

## TiO<sub>2</sub> Supported Pt Based Bimetallic Nanocatalysts for Selective Hydrogenation of Citral<sup>†</sup>

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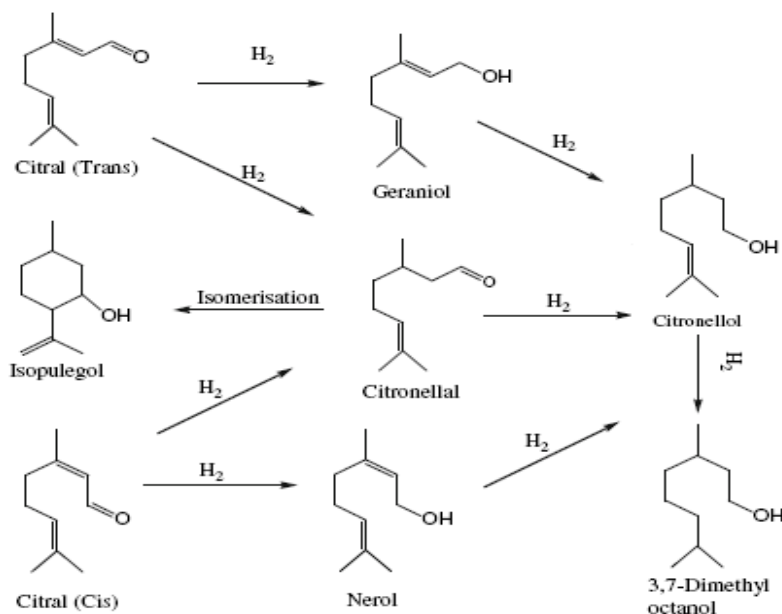
**Abstract:** TiO<sub>2</sub> supported Pt based bimetallic nanocatalysts were prepared by impregnation method and reduced at two different temperatures, 375 °C and 575 °C for the selective hydrogenation of citral to the corresponding unsaturated alcohols namely; geraniol (GOL) and nerol (NOL). The catalysts were characterized by BET surface area measurement, FT-IR, SEM, EDAX, TEM, XRD and XPS. The prepared nanocatalysts are uniformly dispersed with an average particles size 50-100 nm and zero valence metallic state. The SMSI (Strong Metal-Support Interaction) effect shows that the catalysts reduced at higher temperature leads to an increase in selectivity toward unsaturated alcohols (GOL & NOL) for Pt-Ru/TiO<sub>2</sub> compared to Pt-Pd/TiO<sub>2</sub> and Pt-Au/TiO<sub>2</sub> nanocatalysts. In addition a second metal (Ru) also leads to an increase of the GOL & NOL selectivity during the citral hydrogenation. The generated partially oxidized second metal species due to the difference in electronegativity, strongly binds the C=O group and also paves the way for the selective activation of the C=O bond. Metal support interaction and promoter active metal interaction increased the unsaturated alcohol formation.

**Keywords:** Bimetallic nanocatalysts, TiO<sub>2</sub> supported, SMSI effect, Thermal reduction, Citral hydrogenation, Unsaturated alcohols

## Introduction

Selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to their corresponding alcohols is major process of chemical industries, especially in the fine chemical industries<sup>1-3</sup>, such as for the production of pharmaceuticals, detergents, cosmetics, flavors and fragrances<sup>4,5</sup>. 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 cyclization. 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<sup>6-10</sup>. In the present work, selective hydrogenation of citral (Scheme 1) was studied<sup>11,12</sup>. Citral and its related unsaturated alcohols have considerable interest in the perfumery industries<sup>13-14</sup>.

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**Scheme 1.** Reaction path way of citral hydrogenation

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  $\alpha, \beta$ -unsaturated aldehydes catalyzed by different noble metals supported catalysts<sup>15-17</sup>. In addition catalytic hydrogenation of  $\alpha, \beta$ -unsaturated aldehydes are mostly based on supported metals platinum based bimetallic catalysts<sup>18-30</sup>. 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)<sup>31-34</sup> and also addition of second metals at the same phenomena. It has attracted much attention in noble metal supported on reduced oxides (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 bimetallic nanocatalyst by the impregnation method, being reduced in two different temperatures, 375 °C and 575 °C and characterised by BET surface area, FT-IR, XRD, SEM with EDAX, TEM and XPS techniques and their catalytic activity for selective hydrogenation of citral towards unsaturated alcohols (geraniol and nerol).

