Liquid Phase Selective Hydrogenation of Citral over Bimetallic Transition Metal Catalysts

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Abstract
Silica supported bimetallic catalysts of Co-Ni, Ni-Cu and Cu-Co were prepared by deposition precipitation method, calcined at two different temperatures 475°C and 675°C. The prepared catalysts were characterized by BET surface area, SEM, EDX, FT-IR, thermogravimetry and XRD techniques. The XRD measurement of Ni–Cu/SiO2 catalyst has peaks due to CuO and NiO oxides. The catalytic activity and selectivity of these prepared catalysts towards liquid phase selective hydrogenation were studied. Amongst the studied catalysts, Co–Ni/SiO2 calcined at 475°C had presented higher selectivity in terms of citral towards unsaturated alcohols (geraniol and nerol) in a isopropanol solvent medium and 0.2% catalyst loading, at 90°C temperatures under 4 bar pressure with 750 rpm agitation.

Keywords: Silica support, Bimetallic catalysts, XRD, SEM, FTIR, Citral, Selective hydrogenation, Unsaturated alcohols

1. Introduction
The liquid phase selective hydrogenation of unsaturated α, β- aldehydes to the corresponding unsaturated alcohols are an important step in the synthesis of various fine chemicals. An unsaturated alcohol is a very particular important intermediate in several industries such as flavour, fragrance and pharmaceutical industries (Gallezot & Richard, 1998; Bartok & Molnar, 1997; Smith & Notheisz, 1999; Sheldon-Bekkum 2001). Application of heterogeneous catalysts has been increasing because of the virtues of easy separation from the organic media and catalyst reusability, which facilitate the use of continuous process and development of environmental friendly processes. However, this is still a challenge as the reduction of the C=C bond is thermodynamically favoured in comparison with that of the C=O bond. Citral hydrogenation reaction of fine chemical industry Fig. 1 illustrates the main products obtained in this reaction. A lot of studies have been carried out with both catalysts (homogeneous and heterogeneous) in order to obtain results of industrial interest (Malathi & Viswanath, 2001; Lashdaf, Lahtinen, Lindblad, Venalainen & Krause, 2004; Zhu, Liu, Jaenicke & Chuah, 2004). It is known that the choice of the adequate catalyst plays an important role in the activity and selectivity of these reactions. The nature of the active metal, its particle size, supports (Singh, & Vannice, 2000; Lashdaf, Hase, Kauppinen, & Krause, 1988) and the additions of promoters (Bachiller-Baeza, Rodriguez-Ramos & Guerrero-Ruiz, 2001) are some examples of factors that exert influence on the performance of the catalyst. Other parameters like the solvent used have also been taken into consideration (Maki-Arvela, Tiainen, Neyestanaki, Sjoholm, Rantankyla, Laine, Salmil, & Murzin, 2002; Burgener, Ferrer, Mallat & Baiker, 2004; Neri, Mercadante, Donato, Visco, & Galvagno, 1994). Several studies have been carried out employing different active metals and we can conclude that selectivity is towards unsaturated alcohols.

The process of citronellall can be obtained with palladium (Burgener, Wirz, Mallat & Baiker, 2004) nickel (Tiainen, Maki-Arvela & Salmi, 1999; Baijun, Lianhai, Bingchun, Tianxi & Iwatani, 1998) and nickel alloys
Osmium (Singh & Vannice, 2001) and rhodium give rise to the unsaturated alcohols while with the use of platinum and ruthenium the selectivity could be modified by the addition of a second metal (Asedegbega-Nieto, Bachiller-Baeza, Guerrero-Ruiz & Rodriguez-Ramos, 2006; Mali-Arvela, Tiainen, Lindblad, Kumar, Sjoholm, Ollonqvist, Vaynren, Salmi & Murzin, 2003; Richard, Ockelford, Giroir-Fendler & Galiezot, 1989; Galvagno, Milone, Donato, Neri & Pietropaolo, 1993; Galvagno, Donato, Neri & Pietropaolo, 1989). As for the citral hydrogenation, bimetallic catalysts can also improve selectivity towards unsaturated alcohol, when compared to monometallic catalyst, due to electronic and geometric effects (Fouilloux, 1988). Silica supported bimetallic catalysts are very interesting materials in general terms, since one metal can fine tune or modify the catalytic properties of the other metal as a result of both structural and electronic effects. Therefore, bimetallic catalysts usually improve both activity and selectivity and even stability of the catalysts (Ponec, 2001).

