaturated carbonyl compounds is one of the most important research areas in fine chemistry. An overview of the topic is provided in several studies[1-10]. Crotonaldehyde[11,12], methacrolein[13] and particularly, cinamaldehyde[14,15] are the most widely documented compounds in this respect, particularly in relation to the use of single and two metal catalysts supported on various materials such as alumina, polymer, graphite, titania, *etc*. The main problem lies in obtaining catalysts affording the selective reduction of C=O thermodynamically less favoured compared to the C=C hydrogenation.

The hydrogenation of α, β unsaturated carbonyl compounds on single metal catalysts leads to the reduction of the conjugate C=C bond with a high selectivity. Suitable heterogeneous catalysts for the chemoselective hydrogenation of α, β unsaturated aldehydes are mostly based on supported noble metals such as Pd and Ru[16] and Ni supported in Al₂O₃ at lower hydrogenation pressure (2.3 bar)[17]. However, single metal may leads to the reduction of C=O bonds with the use of reducible support such as TiO₂ or Nb₂O₅[18], which are able to produce the SMSI effect. Thus, this kind of system has been successfully used to increase the selectivity to the hydrogenation of C=O bond of the citral when a high reduction temperature of Pt-TiO₂ has been used[19-21]. Similar results have been obtained in the hydrogenation of acrolein over Pt and Ir metal supported on Nb₂O₅. In citral hydrogenation over Ir/TiO₂ catalysts reduced at high temperature (773 K), high selectivity (close to 100 %) to the unsaturated alcohol has been reported[22]. On the other hand, the formation of unsaturated alcohols over bimetallic catalysts have been obtained using Ru-Sn catalysts supported on carbon[23], Ti-Fe supported in SiO₂ and those generated by the addition of Sn to Rh, Pt or Ru catalysts[24]. The favourable effect of the metal ions in these compounds (halides) is related to their Lewis acid character, which activates the carbonyl group by inducing positive charge on the carbon atom[24]. The textural properties of the support, particle size, extent of the metal dispersion and nature of the precursor used to prepare the catalyst have also an effect on the selectivity of the reduction of α, β unsaturated carbonyl compounds[1,19-21,25].

Citral is a very fascinating small molecule for selective hydrogenation, since it has three different double bonds, an isolated, a conjugated and a carbonyl group. Generally citral hydrogenation has been found to be sensitive to the variation of different reaction parameters. Particularly, the solvent used has a strong influence on the product distribution. It has been reported that it is possible to hydrogenate selectively the carbonyl bond with use of appropriate solvent. Arai *et al.*[26] pointed out the influence of solvent and pressure (50 bar H₂ and 170 bar CO₂) in the hydrogenation of three different α, β unsaturated aldehydes, using supercritical CO₂ and ethanol over a conventional Pt/Al₂O₃ catalyst without any promoters. They reported high catalytic activity and selectivity close to

