



Selective hydrogenation of cinnamaldehyde using palladium based bimetallic catalysts Pd-M/TiO₂ (M=Cu, Ag and Au)

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Pd based bimetallic catalysts, Pd-M, (M=Cu, Ag, and Au) supported on TiO₂ P-25, have been prepared by chemical reduction with glucose and characterized by XRD, TEM, XPS, DRS, TPR and H₂TPD. Activity for the conversion of cinnamaldehyde (CAL) and selectivity to hydro-cinnamaldehyde (HCAL), cinnamyl alcohol (COL) and hydrocinnamyl alcohol (HCOL) have been evaluated in the temperature range of 120-140 °C for 1 h and 10 bar hydrogen pressure. For comparison, monometallic Cu, Ag and Au (1% w/w in each case) catalysts supported on TiO₂ P-25 have been prepared and evaluated. DRS and XPS studies reveal nanoscale alloy formation and re-distribution of charges in bimetallic catalysts. Bimetallic Pd-Cu displays higher CAL conversion compared to Pd-Ag and Pd-Au. Besides the favourable electronic and ensemble effects, availability of reactive hydrogen on Pd-Cu, as revealed by the lowest hydrogen desorption temperature, is an additional factor that contributes towards the higher activity of Pd-Cu. Bimetallic catalysts are stable up to five reaction cycles, without any loss of Pd or structural integrity.

Keywords: Bimetallic Pd catalysts, Cinnamaldehyde hydrogenation, Nano scale alloys, Synergistic effect, Reactive hydrogen

Selective hydrogenation of cinnamaldehyde (CAL) to yield hydrocinnamaldehyde (HCAL) or cinnamyl alcohol (COL) is an elegant example of chemoselectivity¹. While both the products find applications in pharma, agro and fine chemicals industries^{2,4}, the scientific challenges involved in the design of catalysts for the hydrogenation of cinnamaldehyde with high selectivity (to HCAL or COL) and maximum CAL conversion continue to be the focus of research in this area. Noble metal (Pt, Pd, Rh, Ru, Os, Ir) based catalysts^{5,6} have proven to be highly effective for this reaction. Several factors, like, the nature of the active metal, its surface structure and exposed crystal planes, metal crystallite size, method of catalyst preparation, characteristics of the support and solvent (polarity and solubility of hydrogen), reaction conditions, additives/promoters/second element used and mode of adsorption of CAL, influence the activity and selectivity¹⁷⁻¹⁹. According to Giroir-Fendler *et al.*⁵, the inherent activity of the Group VIII metal catalysts supported on activated carbon, expressed as TOF (sec⁻¹) (in brackets), increases in the order: Pt (0.02) <Ir (0.04) <Ru (0.05) <Rh (0.5) <<Pd (6.7), with Pd displaying the maximum activity.

Pd based bi-metallic catalysts display further improvements in activity and selectivity as revealed by studies on Pd-Ni^(Ref. 20), Pd-Au^(Ref. 21-24), Pd-Ag^(Ref. 19-25), Pd-Ru^(Ref. 12) Pd-Ir/Cu/Sn^(Ref. 26) catalysts for this reaction. Especially, bimetallic catalysts containing Pd and Group IB metals like Cu, Ag and Au have been investigated extensively for selective hydrogenation of acetylene²⁷⁻²⁹ and cinnamaldehyde²¹⁻²⁶. Investigations on the hydrogenation of cinnamaldehyde are mostly on Pd-Au catalysts, with very few reports on Pd-Ag and Pd-Cu catalysts. Coherent results in these studies have not been observed due to the variations in several parameters that influence the performance. Parvulescu *et al.*²¹ have explored catalysts with 0.6% w/w and 1% w/w total metal loading (50% Pd and 50% Au in colloidal form) embedded onto sol-gel silica and observed that Pd-Au form nanoscale alloys (Pd particle size 5-30 nm) and CAL hydrogenation activity and selectivity for COL formation increase, depending on the catalyst pre-treatment procedure adopted. Yang *et al.*²² prepared Pd-Au catalysts supported on mesoporous silica by co-impregnation, wherein Pd-Au alloy formation (Pd 2% w/w, crystallite size-2-4 nm) was observed. Maximum CAL

