RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF SUPPORTED PT AND RU CATALYSTS: EFFECT OF SMSI FOR SELECTIVE HYDROGENATION

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ARTICLE INFO	ABSTRACT
	Ru/TiO$_2$ and Pt/TiO$_2$ were prepared by impregnation method and reduced at two different temperatures, 375°C (LTR) and 575°C (HTR) for 4 hours. The catalysts were characterized by BET surface area, TPR, HRTEM, XRD and XPS techniques. It was found that the XRD of Pt showed fcc crystalline structure, which is uniformly dispersed with an average particles size of 2.9-4.0nm and zero valence metallic state. The catalysts and their activity and selectivity evaluated in liquid phase selective hydrogenation of citral in a semi-batch Parr reactor at 90°C and a hydrogen pressure of 10 MPa and solvent medium of a isopropanol during 6 hours. Amongst the studied catalysts, 1.5%Pt/TiO$_2$ reduced at 575°C had presented higher selectivity in terms of citral towards unsaturated alcohols (Geraniol and Nerol). This is the influence of strong metal supported interaction (SMSI effect) of supported catalysts reduced at 575°C and selectivity to activate C=O hydrogenation increased.

INTRODUCTION

Heterogeneous catalytic hydrogenation of α,β-unsaturated aldehydes to their corresponding alcohols is a process of major interest for the chemical industries, especially the fine chemical industries, such as for the production of pharmaceuticals, detergents, cosmetics, flavors and fragrances [1-5]. The reaction can lead to variety of products, the C=C double bond is hydrogenated to give a saturated aldehyde or the C=O double bond is involved, yielding an unsaturated alcohol and hydrogenation of both can occur resulting in a saturated alcohol and also formation of cyclisation. Due to the fact that the C=C bond presents a lower binding energy than the C=O bond, the formation of saturated aldehydes is thermodynamically favored, decreasing the selectivity to the unsaturated alcohol [6-12]. In the present work, selective hydrogenation of citral (3, 7–dimethyl-2, 6-octadineal) was studied, this molecule and its unsaturated alcohols being of considerable interest in the perfumery applications [13-14]. The hydrogenation reactions are generally catalyzed by transition metals of group VIII of the periodic table. However, the selectivity of these metals with relation to hydrogenation of C=O bond has shown itself specific for each metal in the order Ir > Pt > Ru > Rh [4]. Vast literature survey is available on the selective hydrogenation of α, β-unsaturated aldehydes catalyzed by different noble metals supported catalysts [15-17]. In addition catalytic hydrogenation of α, β-unsaturated aldehydes are mostly based on supported metals platinum, ruthenium, rhodium and palladium [18-30]. The selectivity towards unsaturated alcohols (geraniol and nerol) could also be increased by metal has deposited on reducible support as TiO$_2$, the hydrogenation of the C=O bond can be

promoted due to the presence of partially reduced species generated upon reduction at high temperature, that is strong metal-support interaction (SMSI effect) [31-34]. It has attracted much attention in noble metal supported on reduced oxides (with SMSI) shows important differences in the catalytic activity and selectivity of hydrogenation reaction when reduced at high temperature, compared with one reduced at lower temperature or the corresponding noble metal supported on un-reducible supports (without SMSI). Most of the studies of SMSI concentrated on titania supported noble metal catalyst.   In this work, we report the preparation of titania supported ruthenium and platinum catalysts by the impregnation method, being reduced in two different temperatures, 375ºC and 575ºC and characterised by BET surface area, TPR, XRD, HRSEM and XPS techniques and their catalytic activity for selective hydrogenation of citral towards unsaturated alcohols (geraniol and nerol).

Experimental

Catalyst preparation

The titanium oxide support (surface area = 52.5 m^2/g) was ground and then sieved to retain particles with sizes between 0.10 and 0.04 mm. After calcinations of the support in flowing air for 4 h at 600 °C, various metal loading 0.25, 0.5, 0.75, 1.0, 1.5, 2.0wt% Pt/TiO$_2$ and Ru/TiO$_2$ monometallic catalysts were prepared by impregnation method   using aqueous solution of RuCl$_3$ (Fluka, 99.8%) and H$_2$PtCl$_6$ (Aldrich, 99.9%) respectively. The formed precipitate filtered and washed with deionized water and dried in a vacuum freeze-dryer for 20 h. The samples were obtained in the

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tubular oven under the atmosphere of 20% H_2/80% N_2 at progressively elevated temperatures for 3 h (120°C). The oven dried samples were calcinad at 400°C for 4 h in air atmosphere, and reduced *in situ* at two different temperatures, 375°C and 575°C for 2 h to characterization for catalyst test.

H_2-Temperature programmed reduction (TPR)

TPR measurements were aimed to test the H_2 consumption during the reduction of Ru/TiO_2 and Pt/TiO_2 catalysts. The resulting powders were subsequently reduced by a mixing gas of 90% Ar/10% H2 at 40 ml min^{-1} and a temperature ramping rate of 10 °C min^{-1} from 25 to 600°C and then maintained at 500 °C. The amount of hydrogenation consumed by the catalyst samples in given temperature range μmol/g catalyst^{-1} was monitored by thermal conductivity detector (TCD) signal intensities.