90 %. Under the conditions used, unsaturated alcohols and saturated aldehydes were the main products. Very small quantities of saturated alcohols were detected and in some cases other products (not identified) should be formed. The explanation given for the enhancement in the selectivity to the unsaturated alcohol is that the dielectric constant increases with an increase in pressure. In other words, the solvent is more polar at higher pressure. This may affect the reactivity of the polar C=O bond, but not the less polar C=C bond. The C=O bonds are activated and easier hydrogenated leading to the selective formation of the unsaturated alcohols. Additionally, the density functional theory (DFT) has been used[27] to calculate and to compare the reactivity of the atoms present in the reactant molecule for a range of solvents with variable dielectric constant in citral hydrogenation under mild conditions using supercritical CO_2. They found that it is possible to hydrogenate selectively the conjugated and isolated C=C double bond of citral to a fully saturated aldehydes (dihydrocitronella). Citral hydrogenation is a complex reaction. There are series and parallel reactions. Products formed over different catalysts include citronellal, citronellol, geraniol, nerol, *etc*. (Fig. 1).
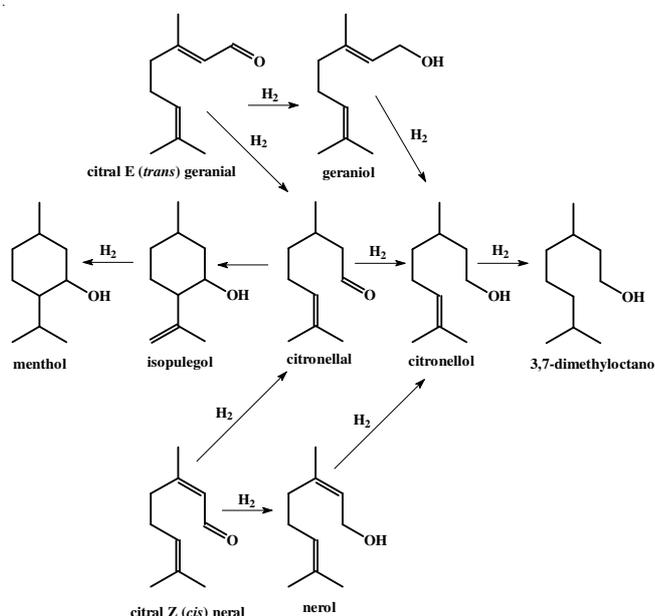
Fig. 1. Schematic representation of citral hydrogenation

It was attributed to the fact that carbon dioxide molecule does not possess a permanent dipole moment. It has a quadrupole moment, which allows a stronger interaction with dipolar solutes. This quadrupole moment enable CO_2 to acts as both a Lewis acid and Lewis base that is recognized as being important in the CO_2 based solvatation. Furthermore, the dielectric constant of supercritical CO_2 varies with the change in density resulted from the pressure variation as observed by Arai *et al.*[26]. Aramendia *et al.*[28] have studied the reduction of citral in gas-phase by hydrogen transfer over acid-basic catalysts ($AlPO_4$/SiO_2, MgO, MgO/B_2O_3 and ZrO_2). The former is predominantly acid whereas the MgO and MgO/B_2O_3 are essentially basic, containing only few acid sites and the ZrO_2, which is an amphoteric solid, containing a similar number of acid and basic sites. The TPD-MS profiles for pyridine and dimethylpyiridine were used to characterize the acid sites of the solids.

They used different aliphatic or aromatic alcohols as hydrogen donor and found that the hydrogen-transfer reductions of citral by 1-phenylethanol as hydrogen donor on basic catalysts (MgO or MgO/B_2O_3) lead to the selectivity reduction of the carbonyl group, whereas, acid and amphoteric solids lead to the completely selective reduction of the double bonds. The behaviour is explained in terms of the interaction of the citral molecule and the catalyst surface, whether citral is adsorbed on the surface of the acid-base catalyst *via* its C=O or its C=C group, which in turn depends on the nature and strength of the catalysts sites. Thus, strong sites favour the reduction of the C=O bond whereas weak sites promote the reduction of C=C bond conjugated with the previous one. The alcohol used as hydrogen donor play a crucial role since it influences both conversion and selectivity in the hydrogenation process. Secondary alcohols (both aliphatic and aromatic) are effective hydrogen donors in this context, while the aromatic group provide a somewhat higher selectivity towards the reduction of the C=O group.

EXPERIMENTAL

Citral (E-Merck, 99 %) and solvents are *n*-heptane, *n*-heptane-1-propanol and 1-propanol (Fluka, 95 %) were used without distillation. Pt/TiO_2 catalysts were prepared by wet impregnation of TiO_2 (Baker, UK, S_{BET} = 50 m^2/g) with an aqueous solution of H_2PtCl_6 p.a. (Aldrich) to give a Pt loading of 1 wt. %. The samples impregnates were dried under vacuum at 373 K for 6 h, calcined in air at 673 K for 4 h and reduced *in situ* at 473 or 773 K, respectively for 2 h prior to the characterization or catalyst test. Additionally, bimetallic Pt-Fe catalysts were obtained by impregnation of an aliquot of reduced Pt/TiO_2 catalysts with an aqueous solution of $FeCl_3$ (Fluka) at pH = 3 in an appropriate amount an iron content of 1 wt. %. After the impregnation, the solids were dried at vacuum at 343 K.