## Experimental

The metal precursors  $H_2PtCl_6 \cdot 6H_2O$  (0.1992 g in 10 mL water) and  $PdCl_2$  (0.1250 g in 10 mL water), the both solutions were mixed together with stirring. The  $TiO_2$  (9.85 g) in 50 mL water) dispersion was added to this solution with vigorous stirring and the resulting

suspension was aged at 80 °C for 24 h with stirring. An aqueous solution of NaBH<sub>4</sub> (0.4116 g in 10 mL water) was added drop wise into this suspension with vigorous stirring. The NaBH<sub>4</sub> aqueous solution was prepared in an ice bath and molar ratio of NaBH<sub>4</sub>: (Pt and Pd) are 10:1. The prepared nanocatalysts denoted as Pt-Pd/TiO<sub>2</sub>375 and Pt-Pd/TiO<sub>2</sub>575. The above produce is used to synthesis Pt-Ru and Pt-Au nanocatalysts instead of using Pt-Pd.

#### *BET surface area and X-ray diffraction (XRD)*

The BET surface area measurements were made on a Micromeritics Gemini 2360 instrument by N<sub>2</sub> adsorption at liquid nitrogen temperature. Prior to measurements, samples were oven dried at 393 K 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<sub>α</sub> (0.15418 nm) radiation source range of 20-90° was employed to determine phase of the modified TiO<sub>2</sub> powers. Crystalline phases were identified with the help of ASTM Powder Data Files.

#### *Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM)*

The SEM analyses were carried out with a Jeol JSM 5410 microscope, operating with an accelerating voltage of 15 kV. Micrographs were taken after coating by gold sputtering. Elemental analysis was carried out on a KeveX, Sigma KS3 Energy dispersive X-ray (EDX) instrument operating at a detector resolution of 136 eV. 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. TEM (HRTEM) images were obtained by employing a JEOL-3010 device with 300 kV accelerating voltage.

#### *X-ray photoelectron spectroscopy (XPS)*

X-ray photoelectron spectroscopic (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 K<sub>α</sub>-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<sub>2</sub> demonstrated in the manuscript was constructed by the Ca.R.Ine version 3.1 crystallography program package.

#### *Activity test*

Citral (mixture of E and Z forms, Merck, 99%) and isopropanol (Fluka, 99.5%) were 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 523 K. 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, 10 MPa 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.