BET surface area, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD)

The BET surface area measurements were made on a Micromeritics Gemini 2360 instrument by N_2 adsorption at liquid nitrogen temperature. Prior to measurements, samples were oven dried at 120 °C for 12 h and flushed with argon gas for 2 h. X-ray diffraction (XRD) patterns have been recorded on a Siemens D-5000 diffractometer, using Ni-filtered Cu K_α (0.15418 nm) radiation source range of 20-90° was employed to determine phase of the modified TiO_2 powders. Crystalline phases were identified with the help of ASTM Powder Data Files. X-ray photoelectron spectroscopy (XPS) was used to analyze the atomic surface concentration on each catalyst. The spectra were recorded on a Perkin-Elmer model 5300 X-ray Photoelectron Spectrometer using Mg Kα-1253.6eV as a radiation source at 300W. The spectra were recorded in the fixed analyser transmission mode with pass energies of 89.32 and 35.61 eV for recording survey high resolution spectra, respectively. All binding energies were referenced to the C 1s peak at 284.6 eV, which is invariably present on the film surface. The spectra were fitted by XPSPEAK with a linear background and to 80%Gausssian/20%Lorentzian peak shape. The structure of anatase TiO_2 demonstrated in the manuscript was constructed by the Ca.R.Ine version 3.1 crystallography program package.

High resolution transmission electron microscopy (HRTEM)

TEM studies were carried out on a JEOL-JEM 100 electron microscope. Samples for direct examination were prepared by suspending the powder in ethanol, and a drop of the suspension was allowed to dry on a copper grid coated with a carbon film. Extractive Replica was performed by ultrasonically dispersing the catalyst powder and depositing a drop of the suspension on freshly cleaved mica. After drying, the dispersed powder was covered by a carbon film. The mica was then plunged into a solution containing a mixture of water, acetone and hydrofluoric acid. The acid concentration was chosen in order to dissolve the support without dissolving the metal particles. They remained stuck to the carbon film, which was collected on a copper grid. The area distribution of particles was determined by counting a large number of particles on the TEM micrographs and by plotting $n_i d^2_i$ as a function of d_i (n_i is the number of particles with in different

intervals with a given average diameter d_i). The mean surface diameter of the particles is then given by $d = \sum n_i d^3_i / \sum n_i d^2_i$. High-resolution TEM (HRTEM) images were obtained by employing a JEOL-3010 device with 300 kV accelerating voltage.

Activity test

Citral (mixture of E and Z forms, Merck, 99 %) and isopropanol (Fluka, 99.5 %) are used as received. The liquid phase citral hydrogenation experiments were performed in a stirred semi-batch reactor (model 4574, Parr Instrument Co.). Before the reaction the catalysts were reduced *in situ* under hydrogen (gas purity, 99.995 %) flow (80-100 mL/min) for 2 h under 10MPa at 250 °C. Then, the reactor was cooled to reaction temperature. Reactant mixture (200 mL of 0.1 M citral in isopropanol) was injected into the bubbling unit to remove the dissolved oxygen before it was injected into the reactor and contacted with the catalysts. Citral hydrogenation reaction was performed at 90°C, 10MPa and at a stirring speed of 750 rpm. Preliminary runs carried out at different stirring rates, loading and catalysts grain size demonstrated the absence of internal and external transfer limitations under the selected conditions. Liquid samples were periodically withdrawn through sample tube extending inside the reactor and analyzed in a HP 4890 GC furnished with an HP 5 semi-capillary column of 15 m and 0.53 mm ID. The GC analysis was performed using a flame ionization detector, using helium gas as carrier and the column was kept at a constant temperature *i.e.* at 120 °C. Under these analytical conditions, the products peaks are identified by the use of mass spectroscopy-gas chromatography (GCMS QP2010 Plus). From the results obtained in these analyses, information such as the catalytic activity, selectivity of the reaction and conversion could be derived.

RESULTS AND DISCUSSION

Characterization of the monometallic catalysts of Ru/TiO_2 and Pt/TiO_2

The uptake of H_2 measured at room temperature is usually used to indicate the dispersion and/or exposed surface of the metal particles on the oxide support. The catalyst must be pre-treated in an atmosphere of hydrogen at elevated temperatures to initiate the hydrogenation activity of the supported metal catalyst. However, the H_2 uptake by the catalyst could be suppressed by increasing the pre-reduction temperature, due to the fact that the sintering of the metal or the migration of the partially reduced oxide onto the metal depended on the nature of the support. Fig.1 shows H_2 uptake profiles as the reduction temperature profiles of 1.5%Ru/TiO_2 and 1.5% Pt/TiO_2 catalysts. Between 25 and 300°C, no reduction peak was observed on the TiO_2 sample. It must be reminded that the reduction of bulk oxygen of TiO_2 has been reported to occur at more than 500°C [35-36]. For 1.5%Ru/TiO_2 catalyst the main H_2 uptake is located at 95°C, followed by broader and smaller peak from 220 to 450°C. 1.5%Pt/TiO_2 sample showed two H_2- consumption peaks with a maximum at 94°C and second peak occurred at 360°C. The H_2- consumption peak at around 95°C was associated tothe reduction of PtOx crystallites to metallic Pt, and the peak at around 320°C could

be attributed to the reduction of the surface capping oxygen of TiO_2 [37-39].