Catalyst characterization: Nitrogen physisorption at 77 K and hydrogen chemisorption at 298 K were carried out in a Micromeritic ASAP 2010 apparatus. TEM micrographs were obtained in a microscope Jeol Model JEM-1200 EXII System and XRD in a Rigaku apparatus. Adsorption of NH_3 was studied by a pulse method in a Micromeritics TPD/TPR 2900 apparatus. The samples were heated up to 383 K and maintained at this temperature for 1 h in helium gas flow. Then, doses of NH_3 were sent to the samples up to complete saturation. Later on the samples were cooled down to room temperature and once the base line was restored, the temperature was increases linearly at a heating rate of 10 °/min up to 800 K. Photoelectron spectra (XPS) were recorded using an Escalab 200 R spectrometer provided with a hemispherical analyzer and using non-monochromatic Mg K X-ray radiation Qm = 1253.6 eV). The surface Pt/Ti, Fe/Ti, Fe/Pt and atomic ratios were estimated from the integrated intensities of Pt 4f Fe 2p and Ti 2p$_{3/2}$ lines after background subtraction and corrected by the atomic sensitivity factors[25]. The spectra were fitted to a combination of Gaussian-Lorentzian lines of variable proportion. The bonding energy of the Si 2p peak at 103.4 eV was taken as an internal standard.

Activity test: The reaction was conducted in a Parr Instrument Model 4574 autoclave at a constant stirring rate

(1000 rpm) batch. All reactions were performed using an hydrogen pressure of 12 bar, catalyst weight of 300 mg, 40 mL of a 0.10 M solution of citral in solvent (*n*-heptane, *n*-heptane-1-propanol or 1- propanol) and reaction temperature of 363 K. Prior the reaction, the reactor was loaded with the catalyst and reactants at atmospheric pressure during 0.5 h and flowed with helium through the solution to assure the absence of oxygen. Prior the experiment, all catalysts were reduced *in situ* under hydrogen flow of 20 cm³ min⁻¹ at atmospheric pressure and temperature of 363 K. In all reaction, internal diffusion limitations were also shown to be absent by applying the Weisz-Prater parameter, which gave a value maximum of 0.19[29]. Blank experiment showed no catalytic activity due to the support under these conditions. An HP 4890 GC furnished with an HP 5 semi-capillary column of 15 m and 0.53 mm ID analyzed reaction products. The GC analysis was performed using a flame ionization detector, using helium as carrier and the column was kept at a constant temperature, 393 K. Under these analytical conditions, the retention time of the reported reactants and products were citral (E): 30.7; citral (Z): 35.4; nerol: 27.6; geraniol 32.2 and acetals: 41 min. The presence of acetals was confirmed by the use of mass spectroscopy-gases chromatography (GC MS-QP2010 Plus).