conversion is observed at composition Pd Au_{0.2}, but with ~ 90% selectivity towards HCAL. Pd-Au/carbon catalysts with Pd-Au atomic ratio varying from 0.1 to 2.1 (2% w/w Pd and Au 0.4 -0.6w/w%, Pd crystallite size 5-7 nm), prepared by Szumelda *et al.*²³, by adopting reverse water-in-oil microemulsion method, displayed different activity and selectivity pattern, depending on Au content. Catalysts with Au/Pd < 0.8 exhibited slightly lower activity *vis-a-vis* monometallic Pd/C, with marginal increase in selectivity towards COL. However, in the case of catalysts with Au/Pd > 1, substantial reduction in activity, along with a significant increase in selectivity for COL was observed. Such variations in activity and selectivity have been attributed to the changes in the microstructure of the alloy particles and surface composition and consequent geometric and electronic modifications of Pd sites. According to Zhang *et al.*²⁴ ultra-small (1.8 nm) Pd-Au nanoalloy catalysts supported on CeO₂ display 93% conversion and 85% selectivity towards HCAL. In these studies, reaction conditions, like temperature, pressure and solvents used are different in each case. In the case of Pd-Ag catalysts, Jiang *et al.*¹⁹ observed that on 0.5% w/w Pd/Al₂O₃, activity decreases, with the addition of Ag, due to preferential enrichment of Ag on the surface and lowering of surface Pd sites. Selectivity for HCAL formation (~90%), however, remains unaltered as Ag content increases. In a recent report, Li *et al.*,²⁵ investigated hydrogenation of CAL on Pd-Ag supported on high surface area MCM-41 (891 m²/g), wherein Pd-Ag nanoalloys (0.5% w/w Pd and varying Ag content) with the crystallite size range of 3-5 nm, were observed. Pd-Ag catalysts displayed significant improvement in activity (99.9% conversion on PdAg_{0.3} compared to monometallic Pd/MCM-41 (61.2 % conversion) with > 90% selectivity for HCAL. To the best of the knowledge of our knowledge, only one report on hydrogenation of CAL using bi-metallic Pd-Cu has been noted. Mahamoud *et al.*²⁶ in their studies on the influence of addition of Sn, Ir and Cu to sol-gel derived Pd/SiO₂(Pd 3% w/w) have observed that addition of Sn (0.15% w/w) and Ir (2.2% w/w) lead to an increase in COL selectivity, while Cu (0.15% w/w) decreases activity, with no improvement in COL selectivity. However, the addition of Cu to Pt shows an increase in COL selectivity at the same CAL conversion level³⁰. Pd-Cu bimetallic catalysts also display higher activity and selectivity for the selective hydrogenation of acetylene^{31a}.

As discussed above, comparison of the efficacies of the bimetallic Pd-Gr.-IB catalysts has not been possible due to variations in the catalyst composition, metal loading, nature of supports. In order to get a better perspective on the influence of Gr IB metals (Cu, Ag, Au) on Pd catalysts, a systematic study on bimetallic catalysts, Pd-M with M=Cu, Ag, Au, with specific atomic composition Pd_{0.9}M_{0.1} (1% Pd loading) for hydrogenation of CAL has been undertaken. Such a comparative evaluation study would bring out the mode of promotion by Gr. IB metals and helpful in designing catalysts with better performance. TiO₂ as support for heterogeneous catalysts has unique characteristics like tunable surface area, porosity, acid-base properties and metal-support interactions and also good chemical and thermal stability^{31a,31b}. Hence TiO₂ P-25 (EVONIK P-25) has been selected as the support for this investigation.

Materials and Methods

Palladium chloride, polyvinyl pyrrolidone, auric chloride, and cinnamaldehyde from Sigma Aldrich, ethylene glycol (EG) and sodium hydroxide (NaOH), auric chloride, silver nitrate and copper nitrate pentahydrate from Qualigens were used as such.

Preparation and characterization and evaluation of catalysts

Details on the preparation of monometallic Pd (1% w/w) and bimetallic Pd_{0.9}-M_{0.1} (M=Cu/Ag/Au) catalysts supported on TiO₂ (P-25) and their characterization by different techniques are covered in an earlier publication³².