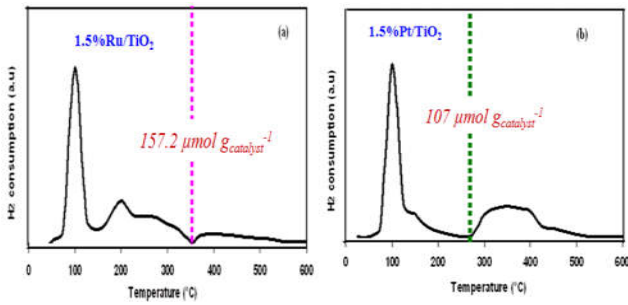activate component until the monolayer coverage of impregnated components is completed. The synthesized monometallic catalysts were subjected to TEM analysis for the measurement of the size of the particles formed and level of dispersion. The micrographs show that the particles were well dispersed and the average particles size calculated was in nm range and the data are shown in Table 1. TEM image of $1.5\%Ru/TiO_2$ reduced at LTR and HTR are given in Fig.2. The Fig.2 seems to catalyst reduced at LTR has smaller particle size than catalyst reduced at HTR. TEM image of $1.5\%Pt/TiO_2$ catalyst is shown in Fig.3. It seems that the catalyst reduced at LTR have an average particle size is low (2.8 nm) compared to HTR (3.4 nm).
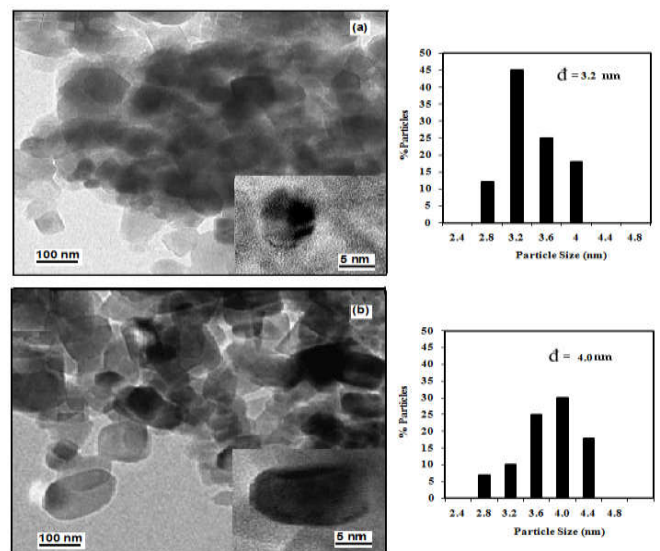
Table 1. Structural property of the synthesized catalysts

Catalysts	Reduced Temp.°C	BET (m²/g)	XRD (A°)		BE (eV)		Average particle size (nm)
			Ti(110)	Ru(101)/ or Pt(111)	O 1s Ru/Pt	Ru3d$_{5/2,3/2}$ or Pt4f$_{7/2, 5/2}$	
TiO_2	375	52.5	25.6	52..5	529.83;531.63		-
	575	48..1	25.4	48.0	529.80;531.60		-
0.25%Ru/TiO₂	375	54.3	25.5	43.8	-	-	-
	575	51.4	25.5	43.8	-	-	-
0.5%Ru/ TiO₂	375	55.2	25.3	43.9	529.81;531.52	280.6;284.8	2.9
	575	52.5	25.4	43.9	529.72;531.50	280.5,284.8	3.2
0.75%Ru/TiO₂	375	56.1	25.5	43.8	-	-	3.1
	575	53.2	25.5	43.9	-	-	3.5
1.0%Ru/TiO₂	375	57.4	25.3	43.8	-	-	3.2
	575	54.3	25.4	43.9	-	-	4
1.5%Ru/TiO₂	375	58.3	25.5	43.8	529.70;531.48	280.6,284.8	3.2
	575	55.2	25.5	43.8	529.70;531.46	280.5,284.8	4.0
2.0%Ru/TiO₂	375	59.2	25.5	43.9	-	-	3.4
	575	55.8	25.5	43.8	-	-	3.9
0.25%Pt/TiO₂	375	52.4	25.4	39.9	-	-	-
	575	51.9	25.5	40	-	-	-
0.5%Pt/TiO₂	375	53.2	25.5	40	529.88;531.63	70.0, 74.3	2
	575	52.8	25.4	38.8	529.86;531.62	70.1, 74.3	2.9
0.75%Pt/TiO₂	375	54.6	25.5	40.1	-	-	2.5
	575	53.7	25.4	40.2	-	-	2.9
1.0%Pt/TiO₂	375	55.4	25.5	39.9	-	-	2.5
	575	54.2	25.5	40	-	-	2.9
1.5%Pt/TiO₂	375	56.8	25.3	40.1	529.87;531.61	70.0, 74.3	2.8
	575	55.2	25.5	40.1	529.85;531.59	70.1, 74.3	3.4
2.0%Pt/TiO₂	375	57.2	25.6	40	-	-	2.6
	575	55.1	25.5	40.1	-	-	2.9

Thus the consumption obtained at higher temperature for our samples can be attributed to the partial reduction of TiO_2 support that is SMSI effect which includes TiO_{2-x} species (x-2). Indeed, the total H_2 uptake is deduced from TRP profiles of 157.2 µmol g catalyst^{-1} for $1.5\%Ru/TiO_2$ and 107 µmol g catalyst^{-1} for 1.5% Pt/TiO_2. Ru and Pt atoms are reduced before the support; the index temperature would then correspond to the beginning of the partial reduction of TiO_2. The BET surface area of the TiO_2 anatase sample obtained by nitrogen physisorption at -198°C was found to be 50 m² g^{-1}. In order to simulate the doping process for the loading of the Ru and Pt series, we exposed the titania on water followed by reduced at 375 and 575°C for 4 h, the surface area dropped to 48 m² g^{-1}. The crystalinity, particle size and surface are of various amounts of Ru/or Pt loading TiO_2 supported catalysts reduced at 375 and 575°C are shown in Table 1. In the case of Ru/or Pt loading TiO_2 anatase catalysts, a consistently decreasing trend with increasing Ru and Pt loading are noted in the series of the samples. In general the surface area of the catalyst material decreasing with increases quantity of the

