Promotion of carbon xerogel supported Pt catalyst by Co and Zn for liquid phase hydrogenation of cinnamaldehyde

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Pt catalysts, supported on mesoporous carbon xerogel and promoted by Co and Zn, were prepared following impregnation method. The catalysts were assessed in liquid phase hydrogenation of cinnamaldehyde. Characterisation of the catalysts was done by elemental analysis, N_2 adsorption, H_2 pulse chemisorptions and X-ray photoelectron spectroscopy. The promoters, Co and Zn, were found to improve the cinnamaldehyde hydrogenation activity of Pt remarkably. The promoters also greatly increased cinnamyl alcohol selectivity. When both the promoters were applied together a further augmentation of cinnamyl alcohol selectivity was observed. XPS analysis revealed electron transfer from the promoters to Pt.

Keywords: Cinnamaldehyde, hydrogenation, Pt catalyst, impregnation, cinnamyl alcohol.

Introduction

Allylic alcohols are highly demanding in pharmaceutical and fine chemical industries. They are extensively used as building blocks/raw materials in the synthesis of value added products like drugs, food additives, fragrances, perfumes, cosmetics, etc.[1–6]. Allylic alcohols can be obtained by selective semi-hydrogenation of α,β-unsaturated aldehydes. Thus, reduction of α,β-unsaturated aldehydes is very valuable from academic as well as industrial point of view. Selective hydrogenation at the olefinic double bond leads to the saturated aldehyde, whereas selective reduction of the aldehydic group leads to the allylic alcohol. Thermodynamics favours the hydrogenation at the C=C function over the aldehydic group[1]. In spite of that, the total selectivity towards saturated aldehyde is not easy to achieve because always there is some chance of hydrogenation of the aldehydic function. On the other hand, high selectivity towards allylic alcohol, being thermodynamically unfavourable, is very difficult to achieve. Hence, selective reduction of the aldehydic group in α,β-unsaturated aldehydes to achieve improved yield of allylic alcohol is very important and demanding. Heterogeneous catalytic hydrogenation is environmentally friendlier process because it produces less amount of waste; also, the catalyst can be separated easily from the reaction mixture and may be reused. The importance of heterogeneous catalytic hydrogenation of α,β-unsaturated aldehydes is indeed reflected in number of studies reported in the available literature[1–9].

Cinnamaldehyde (CMD) is an α,β-unsaturated aldehyde; it is frequently used as model substrate. The selective semi-hydrogenation at aldehydic group results in cinnamyl alcohol (CML), a value added outcome useful in fine chemical industry[1,2]. On the other hand, the selective semi-hydrogenation at C=C function results in hydrocinnamaldehyde (HCMD). HCMD is used in the synthesis of a drug that is useful in the treatment of HIV[4,5]. In addition, both CML and HCMD are used as intermediate in number of organic synthesis[1,6]. The complete hydrogenation results in 3-phenyl-1-propanol (PPL). Supported group VIII metal catalysts exhibit excellent hydrogenation activity. There is room for manipulation of product selectivity by means of application of suitable promoter[2,10–12].

In the present study, Pt based catalysts were prepared using carbon xerogel as support. Co and Zn were applied as promoters. The catalysts were characterised and assessed in the selective hydrogenation of CMD to CML.

Experimental

Carbon xerogel was prepared by carbonisation of dried organic gel that was obtained through sol-gel condensation of resorcinol with formaldehyde[13]. Sol-gel condensation was done at pH 5.6 (adjusted by NaOH solution) with formaldehyde/resorcinol ratio of 2.1 to obtain the organic gel. Curing of the organic gel was done at 75°C for 30 h. The hard gel was ground (0.2–2.0 mm) and washed with 2(N) acetic acid for several times (to remove NaOH) followed by deionised water for several times (to remove acetic acid). Subsequently, the organic gel was dried at 105°C for 24 h. The organic gel was then taken in a tubular reactor and the reactor was placed inside of a tubular furnace and N_2 flow was established. The material was heated to 800°C at a rate of 3°C min^{-1} and carbonized for 3 h under N_2 flow (50 mL min^{-1}). The reactor was finally cooled to ambient temperature and the carbon xerogel (CX) was collected.

Four catalysts, Pt/CX, PtCo/CX, PtZn/CX, and PtCoZn/CX, were prepared by impregnation method using CX as support. Co-impregnation method was applied to prepare the multi-metallic catalysts. $H_2PtCl_6.6H_2O$, $Zn(OOCCH_3)_2.2H_2O$ and $Co(OOCCH_3)_2.4H_2O$ were used as Pt, Zn and Co precursors, respectively. Concentrations of metal precursors were adjusted in the impregnating solutions in such a way that the loading (wt%) of Pt, Co, and Zn in the catalysts were 5.0, 0.8 and 0.4, respectively. Methanol-water mixture (50:50 v/v) was used as solvent. In a typical preparation, precursor(s) solution was added to CX support and stirred periodically for 5 h. The solvent was evaporated leisurely at 50°C and subsequently the catalyst was dried at 100°C for 12 h. The catalysts were then calcined at 350°C for 4 h under 2% O_2 in N_2 flow [(10 mL Air + 90 mL N_2) per min]. Reduction of the catalysts was done at 400°C for 5 h under H_2 flow. Finally, the catalysts were collected and kept under argon.

