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Silica Supported Bimetallic Catalysts for Liquid Phase Selective Hydrogenation of Citral

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Three series of bimetallic catalysts Co-Ni, Ni-Cu and Cu-Co in silica supported were prepared by deposition precipitation method and calcined at 773 and 923 K. The prepared catalysts were investigated by BET surface area, XRD, thermogravimetry, EDX, SEM and FT-IR techniques. The XRD measurements reveal formation of a specific solid solution in the case of Co-Ni/SiO_2 and Cu-Co/SiO_2 catalysts. However, in the case of Ni-Cu/SiO_2 catalyst only peaks due to CuO and NiO were observed. The SEM measurements suggest that the prepared bimetallic catalysts are in a highly dispersed form over the surface of the colloidal silica support. These catalysts were evaluated for liquid phase selective hydrogenation of citral to unsaturated alcohols under ranges of temperature, pressure and loading of catalyst. Among these catalysts investigated, the 773 K calcined Co-Ni/SiO_2 catalyst exhibited a high conversion in a isopropanol as a solvent medium, the maximum selectivity of geraniol and nerol obtained by 363 K temperature, 4 bar pressure, 0.2 % w/v catalyst load with 750 rpm agitation.

Key Words: Citral, Liquid phase hydrogenation, Unsaturated alcohol, Bimetallic catalysts, Silica supported, XRD, SEM, EDX.

INTRODUCTION

The selective hydrogenation of α,β-unsaturated aldehyde to α,β-unsaturated alcohol, such as citral to geraniol and nerol is of importance in fine chemicals manufacture and particularly in respect of fragrances and flavorings. The heterogeneous catalysts used in the fine chemical industry is expanding daily due to their separate advantages, such as its easier separation and reuse after reaction, which is commercially more advantaged. The hydrogenation of unsaturated aldehydes to the corresponding alcohols is an important step in the preparation of various fine chemicals. 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 homogeneous and heterogeneous catalysts in order to obtain results of industrial interest[1-3]. 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[4], its particle size, support[5,6] and the addition of promoters[7,8] 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[9-11]. The catalytic hydrogenation of citral have been carried out employing different active metals.

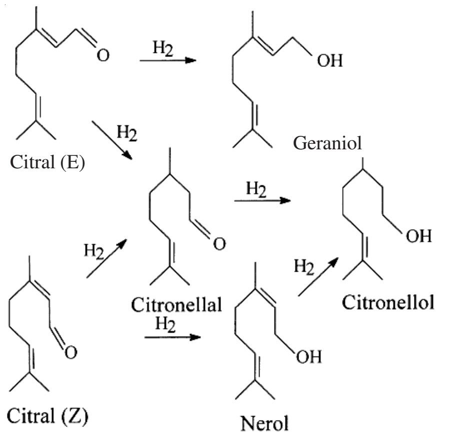


Fig. 1. Scheme of citral hydrogenation

The production of citronellal can be obtained with palladium[12], nickel[13,14] and nickel alloys[15,16]. Osmium[17] and rhodium[18] 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[19-23]. As for the citral hydrogenation, bimetallic catalysts can also improve selectivity towards unsaturated alcohol[24], when compared to mono metallic catalyst, due to electronic and geometric effects[24,25].

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[26]. In the field of hydrogenation, bimetallic catalysts are most often used in order to improve selectivity and stability of the single component metal catalysts[27,28]. 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[29]. 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[26]. 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 behavioour 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/SiO_2; Ni-Cu/SiO_2; Cu-Co/SiO_2 catalysts have been prepared by deposition-precipitation method and characterized by various techniques namely, XRD, FT-IR, SEM-EDX and BET surface area methods. The catalytic properties of these materials were evaluated for hydrogenation of citral to unsaturated alcohols (geraniol and nerol) in liquid phase under condition of temperatures range 333-383 K, 1-6 bar pressure and 0.1 to 0.3 w/v of catalyst load.