Fig. 2. TEM images and metal particle size distributions of 1.5%Ru/TiO₂ catalyst reduced at (a) 375°C, (b) 575°C
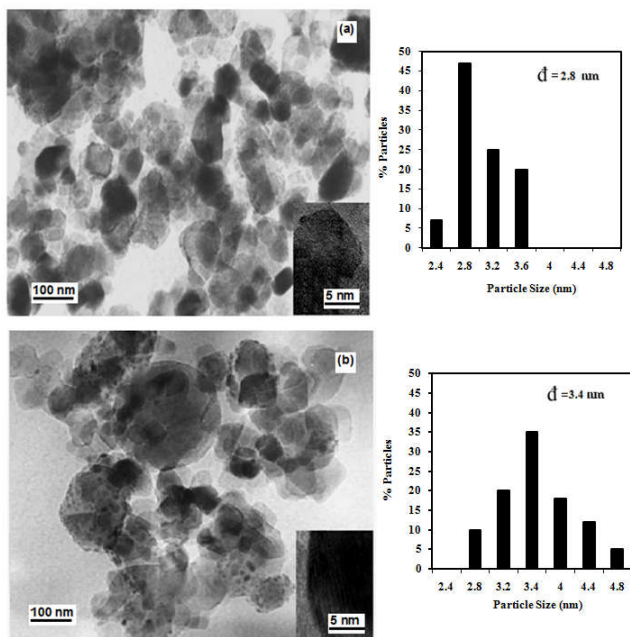
Fig. 3. TEM images and metal particle size distributions of 1.5%Pt/TiO$_2$ catalyst reduced at (a) 375°C, (b) 575°C

The crystalline of the synthesized samples were characterized by X-ray diffraction (XRD). Fig. 4 and 5 shows the XRD patterns for the different loading of Ru/TiO$_2$ and Pt/TiO$_2$ catalysts. The peaks at 25.5, 53.8, 58, 71.1 and 75.2° correspond to the facets of anatase TiO$_2$ [40]. The Fig.5 shows, Pt diffraction peaks are assigned to (111), (200), (220) and (311) planes, indicating a face-centered cubic (fcc) lattice structure characteristic of the Pt crystal [39]. The Fig.4 shows, Ru diffraction peaks at 38.2, 42.3, 43.8, 58.1 69.2 and 79.4 are assigned to (100), (002), (101), (102), (110), and (103) planes. The XRD patterns also indicated that the intensity of the peaks of Ru/Pt reflection of metal particles increased as the metal loading was increased, the reduction temperatures increases from 375 to 575°C, the diffraction peaks of Ru and Pt become very sharper [41,42].
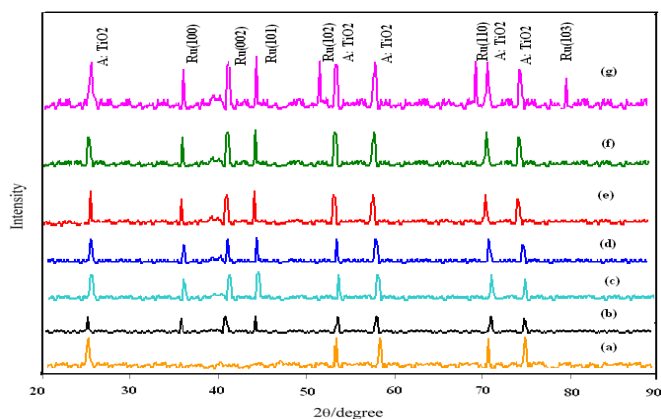

Fig. 4. X-ray diffraction of various metals loading of Ru/TiO$_2$ catalysts (a) TiO$_2$, (b) 0.25% Ru/TiO$_2$, (c) 0.5%Ru/TiO$_2$, (d) 0.75%Ru/TiO$_2$, (e) 1.0%Ru/TiO$_2$, (f) 1.5% Ru/TiO$_2$ (g) 2.0%Ru/TiO$_2$

XPS analysis was conducted to determine the chemical and electronic structure of Ru/TiO$_2$ and Pt/TiO$_2$ catalysts. The XPS spectra studied for O1s within TiO$_2$, Ru3d and Pt4f core level region. This spectra of O1s with in TiO$_2$ can be

principally assigned to the crystal lattice of oxygen (Ti^{4+}-O) and surface adsorbed OH (Ti-OH) with binding energies of 529.81 and 531.64 eV respectively [43]. The Fig.6 show the deconvoluted O1s bands of Pt/TiO$_2$ and Ru/TiO$_2$, respectively, which indicate the presence of Ti^{4+}O (529.81) and Ti-OH (531.69). The concentration of Ti-OH increases after the modification by Pt and Ru doping, suggesting the doped TiO$_2$ enhance the formation of OH•. Regarding the Ti species for Ru/TiO$_2$ and Pt/TiO$_2$, curve fitting indicated the presence of Ti^{3+} in addition to the dominant Ti^{4+} peak. This evidenced the existence of reduced states (Ti^{3+}) with the line position at 457.5 eV, while the bonding energy of Ti^{4+} is located at 459 eV.
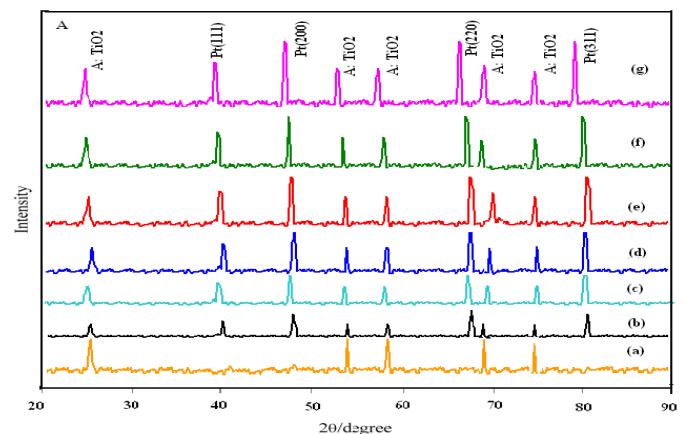

