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ARTICLE

Selective hydrogenation of cinnamaldehyde on nickel nano particles supported on titania- Role of catalyst preparation methods

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With nickel acetate as the precursor, 15% (w/w) Ni/TiO₂(P-25) catalysts have been prepared by four different methods, namely, direct impregnation (IM), deposition precipitation (DP) with urea and by chemical reduction, using hydrazine hydrate (HH) and glucose (GL) as reducing agents. XRD, hydrogen chemisorption, TEM and TPR analyses reveal that smaller Ni crystallites, 8-12 nm in size, are obtained by adopting HH & GL methods compared to 15-20 nm crystallites by IM and DP methods. Nature of metal support interactions (MSI) vary depending on the method of preparation. XPS studies reveal the presence of residual Ni²⁺ ions along with Ni metal. All the catalysts exhibit good conversion of cinnamaldehyde (CAL) (in methanol, at 20 Kg/cm² H₂ pressure, 80-140°C) and selectivity to cinnamyl alcohol (COL) / hydrocinnamaldehyde (HCAL) up to 1hr, beyond which, further hydrogenation of COL to hydrocinnamyl alcohol (HCOL) occurs. Catalysts prepared by HH & GL display higher CAL conversion and selectivity to COL. Conversion of HCAL to HCOL proceeds at a slower rate compared to that of COL to HCOL. Introduction of HCAL along with CAL as feed increases selectivity to HCOL, while introduction of COL in the same manner decreases selectivity to HCOL. Infra-red spectra of CAL adsorbed on the catalysts reveal surface bonding through C=C and C=O groups. Steric hindrance due to adsorption of COL and the presence of small amounts of Ni²⁺ favour adsorption of CAL through C=O group leading to higher selectivity to COL.

Key words: Nickel nano particles, Chemical reduction, Titania, Selective hydrogenation, Cinnamaldehyde, C=O activation

Introduction

Selective hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL) is a challenging proposition, as it involves the competitive hydrogenation of carbonyl double bond vis-à-vis thermodynamically favourable hydrogenation of olefinic double bond.¹ Design of suitable catalysts and adopting appropriate reaction conditions are the two key factors to be addressed. A number of noble metal (Pt, Pd, Ir, Ru, Rh and Os), non-noble metal (Fe, Co, Ni, Cu), as well as bimetallic (noble and non-noble) catalysts on different supports (carbon, alumina, silica & titania etc.) are known to be effective for this conversion.²⁻⁴ In general, Os, Ir, Ru, Pt, Co & Cu are reported to be selective for the formation of COL, while, Rh, Pd & Ni towards hydrocinnamaldehyde (HCAL) and hydrocinnamyl alcohol (HCOL). A number of parameters, like, the nature of the active metal, its surface structure and exposed crystal planes, method of catalyst preparation, characteristics of the support, solvent (polarity and solubility of hydrogen), reaction conditions and additives/promoters/second element used could influence the activity and selectivity.^{5,6} Electronic as well as geometric factors, that

manifest in different modes of adsorption of CAL and in the selectivity displayed by different crystal planes exposed (facet selectivity), are related to the nature of the active metal. While a number of reports⁷⁻¹⁷ attribute activity and COL selectivity to the metal nano particle size and shape, a recent publication by Zhu and Zaera¹⁸ has concluded that the selectivity is independent of the particle size within a narrow range of 1.25 to 1.5 nm Pt nano particles supported on silica. Hence the final word on this front is yet to emerge.

From the process economics point of view, it is always desirable to develop non-noble metal based catalysts. Lin et al.¹⁹ have reported that the addition of Ir to Ni/TiO₂ brings in several changes, like, formation of bimetallic Ni-Ir species, the reducibility of Ni²⁺ is improved, the electronic structure of Ni is modified and hydrogen spill over is promoted. The improvement in activity of Ni-Ir/TiO₂ vis- a-vis Ni/TiO₂ is attributed to these changes. Ni₂P supported on SiO₂²⁰ Cu-Ni based hydrotalcites,²¹ layered Zn-Ni-Cu-Al hydrotalcites,²² Co-Al and Ni-Al based hydrotalcites²³ are some of the non-noble metal based catalysts explored for this reaction. Earlier work²⁴ in this laboratory has shown that supported cobalt catalysts, especially on titania, display high activity and good

selectivity for COL. However, arriving at non-noble metal based catalysts with maximum activity and selectivity remains a challenge. Unlike the noble metals, Co, Ni & Cu based catalysts are characterized by relatively strong metal support interactions (SMSI) which influence the degree of reduction, metal dispersion and the evolution of the active phase. Metal support interactions are to be moderated to a desirable extent, by adopting suitable methods of preparation, so as to maximize the activity and selectivity. We have therefore, attempted to address these issues through a series of investigations on nickel based catalysts, which are active for selective hydrogenation of α - β unsaturated aldehyde like CAL. Since the desired characteristics of supported Ni catalysts evolve during the preparation, as the first step, influence of different preparation methods on the characteristics and performance supported Ni catalysts has been investigated. For this investigation, Ni (15% w/w) loaded on titania (P-25), a well-known reactive support, has been selected.