RESULTS AND DISCUSSION

Hydrogen chemisorption results are given in Table-1 the estimated metal particle size obtained by TEM and the NH₃ uptake. These results revealed that the platinum is highly dispersed. In fact, the H/Pt surface ratio of the Pt/TiO₂ low temperature catalysts was 0.27. The Fe-Pt/TiO₂ low temperature catalysts display a substantially lower H/Pt, due to partial coverage of Pt crystallites by oxidized species of iron. In the Fe-Pt/TiO₂ high temperature catalyst, a slight drop in the H/Pt ratio compared with the monometallic catalyst was observed. This is explained taking into account the low value of the H/Pt ratio exhibited by the Pt/TiO₂ high temperature catalyst, due to covering of the Pt particles by TiO₂ moieties generated by the SMSI effect. Studies performed by transmission electron microcopy (TEM) indicate that particle size of Pt/TiO₂ low temperature and Pt/TiO₂ high temperature samples are similar (2.54-2.62 nm) and confirm that the platinum is highly dispersed in all the catalysts. The incorporation of Fe promoter to the reduced Pt catalyst did not modify significantly the metal particle size, showing metal particle size close to 2.73 nm. The Pt/TiO₂ catalysts show higher amount of acid sites than the support and the bimetallic Pt-Fe/TiO₂ display even higher values. The acid sites may be attributed to residual chloride because the catalysts were obtained from chlorine containing precursors H₂PtCl₆, FeCl₃ and also by TiOₓ moieties generated by partial reduction of titanium. The number of desorbed ammonia molecules given in Table-1, may include not only the acid sites but also a contribution of NH₃ physisorbed on the support. After subtracting the adsorption by the support, significant quantities of adsorbed ammonia either on Pt or Pt-Fe catalyst remains, indicative of acid sites, which are present in higher extent in Fe-Pt/TiO₂ catalysts. To have an estimation of the strength of the acid sites, DTP profiles of the chemisorbed NH₃ was also registered (Fig. 2). In spite of a

TABLE-1
H/Pt RATIO, METAL PARTICLE SIZE AND SURFACE ACIDITY OF TiO₂ AND Pt/TiO₂ CATALYSTS

Catalyst	H/Pt	d_{TEM} (nm)	NH₃ adsorbed (mol/g × 10¹⁹)
TiO₂LT			2.58
Pt/TiO₂LT	0.27	2.62	4.47
Pt-FeTiO₂LT	0.07	2.74	8.33
TiO₂HT			2.57
Pt/TiO₂HT	0.18	2.54	4.62
Pt-FeTiO₂HT	0.03	2.73	9.22

LT = Low temperature; HT = High temperature.
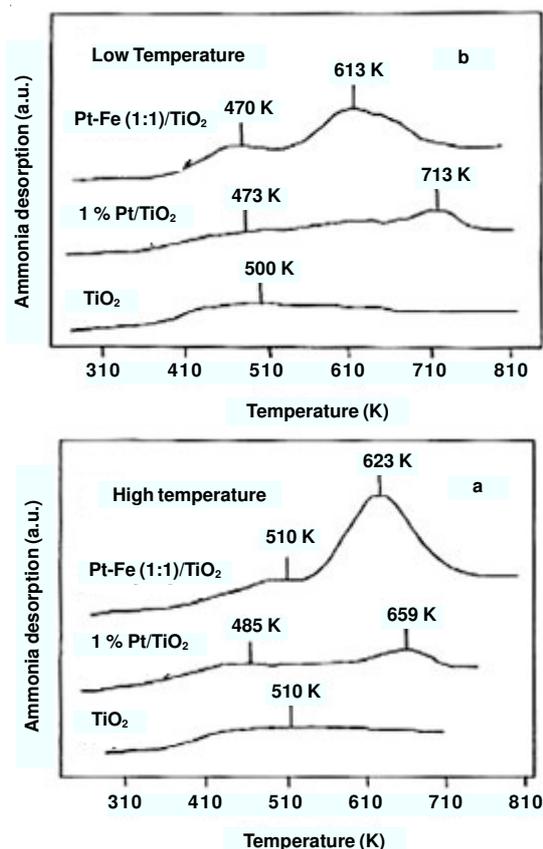
Fig. 2. DTP of ammonia over Pt-supported catalyst (a) low temperature and (b) high temperature

quantitative evaluation of desorbed species was not performed because of a simple integration of the desorption peaks is rather risky considering that the ammonia decomposition can also take place during the DTP experiments, especially on Fe-Pt/TiO₂ catalysts. The profiles exhibit a wide peak centered close to 500 K attributed to the desorption of ammonia adsorbed on weak acid sites and it is likely that they also include NH₃ physically adsorbed on the support.