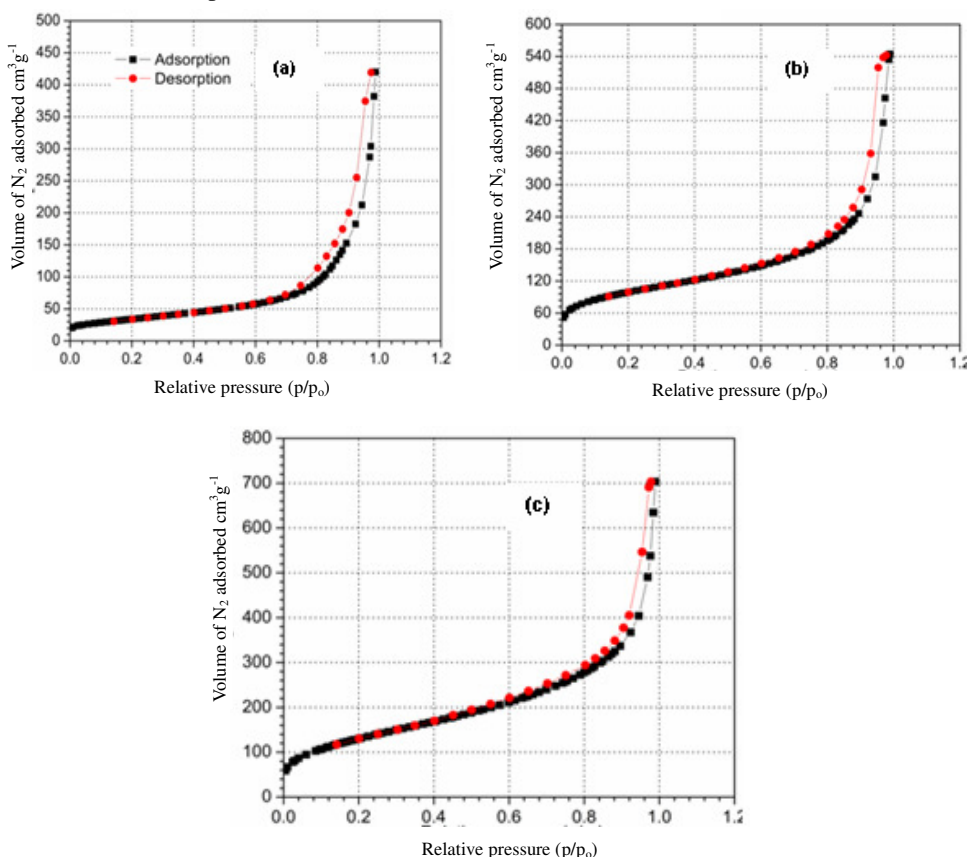
## Results and Discussion

### Physicochemical characterization

#### Surface area measurement

Figure 1 shows  $N_2$  adsorption-desorption isotherm of that Pt-Pd/TiO<sub>2</sub>, Pt-Ru/TiO<sub>2</sub> and Pt-Au/TiO<sub>2</sub> nanocatalysts. According to IUPAC nomenclature, all the isotherms are type IV classification isotherm<sup>35</sup>. A sharp adsorption and desorption steps followed by a plateau at high  $P/P_0$ , which is characteristic of capillary condensation and evaporation in the pores, are clearly observed<sup>36</sup>. While a hysteresis loop close to H<sub>1</sub>-type is observed for the TiO<sub>2</sub> support. The hysteresis loop is changing with the noble metals incorporation. Then, evolution from H<sub>1</sub>-type to H<sub>2</sub>-type is observed (Figure 1). The absence of any sharp rise in the nitrogen uptake as  $P/P_0$  close to 1 also tends to conclude on a homogeneous pore size repartition, without large pores in the support<sup>37,38</sup>.

In addition, pore size ( $D_p$ ) and pore volume ( $V_p$ ) (Table 1) are decreased with the increase in reduction temperature of the prepared nanocatalysts. Further, the nanocatalyst exhibit decrease in surface area at higher temperature reduction than at lower temperature. The decrease of the pore volume is more marked as shown in Table 1.



**Figure 1.**  $N_2$  adsorption/desorption isotherm of bimetallic catalyst of (a) Pt-Pd/TiO<sub>2</sub> (b) Pt-Ru/TiO<sub>2</sub> and (c) Pt-Au/TiO<sub>2</sub> bimetallic catalyst

**Table 1.** N<sub>2</sub> adsorption-desorption measurements for TiO<sub>2</sub> supported bimetallic (Pt-Pd,Pt-Ru and Pt-Au) nanocatalysts

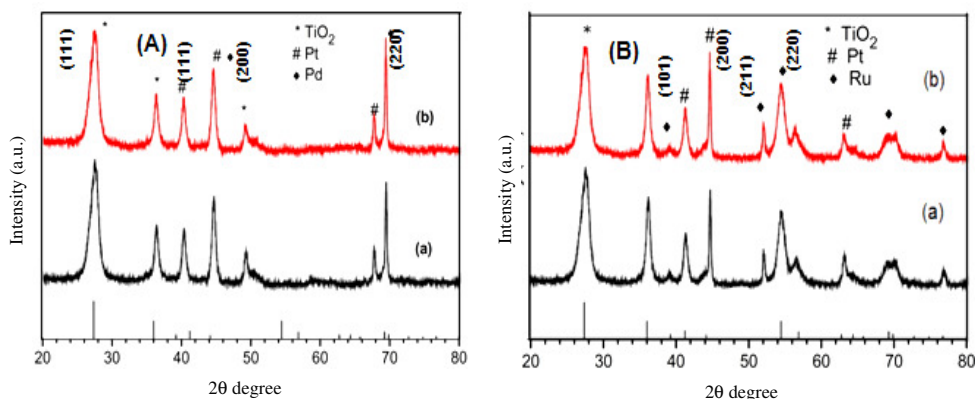
Nanocatalysts	Metal loading, mol % <sup>a</sup>				$S_{BET}$ , m <sup>2</sup> /g <sup>b</sup>	$D_{pore}$ , nm <sup>c</sup>	$V_{Pore}$ , cm <sup>3</sup> /g <sup>d</sup>
	Pt	Pd	Ru	Au			
Pt-Pd/TiO <sub>2</sub> 375	0.8	0.7	-	-	46	18.1	0.27
Pt-Pd/TiO <sub>2</sub> 575	0.9	0.6	-	-	44	20.3	0.22
Pt-Ru/TiO <sub>2</sub> 375	0.8	-	0.7	-	49	17.4	0.21
Pt-Ru/TiO <sub>2</sub> 575	0.7	-	0.8	-	45	21.2	0.15
Pt-Au/TiO <sub>2</sub> 375	0.8	-	-	0.7	58	18.2	0.18
Pt-Au/TiO <sub>2</sub> 575	0.9	-	-	0.7	53	19.8	0.17