2. Experimental

2.1 Preparation of catalysts

P25 TiO₂ (Evonik), Ni(CH₃COO)₂·4 H₂O (CDH), NaOH (SRL), Hydrazine Hydrate, Poly ethylene glycol, 400 Urea, D-glucose (all from Merck), Methanol, Ethanol, Methanol (all from Qualigens) and Cinnamaldehyde (ALDRICH), were used as such.

Four different methods were adopted for the incorporation of nickel on to the support titania.

Method 1 Impregnation (IM)

0.74 g of nickel acetate was dissolved in 20 ml of water with continuous stirring for 30 min. at room temperature, followed by addition of 1 g of TiO₂ (P25). The slurry was refluxed for 5 h at 80°C, cooled to room temperature, centrifuged, washed with anhydrous ethanol and dried at 60°C for 24h. The catalyst was calcined at 450°C for 4 h in air and then pre-reduced at 400°C for 4 h in hydrogen gas flow.

Method 2 Deposition Precipitation with urea (DP)²⁵

0.74 g of nickel acetate and 1 g of TiO₂ were mixed in 20 ml of water and stirred for 30 min at room temperature. 0.5 g of urea was added to the mixture and refluxed for 5 h at 80°C. The slurry was cooled at room temperature, centrifuged, washed with anhydrous ethanol and dried at 60°C in 24 h. The catalyst was calcined at 450°C for 4 h in air and then pre-reduced at 400°C for 4 h in hydrogen gas flow.

Method 3 Chemical reduction by Hydrazine Hydrate (HH)²⁶

0.74 g of nickel acetate and 1.2 g of Poly ethylene glycol were dissolved in 20 ml of anhydrous ethanol and stirred for 30 min at room temperature. 1.5 ml of 0.1M NaOH in ethanol was added drop-wise, followed by 8 ml of hydrazine hydrate. The mixture, after refluxing for 5h at 80°C, changed to black in colour, indicating the reduction to Ni metal and confirmed by UV spectroscopic analysis (Fig1). 1 g of TiO₂ (P25) was added to the solution containing Ni nano particles and stirred for 2h. The mixture was cooled to ambient

temperature, centrifuged, washed with anhydrous ethanol and dried at 60°C for 24h.

Method 4 Chemical reduction by D-Glucose (GL)²⁷

0.74 g of nickel acetate and 40 ml of D-glucose solution (0.15M) were mixed and stirred for 30 min at room temperature. 10 ml of liquor ammonia was added drop-wise to the mixture. Refluxing the mixture for 5 h at 80°C turned its colour to black indicating reduction of Ni²⁺ ions to Ni metal, which was confirmed by UV spectroscopic analysis (Fig.1). 1 g of TiO₂ (P25) was added to the solution containing Ni nano particles and stirred for 2h. The mixture was cooled to ambient temperature, centrifuged, washed with anhydrous ethanol and dried at 60°C for 24h.

Both HH and GL catalysts were pre-reduced in hydrogen gas flow at 300°C for two hours. All characterization and hydrogenation experiments were carried out with pre-reduced catalysts.

2.2 Characterization of catalysts

Quantitative estimation of nickel contents in the finished catalysts were carried out by XRF, after due calibrations. Powder X-ray diffraction patterns for the catalysts were recorded by Rigaku Miniflex II diffractometer, using Cu-K α (λ =0.15418 nm) in 2 θ range of 10° to 80° and a scan rate of 3°/min.

Temperature Programmed reduction (H₂-TPR) and hydrogen pulse chemisorption studies were carried out on Micromeritics Autochem II 2920 chemisorption analyser. Catalysts by IM & DP methods were calcined in air at 450°C and the catalysts by HH and GL methods at 300°C, prior to TPR experiments. 50 mg of catalyst was pre-treated at 300 °C in high purity Ar gas (25cc/min) for 1 h and then cooled to room temperature in Ar flow. The gas was changed in 10 % H₂ in Ar (25cc/min) at room temperature. After the stabilization of the baseline TPR was started from RT to 700° C with a heating rate 10° C/ min.

Ni metal surface area measurements were performed by H₂ pulse chemisorption. 50 mg of catalysts were pre-treated at 300 °C in high purity Ar gas (25cc/min) for 1 h and then cooled to room temperature under Ar flow. The catalysts were reduced (at 400° C for IM & DP catalysts and 300°C for HH &GL catalysts) for 2 h under 10 % H₂/Ar flow, cooled down to RT under Ar. H₂ pulses were injected with Ar as carrier gas, until the eluted peak area of consecutive pulses was constant.

Transmission electron microscopic (TEM) investigations on the pre-reduced catalysts were studied on a CM 20 Phillips transmission electron microscope with an acceleration voltage of 120 KV.

CAL in vapour phase was adsorbed on self-supported disc of the catalysts at 120°C in the IR gas cell attached to Perkin-Elmer FT-IR unit. After equilibration, the sample was cooled to room temperature, excess vapour evacuated and spectra of adsorbed CAL were recorded.

X-ray photoelectron spectra of the catalysts were recorded using Omicron Nanotechnology instrument with Mg K α radiation. The base pressure of the analysis chamber during the scan was 2*10⁻¹⁰ millibar. The pass energies for individual scan and survey scan are 20 and 100 eV, respectively. The spectra were recorded with step width of 0.05 eV. The data were processed with the Casa XPS

program (Casa Software Ltd, UK), and calibrated with reference to the adventitious carbon peak (284.9 eV) in the sample.