EXPERIMENTAL

Preparation of catalysts: Various bimetallic catalysts of Co-Ni/SiO_2; Ni-Cu/SiO_2 and Cu-Co/SiO_2 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 SiO_2. 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 383 K for 16 h. The oven-dried sample was finally calcined at 773 K for 4 h in air atmosphere. A small portion of the finished catalyst was further heated at 923 K for 4 h to evaluate thermal stability.

Characterization of catalysts: 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 393 K for 12 h and flushed with argon gas for 2 h.

Powder X-ray diffraction (XRD) patterns have been recorded on a Siemens D-5000 diffract meter, using Ni-filtered Cu K_α (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. 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 Kevex, Sigma KS3 energy dispersive X-ray (EDX) instrument operating at a detector resolution of 136 eV.

Catalyst testing: Citral (mixture of E and Z forms, Merck, 99 %) and isopropanol (Fluka, 99.5 %) are used. 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 4 bars at 523 K. Then, the reactor was cooled to reaction temperature. Reactant mixture (200 mL of 0.1 M citral in isopropanaol) 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 323 K 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 analyzed reaction products. 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 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). 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

The N_2 BET surface areas of various catalysts prepared in this investigation and calcinied at 773 and 923 K are shown in Table-1. As can be noted from Table-1, all samples exhibited reasonably high specific surface areas. Among three combinations synthesized, the Co-Ni/SiO_2 sample calcined at 773 K exhibited a high BET surface area of 192 m^2 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 precursors over the colloidal silica is expected to yield smaller crystallites of bimetallic oxides on the surface of the SiO_2 and exhibit a high specific surface area. However, upon calcinations at slightly higher temperature (923 K) a decrease in the surface area is observed (Table-1). This decrease in the surface area is due to sintering of the samples.

The primary 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

TABLE-1
VARIOUS BIMETALLIC (Co-Ni; Ni-Cu AND Cu-Co) SILICA SUPPORTED CATALYSTS CALCINED AT 773 AND 923 K, BET SA MEASUREMENTS OF AND ACTUAL METAL LOADING, METAL LOADINGS FROM EDX ANALYSIS, XRD PHASE OBSERVED

Bimetallic catalyst	Calcination temp. (K)	BET SA ($m^2 g^{-1}$)	Actual metal loading (wt. %)			Metal loading from EDX analysis (wt. %)			XRD phases identified
			Co	Ni	Cu	Co	Ni	Cu	
$Co-Ni/SiO_2$	773	192	10.0	10.00	0	9.80	9.50	0	$Co_{1.29}Ni_{1.71}O_4$
	923	164	10.1	9.89	0	9.82	9.40	0	$Co_{1.29}Ni_{1.71}O_4$
$Ni-Cu/SiO_2$	773	159	0	9.60	10.40	0	11.10	12.50	NiO; CuO
	923	132	0	9.40	10.60	0	11.09	12.58	NiO; CuO
$Cu-Co/SiO_2$	773	160	10.28	0	9.62	10.4	0	11.30	$Cu_{0.76}Co_{2.24}O_4$
	923	121	10.30	0	9.64	10.5	0	11.10	$Cu_{0.76}Co_{2.24}O_4$; CuO

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 should also 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 $m^2 g^{-1}$. The surface area will be typically constant up to the calcination temperatures of 923-1073 K. However, the porosity is normally lost at temperatures higher than 1473 K. 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[30]. The physically adsorbed water can be removed by treating at 573 K. 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[31].

The X-ray powder diffractgrams of various samples calcined at 773 and 923 K are shown in Fig. 2. 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 SiO_2 phase are noted from XRD results. The absence of SiO_2 diffraction patterns indicates that silica is in the amorphous state. In general, the XRD patterns of 773 K calcined samples are relatively broad indicating partly amorphous nature of the samples. The XRD patterns of $Co-Ni/SiO_2$ sample revealed the presence of a definite compound between cobalt and nickel with the composition $Co_{1.29}$ $Ni_{1.71}O_4$. With increase in calcinations temperature from 773 to 923 K, an increase in the intensity of the peaks pertaining to this phase was noted. 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 $Ni-Cu/SiO_2$ sample revealed the presence of both CuO and NiO phases. With increase in calcination temperature from 773-923 K and increase in the intensity of the lines due to better crystallization of these phases was observed.