Fig. 5. X-ray diffraction of various metals loading of Pt/TiO$_2$ catalysts (a) TiO$_2$, (b) 0.25% Pt/TiO$_2$, (c) 0.5%Pt/TiO$_2$, (d) 0.75%Pt/TiO$_2$, (e) 1.0%Pt/TiO$_2$, (f) 1.5% Pt/TiO$_2$ (g) 2.0%Pt/TiO
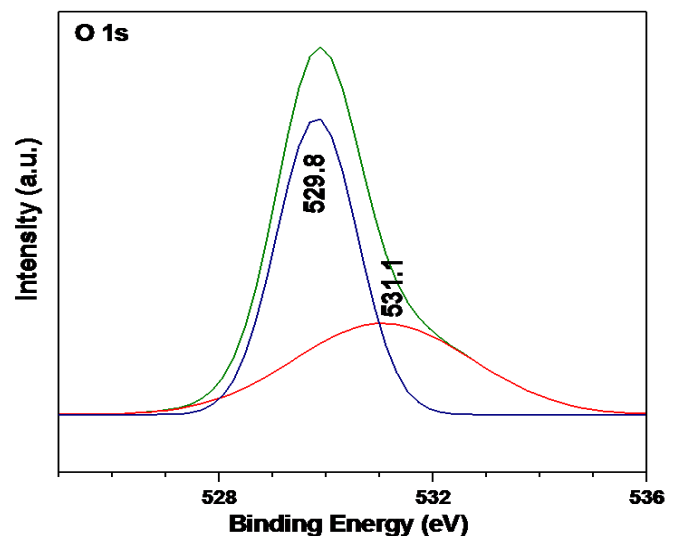

Fig .6. The XPS of spectra of (a) 1.5% Ru/TiO$_2$, (b) 1.5%Pt/TiO$_2$ for O 1s region

The formation of Ti^{3+} implies that the interaction between Ru/Pt species and TiO$_2$ matrix occurred during the reduction reaction [44]. The Pt (II) chlorinated species after reduction at 375°C, while Pt^0 was dominant in the case of samples reduced at 575°C. Fig. 7 peak binding energies of Pt 4f$_{7/2}$ at 71.29 eV and 4f$_{5/2}$ at 74.52 eV, suggest that the Pt particles are present in the zerovalent state. This indicates that the successive reduction from Pt^{2+} to Pt^0 needs to be driven at 575°C. The Ru3d spectrum has been obscured by the C 1s (284.5 eV) spectrum, but the deconvoluted spectrum shows a doublet with

peak binding energies of 279.77 eV $(3d_{5/2})$ and 284.12 eV $(3d_{3/2})$, it was difficult to resolve the small Ru peak out from the large peak of C 1s. The Ru3d spectra revealed the presence of two different chemical states on the surface (Ru^0 at 281.0 eV and Ru^{4+} at 283.3 eV) except Ru species on titania shows chemical state of Ru^0 species in Fig.8. According Balaraju et al. to the B.E value of Ru^0 species was in the range 280- 281 eV. The presence of Ru^{4+} species indicated that the Ru exists as oxide form and this species might be formed during reduction temperature at 575°C. In addition, the peak shift was observed in the cases of Ru/TiO_2 and Pt/TiO_2, which can be ascribed to either diameter change of Ru/Pt particles size or transfer from the partial reduced TiO_x Ru/Pt particles (i.e. SMSI effect) [45-47].

The strong metal-support interaction (SMSI) effect, a phenomenon widely studied for more than 30 years, is characterized by a strong change in the physical and chemical properties of metal particles dispersed over reducible oxides. The more important signature of the SMSI effect is the almost complete inhibition of hydrogen chemisorption capacity, with modifications of the catalytic performance of the metal/oxide system. Evidence of the structural changes brought by SMSI has been obtained by high resolution electron microscopy imaging, which shows decoration of the metal particles with oxide moieties of the support after reduction in hydrogen at high temperature. Particularly, in titania supported systems, it has been well established how upon high temperature reduction in hydrogen (575 °C).
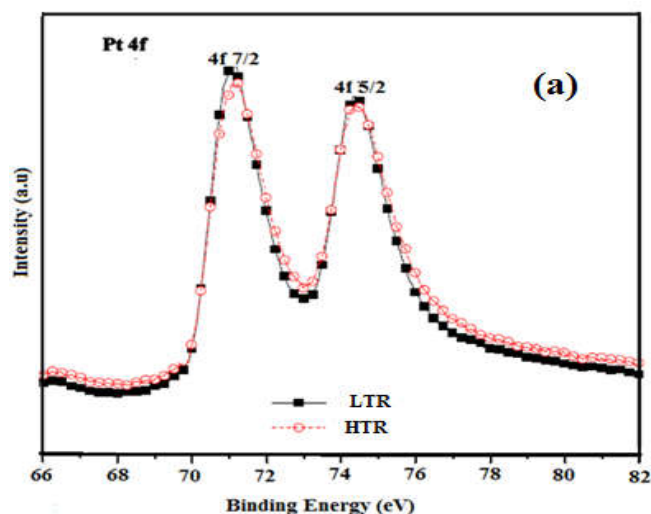