2.3 Reaction studies

Hydrogenation reactions were performed in liquid phase, in a 100 ml Parr reactor (Model-4848). The autoclave was charged with 150 mg of pre-reduced catalyst, 1.2 g of cinnamaldehyde and 16 ml of methanol. After purging first with nitrogen (three times) and then with hydrogen (three times) the autoclave was pressurized with hydrogen to the desired value of 20 Kg/cm² at 298K. The reaction was performed at 120° C for 1 h with stirring at 600 rpm. No increase in conversion was observed at stirring rates higher than 600 rpm indicating that at this rate mass transfer limitations could be ruled out. Actual pressure during reaction was 23 Kg/cm². Further experimental details on reaction studies are given in ESI-1. The reaction products were separated by filtration and analysed on Perkin Elmer Clarus-500 GC with ZB-1 capillary column and FID detector

3. Results and discussion

XRD patterns for the catalysts prepared by IM and DP methods indicate the presence of NiO and titania P-25 phases after drying and calcination in air at 450°C. Low temperature chemical reduction of Ni²⁺ ions to Ni metal in solution by HH and GL methods is confirmed by the absence of absorption maximum at 396 nm due to d-d transition for Ni²⁺ (Fig.1)

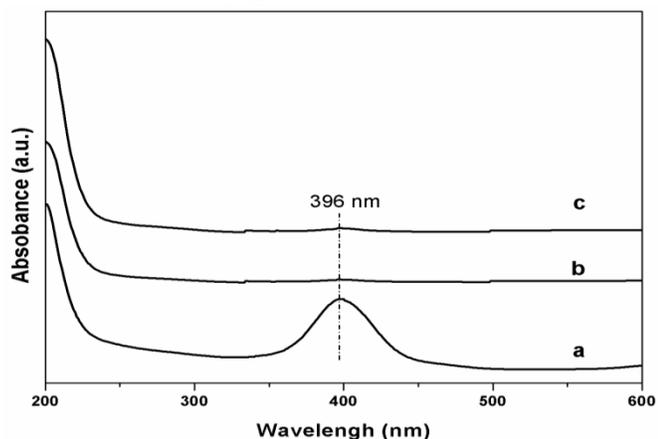


Fig. 1 Electronic spectra of impregnation solutions by HH & GL methods- a-before and after reduction by b-HH and c-GL methods

Table 1 Properties of catalysts prepared by different methods

Prepn. Method	Ni content (wt %) ^a	Metal Disp. ^b %	Cryst. Size ^c (nm)	Cryst. Size ^d	Cryst. Size ^e (nm)	TPR Redn. Maxima (°C)
IM	16.1	5.3	19	16.6	15	299, 388, 448, 611, 637
DP	16.5	4.6	20	18	16	370, 502, 570
HH	15.2	8.7	11	11	8	293, 320, 668
GL	15.5	10.7	9.5	12	10	352, 690

a-by XRF, b & c-by H₂ chemisorption, d- by TEM, e- by XLBA

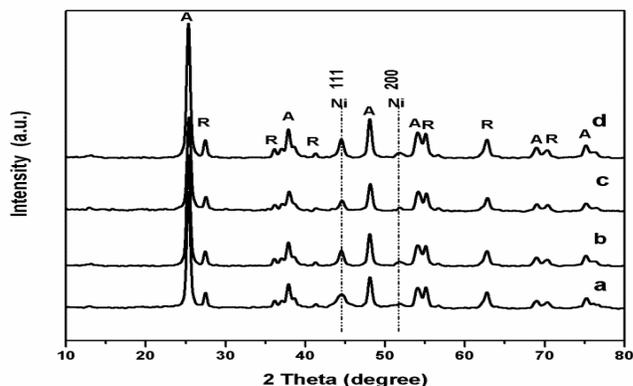


Fig. 2 XRD patterns for the catalysts in reduced state: a-IM, b-DP, c-HH and d-GL methods.

Table 1 lists the physico-chemical properties of the catalysts. Nickel contents estimated by XRF method match closely with the expected values. XRD patterns for all the four catalysts in reduced state are shown in Fig.2. Along with the d-lines for P-25-titania, two major lines corresponding to Ni metal with fcc structure (JCPDC #870712) at 2θ values at 44.4- 44.6° and 51.8° (corresponding to (111) and (200) planes respectively) are observed. Absence of d-lines due to NiO indicates nearly complete reduction to Ni metal in all the four catalysts. However, presence of residual NiO, at levels below the detection limits of XRD, could not be ruled out.

Ni crystallite sizes estimated by Debye-Scherer method are given in Table.1, which also includes the values obtained by pulse chemisorption of hydrogen and TEM techniques (Fig.3). Fairly good agreement between the size values from three different methods, XRD, chemisorption and TEM is observed. As expected, the crystallite size values obtained by chemical reduction at lower temperature (HH & GL methods), are smaller than those by reduction with hydrogen at higher temperature (IM & DP methods). Ni crystallite size values for the IM & DP catalysts are higher (15-20 nm) compared to 12.7 nm reported earlier for 11% w/w Ni on high surface area titania.¹⁹ Chemical reduction methods, HH and GL, yield Ni crystallites of smaller size, 8-12 nm, comparable with earlier report,¹⁹ in spite of higher Ni loading (15- 16 Vs 11 %w/w) and lower surface area of TiO₂ support (50 Vs 150 m²/g).