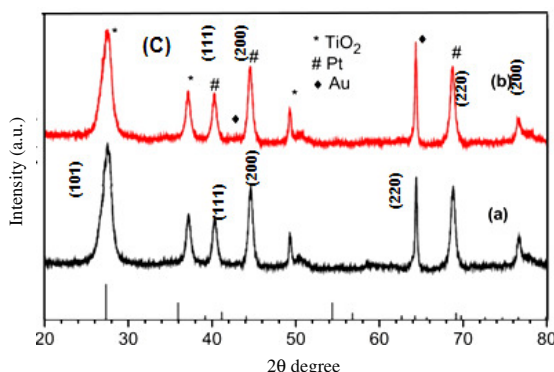
<sup>a</sup>ICP method, <sup>b</sup>Specific surface area deduced from the isothermal analysis at liquid nitrogen temperature in the relative pressure range from 0.05 to 1.00. <sup>c</sup>Total pore volume. <sup>d</sup>Pore diameter calculated using BJH method

### XRD analysis

Powder XRD pattern of Pt-Pd/TiO<sub>2</sub>375 and Pt-Pd/TiO<sub>2</sub>575 nanocatalysts are given in Figure 2A, which exhibit diffraction peaks at 25.5°, 37.7° and 48.2° that are consistent with the (101), (004) and (200) is characteristic planes (JCPDS no.: 84-1286) of anatase TiO<sub>2</sub> [39,40] also exhibit other peaks at 39.9°, 46.3° and 67.45° with corresponding planes of (111), (200) and (220) is characteristic of Pt (JCPDS 04-802) and the peaks at 40.1°, 46.7° and 68.1° with corresponding planes of (111), (200) and (220) of Pd (JCPDS 05-0681) face centered phase.

Powder XRD pattern of Pt-Ru/TiO<sub>2</sub>375 and Pt-Ru/TiO<sub>2</sub>575 nanocatalysts are given in Figure 2B. In Figure 2B the diffraction peaks at 38.3°, 42.2°, 44.0°, 58.3°, 69.5° and 78.4° with corresponding to (100), (002), (101), (102), (110) planes is due to (JCPDS 06-0663) of hexagonal Ru. Furthermore, the diffraction peaks corresponding to Pt and TiO<sub>2</sub>. Figure 2C shows that the powder XRD pattern of Pt-Au/TiO<sub>2</sub>375 and Pt-Au/TiO<sub>2</sub>575 nanocatalysts. The diffraction peaks 38.1°, 44.4°, 64.3° and 77.5° corresponding to (111), (200), (220), (311) and (112) planes are due to fcc phase (JCPDS card no. 06-0663) of Au. Further, the diffraction peaks corresponding Pt and TiO<sub>2</sub> is also found in Figure 2C.