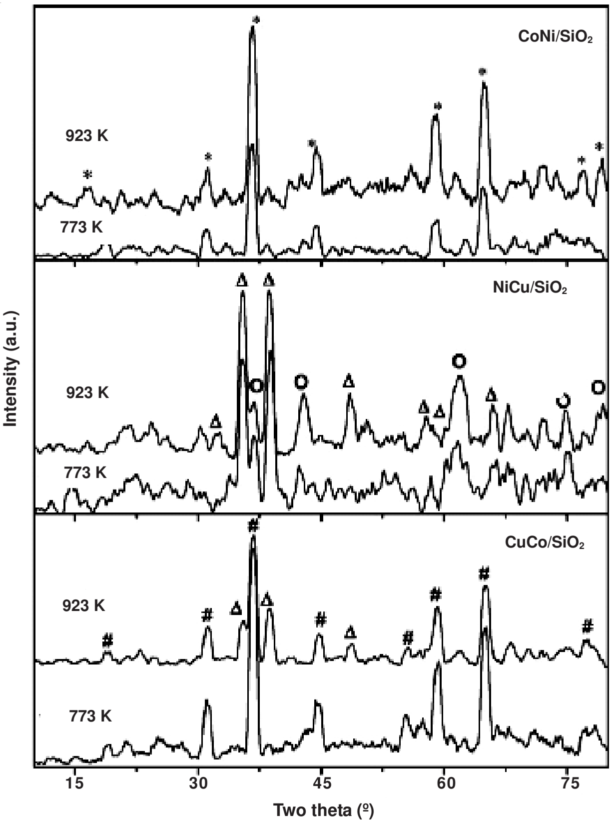
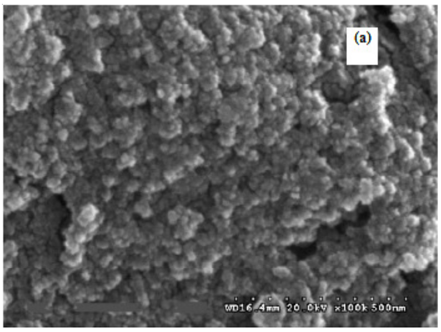


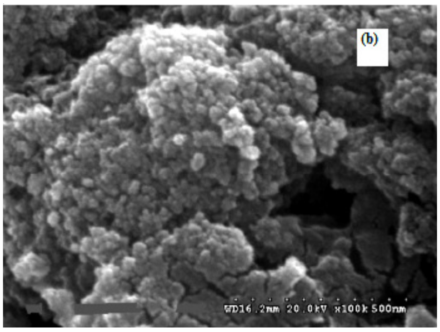
Fig. 2. X-Ray diffraction patterns of various bimetallic catalysts calcined at 773 and 923 K (*) lines due to $Co_{1.29}Ni_{1.71}O_4$ phase: (Δ) lines due to CuO phase; (O) lines due to NiO phase; (#) lines due to $Cu_{0.76}Co_{2.24}O_4$ phase

However, as reported by Davies[32], the formation of tetragonal or orthorhombic phases is not found probably due to a different preparation method adopted and the lower calcination temperatures[33].