Support being the same, the influence of preparation methods on the degree of Ni-support interactions is clearly evident in the TPR patterns (Fig.4). TPR reduction maxima observed in each case are listed in Table.1. For the catalysts prepared by IM & DP the reduction behaviour is as per the literature report.¹⁹ In the case of the catalyst by IM method, major TPR maximum located at 448°C is due to the Ni species having strong interaction with the support. A shoulder on the low temperature side, at 288°C, signifies free/weakly bound NiO. Two high temperature reduction maxima at 388°C and 448°C are due to the species that have strong interaction with the support. Other higher temperature reduction peaks could possibly be due to the reduction of the support.

The catalyst prepared by DP method shows two reduction maxima at 370 & 505°C and the third one at 570°C due to reduction

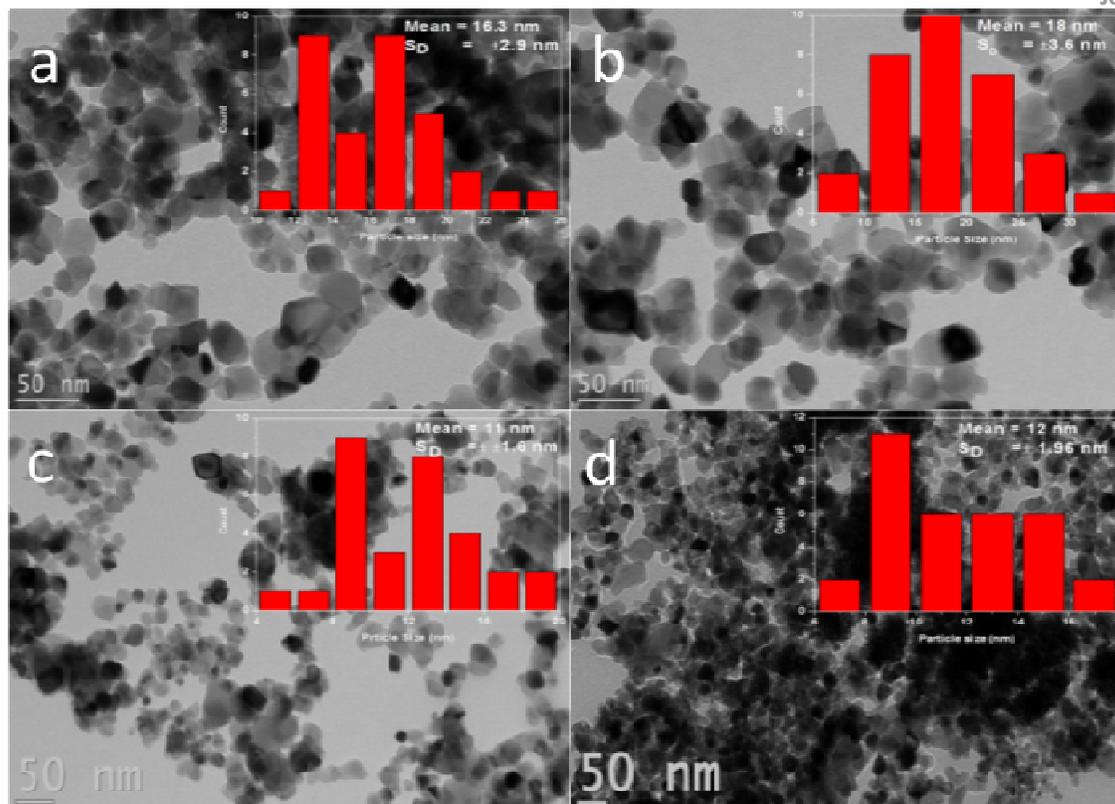


Fig. 3 TE micrographs with histograms for the catalysts by: a-IM, b-DP, c-HH and d- GL methods

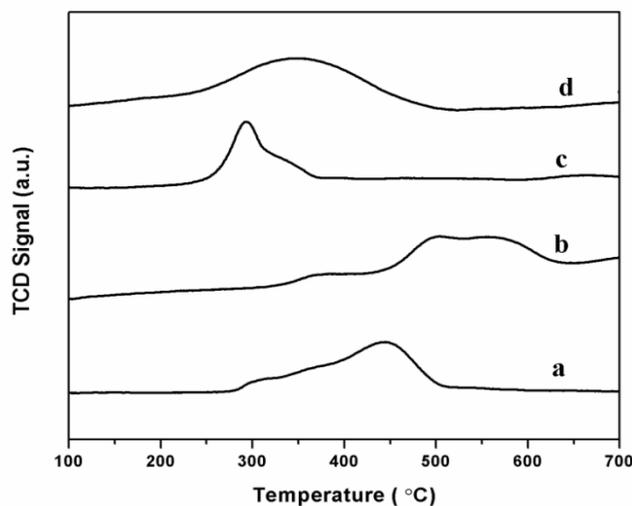


Fig. 4 TPR profiles for the catalysts by -a- IM, b-DP, c-HH and d- GL methods.