Fig.7. XPS spectra of 1.5%Pt/TiO2 for Pt 4f core level region

oxide moieties from the support migrate over the metallic particles, blocking the surface and modifying its adsorption and catalytic properties [48]. It has also been stated that modifications of the electronic properties of the metal particles occur before the migration of support can be detected. This is the case for supports such as TiO_2, where the electronic effects related with SMSI are already important after reduction in hydrogen at 575°C, even though decoration of metallic particles is only detected by TEM.

Selective hydrogenation of citral over of Pt/TiO₂ and Ru/TiO₂ catalysts

The reaction network, hydrogenation starting from citral is shown in Scheme 1. The geraniol and nerol (G&N) isomers

are obtained by selectively hydrogenating the citral C=O functional group, while citronellal (CNA) is obtained by the selective hydrogenation of the conjugated C=C bond. In turn, citronellol (CNO) can be obtained by the selective hydrogenation of the citronellal C=O group or from the C=C bond of geraniol and nerol. The hydrogenation of the isolated C=C bond is not desirable since compounds such as 3,7-dimethyloctanal and 3,7-dimethyloctanol (DMO) give an unpleasant odour to the geraniol and nerol, ctironellal and citronellol mixtures. Beside these reactions, processes of cylization or of reaction with the solvent (isopropyl alcohol) can lead to other by products likes isopulegol (ISOP) or acetals formation respectively.
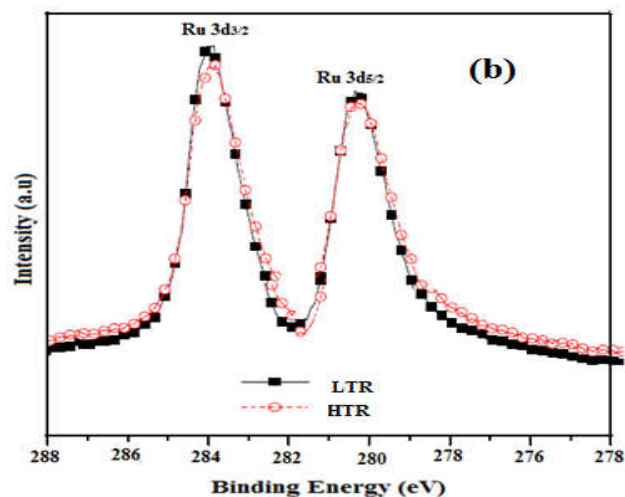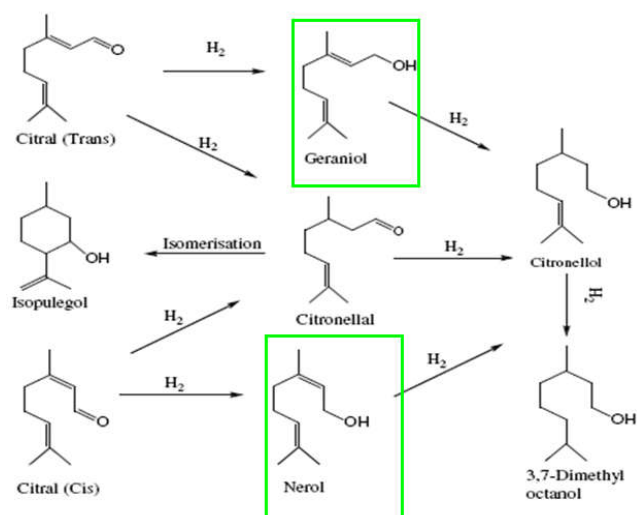

Fig. 8. XPS spectra of 1.5%Ru/TiO2 for Ru 3d core level region

Scheme 1. Reaction network of citral hydrogenation

Influence of the reduction temperature of monometallic Ru/TiO₂ catalysts

The fig.9 shows, the citral conversion as function of time for various metal loading of Ru/TiO_2 catalysts reduced at 375°C (LTR) and 575°C (HTR). For both the series of HTR and LTR catalysts, whatever be the reduction temperature, citral is converted within 330 minutes reaction time. The catalysts reduced at HTR show lower actives than their counterparts reduced at LTR. This phenomenon is explained by the presence of partially reduced support species ($TiO_{(2-x)}$ ($x < 2$))