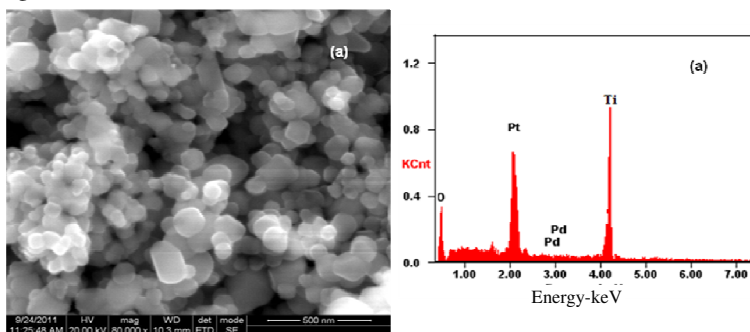




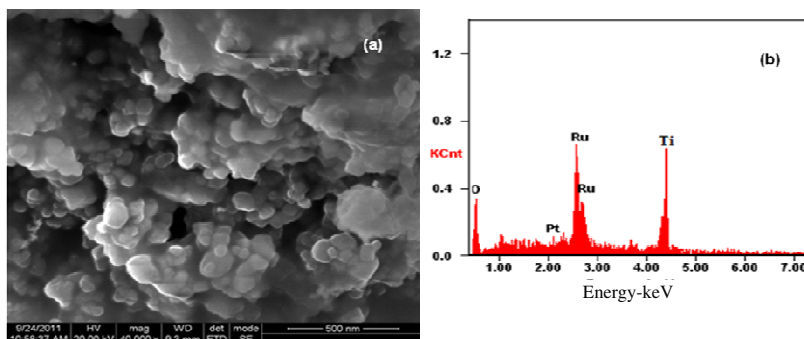
**Figure 2.** XRD pattern of (A) Pt-Pd/TiO<sub>2</sub>, (B) Pt-Ru/TiO<sub>2</sub> and (C) Pd-Au/TiO<sub>2</sub> Nanocatalysts thermally reduced (a) 375 °C and (b) 575 °C

### Scanning electron microscopy

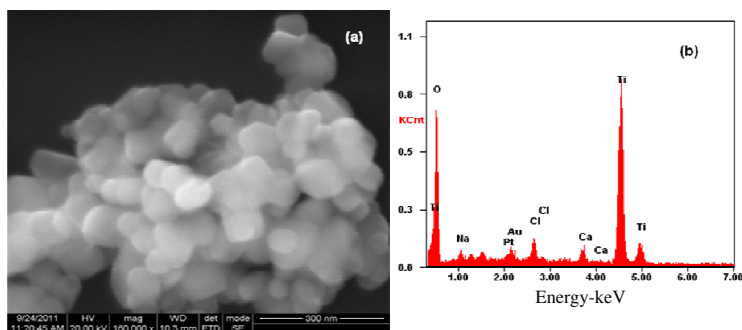
The morphology of the synthesized nanocatalysts was investigated using SEM analysis. SEM images and the corresponding EDAX spectra of Pt-Pd/TiO<sub>2</sub>, Pt-Ru/TiO<sub>2</sub> and Pt-Au/TiO<sub>2</sub>, reduced at 575 °C are given in Figure 3 to 5 respectively. The micrographs show that the particles were spherical-like irregular particles with the average diameter is in nm range. For the nanocatalysts, reduced at higher temperature relatively larger particles are observed due to agglomeration at sintering process. The EDAX spectrum shows the presence of Pt, Pd, Au and Ru along with Ti and O.



**Figure 3.** (a) SEM image of Pt-Pd/TiO<sub>2</sub>/575 (b) EDAX spectrum of Pt-Pd/TiO<sub>2</sub>/575



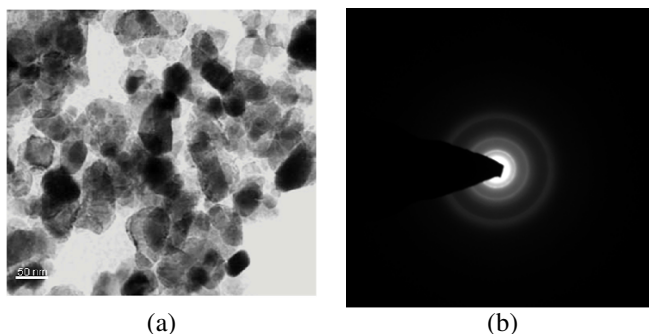
**Figure 4.** (a) SEM image of Pt-Ru/TiO<sub>2</sub>/575 (b) EDAX spectrum of Pt-Ru/TiO<sub>2</sub>/575