of the support. Compared to the sample by IM method, DP method results in stronger metal-support interactions, as indicated by the shift in reduction maxima to higher temperatures. On the contrary, the catalyst prepared by HH method shows a well-defined reduction maxima at lower temperatures, at 295°C and a shoulder at 320°C, both due to relatively weaker MSI. This is expected, since the chemical reduction of Ni^{2+} takes place at lower temperature. A small high temperature peak at 668°C, possibly due to the reduction of the support, is observed. The catalyst by GL method shows a single reduction peak at 352°C and a weak high temperature reduction peak

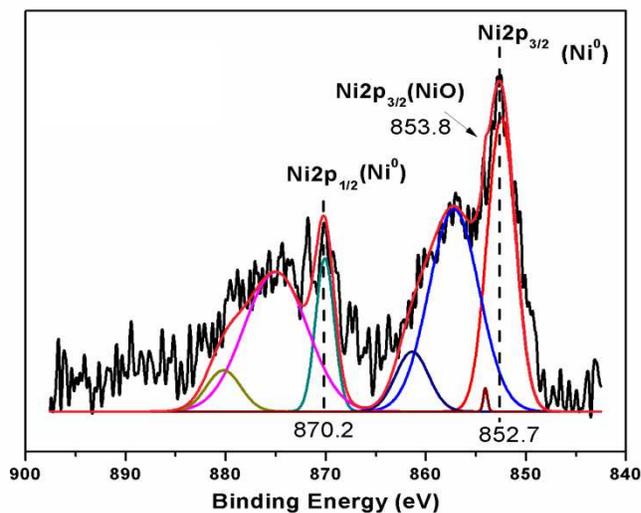


Fig. 5 XPS line profile for pre-reduced catalyst prepared by GL method

at 690°C. To summarize, TPR data indicate that preparation methods profoundly influence the degree of metal-support interactions. XPS line profile for pre-reduced GL catalyst is presented in Fig.5. Major peaks at 870.2 eV and 853.2 eV are close to the respective values of 870 eV and 853 eV reported in literature for $\text{Ni}2p_{3/2}$ and $\text{Ni}2p_{1/2}$ lines. On deconvolution, a minor peak at 853.8 eV due to residual NiO is observed. XPS data for other catalysts also indicate the presence of very small quantities of Ni^{2+} . Since the NiO contents are very small they are not revealed in X-ray diffractograms.

The data on the conversion and selectivity for hydrogenation of CAL on the four catalysts at 120 °C for one hour reaction time are given in Table.2. Based on the TOF values, catalysts prepared by IM & DP methods with larger Ni crystallite size (15-20 nm) are a shade more active than catalysts prepared by HH & GL methods with relatively smaller crystallite sizes, (8-12 nm) respectively.

Table 2 Conversion and selectivity data for hydrogenation of cinnamaldehyde at 120 °C

Catalyst Prepn. method	Conv. %	Products selectivity %				TOF s ⁻¹ x 10 ⁴
		HCAL	COL	HCOL	Others	
IM	84	38.9	43.6	17.4	0.1	7.7
DP	70	64.6	29.9	5.3	0.2	6.7
HH	99	25.3	53.2	21.3	0.2	6.0
GL	91	31.0	61.0	6.9	1.1	6.0

Wt. of catalyst -150 mg, CAL-1.2 g, Methanol-16 ml, Pressure-20 Kg/cm², Reaction time -1 hr

Crystallite size effects on activity are not expected in this size range (10-20 nm). However, contrary to the literature reports, all the four catalysts display significant but moderate selectivity towards COL and lower selectivity for HCOL during the initial 1 hr reaction time. The catalysts prepared by low temperature chemical reduction methods display relatively higher selectivity towards COL indicating that factors other than size could play a role in directing selectivity at the initial stages. On continuing the reaction beyond 1 hr, further hydrogenation of COL to HCOL is observed, as indicated by the typical data given in Table.3 for the catalyst prepared by GL method.

Table 3 Typical conversion and selectivity data for extended runs

Prepn. method	Conv. %	Products selectivity %			
		HCAL	COL	HCOL	Others
GL (1 hr)	91	31.0	61.0	6.9	1.1
GL (4 hrs)	100.0	20.1	-	79.0	0.9
GL (8hrs)	100.0	-	-	99.4	0.6

Catalyst GL wt.-150 mg, CAL-1.2 g, Methanol-16 ml, Pressure-20 Kg/cm², Temp.120 °C

In order to unravel the mechanistic pathways during hydrogenation, experiments have been conducted with different feedstock compositions and reaction temperatures and the results are presented in Table 4 & 5. Results on experiments with HCAL, COL and mixture of HCAL and COL as feed on catalyst GL are given in Table.4. In the absence of CAL, COL gets hydrogenated completely to HCOL. The rate of hydrogenation of HCAL is very slow and the same trend is observed with 50/50 (V/V %) mixture of COL & HCAL as well, resulting mainly in HCOL.