Catalysts were evaluated for liquid phase hydrogenation of cinnamaldehyde (CAL) in 100 mL Parr reactor (Model-4848). Initially, the reactor was filled 15 g of isopropanol and 1.65 g of water as a solvent. Use of this mixture as solvent³³ resulted in the very little formation of acetals during hydrogenation. 2.4 g of CAL and 40 mg of catalyst were then added to the solvent mixture. The reactor was purged three times with H₂ gas and then pressurized to 10 bar and the reaction was carried out for 1 h in the temperature range 120-140 °C. 1 h time is noted from the moment the reactor reaches the specified temperature. After each reaction, the reactor is allowed to cool naturally to room temperature, catalyst and reaction products were separated by filtration and the product stream was analyzed in Perkin Elmer Clarus-500 GC equipped with ZB-1 capillary column and FID.

Results and Discussion

Characterization of catalysts

Chemical composition

Palladium and Gr. IB metal contents in the catalysts were analyzed by ICP-AES technique and the results are presented in Table 1. Experimentally determined metal contents are in close agreement with the nominal metal contents considered during preparation of the mono and bi-metallic catalysts.

Characterization of catalysts using different techniques

Details on XRD, DRS, TPR and XPS data and the inferences therein for Pd-M/TiO₂ (M=Cu, Ag and Au) catalysts have presented in an earlier publication³². Experimental data and figures on all characterization techniques have been included in the Supplementary Data. Detailed characterization of Pd-M/TiO₂ catalysts³² has shown that no significant changes in the XRD patterns for bimetallic Pd-M/TiO₂ catalysts *vis-à-vis* the pattern for monometallic Pd/TiO₂ were

Table 1 — Chemical composition of the catalysts

Catalysts	Expected metal content		Actual metal content	
	At.(frac)		At.(frac)	
	Pd	Other	Pd	Other
Pd/TiO ₂	1.00	-	1.02	-
Pd-Au/TiO ₂	0.90	0.10	0.93	0.09
Pd-Ag/TiO ₂	0.90	0.10	0.95	0.09
Pd-Cu/TiO ₂	0.90	0.10	0.90	0.10
Pd- Cu/TiO ₂ (used)	0.90	0.10	0.93	0.11

observed. Characteristic surface plasmon resonance (SPR) bands due to Ag & Au were not observed in the diffuse reflectance spectra (DRS) for bimetallic Pd-Ag and Pd-Au catalysts (Fig. S1, Supplementary Data) due to alloy formation between the constituent metals. Alloy formation in Pd-Cu has been well documented in the literature³⁴⁻³⁵. Changes in binding energy values for Pd 3d_{5/2} core level for Pd-M catalysts vs. the corresponding value for monometallic Pd indicate charge transfer from Gr. IB metals to Pd (Table S1). TPR patterns of calcined catalysts (Fig. S2) display sharp hydrogen evolution peaks due to decomposition of Pd hydride. Suppression of hydride formation is dependent on the Pd-M atomic ratio, being more effective at higher loading of Gr. IB metal. Cai *et al.*³⁶ observed hydride decomposition on Pd_{0.9}Cu_{0.1}/Al₂O₃ catalyst at 70 °C, but not on Pd_{0.8}Cu_{0.2} and Pd_{0.5}Cu_{0.5}. In the present case, due to low loading of Gr. IB metals hydride decomposition peaks are observed. The intensity of the hydride decomposition peaks varies with the nature of Gr. IB metals, with Pd-Au displaying a maximum reduction in intensity, possibly due to extent charge re-distribution during alloy formation.

Temperature programmed desorption (TPD) of hydrogen

Since activation of hydrogen is known to play a key role in the hydrogenation of CAL, H₂-TPD measurements have been carried out on mono and bimetallic catalysts. H₂ TPD patterns (Fig. 1) reveal the reactivity of adsorbed hydrogen species on