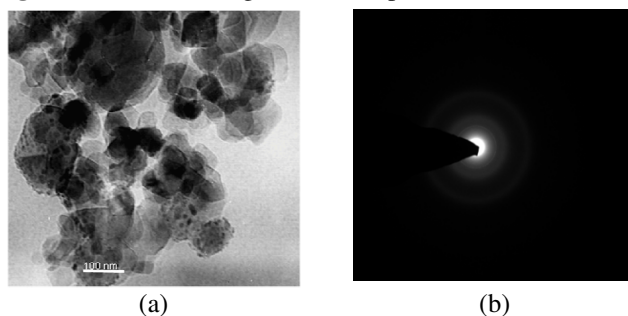
**Figure 5.** (a) SEM image of Pt-Au/TiO<sub>2</sub>575 (b) EDAX spectrum of Pt-Au/TiO<sub>2</sub>575

### Transmission electron microscopy

The prepared nanocatalysts were subjected to TEM analysis to study the morphology of prepared samples. The TEM images and SAED pattern of the Pt-Pd/TiO<sub>2</sub> and Pt-Au/TiO<sub>2</sub> nanocatalysts thermally reduced at 375 and 575 °C are given in Figure 6 and 9 respectively. The morphology of samples was spherical and well dispersed and the sizes of the particles were in the range of 50-100 nm. It is observed that the catalysts reduced at 375 °C have smaller particle size than catalysts reduced at 575 °C. The SAED patterns show that the nanocatalysts are crystalline in nature. Reduction at higher temperatures lead to significant increase in size and agglomeration of nanoparticles at the exterior surface compared to the catalysts reduced at lower temperature. The high magnification HRTEM images reveal the presence of orderly crystallites in the particles.

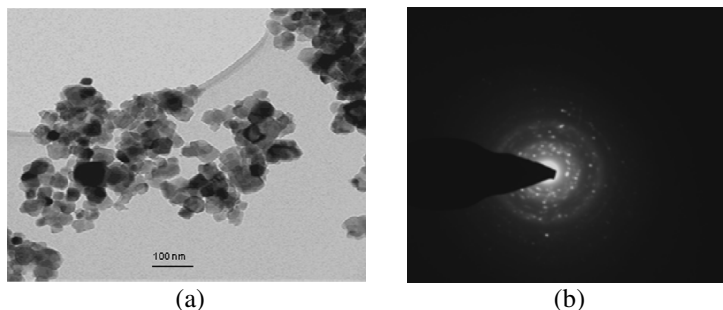


**Figure 6:** (a) TEM image (b) SAED pattern of Pt-Pd/TiO<sub>2</sub>375

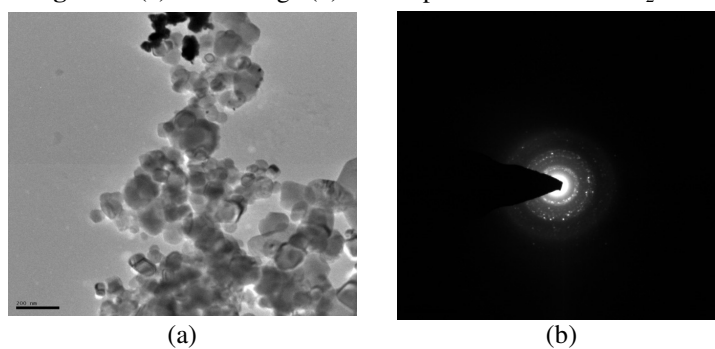


**Figure 7** (a) TEM image (b) SAED pattern of Pt-Pd/TiO<sub>2</sub>575





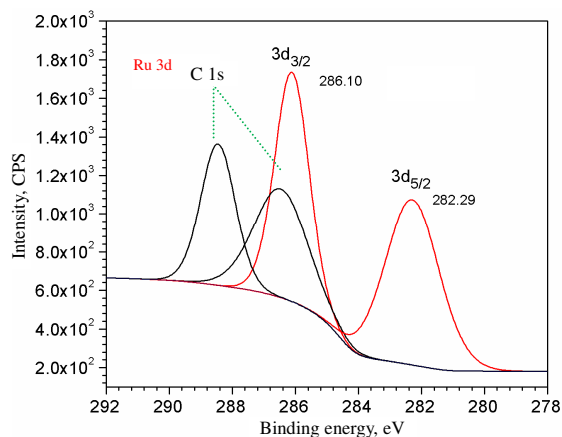
**Figure 8.** (a) TEM image (b) SAED pattern of Pt-Au/TiO<sub>2</sub>375