In the field of hydrogenation, bimetallic catalysts are most often used in order to improve selectivity and stability of the single component metal catalysts (Savargaonkar, Khanra, Pruski, & King, 1996; Coq & Figueras, 2001). The catalytic performance of bimetallic catalysts differ significantly from that of the individual components; often show mutual promotion effects towards reduction and increasing thermal stability against sintering (Kulkarni, Sankar & Rao, 1991). Bimetallic catalysts supported on high specific surface area carriers, such as silica and alumina, have attracted considerable attention recently because of their better performance when compared to the corresponding monometallic counterparts (Ponec, 2001). Additionally, the preparation of supported bimetallic catalysts by different methods could lead to catalysts with new characteristics, where a specific interaction between the two metals could produce a hybrid catalyst whose behavior may differ significantly from that of the catalysts prepared by conventional methods.

In the present study, a series of transition metal-based bimetallic Co-Ni/SiO2; Ni-Cu/SiO2; Cu-Co/SiO2 catalysts have been prepared by deposition precipitation method, calcined at low (475°C) and high (675°C) temperatures. The catalysts have been characterized by various techniques like, Brunauer-Emmett-Teller (BET) surface area, Scanning electron microscopy (SEM), EDX, FT-IR and X-ray Diffraction (XRD). The catalytic activity and selectivity of these bimetallic catalysts were evaluated for liquid phase selective hydrogenation of citral to unsaturated alcohol (geraniol and nerol) in an isopropanol medium under condition of temperatures range 60-110°C, 1 to 6 bar pressures and 0.1 to 0.3 catalyst loads.

2. Experimental
2.1 Preparation of Catalysts
Various bimetallic catalysts of Co-Ni/SiO2; Ni-Cu/SiO2 and Cu-Co/SiO2 were prepared by deposition-precipitation method. Bimetals were deposited over silica support in 1:1 molar ratio (based on metals) keeping the loading amount constant at 20 wt.% with respect to SiO2. In a typical preparation procedure, the required quantities of the respective metal nitrate salts (Fluka, AR Grade) were dissolved separately in double distilled water and mixed together. To this mixture solution, the required quantity of colloidal silica (40 wt. %, Fluka, AR Grade) was added and the resultant slurry was stirred for 4 h to obtain homogeneous mixture. Subsequently, the homogenized slurry was titrated with aqueous ammonia until pH=8.5. Thus formed precipitated gel was filtered, washed several times until free from anion impurities and dried at 120°C for 16 h. The oven-dried sample was finally calcined at 475°C for 4 h in air atmosphere. A small portion of the finished catalyst was further heated at 675°C for 4 hours to evaluate thermal stability.

2.2 Characterization of Catalysts
The BET surface area measurements were made on a Micromeritics Gemini 2360 instrument by N2 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 hours.

Scanning electron microscopy (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 Keveex, Sigma KS3 Energy dispersive X-ray (EDX) instrument operating at a detector resolution of 136 eV. Powder X-ray diffraction (XRD) patterns have been recorded on a Siemens D-5000 diffract meter, using Ni-filtered Cu Kα (0.15418 nm) radiation source. Crystalline phases were identified with the help of ASTM Powder Data Files. The infrared spectra were recorded on a Nicolet 740 FT-Infrared spectrometer at ambient conditions, using KBr disks with a normal resolution of 4 cm⁻¹ and averaging 100 spectra.
2.3 Catalyst Testing

Citral (mixture of E and Z forms, Merck, 99%) and isopropanol (Fluka, 99.5%) are used as received without further purification. 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 4 bars a 120°C. Then, the reactor was cooled to reaction temperature. Reactant mixture (200 ml of 0.1M 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 60°C 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, 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 - Gas chromatography (GC MS-QP2010 Plus). From the results obtained in these analyses, information such as the catalytic activity, selectivity of the reaction and conversion could be derived.