Accordingly, a reaction pathway is depicted in Scheme.1. Conversion of CAL proceeds simultaneously through two routes, to

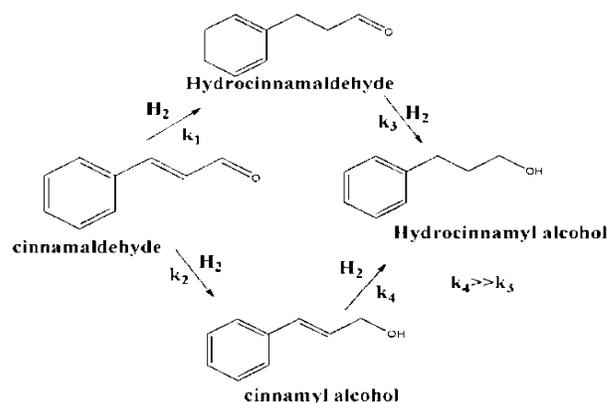
Table 4 Conversion and selectivity data for hydrogenation with different feeds at 120 °C

Feed	Conv. %	Products composition %			
		HCAL	COL	HCOL	Others
COL	88.6		11.4	88.0	0.6
HCAL	19.0	81.0	0.0	18.8	0.2
COL+HCAL- 50/50		33.0		66.0	0.1

Catalyst GL wt.-150 mg, Feed-1.2 g, Methanol-16 ml, Pressure-20 Kg/cm², Reaction time-1hr

COL and HCAL, which on further hydrogenation yield HCOL. Based on the data presented in Table 4, conversion of COL to HCOL proceeds with a rate of 20.7 hr⁻¹ (moles of COL converted per hour per mole of Ni) while the corresponding rate for the conversion of HCAL is 4.4 hr⁻¹. It is clear that HCOL is formed from COL and not from HCAL

Scheme 1 Reaction pathways for hydrogenation of cinnamaldehyde on Ni/TiO₂ catalysts



Similar observations have been reported by Nitta et al.²⁸ on Co/SiO₂ catalysts and Mahmoud et al.²⁹, Hammudeh et al.³⁰, and Cairns et al.³¹ on Pd based catalysts. Weak adsorption of HCAL on the surface, relative to that of CAL & COL, could lead to its slower rate of hydrogenation. Besides, addition of small amount HCAL (0.1g) along with feed CAL (1.1g) increases the selectivity to HCOL at 120 °C, while the addition of COL (0.13g) to CAL (1.07g) in the same manner, lowers the selectivity towards HCAL, from 31.0% to 19.6% on GL catalyst and 38.9% to 25.1% on IM catalyst. It is likely that adsorbed COL promotes adsorption of CAL in on-top η_1 mode^{5,32} via C=O due to steric hindrance. Breen et al.³³ have observed that on Ir supported on carbon, adsorbed COL causes steric hindrance, thus inhibiting the adsorption of CAL via C=C bond. On increasing the reaction temperature from 80 to 120 °C, the selectivity to COL increases on all four catalysts. But at 140 °C, HCOL is formed at the expense of COL (Table 5). Like Pd, Ni surface facilitates adsorption of CAL in η_4 or η_2 (di π) mode^{5,32}, wherein the formation of both HCAL and COL are possible. This is corroborated by the FT-IR spectra for CAL adsorbed on the catalysts at 120 °C presented in Figure.6. CAL in vapour phase displays absorption bands at 1625 cm⁻¹ due to conjugated C=C bond stretching vibration and at 1720 cm⁻¹ due to C=O bond asymmetric

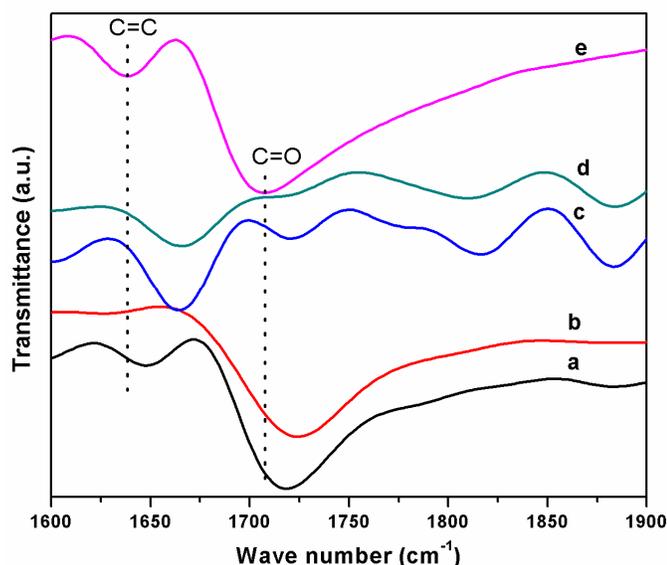


Fig. 6 FTIR spectra of adsorbed cinnamaldehyde on: a) GL b) HH c) IM d) DP catalysts. e) CAL in vapour phase

stretching vibration of unsaturated aldehyde^{34,35}. Corresponding spectra for all the four catalysts show shifts on the absorption maxima due to bonding of CAL with the surface.

However, experimental data from the present work indicate that the formation of kinetically controlled product, COL, is favoured in the first one hour of reaction. With the increase in reaction time or temperature, HCOL, which is thermodynamically the most stable product, is formed.