Binding energies of core-level electrons and metal surface composition were obtained from XP spectra. For the Pt/TiO₂ low temperature catalyst, the binding energy of Pt ⁴f₇/₂ peak is approximately 69.4 eV, which corresponds to Pt⁰ species. A slight increase in the BE of Pt ⁴f₇/₂ peak is consistent with the general trend observed for small particles of transition metal deposited on inorganic substrates and agrees with metal particle size obtained from TEM data. Catalysts promoted by Fe and titania-supported iridium catalysts reduced at high temperature

display similar BE values. However, a slight broadening to higher binding energies suggests the presence of Pt^0 and Pt^{6+} species in these samples. Fig. 3 display XP spectra for some representative Pt-supported catalysts. It can be seen that three component had to be included to fit experimental spectra because the Ti 3s peak coming from the support falls just between the two spin-orbit split levels of platinum. The hydrogenation, expressed as micromole converted per second per gram of catalyst and the initial turnover frequency, evaluated by means of the average of TOF at 10 % conversion for the low temperature series. It should be pointed out that in the Pt/TiO_2 and Pt-Fe/ TiO_2-low temperature catalysts the selectivity towards the products obtained by hydrogenation of the C=O bond (geraniol and nerol) was 100 %. The proportion of nerol and geraniol is the same of the existing in the starting citral mixture 65:35, indicating that the hydrogenation of both isomers occurs at the same reaction rate. Table-2 observed $(Pt/Ti)_s$ and $(Fe/Ti)_s$ surface ratios for the studied catalysts. The Pt/TiO_2-high temperature catalysts show lower Pt/Ti ratios than their low temperature counterparts due presumably to the migration of TiO_x moieties on the Pt particles. For the Fe promoted titania-supported Pt catalysts, partial reduction of Fe additives in inferred as judging from the binding energies of Fe $2p_{3/2}$ levels. The (Pt/Ti) atomic surface ratio is comparable in both monometallic Pt/TiO_2 catalysts and a slight decrease in that ratio takes place after the addition of Fe in both series.

hand, the surface $(Fe/Pt)]_s$ ratios of both Pt-Fe/TiO_2 (high temperature and low temperature) catalysts, were approximately two times higher than the bulk the slight increases in the mentioned ratio in the high temperature series suggest that the Fe species are covering not only the titania but also the Pt crystallites.

Catalytic hydrogenation results at 363 K and 8.27 bars, expressed as the evolution of the conversion level with time over Pt or Pt -Fe/TiO_2 low temperature catalysts on the studied at different solvents. It can be seen that all the catalysts showed similar trends. The reaction rates are higher at the beginning of reaction (below 2 h) and progressively decrease as the conversion increases. In both catalysts series an increase in the polarity of the solvent leads to an enhancement in the conversion level (Table-3). The conversion level at the same reaction time (1 h) as well as the initial activity for citral hydrogenation, expressed as micromole converted per second per gram of catalyst and the initial turnover frequency, evaluated by means of the average of TOF at 10 % conversion for the low temperature series. It should be pointed out that in the Pt/TiO_2 and Pt-Fe/TiO_2 low temperature catalyst the selectivity towards the products obtained by hydrogenation of the C=O bond (geraniol and nerol) was 100 %. The proportion of nerol and geraniol is the same of the existing in the starting citral mixture 65:35 indicating that the hydrogenation of both isomers occurs at the same reaction rate.