generated after reduction at high temperature, which can cover part of the metallic surface. In addition of the selectivity of product is shown in fig.10. For 1.5% Ru/TiO_2 catalyst, citronellal and citronellol are formed in larger extend after reduction at 575°C to that of isopulegol. This phenomenon can be explained by an evaluation of the metal particle size, the average particle diameters of HTR has higher (4.0 nm) than LTR (3.2nm). The drop of isopulegol formation after reduction at high temperature can be explained by the removal of chloride ions that means the elimination of acid sites on the catalyst surface. The monometallic catalysts of 1.5%Ru/TiO_2, the SMSI is slightly beneficial on the unsaturated alcohols formation. Nevertheless, once the citral conversion reaches 100%, the unsaturated alcohols keep being hydrogenated. Thus, the presence of $TiO_{(2-x)}$ species does not poison unsaturated carbon hydrogenation sites, but modifies the unsaturated carbon/carbonyl group adsorption competition by enhancing the activation of the oxygen electronic doublet of the carbonyl group.
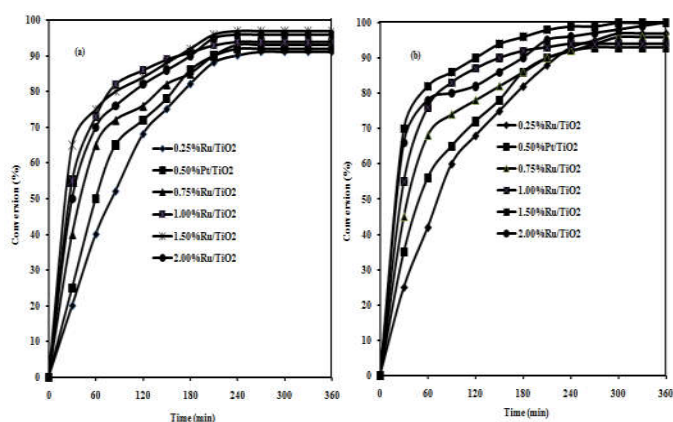

Fig. 9. Conversion of Various loading of metal in Ru/TiO_2 catalysts reduced at (a) 375°C (LTR), (b) 575°C (HTR).
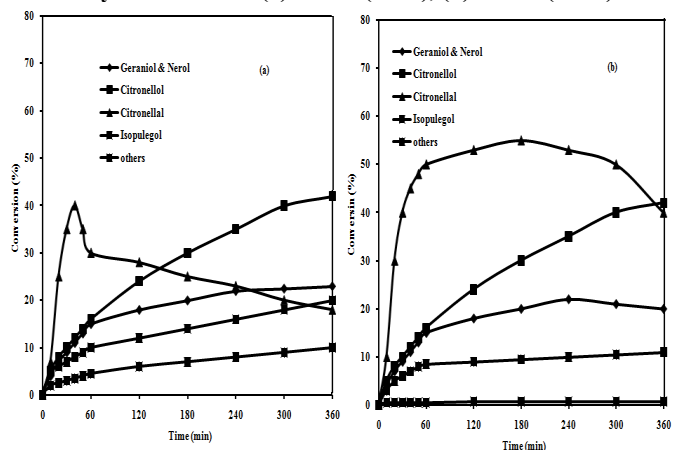

Fig. 10. Product distribution as function of time for the hydrogenation of citral over 1.5% Ru/TiO2 catalysts reduced at (a) 375°C (LTR), 575°C (HTR)

Influence of the reduction temperature of monometallic Pt/TiO₂ catalyst

The Fig.11 shows, citral conversion as a function of time for various metal loading of Pt/TiO_2 catalysts reduced at two different temperatures 375°C (LTR) and 575°C (HTR). For both of HTR and LTR catalysts, whatever be the reduction temperature, citral is converted within 330 minutes reaction time. As observed for Ru/TiO_2 catalysts, the sample reduced at

375°C is more active than the one reduced at 575°C, but both are rapidly deactivated. The deactivation process is independent of the nature of metal. The graphs reported in fig.12 indicate that the increase of reduction temperature from 375°C to 575°C allows one to double the amount of unsaturated alcohols, while this phenomenon is not observed by using a support as silica and alumina. The opposite behaviour is observed for the hydrogenation of the conjugated
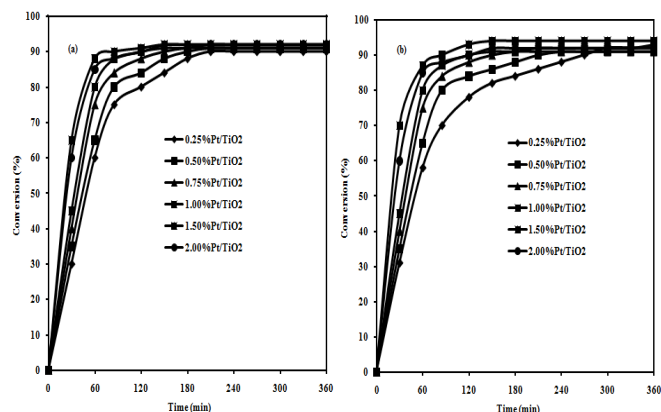

Fig. 11. Conversion of Various loading of metal in Pt/TiO_2 catalysts reduced at (a) 375°C (LTR), (b) 575°C (HTR)
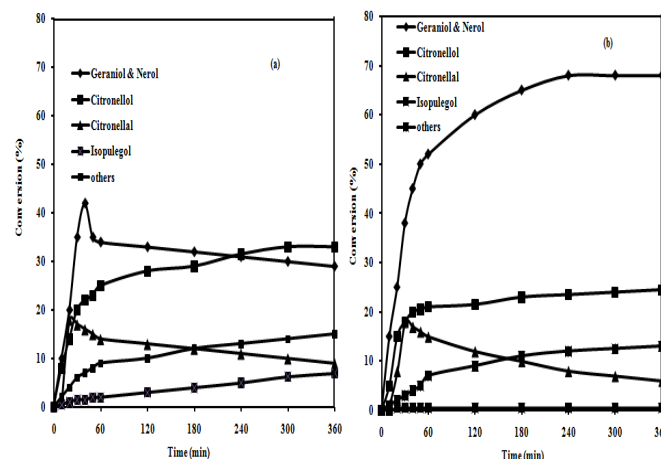