Supported Ni catalysts are reported to be selective for C=C hydrogenation, with nearly zero selectivity for COL,^{29, 36-40} while in the present work, significant COL selectivity is observed, with all four catalysts when the reaction is carried out for 1 hr. Though studies on supported Ni catalysts have been reported earlier (Table 6), the nature of support, Ni dispersion, metal-support interactions,

Table.5 Effect of reaction temperature on CAL conversion and selectivity to different products

	Catalysts	CAL Conv. %	HCAL	Selectivity (%)		
				COL	HCOL	others
1	GL-80 °C	44.6	72.8	23.8	2.9	0.5
	GL-100° C	73.0	53.9	40.1	5.0	1.0
	GL-120 °C	91.0	31.0	61.0	6.9	1.1
	GL-140 °C	98.0	29.0	27.3	43.6	0.1
2	IM-80 °C	38.6	81.2	13.2	5.2	0.4
	IM-100 °C	63.5	63.3	24.2	12.1	0.4
	IM-120° C	84.0	38.9	43.6	17.4	0.1
	IM-140 °C	89.2	35.4	19.8	43.8	1.4
3	DP-80 °C	27.9	88.4	10.1	1.1	0.4
	DP-100 °C	43.2	76.3	18.3	3.4	2.0
	DP-120 °C	70.0	64.6	29.9	5.3	0.2
	DP-140 °C	74.3	61.0	14.2	23.7	1.1
4	HH-80 °C	49.1	71.0	19.3	8.6	1.1
	HH-100° C	78.3	52.0	34.7	12.6	0.7
	HH-120 °C	99.0	25.3	53.2	21.3	0.2
	HH-140 °C	99.2	24.9	23.3	44.5	7.3

Catalyst wt.-150 mg, CAL-1.2 g, Methanol-16 ml, Pressure-20 Kg/cm²

and the experimental conditions adopted vary widely, thus making comparison, a difficult task. Lin et al (19), in their studies on hydrogenation of CAL on Ni/TiO₂ with iso-propyl alcohol as solvent at 80°C, have reported conversion of 66.2% in one hour, with nearly total selectivity to HCOL and COL is not observed. Besides, it is to be noted that HCOL formation is less, even after 5 hr of reaction, when conversion reaches 71%.

Table 7 presents activity/selectivity data as observed by Lin et al., along with the data for the catalyst GL from the present study, but under the experimental conditions adopted by them (19). It is observed that CAL conversion is less (42 & 51%) in the present case, compared to 66.2% reported by Lin et al.

Table 6 Liquid phase hydrogenation of cinnamaldehyde over Ni based catalysts-Data from the literature

Catalyst/ (Wt. mg)	Ni Cryst. Size (nm)	Solvent (Vol-ml)	Temp. (°C) /Pressure (Kg/cm ²)	Time (h)	Conv. (%)	COL Selec (%)	Ref
15%Ni/TiO ₂ (150)	10-20	Methanol (16)	120/20	1	70-99	30-61	Present work
11%Ni/ TiO ₂ (50)	12.7	Iso-propyl alcohol (80)	80/20	1	66.2	1.8	19
5% Ni/ SBA-15(265)	3.6	Propylene carbonate (25)	150/ atmos	3	57.2	1.6	36
10%Ni/CNF/AC (50)	4.2-5.5	Toluene (20)	160/30	1.5	80-90	-	39
Ni w/o support (1000)	50	Ethanol (100)	100/15	3	97.0	-	37
10% Ni ₁₂ P ₅ /SiO ₂ (500)		Cyclohexane (115)	120/30	2	78.1	3	20

Table 7 Conversion and selectivity data at 80°C for GL catalyst

Solvent	Conv. %	Products selectivity %				TOF s ⁻¹ x 10 ⁴
		HCAL	COL	HCOL	Others	
Methanol	42.0	72.2	23.2	2.6	2	7.7
Iso-propyl alcohol	51.0	81.0	12.4	3.1	3.5	6.7
Lin et al (19)	66.2	98.2	nd	1.8	-	-

Cat. (GL) Wt.- 50 mg, CAL-3 mmol., Temp-80°C, Solvent-10 ml, Pressure-20 kg/cm

Nature of titania supports used (low surface area P-25 Vs high surface area nano size titania) and metal-support interactions, could in part, explain the difference in activity. Ni crystallite sizes are in the same range and in this size range no significant variations in the coordinative unsaturated sites or relative population exposed crystal planes, (111),(110),100, are expected. Besides, the effect of solvent is seen clearly, with higher TOF values and higher selectivity for COL with GL catalyst, when methanol is used instead of isopropyl alcohol. Higher solubility of hydrogen in methanol⁴¹ and its higher dipole moment vis-à-vis isopropyl alcohol⁴² which could activate C=O, could be one of the factors responsible for higher selectivity.

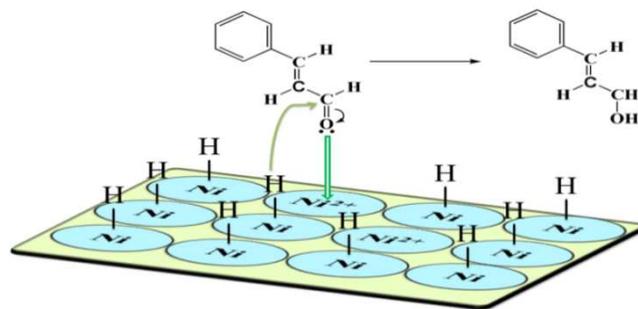
Ungureanu et al.³⁶ have investigated selective hydrogenation of CAL with propylene carbonate as solvent on Ni, Cu and Ni-Cu bimetallic nano particles confined in the channels of ordered mesoporous SBA-15 and observed that mono metallic Ni nano particles (5 wt Ni, 3.5 nm in size) are moderately active (57.2 % conversion) with very high selectivity to HCAL (94.2%). Addition of Cu up to atomic fraction 0.2, increases conversion from 57.2% to 99.3% with a concurrent decrease in HCAL selectivity (94.2 to 90.8%) and small increase in COL selectivity (1.6 to 5.4%).