Fig. 3. Pt 4f core-level spectra for Pt supported catalysts

TABLE-2
XPS ATOMIC RATIO OF Pt-SUPPORTED CATALYSTS

Catalyst	$(Pt/Ti)_s$	$(Fe/Ti)_s$	$(Fe/Ti)_b$	(Fe/Pt)
Pt/TiO_2LT	0.0244	–	–	–
Pt-FeTiO$_2$LT	0.0202	0.116	3.45	5.78
Pt/TiO_2HT	0.0274	–	–	–
Pt-FeTiO$_2$HT	0.0195	0.127	3.45	6.45

This decreases account a surface coverage by iron species. On the other hand no significant changes in the (Fe/Ti) was observed in both bimetallic catalysts being these ratio 0.117 and 0.126, approximately 5 times higher than the bulk Fe/Ti ratio, confirming the surface enrichment in Fe. On the other

TABLE-3
CATALYTIC ACTIVITY IN THE CITRAL HYDROGENATION AT 363 K AND 8.27 bar, CONVERSION LEVEL AT 1 h, INITIAL ACTIVITY, TURNOVER FREQUENCY (TOF) OF 10 % OF CONVERSION OVER Pt SUPPORTED CATALYSTS. SERIES LOW TEMPERATURE

Catalyst	Solvent	Conversion % (t = 1h)	Initial activity (µmol g^{-1} s^{-1})	TOF (s^{-1})
Pt/TiO_2	*n*-Heptanes	3.1	0.12	0.011
	n-Heptane-1-propanol	9.5	0.34	0.027
	1-Propanol	10.2	0.37	0.029
Pt-Fe/TiO_2	*n*-Heptanes	19.2	0.76	0.292
	n-Heptane-1-propanol	21.3	0.78	0.305
	1-Propanol	22.5	0.88	0.341

It is well known that the reaction rate in a given solvent depends on the differences in the characteristics of the solvent and reactant and the solvent and the activated complex. If the activated complex is similar to the solvent but the reactant are not, the rate will be the rate in an ideal solution in which no interactions between the reactant and solvent take place. If the reactant resemble the solvent but the transition state does not, the rate will be small compared to the ideal situation. Especially reactions producing products more polar than reactants will go well in polar solvent reactions giving product less polar than the reactants will go well in non polar solvents. Thus, taking into account that during the reaction the citral molecule is adsorbed on the active center partially polarized in the carbonyl bond it should be expected that this adsorbed activated specie should reacts easier in the presence of polar solvent, in agreement with our obtained results. It can be seen

in Table-3 that Pt-Fe/TiO$_2$ low temperature catalyst displays much higher activity than it monometallic counterpart. This behaviour is attributed to the higher polarizability of the carbonyl bond induced by the acidity of the catalyst. In this sample, this is an important effect, which may lead to an almost negligible effect of the dielectric constant of the solvent. Conversion against time at high temperature catalyst series. The liquid phase catalytic hydrogenation of citral at 363 K and 8.27 bars by using Pt or Pt-Fe/ TiO$_2$ high temperature catalysts to n conversion and time, for the different solvents. The observed trends are similar to those previously discussed, being higher the reaction rates at the beginning of the reaction and progressively decrease with the time on stream. The Pt/TiO$_2$ high temperature catalyst exhibits higher activity compared to the low temperature counterpart, which is attributed to the presence of modified metallic sites by decoration with TiO$_x$ species. Conversely, the Pt-Fe/TiO$_2$ high temperature catalyst shows lower activity than the low temperature counterpart. This behaviour is not unusual and it has been previously reported. It is attributed to the migration of TiO$_x$ species on the Ir-Fe which produces a decrease in the activity due to decreases in the amount of Pt surface atoms and a drop in the polarization sites. Table-4 compiles the catalytic activity results obtained in the citral hydrogenation over Pt/TiO$_2$ high temperature and Pt-Fe/TiO$_2$ high temperature catalysts.