The XRD profiles of $Cu-Co/SiO_2$ sample calcined at 773 K revealed the formation of a non-stoichiometric cobalt-copper-oxide solid solution $Cu_{0.76}Co_{2.24}O_4$. This solid solution of general formula $Cu_xCo_{3-x}O_4$ exhibits spinel structure formed by partial migration of copper into the spinel structure of Co_3O_4 compound. Although the standard XRD patterns of $Cu_xCo_{3-x}O_4$ are very similar to that of Co_3O_4, 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[34]. Porta *et al.*[35] investigated Cu- and Co-mixed oxides of different atomic ratios and observed the presence $Cu_xCo_{3-x}O_4$ and CuO for an atomic ratio of 50:50. They suggested that a change of 0.005 Å in the a_0 cell parameter of the Co_3O_4 phase indicates mixed oxide formation. The formation of a Cu-Co spinel is very difficult and reveals a lower thermal stability. Li *et al.*[34] synthesized Cu-Co mixed oxides with a Cu/Co atomic ratio of 0.25-1.0 and observed that the Cu-Co spinel is formed above 588 K and stable up to 623 K for Cu/Co < 1. For the sample with Cu/Co = 1, a facile transformation of Cu-Co spinel into CuO and Co_3O_4 was noted. In the present study with increase in calcination temperature from 773-923 K, in addition to the existence of $Cu_{0.76}Co_{2.24}O_4$ phase, emergence of a new crystalline CuO phase was noted. This observation is in accordance with the earlier cited literature. With increase in calcination temperature a better crystallization of various phases in the sample is a known phenomenon, which clearly signifies the influence of calcinations temperature on the crystallization and formation of new phases in line with literature. It is a reported fact that after reduction and 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[36] of the Cu-Co/Al_2O_3 and transmission electron microscopy of the Cu-Co/SiO_2 catalysts. Therefore, it can be concluded that the alloy formation is favoured by the presence of $Cu_xCo_{3-x}O_4$ phase in the precursor.

To understand the surface morphology and to assess the dispersion of bimetallic active components over the SiO_2 support, SEM investigation was performed on various samples calcined at 773 K. The representative electron micrographs obtained are presented in Fig. 3. The particle size estimation from SEM data reveals that an average particle size in the case of Cu-Co/SiO_2 and Ni-Cu/SiO_2 samples is less than 14 µm and that of Cu-Co/SiO_2 sample is between 10 and 15 µm. Among the three samples investigated, the Co-Ni/SiO_2 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 Table-2. For the purpose of comparison the actual metal loadings deposited during the preparation are also shown in Table-2. The EDX results corroborate well, within the limit of permissible error, with the actual metal loadings of the samples.





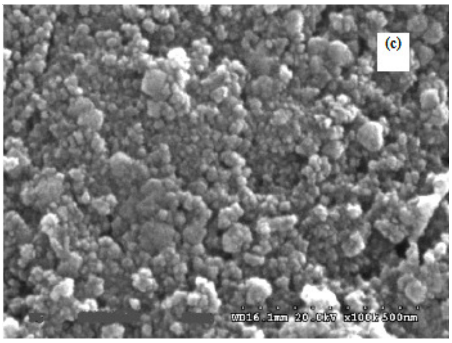


Fig. 3. SEM micrographs of (a) Co-Ni/SiO_2; (b) Ni-Cu/SiO_2; (c) Cu-Co/SiO_2 calcined at 773 K

TABLE-2
PERCENTAGE CONVERSIONS AGAINST TEMPERATURE FOR BIMETALLIC SUPPORTED CATALYSTS CALCINED AT 773 AND 923 K[#]

Temp. (K)	Co-Ni/SiO_2		Ni-Cu/SiO_2		Cu-Co/SiO_2	
	773 K	923 K	773 K	923 K	773 K	923 K
333	10	8	7	2	6	3
343	25	10	14	8	13	9
353	38	18	17	10	17	11
363	52	25	22	12	20	13
373	50	20	20	10	21	11
383	38	24	20	11	19	11

[#]The selectivity is 100 % towards unsaturated alcohols is all the cases. Conditions: Catalyst loading, 0.2 % w/v; citral, 1.67 mol dm^{-3}; solvent 3.5 mol dm^{-3}; pressure 4 bar; rmp 750.