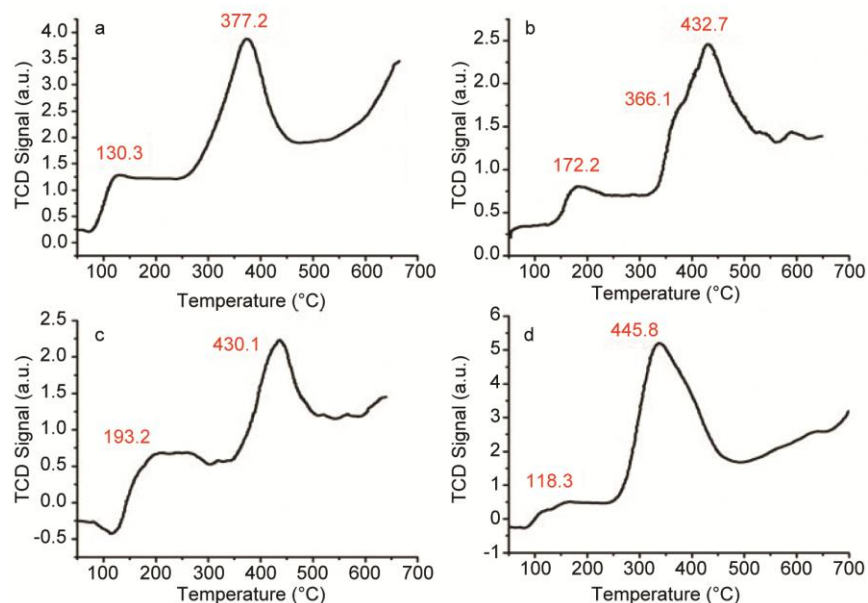


Fig. 1 — H₂ Temperature programmed desorption patterns for Pd-M/TiO₂ catalysts: (a) Pd/TiO₂, (b) Pd-Au/TiO₂, (c) Pd-Ag/TiO₂ and (d) Pd-Cu/TiO₂

different catalysts. H₂ desorption peaks up to 200 °C are due to chemisorbed hydrogen, which could be relevant to the hydrogenation process. It is observed that the hydrogen chemisorbed on Pd-Cu catalyst desorbs at the lowest temperature (118 °C), in comparison with desorption temperatures for Pd-Au (172 °C), Pd-Ag (193 °C) and mono-metallic Pd (130 °C). Availability of active surface hydrogen for hydrogenation reaction is facilitated on Pd-Cu due to lowest desorption temperature.

Transmission electron microscopy (TEM)

In order to ensure that Pd is in the metallic state during the reaction, as prepared catalysts were reduced in hydrogen gas flow at 300 °C for 2 h prior to evaluation of activity for hydrogenation of cinnamaldehyde. Particle sizes of the reduced catalysts as measured by TEM (Fig. 2) are in the range of 5-6 nm and in line with the particle sizes measured for as prepared catalysts³².

Hydrogenation of cinnamaldehyde

Activity and selectivity

Results on hydrogenation of CAL on monometallic Pd, Cu, Ag and Au and bimetallic Pd-M catalysts in the temperature range of 120-140 °C are presented in Table 2. Use of a mixture of isopropyl alcohol and water as a solvent has resulted in minimum selectivity for acetal formation, i.e., 5% max. All three Gr. IB elements act as efficient promoters. Bi-metallic Pd-M

(M=Cu, Ag Au) catalysts display higher CAL conversion compared to that on monometallic Pd, Cu, Ag and Au catalysts due to synergistic interactions. For detailed comparative analysis, CAL conversion and selectivity for HCAL, COL and HCOL at 140 °C on different catalysts are considered, as shown graphically in Fig. 3. CAL conversion decreases in the following order: Pd-Cu >Pd-Au >Pd-Ag> Pd> Cu> Ag> Au.

DRS and XPS studies on Pd-M catalysts reveal the formation of nanoscale alloys and charge transfer from Cu/Ag/Au to Pd, resulting in charge redistribution. Besides, the introduction of Cu/Ag/Au into Pd lattice could lead to lattice strain due to the difference in atomic size with respect to Pd³⁷. Such electronic, as well as geometric factors contribute towards the higher CAL conversion displayed by the three bi-metallic catalysts, in comparison with the activity of monometallic Pd catalyst. In the case of Pd-Cu, availability of active hydrogen, as revealed by the lowest hydrogen desorption temperature (Fig. 1), is an additional factor contributing towards the higher activity of Pd-Cu *vis-à-vis* Pd-Ag and Pd-Au.