3. Results and discussions

3.1 Characterization

The N2 BET surface areas of various catalysts prepared in this investigation are shown in Tab 1. As can be noted from Tab 1, all samples exhibited reasonably high specific surface areas. Among three combinations synthesized, the Co–Ni/SiO2 sample calcined at 475°C exhibited a high BET surface area of 191 m2 g−1. The occurrence of high surface areas in the present investigation could be attributed to the employment of colloidal silica support and also to the preparation method adopted (deposition–precipitation). The co-precipitation of bimetallic precursor over the colloidal silica is expected to yield smaller crystallites of bimetallic oxides on the surface of the SiO2 and exhibit a high specific surface area. However, upon calcination at slightly higher temperature (675°C) a decrease in the surface area is observed (Tab 1). This decrease in the surface area is due to sintering of the samples. The surface area of Cu–Co/SiO2 catalyst has been very low at 475°C compared to others catalysts.

The surface morphology and to assess the dispersion of bimetallic active components over the SiO2 support, SEM investigation was performed on various samples calcined at 475°C. The representative electron micrographs obtained are presented in Fig. 2. The particle size estimation from SEM data reveals that the average particle size for all the three catalysts Cu-Co/SiO2 and Ni–Cu/SiO2 and Co-Ni/SiO2 is between 10 and 15 nm. Among the three samples investigated, the Co-Ni/SiO2 exhibited more porous texture, hence, was also found to exhibit more specific surface area. To get information on the surface composition of the samples, the energy dispersive X-ray microanalysis (EDX) was also performed. As expected, the EDX results revealed the presence of Si, O, Co, Ni and Cu elements in the respective samples in appropriate proportions. The quantitative metal loadings detected (wt. %) in the respective samples are presented in Fig.7. For the purpose of comparison the actual metal loadings deposited during the preparation are also shown in Fig.7. The EDX results corroborate well, within the limit of permissible error, with the actual metal loadings of the samples.

The FT-IR spectra of various bimetallic catalysts prepared in this study were recorded in range of 4000–400 cm−1. Normally, strong bands associated with –OH stretching vibrations of water and surface hydroxyl groups occur between 3200 and 3700 cm−1. A sharp and strong absorption band in the region 3650–3700 cm−1 was noted in all cases characterizing the presence of hydroxyl groups. Water of hydration usually exhibits one strong band near 3600 cm−1and one or more sharp bands near 3400 cm−1. Water of hydration can be easily distinguished from hydroxyl groups by the presence of the H–O–H bending motion, which produces a medium band in the region 1600–1650 cm−1. Free water has a strong broad absorption band centered in the region 3200–3400 cm−1. Interestingly, all the three bimetallic samples exhibited fairly similar IR patterns, signifying the predominance of silica IR features in the spectra. The FTIR spectra of catalysts are given in Fig.3.

Aim of employing a support is to achieve an optimal dispersion of the catalytically active components and to stabilize them against sintering. The deposition–precipitation technique takes the advantage of the fact that precipitation onto the preformed carrier needs a lower super saturation than formation of new phases directly from the liquid. The selected support also should be stable under reaction and regeneration conditions and should adversely interact with the solvent, reactants and reaction products. Therefore, the colloidal silica support has
been advantageously employed in the present investigation. The term colloidal silica refers to a stable dispersion or sols of discrete nanometric particles of amorphous silica, commonly suspended in water with a size of about 7–12 nm in diameter. Depending on the synthesis conditions, the structure of the colloidal particles may differ from isolated spherical particles to agglomerates of complex structures. Colloidal silica exhibits reasonably high specific surface area ranging between 140 and 345 m² g⁻¹. The surface area will be typically constant up to the calcinations temperatures of 475 - 675°C K. However, the porosity is normally lost at temperatures higher than 1200°C. Since silica is a neutral oxide, there are no strong Bronsted or Lewis acid–base sites on the surface. Untreated silica is totally hydroxylated and the hydroxyl layer is covered with physically adsorbed water (Kinney, Chuang & Maciel, 1993). The physically adsorbed water can be removed by treating at 300°C (Tsyrsganenko & Filimonov, 1973). Thermal treatment of the support leads first to removal of water (dehydration) and then to combination of adjacent hydroxyl groups to form water (dehydroxylation). On silica, the dehydroxylation leads to the formation of surface siloxane bridges (Porta, Dragone, Fierro, Inversi, Jaco & Moretti, 1992).