TABLE-4
CATALYTIC ACTIVITY IN THE CITRAL HYDROGENATION AT 363 K AND 8.27 bar CONVERSION LEVEL AT 1 h, INITIAL ACTIVITY, TOF AND SELECTIVITY AT 10 % OF CONVERSION OVER Pt SUPPORTED CATALYSTS. SERIES HIGH TEMPERATURE

Catalysts	Solvent	Conversion % (t = 1 h)	Initial activity (μmol s^{-1} g^{-1})	TOF (s^{-1})	Selectivity (%)	
					Geraniol + nerol	Acetals
Pt/TiO₂	n-Heptanes	9.50	0.32	0.04	100	0
	n-Heptane-1-propanol	0.11	0.41	0.05	95	5
	1-Propanol	25.50	1.18	0.14	75	25
Pt-Fe/TiO₂	n-Heptanes	5.90	0.17	0.18	100	0
	n-Heptane-1-propanol	14.00	0.46	0.45	70	30
	1-Propanol	15.20	0.53	0.51	55	45

The values of conversion level at the same reaction time (1 h), the initial activity, the turnover frequency (TOF), the selectivity and the yield to geraniol + nerol are given. As it was mentioned the catalytic activity-conversion level and the initial activity- of the Pt/TiO$_2$ high temperature catalyst is higher that the low temperature monometallic catalysts in the three studied solvents and increases with the polarity of the solvent, behaviour explained on the basis of the modification of the active sites induced by the SMSI effect. The enhancement in the turnover frequency values is even more important due to a decrease in the amount of Pt surface atoms. However, this catalyst displays lower selectivity to the products generated by hydrogenation of the C=O bond because by a parallel pathway the formation of acetals by reaction between the reactant and the polar solvent takes place. The formation of acetals increases with the dielectric constant of the solvent. With regard to Pt-Fe/TiO$_2$ high temperature catalyst the conversion level is lower compared to the low temperature counterpart and to the monometallic Pt/TiO$_2$ catalyst whatever the solvent used. This behaviour is explained on the basis of destruction of surface interface sites produced by the migration of TiO$_x$ species on Pt-Fe^{3+} sites leading to a decrease in the amount of Pt surface atoms and a drop in the polarization sites. The possible route of acid sites to produce acetalsr and line by Capelletti et al.[27] suggestions. It is a similar mechanism to that proposed for the reaction in homogeneous phase to obtain acetals from aldehydes. Thus, the protonation of the oxygen atom in the carbonyl bond takes place in the initial step. This protonation is caused by an acid site from the catalytic surface followed by a subsequent nucleophilic attack of an alcohol molecule and then lost of proton from the generated specie (protonated hemiacetal) to produce water. Finally, the acetal is obtained between a second alcohol molecule and the formed carbocation.

Conclusion

• Supported platinum systems obtained results; Pt/TiO$_2$ catalysts are active and selective to get geraniol and nerol by hydrogenation of citral. Increasing the reduction temperature from 473-773 K, low temperature and high temperature, respectively lead to an important enhancement due to decoration of Pt crystals by SMSI effect. In the Pt/TiO$_2$ low temperature, the addition of Fe increases significantly the activity due to the modification of the active sites by creation of more polarizing sites. However, the Pt-Fe/TiO$_2$ high temperature catalyst displays lower activity because of the destruction of these polarizing sites by migration of TiO$_x$ species.

• The effect of the nature of the solvent was also studied. The results demonstrated that in the low temperature series, the activity increases as the dielectrical constant of the solvent increases. In these catalysts, only geraniol and nerol, the products generated by hydrogenation of the carbonyl bond, takes place. In the high temperature series, it was found that as the polarity of the solvent increases, a side reaction occurring on the acid sites of the catalysts lead to acetals, therefore the selectivity to the unsaturated alcohols decreases.