Fig. 12. Product distribution as function of time for the hydrogenation of citral over 1.5% Pt/TiO2 catalysts reduced at (a) 375°C (LTR), 575°C (HTR)

unsaturated carbon leading to citronellal. For the reduction temperatures, citronellal decreases while citronellol increases as a function of time, indicating the hydrogenation of the carbonyl function of citronellal. However, isopulegol is obtained at LTR, whereas reducing the catalysts at HTR leads almost its disappearance. This phenomenon was observed in recent reports on Ru/TiO_2 catalyst and explained by the decrease in acidity after high temperature reduction (575°C). Nevertheless, it should be noticed that isopulegol formation is rather limited on the Pt/TiO_2 catalysts reduction at 300°C compared to the Ru/TiO_2 sample prepared and activated in the same conditions. TEM analysis revealed small (2.8–4.0 nm) well-dispersed particles of Ru and Pt on the support. TPR experiments highlighted the partial reduction of TiO_2 species above 375°C as reduction temperature. Selective hydrogenation of citral was performed at 90°C on all samples and under 10MPa hydrogen pressure. When Ru and Pt salts are impregnated in HCl medium, reducing the resulting catalysts at LTR (375°C) leads mainly to citral cyclization

towards isopulegol, due to the presence of acidic sites induced by chloride species. A reduction of these catalysts at HTR (575°C) allows one to decrease chlorine content and consequently isopulegol formation. For all catalysts, the presence of $TiO_{(2-x)}$ moieties (x < 2) on the Ru and Pt active surface after reduction at 575°C involves a slight decrease of the citral conversion. Nevertheless, the SMSI effect promotes the formation of unsaturated alcohols (intended products), this effect being more pronounced with Pt/TiO2 catalyst. The $TiO_{(2-x)}$ species are responsible for the activation of the C=O group of citral according to the Scheme 2 in this reaction.
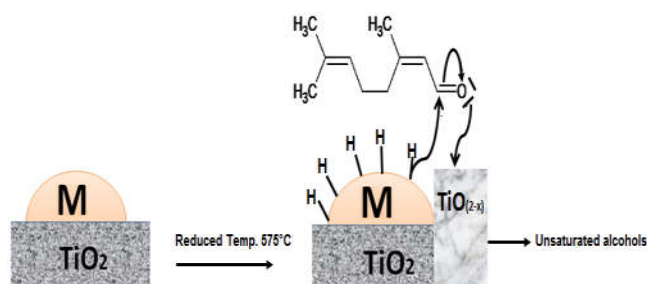
Scheme 2. Schematic evolution of the adsorption mode of citral on M/TiO2 catalyst reduced at 575°C (HTR); (◯) support in a partially reduced state $TiO_{(2-x)}$ (x<2)

The conversion and selectivity results obtained on various catalysts are shown in fig.13. As can be noted from this figure, the 1.5% Ru/TiO_2 shows 96% and 98% conversions respectively in LTR and HTR but selectivity of unsaturated alcohol (geraniol and nerol) 20% for LTR and 23% for HTR. Fig.13b shows recycling In the case of 1.5% Pt/TiO_2 catalysts 68% selectivity of HTR due to SMSI effect.
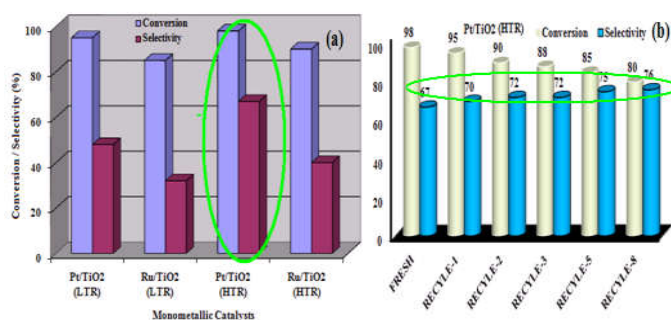
Fig. 13. (a) Conversion and selectivity of 1.5% Ru/TiO_2 and 1.5% Pt/TiO_2 catalysts reduced at 375°C (LTR) and 575°C (HTR) for selective hydrogenation of unsaturated alcohols (b) Recyling of 15% pt/TiO_2 (HTR)

Conclusions

Monometallic catalysis of Ru and Pt supported on titania(IV) oxide were prepared by impregnation and reduced either at 375°C or at 575°C (high temperature required to generate SMSI effect). The catalysts have been characterized by physisorption and chemisorptions. TEM micrograph and XRD study of these catalysts proven that the particles are well dispersed, XPS analysis revealed that the catalysts contained mostly zerovalent Pt and Ru, with a little Pt(II), Pt(IV) and Ru (IV). The C=O bonds are hydrogenated rather the thermodynamically favourable C=C bond on supported metal systems. This is attributed to the influence of the SMSI state in these supported metal catalysts. With the metal oxide

decoration of the Pt particles by titania suboxides (SMSI state) after high temperature reduction (575°C), the presence of coordinative unsaturated Ti cations strengthens the interaction of the catalyst with the C=O bond of citral and enhances the selectivity for C=O bond hydrogenation. Among these catalysts 95% of conversion and 68% of selectivity of unsaturated alcohols (geraniol and nerol) is obtained in 1.5%Pt/TiO_2 reduced higher temperature. It can be used for more than 12 recyles.

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