Evidence for the synergistic interactions between Pd and Gr. IB metal is observed in the activity for CAL conversion on the mechanical mixtures of mono metallic Pd/TiO₂ and Cu/TiO₂ catalysts in the proportion of 9:1. The reduced mechanical mixture displays CAL conversion of 32.1% at 140 °C compared to 69.8% conversion observed for

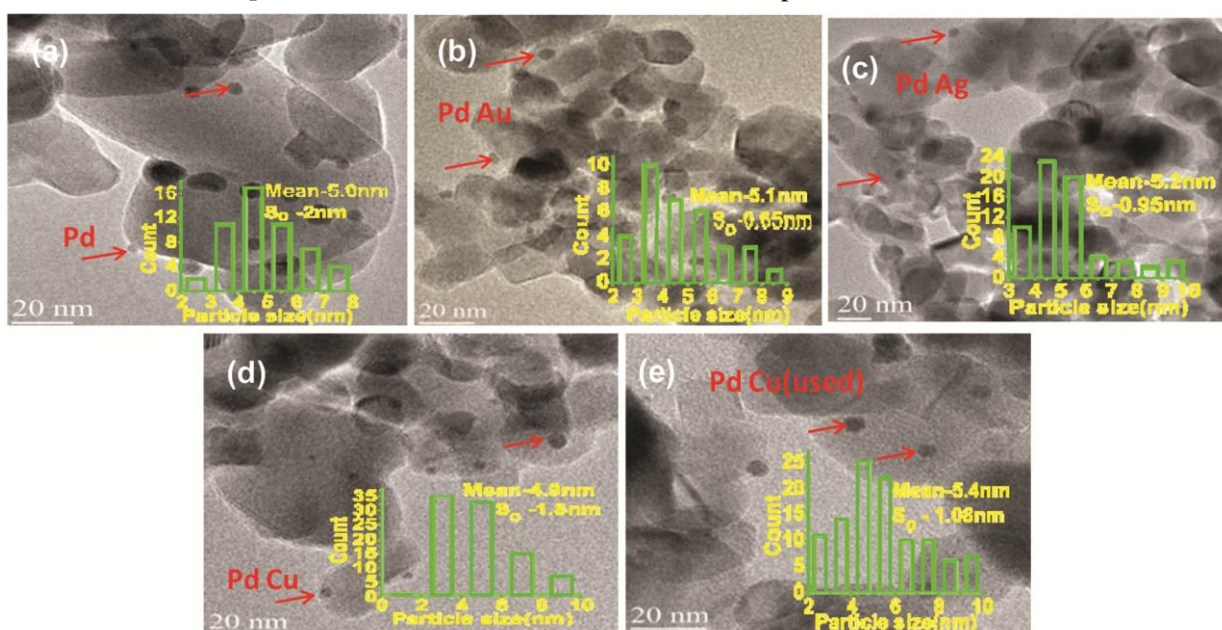


Fig. 2 — Transmission electron micrographs for Pd-M series of catalysts after reduction in hydrogen at 300 °C: (a) Pd/TiO₂, (b) Pd-Au/TiO₂, (c) Pd-Ag/TiO₂, (d) Pd-Cu/TiO₂ and (e) Pd-Cu/TiO₂ (used)

Table 2 — Hydrogenation of cinnamaldehyde (CAL) on Pd based catalysts at different reaction temperatures

Catalyst	Temp. (°C)	Conv. (%)	S-HCAL (%)	S-HCOL (%)	S-COL (%)	S-ACTL (%)
Pd	120	36.6	28.4	39.9	29.7	1.9
	130	46.4	39.1	32.8	25.1	3.0
	140	47.9	33.9	45.0	18.4	2.5
Pd- Au	120	57.8	35.0	38.3	22.6	4.0
	130	63.0	31.2	45.8	18.5	4.5
	140	71.4	27.8	57.6	10.6	4.0
Pd- Ag	120	43.3	57.3	15.3	22.0	5.4
	130	52.5	55.0	19.4	20.1	5.0
	140	66.9	50.5	25.0	20.0	4.4
Pd- Cu	120	61.0	58.9	27.4	10.4	3.2
	130	69.8	65.6	22.4	8.2	3.8
	140	84.0	51.7	42.2	3.3	2.7
Au	120	6.2	70.3	13.9	13.4	2.4
	130	9.6	74.1	10.3	12.7	2.7
	140	11.7	74.2	10.9	12.4	2.4
Ag	120	9.5	75.0	12.1	12.1	0.8
	130	16.3	76.2	11.2	11.6	1.0
	140	20.1	73.3	12.2	12.4	2.0
Cu	120	13.5	76.2	10.0	12.9	0.7
	130	17.2	74.4	10.6	13.8	1.2
	140	22.1	77.0	11.7	10.3	0.9
Pd & Cu Mech. mix	140	32.3	76.6	6.7	12.1	4.4