**Figure 9.** (a) TEM image (c) SAED pattern of Pt-Au/TiO<sub>2</sub>575

#### *XPS of bimetallic supported on TiO<sub>2</sub> nanocatalysts*

Figure 10 show the core level spectra of Ru 3d and Pt 4f of Pt-Ru/TiO<sub>2</sub>375 nanocatalyst. The core level spectrum of Ru 3d spectrum has been obscured by the C 1s (286.6 eV) spectrum, but the deconvoluted spectrum shows a doublet with peak binding energies of 282.29 eV (3d<sub>5/2</sub>) and 286.286.1 eV (3d<sub>3/2</sub>). It is difficult to resolve the small Ru peak from the large peak of C 1s. The Ru 3d spectra revealed the presence of only Ru<sup>0</sup> at 3d<sub>5/2</sub> at 282.32 eV<sup>41-43</sup>.



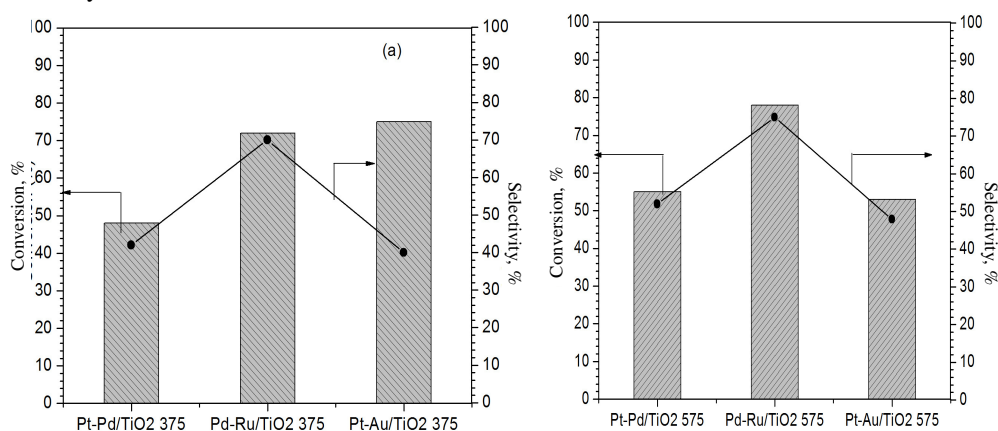
**Figure 10.** XPS Ru d 3d core level spectra of Pt-Ru/TiO<sub>2</sub> 375 °C