The X-ray powder diffractograms of various samples calcined at 475 and 675°C are shown in Fig. 4. The oxide mixtures that were observed either contained segregated phases of NiO, CuO and CoO or solid solutions of these combinations. Silica normally exists in any of the three crystallographic forms namely, cristobalite, quartz and tridymite. However, no diffraction patterns pertaining to crystalline SiO₂ phase are noted from XRD results. The absence of SiO₂ diffraction patterns indicates that silica is in the amorphous state. In general, the XRD patterns of 475°C calcined samples are relatively broad indicating partly amorphous nature of the samples. The XRD patterns of Co–Ni/ SiO₂ sample revealed the presence of a definite compound between cobalt and nickel with the composition Co₁₃₈Ni₆₁₆O₄. The increase in the intensity of the peaks is due to better crystallization of the sample under the impact of high temperature calcination. The XRD patterns of Ni–Cu/SiO₂ sample revealed the presence of both CuO and NiO phases. With increase in calcination temperature from 475 and 675°C and increase in the intensity of the lines due to better crystallization of these phases was observed. However, as reported by Davies et al., the formation of tetragonal or orthorhombic phases is not found probably due to a different preparation method adopted and the lower calcination temperature has studied (Maki-Arvela, Tiaine, Lindblad, Demirkan, Kumar, Sjoholm, Ollonqvist, Vayrynen, Salmil, & Murzin, 2003).

The XRD profiles of Cu–Co/SiO₂ sample calcined at 475°C revealed the formation of a non-stoichiometric cobalt–copper-oxide solid solution Cu₀.₇₆Co₂.₂₄O₄. This solid solution of general formula CuₓCo₃−ₓO₄ exhibits spinel structure formed by partial migration of copper into the spinel structure of Co₃O₄ compound. Although the standard XRD patterns of CuₓCo₃O₄ are very similar to that of Co₃O₄, the presence of these Cu–Co oxide solid solutions have been identified in the literature by using the differences in the diffraction patterns from the 311, 511 and 111 planes, corresponding to the differences in d values of around 0.01 Å. The surface area will be typically constant up to the passivation of the Cu–Co solid solution the XRD analysis revealed disappearance of the mixed oxide with the formation of a metallic phase with fcc structure whose lattice values (a = b = c = 0.3594 nm) are intermediate of Cu (a = 0.3615 nm) and Co (a = 0.3545 nm) metallic phases confirming formation of a Cu–Co alloy system. This was also substantiated by IR spectroscopy (BaiJliard-Letoumel, Cobo, Mirodotos, Primet & Dalmon, 1989) of the Cu–Co/Al₂O₃ and transmission electron microscopy of the Cu–Co/SiO₂ catalysts. Therefore, it can be concluded that the alloy formation is favoured by the presence of CuₓCo₃−ₓO₄ phase in the precursor.

3.2 Catalytic reaction

Liquid phase hydrogenation of citral can be observed in the scheme of Fig. 1, citral can give rise to a large variety of products depending on which double bond is attacked by hydrogen. The three main primary hydrogenation products obtained by the reaction of one of the conjugated double bonds are citronellal (saturated aldehydes), geraniol and nerol (unsaturated alcohols). These compounds still have two double bonds and so further hydrogenation can give citronellol. In the hydrogenation of citral, both activity and selectivity were...
studied to assess those factors which might lead to higher active and improved selectivity to prepared bimetallic silica supported catalysts. The data are shown in Tab. 1. It can be observed that all cases in the present investigation, the reaction produces unsaturated alcohol (geraniol and nerol), selectively in three series of catalysts calcined at 475°C and 675°C temperature with various conditions of temperature, pressure, agitation rpm and catalyst load.

3.2.1 Effect of pressure
The hydrogenation reaction was carried out at hydrogen pressures ranging 1 to 6 bars while maintaining a constant temperature and initial citral concentration. The results showed that increasing the hydrogen pressure, resulted in increase in the rate of conversion of citral in Fig. 5 indicates that the rate of reaction is directly proportional to the hydrogen pressure, effectively exhibiting a first order dependency on hydrogen. The reaction selective and conversion of unsaturated alcohols (geraniol and nerol) under such condition of difference range of hydrogen pressure. The rate of reaction has been studied with higher selective of citral hydrogenation were obtained with the optimum hydrogenation rate and with catalysts having an optimum specific mental surface area. Among series of bimetallic catalysts higher selective conversion at 4 bar pressure and more favored in Co-Ni/SiO2 catalyst.