REFERENCES

1. V. Ponec, *Appl. Catal. A: General*, **149**, 27 (1997).
2. U.K. Sing and M.A. Vannice, *J. Catal.*, **191**, 165 (2000).
3. W.K. Amornpattana and J.M. Winterbottom, *Catal. Today*, **66**, 277 (2001).
4. Z.M. Michalska, B. Ostaszewski, J. Zientarska and J.M. Rynkowski, *J. Mol. Catal. A: Chem.*, **185**, 279 (2002).
5. M. Lashdaf, J. Lahtinene, M. Lindblad, T. Venäläinen and A.O.I. Krause, *Appl. Catal A: General*, **276**, 129 (2004).
6. G. Lafaye, T. Ekou, C.M. Especel, C. Montassier and P. Marecot, *Appl. Catal. A: General*, **257**, 107 (2004).
7. P. Reyes and H. Rojas, *React. Kinet. Catal. Lett.*, **88**, 363 (2006).
8. M.C. Aguirre, J.L.G. Fierro and P. Reyes, *React. Kinet. Catal. Lett.*, **84**, 351 (2005).
9. P. Reyes, M.C. Aguirre, G. Pecchi, J.L.G. Fierro, G. Santori and O. Ferretti, *J. Mol. Catal. A. Chem.*, **184**, 431 (2002).
10. P. Reyes, M. Aguirre, G. Pecchi and J.L.G. Fierro, *J. Mol. Catal. A Chem.*, **164**, 245 (2000).
11. P. Reyes, G. Pecchi and J.L.G. Fierro, *Langmuir*, **17**, 522 (2001).
12. P. Reyes, M. Aguirre, I. Melián-Cabrera, M. López-Granados and J.L.G. Fierro, *J. Catal.*, **28**, 229 (2002).

13. M. Uestima and Y. Shimasaki, *Catal. Lett.*, **15**, 405 (1992).
14. V. Satagopan and S.B. Chandalia, *J. Chem. Tech. Biotech.*, **60**, 17 (1994).
15. P. Reyes, C. Rodriguez, G. Pecchi and J.L.G. Fierro, *Catal. Lett.*, **69**, 27 (2000).
16. M. Lashdaf, A.O.I. Krause, M. Lindblad, M. Tiitta and T. Venäläinen, *Appl. Catal A: General*, **241**, 65 (2003).
17. P. Maka-Arvela, L.P. Tiainen, M. Lindblad, K. Demirkan, N. Kumar and D. Yu. Murzin, *Appl. Catal. A: General*, **241**, 271 (2003).
18. M.A. Vannice, *Top. Catal.*, **4**, 241 (1997).
19. R. Malathi and R.P. Viswanath, *Appl. Catal. A: General*, **208**, 323 (2001).
20. R. Poltranzewski, S. Galvagno, R. Oietropaolo, P. Staiti and Malathi, *J. Catal.*, **102**, 190 (1986).
21. M.A. Vannice and B. Sen, *J. Catal.*, **115**, 65 (1989).
22. M.A. Aramendia, V. Borau, C. Jimenez, J.M. Marinas, A. Porras and F.J. Urbano, *J. Catal.*, **172**, 46 (1997).
23. S. Galvano, C. Milone, A. Donato, G. Neri and R. Pietropaolo, *Catal. Lett.*, **17**, 55 (1993).
24. P. Claus, *Topics Catal.*, **5**, 51 (1998).
25. C.D. Wagner, L.E. Davis, M.V. Zeller, J.A. Taylor, R.H. Raymond, L.H. Gale, *Surf. Inter. Anal.*, **3**, 211 (1981).
26. B.M. Banaghe, Y. Ikushima, M. Shirai and M. Arai, *Catal. Lett.*, **62**, 175 (1999).
27. A. Chatterjee, M. Chaterjee, Y. Ikushima and F. Mizukami, *Chem. Phys. Lett.*, **395**, 143 (2004).
28. M.A. Aramendia, V. Boreal, C. Jiménez, J.M. Marinas, A. Porras and F.J. Urbano, *Appl. Catal. A: General*, **172**, 31 (1998).
29. M. R. Capeletti, L. Balzano, G. De la Puente, M. Laborde and U. Sedran, *Appl. Catal. A: General*, **198**, L1 (2000).