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 3700-3650 cm^{-1} was noted in all cases characterizing the presence of hydroxyl groups. Water of hydration usually exhibits one strong band near 3600 cm^{-1} and 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 1650-1600 cm^{-1}. Free water has a strong broad absorption band centered in the region 3400-3200 cm^{-1} [37]. Interestingly, all the three bimetallic samples exhibited fairly similar IR patterns, signifying the predominance of silica IR features in the spectra.

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 (unsaturated alcohol) and nerol (unsaturated alcohol). These compounds still have two double bonds and so further hydrogenation can give citronellol . 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 are shown in Table-1. It can observed that all cases in the present investigation, the reaction produces unsaturated alcohol (geraniol and nerol), selectivity in three series of catalysts calcined at 773 and 923 K temperature with under various conditions of temperature, pressure, agitation rmp and catalyst load.

Effect of temperature: The selectivity of both bimetallic catalysts is shown in Table-2. The influence of temperature on the kinetics of the hydrogenation reaction was studied at 333, 343, 353, 363, 373 and 383 K with under such conditions of catalyst loading, 0.2 % w/v; citral, 1.67 mol dm^{-3}; solvent 3.5 mol dm^{-3}; pressure 4 bar; rmp 750. Among the series of catalysts investigated citral hydrogenation higher selective at 363 K temperature for conversion in unsaturated alcohol (geraniol). 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 favoured.

Effect of pressure: The hydrogenation reaction was carried out at hydrogen pressures ranging 1-6 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. Table-3 indicates that the rate of reaction is directly proportional to the hydrogen pressure, effectily exhibiting a first order dependency on hydrogen. The selective conversion of geraniol under various range of hydrogen pressure. The rate of reaction has been studied with higher selectivity of citral hydrogenation which 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 favoured in Co-Ni/SiO$_2$ catalyst.

TABLE-3
PERCENTAGE CONVERSION AGAINST PRESSURE FOR BIMETALLIC SUPPORTED CATALYSTS CALINATED AT 773 AND 923 K[#]

Pressure (bar)	Co-Ni/SiO$_2$		Ni-Cu/SiO$_2$		Cu-Co/SiO$_2$	
	773 K	923 K	773 K	923 K	773 K	923 K
1	15	7	5	3	5	4
2	30	12	13	7	10	7
3	44	19	16	11	15	11
4	52	28	25	13	21	12
5	50	19	21	12	20	11
6	48	20	21	11	19	9

[#]The selectivity is 100 % towards unsaturated alcohol is all the cases. Conditions: Catalyst loading, 0.2 % w/v; citral, 1.67 mol dm^{-3}; solvent 3.5 mol dm^{-3}; temperature 363 K; rmp 750.

Effect of catalyst loading: From Table-4, it is suggested that 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 and 0.30 % w/v catalyst loaded with under such conditions. Among the three series of bimetallic catalysts, indicate in Table-4 higher selective conversion citral to geraniol which in catalyst load is load 0.2 % w/v. The most favoured bimetallic catalyst of Co-Ni/SiO$_2$ calinated at 773 K.

TABLE-4
PERCENTAGE CONVERSION AGAINST CATALYST LOADING FOR BIMETALLIC SUPPORTED CATALYSTS CALINATED AT 773 AND 923 K[#]

Catalyst (w/v)	Co-Ni/SiO$_2$		Ni-Cu/SiO$_2$		Cu-Co/SiO$_2$	
	773 K	923 K	773 K	923 K	773 K	923 K
0.10	35	7	5	8	8	3
0.15	50	11	11	7	11	2
0.20	70	33	16	11	18	14
0.25	58	28	12	13	10	11
0.30	47	19	10	12	4	7

[#]The selectivity is 100 % towards unsaturated alcohol is all the cases. Conditions: Citral, 1.67 mol dm^{-3}; solvent 3.5 mol dm^{-3}; temperature 363 K; pressure 4 bar; rmp 750.