CAL: 2.4 g, Solvent: 15 g Isopropanol+1.65 g water, Catalyst: 40 mg, H₂: 10 bar, Reaction time:1 h, Agitation speed: 600 rpm

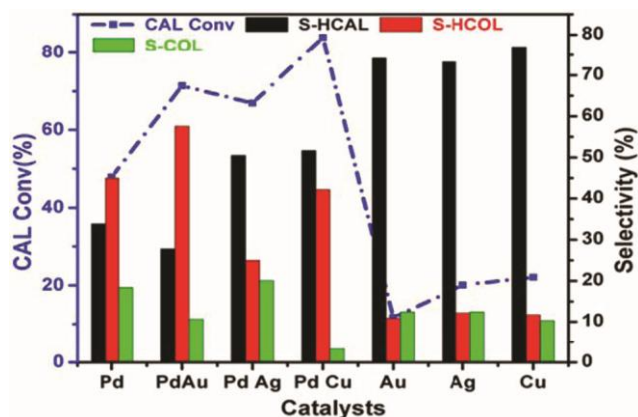


Fig. 3 — Activity and selectivity for hydrogenation of cinnamaldehyde at 140 °C on monometallic and bimetallic Pd-M (M=Cu, Ag, Au)

bimetallic Pd-Cu/TiO₂ catalyst (Table 2 Sr. No 8) at the same temperature signifying the importance of synergistic interactions in bi-metallic catalysts. Significance of such synergistic interactions, especially in the high activity for total hydrogenation of CAL to hydrocinnamyl alcohol (HCOL), displayed bimetallic Ni-Ru catalysts supported on Mg-Al hydrotalcite, has been illustrated in a recent publication³⁸. Bio-mass derived eugenol is also

hydrogenated³⁹ in facile manner over bimetallic Ni-Ru catalysts supported on hydrotalcite.

Product selectivity patterns on bimetallic catalysts, however, display different trend. Pd-Cu catalyst displays maximum activity in terms of CAL conversion, lowest selectivity towards COL and maximum selectivity towards HCAL. Pd-Ag, on the other hand, shows relatively higher selectivity towards COL and maximum selectivity again for HCAL. Pd-Au however, displays maximum selectivity for HCOL. As discussed in the introduction section, the literature reports on activity and selectivity patterns for CAL hydrogenation on Pd-M (M=Cu, Ag Au) catalysts do not present any regular pattern, since the catalyst composition, supports, characteristics and reaction conditions vary in each case. No activity pattern for CAL conversion among Pd-M catalysts has been reported for comparison with the results from the present work.

Monometallic Pd, on the other hand, shows moderate selectivity for all three products, HCAL, COL and HCOL. As the reaction temperature increases from 120 °C to 140 °C, (Table 2) as expected, selectivity to HCOL increases at the expense of COL selectivity and HCAL selectivity

Table 3 — Influence of feedstock composition on CAL conversion

Catalysts	Feed	Conv (%)	S-HCAL (%)	S- HCOL (%)	S-COL (%)
Pd	100% CAL	36.6	28.4	39.9	29.7
	100% HCAL	27.1	-	83.0	16.9
	100% COL	98.8	-	100	-
	50% HCAL+ 50% COL	14.2+63.8	-	100	-
	50% CAL+ 50% COL	84.3+71.6	18.2	81.7	-
Pd-Cu	100% CAL	61	58.9	27.4	10.4
	100% HCAL	14.4	-	83.4	16.6
	100% COL	98.8	-	96.4	-
	50%HCAL + 50% COL	25.8+98.6	-	100	-
	50% CAL + 50% COL	63.1+64.3	27.3	72.7	-

CAL: 2.4 g, Solvent: 15 g Isopropanol+1.65 g water, Catalyst: 40 mg, H₂: 10 bar, Reaction time: 1 h, Agitation speed: 600 rpm