3.2.2 Effect of temperature
The selectivity of both bimetallic catalysts in shown in Fig. 6, the influence of temperature on the kinetics of the hydrogenation reaction was studied at 60-110°C with under such conditions of catalyst loading, 0.2%w/v; Citral, 1.67 mol dm-3; Solvent 3.5mol dm-3; Pressure 4 bar; rpm 750. Among the series of catalysts investigated citral hydrogenation higher selective at 90°C temperature for conversion in unsaturated alcohol (geraniol and nerol). The hydrogenation selective depends on reaction temperature, increasing temperature the selective hydrogenation of the C=O group is much more difficult in the presence of C=C bond, because the hydrogenation of the C=C bond is thermodynamically more favored.

3.2.3 Effect of catalyst loading
From Fig.7, the liquid phase hydrogenation rate increase with catalyst loading especially at lower temperature and have studied at 0.10, 0.15, 0.2, 0.25,0.27 and 0.30 % w/v catalyst loaded with under such conditions. Among the three series of bimetallic catalysts, indicate in Fig. 7 higher (70%) selective conversion citral to unsaturated alcohols, which in catalyst load is load 0.2%w/v. The most favored bimetallic catalyst of Co-Ni/SiO2 calinated at 475°C.

3.2.4 Selective conversion of unsaturated alcohol
The experimental studies of the initial stages of the hydrogenation of citral showed that the selectivity towards geraniol (unsaturated alcohol) increase with increasing conversion, suggesting that a modification of the bimetallic catalyst surface takes place as the reaction proceeds. In order to explain this behavior it is useful to investigate the way the products affect the reaction. From Fig. 8(a), it can be observed in the present investigation, the reaction carried out under conditions of catalyst loading, 0.2%w/v; Citral, 1.67 mol dm-3; Temperature 90°C; Pressure 4 bar; rpm 750. Three series of catalysts investigated for liquid phase citral hydrogenation, higher selectivity of Co-Ni/SiO2 at 90°C temperature for conversion of unsaturated alcohols (59%). At that same time Ni-Cu/SiO2 is much better than Cu-Co/SiO2. The high temperature calcined at 675°C bimetallic catalysts, in Fig. 8(b), the rate of reaction and conversion of unsaturated alcohols (geraniol and nerol) was poor compared to calcined at 475°C the catalysts. Among the series of bimetallic catalysts investigated higher activity and selectivity is for Co-Ni/SiO2 catalyst for or liquid phase hydrogenation of citral towards unsaturated alcohols product.

4. Conclusions
The preparation and the characterization of silica supported bimetallic catalysts and their application in liquid phase hydrogenation of citral towards unsaturated alcohols (gerraiol and nerol) has been studied.

- Three series of bimetallic catalysts calcinated at low and high temperature (475°C and 675°C), incorporation of silica support in the colloidal form during deposition precipitation of bimetallic resulted in stable and well formed catalysts with high specific surface area when calcinated at 475°C. SEM micrograph of the particles was good and particles size are in the nm range (10-14), and show higher surface area for catalysts calcined at 475 °C than the catalysts calcined at 675°C.
- The XRD patterns of Co–Ni/ SiO2 shows the composition of catalyst as Co1.38 Ni1.61O4. The increase in the intensity of the peaks is due to better crystallization of the sample under the impact of high temperature.
calcinations and Ni–Cu/SiO$_2$ catalyst contains, CuO and NiO phases. With increase in calcination temperature from 475-675°C increase in the intensity of the lines is observed which is due to better crystallization of these phases at high temperature.

- The catalytic activity has been investigated in reaction conditions and compared with the performance of low and high temperature calcinated catalysts. The catalyst Co-Ni/SiO$_2$ calcinated at 475°C is found to give the highest selectivity towards unsaturated alcohols.

- It can be observed that for all the cases in the present investigation, the reaction produces unsaturated alcohols (geraniol and nerol), in activity and selectivity for Co-Ni/SiO$_2$ calcined at 475°C under conditions of Catalyst loading, 0.2%sw/v; Citral, 1.67 mol dm$^{-3}$; Solvent 3.5mol dm$^{-3}$; Temperature 90°C; Pressure 4 bar; rpm 750. Liquid phase citral hydrogenation is most selective for Co-Ni/SiO$_2$. Among these experiments the overall conversion observed is 99% but selectivity is only 59% towards unsaturated alcohols (geraniol and nerol). The hydrogenation of citral over these synthesized catalysts indicated that they can be used as the catalysts for other hydrogenation reactions also.