### Nanocatalyst testing

#### *Effect of second metal addition for higher selectivity of unsaturated alcohols*

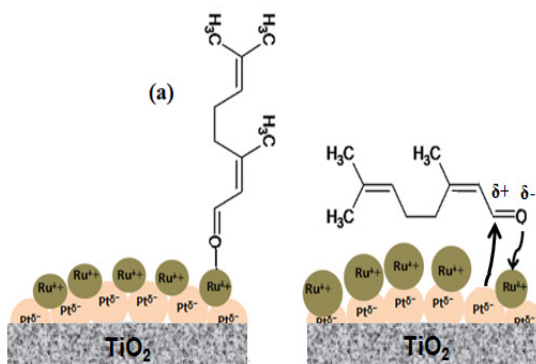
The Figure 11 shows, the unsaturated alcohols conversion and selectivity as a function of Pt-Pd/TiO<sub>2</sub>, Pt-Ru/TiO<sub>2</sub> and Pt-Au/TiO<sub>2</sub> catalysts, thermally reduced at 375 °C and 575 °C. The catalysts reduced at low temperature (375 °C) shows the overall conversion and selectivity of GOL & NOL 48, 72 and 45% and 45,70 and 40% for bimetallic catalysts Pt-Pd/TiO<sub>2</sub>, Pt-Ru/TiO<sub>2</sub> and Pt-Au/TiO<sub>2</sub> respectively, which is shown in Figure 11a. The catalysts thermally reduced at high temperature (575 °C) exhibit the overall conversion and selectivity of GOL & NOL 55, 78 and 53% and 52, 75 and 48% for bimetallic Pt-Pd/TiO<sub>2</sub>, Pt-Ru/TiO<sub>2</sub> and Pt-Au/TiO<sub>2</sub> catalysts respectively, which is shown in Figure 11b. The catalysts reduced at 575 °C show higher activities than their counterparts reduced at 375 °C. This phenomenon is explained by the presence of partially reduced support species TiO<sub>(2-x)</sub> generated after reduction at high temperature, which can cover part of the metallic surface<sup>44-47</sup>. The bimetallic catalysts relatively show higher activity than the monometallic catalysts, which may be due to the cooperative activity of the two metals<sup>48-53</sup>.



**Figure 11.** Conversion and selectivity towards unsaturated alcohols as a function of reduction temperature of catalyst (a) 375 and (b) 575 °C at 90 °C, 10 MPa, 750 rpm, IPA solvent, 1.5% metal content and m= 250 mg

#### *Effects of ruthenium promoter on Pt catalysts*

Among the prepared TiO<sub>2</sub> supported bimetallic (Pt-Pd/TiO<sub>2</sub> and Pt-Ru/TiO<sub>2</sub> and Pt-Au/TiO<sub>2</sub>) nanocatalysts Pt-Ru/TiO<sub>2</sub> shows the highest overall conversion and selectivity towards GOL & NOL. The XPS analysis shows the presence of Pt<sup>0</sup> and Ru<sup>0</sup>. In the Pt-Ru/TiO<sub>2</sub> nanocatalyst the contact between Pt and Ru atoms favors the partial electronic transfer from Ru<sup>0</sup> towards Pt<sup>0</sup> due the difference in electronegativity. In this way, there is + $\delta$  charge density in the Ru atoms and a - $\delta$  charge density in the Pt atoms (Scheme 2). Eventhough, Ru, Pd and Au have the same electronegativity; Ru is a hard acid, whereas Pd and Au are soft acids. Considering a molecule of  $\alpha$ ,  $\beta$ -unsaturated aldehyde, it is accepted that the C=O group could be adsorbed on to the Ru metal surface<sup>52</sup> due to partial negative charge (- $\delta$ ) on the O atom. Which favours the hydrogenation of the C=O group resulting in the formation of unsaturated alcohols. The mode of adsorption of citral over Pt-Ru/TiO<sub>2</sub> catalyst is shown in the Scheme 2.



**Scheme 2.** Adsorption mode of citral

## Conclusion

The characterization techniques showed that the  $\text{TiO}_2$  supported platinum based bimetallic nanocatalysts have a porous nature with high surface area and pore volume. The SMSI effect was evaluated by performing the hydrogenation on the catalysts, thermally reduced at low ( $375^\circ\text{C}$ ) and high ( $575^\circ\text{C}$ ) temperatures. The bimetallic nanocatalysts are able to generate reactive  $\text{TiO}_{(2-x)}$  species after reduction at high temperature ( $575^\circ\text{C}$ ), leading to a SMSI effect comparable or superior to that on Pt-Ru supported on bulk titania. The SMSI effect shows that the catalysts reduced at higher temperature leads to an increase in selectivity toward unsaturated alcohols (GOL & GOL) for Pt-Ru/ $\text{TiO}_2$  compared to Pt-Pd/ $\text{TiO}_2$  and Pt-Au/ $\text{TiO}_2$  nanocatalysts. In addition a second metal (Ru) also leads to an increase of the GOL & NOL selectivity during the citral hydrogenation. The generated partially oxidized second metal species due to the difference in electronegativity, strongly binds the  $\text{C}=\text{O}$  group and also paves the way for the selective activation of the  $\text{C}=\text{O}$  bond. Metal support interaction and promoter active metal interaction increased the unsaturated alcohol formation.

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