However, Zhao et al.³⁷ have reported that unsupported Ni nano particles of size 50 nm are highly active (94.2 % conversion after 3 hrs, at 100°C, 15 MPa hydrogen pressure, with 20 ml of CAL and 1g of catalyst dispersed in 100 ml of ethanol as solvent) with selectivity to HCAL at ~55%, which increases drastically with the addition of Ru. It is likely that with larger Ni crystallites, further hydrogenation to HCOL is catalysed. Nickel phosphides, like Ni₂P and Ni₁₂P₅, when supported on silica²⁰, display very high selectivity towards HCAL. Chen et al.³⁸ observed that Ni-Si intermetallics display higher selectivity towards HCAL vis-a vis HCOL, due to the electronegative character of Si and the consequent repulsive force between Si & oxygen in C=O. Gryglewicz et al.³⁹ have observed that the hydrogenation of CAL on 10% w/w Ni supported on two different types of CNF & activated carbon supports proceeds selectively towards HCAL and hydrogenation of COL to HCOL is faster than that of HCAL.

Structural and electronic environment of Ni in the catalyst matrix could direct the orientation of the CAL molecule on the surface (adsorption through C=C or C=O) and hence the selectivity^{21-23,39}. Apestiguia and co-workers⁴⁰ have carried out detailed investigations on the characterization, activity, selectivity

and kinetic analysis of hydrogenation of CAL (with iso-propyl alcohol as solvent) on Cu/SiO₂, Cu-Al binary oxide, Cu-Al-Zn ternary and Cu-Al-Zn-Ni/Co quaternary oxides with spinel structure. With metallic Cu as the active phase, HCAL was formed as the major product on Cu/SiO₂ and Cu-Al binary oxides. However, modification of the Cu-Al spinel matrix composition by the introduction of Zn, Ni & Co and controlled pre-reduction (with hydrogen at 473K) resulted in the generation of Cu_{0.5}[MO]_{0.5}ZnAl₂O₄ phase, with M= Zn, Co or Ni, which displayed increase in activity as well as selectivity towards COL when compared to Cu/SiO₂ and Cu-Al binary spinel. Under the pre-reduction conditions employed, only Cu²⁺ could be reduced to metallic state, leaving the divalent cations as such. Such a situation resulted in the formation of Cu⁰-M²⁺ sites which facilitate adsorption of CAL in a linear configuration, via C=O, thereby leading to higher selectivity towards COL. However, kinetic runs over extended periods lead to further hydrogenation of COL to HCOL. Similar observations have been reported by Dragoi et al. on non-calcined and mildly reduced (at 150°C) hydrotalcites based on Mg & Al²¹ and Zn-Al²² with propylene carbonate as solvent. Partial substitution of Mg²⁺ /Zn²⁺ in the hydrotalcites with Cu²⁺-Ni²⁺ resulted in the increase in COL selectivity, due to the formation of Cu⁰-Ni²⁺ sites, which are likely to act as Lewis acid sites, promoting preferential adsorption of CAL through C=O⁴³⁻⁴⁷ and leading to the formation of COL.

However, Ni-Al and Co-Al based catalysts derived from takovite type LDH precursors, on calcination and high temperature reduction form Ni & Co metal nano particles of size 3.6-5.8 nm and <3.0 nm respectively.²³ While COL is formed selectively on Co-Al based catalysts, (60% selectivity at 50% conversion) Ni-Al based catalysts yield HCAL with 95% selectivity at complete conversion with propylene carbonate as solvent. Presence of M⁰-Nⁿ⁺ sites are thus essential for polarization and activation of C=O bond.



Scheme 2 Proposed mode of adsorption of cinnamaldehyde on Ni/TiO₂ - Adsorption and activation of cinnamaldehyde

In the present case, the observed selectivity to COL could be due to the adsorption of CAL through C=O bond, which is facilitated by the presence of small amounts of Ni²⁺ as observed in XPS studies, along with Ni⁰, as depicted in Scheme 2. The quantity of Ni²⁺ may be too small to be revealed by XRD studies. The nature of metal-support interactions, which vary depending on the method of preparation (HH & GL) and the use of methanol as solvent could be the other contributing factors for the higher selectivity to COL.

Conclusions

Nickel (15% w/w) supported on TiO₂-P-25 catalysts have been prepared by conventional high temperature hydrogen reduction (IM & DP) and low temperature chemical reduction (HH & GL) methods. HH and GL methods yield relatively smaller Ni crystallites. Preparation methods adopted profoundly influence the nature of metal-support interactions. All four catalysts exhibit good conversion of CAL and significant selectivity to COL in the initial stages of the reaction. With the increase in reaction time, COL is hydrogenated further to HCOL. Catalysts prepared by HH & GL methods display higher CAL conversion and selectivity to COL. Presence of small amounts of Ni²⁺ along with Ni⁰ and steric hindrance due to adsorbed COL could favour the adsorption of CAL through C=O, leading to the formation of COL, which gets hydrogenated further to HCOL with the increase in reaction time.

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