References


Table 1. Various bimetallic (Co-Ni; Ni-Cu and Cu-Co) silica supported catalysts calcined at 475 and 675°C, BET SA measurements of and actual metal loading, metal loadings from EDX analysis, XRD phase observed

<table>
<thead>
<tr>
<th>Bimetallic catalyst</th>
<th>Calcination Temp. (°C)</th>
<th>XRD phases Identified</th>
<th>Actual metal loading (wt%)</th>
<th>Metal loading from EDX analysis (wt%)</th>
<th>BET SA (m²g⁻¹)</th>
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<tr>
<td>Co-Ni/SiO₂</td>
<td>475</td>
<td>Co₁₃₈Ni₁₆₁O₄</td>
<td>10 10 0</td>
<td>9.7 9.32 0</td>
<td>191</td>
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<tr>
<td></td>
<td>675</td>
<td>Co₁₃₈Ni₁₆₁O₄</td>
<td>10.23 9.77 0</td>
<td>9.88 9.41 0</td>
<td>163</td>
</tr>
<tr>
<td>Ni-Cu/SiO₂</td>
<td>475</td>
<td>NiO; CuO</td>
<td>0 9.7 10.3</td>
<td>0 11.42 12.41</td>
<td>158</td>
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<tr>
<td></td>
<td>675</td>
<td>NiO; CuO</td>
<td>0 9.81 10.19</td>
<td>0 11.09 12.58</td>
<td>131</td>
</tr>
<tr>
<td>Cu-Co/SiO₂</td>
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<td>Cu₀.₇₅Co₂.₂₅O₄</td>
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<td>10.42 0 11.32</td>
<td>165</td>
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<tr>
<td></td>
<td>675</td>
<td>Cu₀.₇₆Co₂.₂₅O₄;CuO</td>
<td>10.83 0 9.17</td>
<td>10.52 0 11.13</td>
<td>125</td>
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</table>

Figure 1. Scheme of Citral hydrogenation
Figure 2. SEM micrographs of (a) Co-Ni/SiO₂; (b) Ni–Cu/SiO₂; (c) Cu-Co/SiO₂ calcined at 675°C

Figure 3. FT-IR spectra of (a) Co-Ni/SiO₂; (b) Ni–Cu/SiO₂; (c) Cu-Co/SiO₂ Samples calcined at 475°C
Figure 4. X-ray diffraction patterns of various bimetallic catalysts calcined at 475 and 675°C, (*) lines due to $\text{Co}_{1.38}\text{Ni}_{1.61}\text{O}_4$ phase; (Δ) lines due to CuO phase; (O) lines due to NiO phase; (#) line due to $\text{Cu}_{0.75}\text{Co}_{2.25}\text{O}_4$ phase.
Figure 5. Percentage of conversions against pressure for Bimetallic supported catalysts calcined at 475 and 675°C. The selectivity is 100% towards unsaturated alcohols (geraniol and nerol) in all cases. Conditions: Catalyst loading, 0.2% w/v; Citral, 1.67 mol dm⁻³; Solvent 3.5 mol dm⁻³; Temperature 363 K; rpm 750.

Figure 6. Percentage conversions against temperature for Bimetallic supported catalysts calcined at 475 and 675°C. The selectivity is 100% towards unsaturated alcohols (geraniol and nerol) in all cases. Conditions: Catalyst loading, 0.2% w/v; Citral, 1.67 mol dm⁻³; Solvent 3.5 mol dm⁻³; Pressure 4 bar; rpm 750.
The selectivity is 100% towards unsaturated alcohols (geraniol and neral) in all the cases. Conditions: Citral, 1.67 mol dm$^{-3}$; Solvent 3.5 mol dm$^{-3}$; Temperature 363 K; Pressure 4 bar; rpm 750.

Figure 8. Percentage conversion against Time for Bimetallic silica supported catalysts calcined at (a) 475°C (b) 675°C; Temperature, 90°C; Pressure 4 bar; Agitation rpm, 750; Catalyst loading, 0.2% w/v; Citral, 1.67 mol dm$^{-3}$; Solvent 3.5 mol dm$^{-3}$.