Selective conversion of unsaturated alcohol: The experimental data of the initial stages of the hydrogenation of citral showed that the selectivity towards geraniol and nerol (unsaturated alcohols) increases, suggesting that a modification of the bimetallic catalyst surface takes place as the reaction proceeds. In order to explain this behavioour it is useful to investigate the way the products affect the reaction. In the present investigation, the reaction carried out under conditions catalyst loading, 0.2 % w/v; citral, 1.67 mol dm^{-3}; temperature 363 K; pressure 4 bar; rmp 750 (Fig. 4a). Three series of catalysts

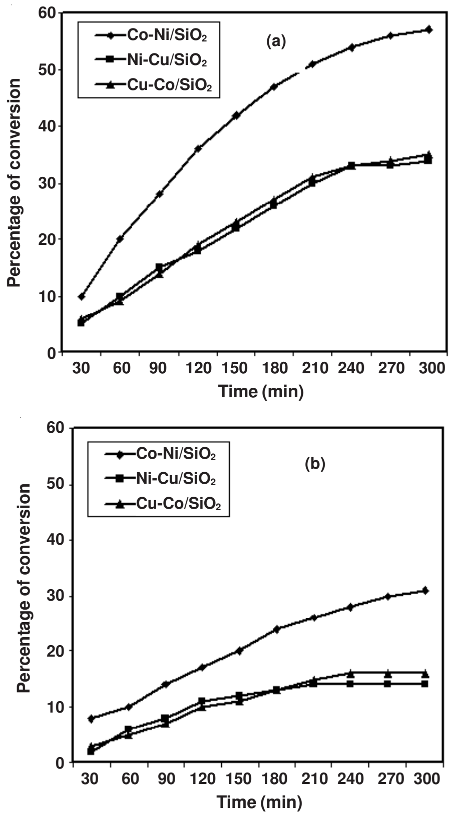


Fig. 4. Percentage conversion against time for bimetallic silica supported catalysts (Co-Ni/SiO$_2$; Ni-Cu/SiO$_2$; Cu-Co/SiO$_2$) calcined at (a) 773 K (b) 923 K; temperature, 363 K; pressure 4 bar; agitation rpm,750; catalyst loading, 0.2 % w/v; citral, 1.67 mol dm^{-3}; solvent 3.5 mol dm^{-3}

investigated liquid phase cital hydrogenation higher selectivity of Co-Ni/SiO_2 with 363 K temperature for conversion of unsaturated alcohols (57 %). At that same time Ni-Cu/SiO_2 much better than Cu-Co/SiO_2. The high temperature calcined at 923 K bimetallic catalysts in Fig. 4 (b) rate of reaction and conversion of geraniol and nerol was poor compared to calcined at 773 K.

Among the series of bimetallic catalysts, it is suggested that the higher active and selectivity catalyst is Co-Ni/SiO_2 for liquid phase hydrogenation of citral to geraniol and nerol.

Conclusion

The Co-Ni/SiO_2, Ni-Cu/SiO_2 and Cu-Co/SiO_2 bimetallic catalysts exhibit increasing activity and selectivity for the liquid phase hydrogenation of citral. Incorporation of silica support in the colloidal form during deposition precipitation of bimetallic resulted in stable and well formed catalysts with high specific surface are for calcinated at 773 K. The optimum catalyst reduction temperature which could give the highest selectivity to unsaturated alcohol was investigated over Co-Ni/SiO_2 catalyst calcinated at 773 K. Three series of catalysts calcinated at low and high temperature (773 and 923 K) were prepared and used for liquid phase hydrogenation at various temperature and pressure and rpm agitation. It can observed that in all cases, the present investigation, the reaction produces unsaturated alcohols, in activity and selectivity catalyst of Co-Ni/SiO_2 calcined at 773 K temperature with under conditions of catalyst loading, 0.2 % w/v; citral, 1.67 mol dm^{-3}; solvent 3.5 mol dm^{-3}; temperature 363 K; pressure 4 bar; rmp 750, liquid phase cital hydrogenation most selective Co-Ni/SiO_2. Among these experiments overall conversion of is 99 % but selectivity is 57 % of geraniol and nerol.

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