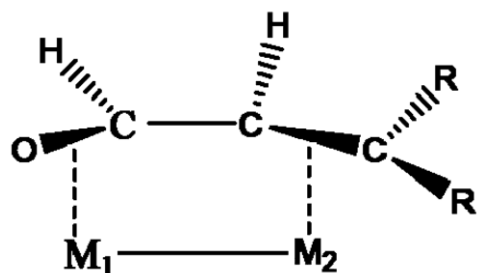


Fig. 4 — Mode (η_4) of adsorption of cinnamaldehyde on Pd metal surface

remains nearly constant. Other monometallic Cu, Ag & Au catalysts display very low CAL conversion and maximum selectivity for HCAL. Similar trends on monometallic Cu/TiO₂, Ag/TiO₂ Au/TiO₂ catalysts have been observed earlier⁴⁰ wherein all the three catalysts display very high selectivity towards HCAL. Thus, bimetallic catalysts, display higher CAL conversion, with high selectivity for HCAL by Pd-Ag and Pd-Cu catalysts and high selectivity for HCOL in the case of Pd-Au.

Effect of feedstock composition

Table 3 presents the influence of feedstock composition on CAL conversion typically on Pd-Cu-TiO₂ at 120 °C. It is observed that monometallic Pd and bi-metallic Pd-Cu based catalysts are highly effective for the conversion of 100% COL to HCOL, but the activity of both catalysts for the conversion of HCAL is lower at 27.1% and 14.4%, which could be due to weaker adsorption HCAL through C=O bond. A similar trend is indicated with mixtures of HCAL+COL (50/50), wherein the conversion of COL is faster compared to that of HCAL with 50/50 mixture of CAL+COL, mono and bimetallic catalysts display different behaviour. On monometallic Pd, the addition of COL with CAL increases CAL conversion from

Table 4 — Recyclability of the catalysts

No. of Cycle	Conv (%)	S-HCAL (%)	S-HCOL (%)	S-COL (%)
1	84.0	51.7	42.2	3.3
2	84.7	52.1	42.1	3.1
3	83.6	52.4	42.3	2.1
4	83.8	52.4	41.5	2.4
5	82.5	54.7	40.5	1.4

CAL: 2.4 g, Solvent: 15 g Isopropanol+1.65 g water, Catalyst: 40 mg, Temp. : 120 °C, H₂: 10 bar, Reaction time: 1 h, Agitation speed: 600 rpm

36.6% to 84.3% accompanied by a decrease in HCAL selectivity from 28.4% to 18.2 % and increase in HCOL selectivity from 39.9% to 81.7%. On Pd sites, CAL is expected to get adsorbed in η_4 or $d-\pi \eta_2$ mode (Fig 4) with equal probability for the formation of HCAL and COL⁴¹. Though the hydrogenation of the olefinic group is kinetically faster, further hydrogenation of COL to HCOL increases the selectivity towards HCOL. On Pd-Cu, adsorption of CAL and COL is relatively weaker, and hence their conversions are lower compared to the conversions on monometallic Pd. Adsorption of products *vis-à-vis* the reactant thus influences the reaction pathway.

Stability and recyclability of the catalysts

The catalysts after the reaction could be separated, washed with alcohol and re-used. Table 4 gives the CAL conversion and selectivity data for re-use of catalysts up to 5 cycles. It is observed that nearly stable activity and selectivity to different products are obtained up to five cycles No change in Pd content (Table 1) or Pd particle size is observed in the used catalyst (Table 1) & (Fig. 2d and 2e) indicating the stability of the catalysts with respect to recycling.

Conclusions

Palladium based bimetallic catalysts Pd-M, with M= Cu, Ag and Au, supported on TiO₂, display higher activity for hydrogenation of cinnamaldehyde and selectivity for hydrocinnamaldehyde in comparison with the component monometallic catalysts. Nanoscale alloy formation, charge redistribution, ensemble effects and synergistic effects in bimetallic catalysts are responsible for the observed higher activity. Bimetallic Pd-Cu displays higher activity compared to Pd-Ag & Pd-Au. Presence of active hydrogen on Pd-Cu, characterized by lowest hydrogen desorption temperature, is an additional contribution towards its higher activity. Bimetallic catalysts display stable activity and selectivity up to five reaction cycles. No changes in Pd content or Pd particle size of the catalysts are observed on re-use.

Supplementary Data

Supplementary Data associated with this article are available in the electronic form at [http://www.nopr.niscair.res.in/jinfo/ijca/IJCA_60A\(10\)1296-1302_SupplData.pdf](http://www.nopr.niscair.res.in/jinfo/ijca/IJCA_60A(10)1296-1302_SupplData.pdf).

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