Textural properties of the catalysts were obtained from N_2 adsorption-desorption isotherms measured at –196°C in an automatic adsorption apparatus (Nova Touch LX4, Quantochrome Instruments). Brunauer-Emmett-Teller (BET) equation was employed to determine the total surface area (S_{BET}). Mesoporous area (S_{meso}) and microporous volume (V_M) were calculated applying t-plot. Total pore volume was determined from the data at relative pressure of 0.99. Barrett-Joyner-Halenda (BJH) technique was applied on the desorption isotherms to ascertain pore size distribution[13]. Metal (Pt, Co, Zn) contents of the catalysts were assessed by elemental analysis. XPS analyses were performed on pre-reduced catalysts to determine the Pt^0 binding energy. Pt dispersion was measured by dynamic pulse chemisorption of H_2 at room temperature in a Chem BET Pulsar apparatus, considering H/Pt stoichiometric ratio equals to 1. H_2 chemisorption on Zn and Co surface was assumed to be negligible. Particle size (d) of Pt was calculated applying the equation, d[nm] = 1.122/D, where D is the fractional dispersion[2].

Hydrogenation of cinnamaldehyde (CMD) was performed in a stainless steel batch reactor at 75°C under 16 bar H_2. Typically, solvent, CMD, and catalyst were taken in the reactor and purged 6 times with H_2. Subsequently, the reactor was heated to the reaction temperature, 75°C, at a heating rate of 10°C min^{-1} under 0.05 bar H_2. Finally, H_2 pressure was tuned to reaction pressure, 16 bar, and the reaction was initiated by starting stirring.

Liquid samples were collected periodically and analysed chromatographically to monitor the progress of the reaction. CMD conversion and products selectivities were calculated as follows:

CMD conversion (%) = [1 – {concentration of CMD/(concentration of all products + concentration of CMD)}] × 100%.

Selectivity of product, **P** (%) = (concentration of **P**/concentration of all products) × 100%.

Results and discussion

Textural characteristics of the catalysts are listed in Table 1. The results reveal that considerable extent of surface is mesoporous in nature (169–175 m^2 g^{-1}). Total surface area as well as mesoporous area remained practically unchanged

Table 1. Textural properties of the carbon xerogel support and the supported catalysts

Sample	S_{BET} (m^2 g^{-1})	S_{meso} (m^2 g^{-1})	V_T (cm^3 g^{-1})	D_P (nm)
CX	511	172	0.802	15.8
Pt/CX	510	175	0.799	15.7
PtCo/CX	513	169	0.792	15.7
PtZn/CX	507	173	0.805	15.8
PtCoZn/CX	505	169	0.789	15.6

S_{BET} = Total surface area, S_{meso} = mesoporous area, V_T = total pore volume, D_P = average pore diameter.

upon metal loading; this was because the amount of metal(s) loaded was low. Also, it can be anticipated that the metal(s) is/are uniformly dispersed over the carbon xerogel surface; and thus, possibility of pore blockage may be ruled out. Another important point is that the catalysts exhibited large average pore diameter (~ 16 nm). This is particularly beneficial in liquid phase applications; mass transfer limitations can be avoided effectively[2].

Table 2. Pt dispersion and Pt[0] binding energy (B.E.) along with metal loading of the catalysts

Catalyst	Metal loading (wt%) (by AES)			Pt dispersion (%)	Pt[0] B.E. (eV)
	Pt	Co	Zn		
Pt/CX	5.01	–		54	72.21
PtCo/CX	4.98	0.81		27	71.75
PtZn/CX	4.99	–	0.41	33	71.81
PtCoZn/CX	4.99	0.80	0.39	11	71.89

Table 2 presents the metal loadings (determined by AES), Pt dispersion (determined by H_2 chemisorption), and Pt[0] binding energy (determined by XPS). H_2 chemisorption study reveals well dispersion of Pt in the monometallic Pt/CX catalyst; 53% Pt is exposed on the surface. However, the chemisorptions of H_2 was decreased significantly in presence of a second metal (Co or Zn), resulting in considerable lower Pt dispersion (27% in PtCo/CX and 33% in PtZn/CX). Amount of H_2 chemisorption i.e. Pt dispersion decreased further in the trimetallic PtCoZn/CX catalyst (11%). Decreased H_2 chemisorption i.e. lower Pt dispersion in the bi- and tri-metallic catalysts may be due to decoration of Pt surface by Co and/or Zn; alloy formation may also be responsible. Decrease in amount of H_2 chemisorption over noble metal catalysts in presence of first row transition metal promoter is reported in the literature[2,10,11]. XPS analysis of the catalysts was conducted to determine the binding energy of Pt[0]. The results (Table 2) show that binding energy of Pt[0] noticeably decreased in the bi- and tri-metallic catalysts. This indicates electron transfer from Co and Zn to Pt.

Cinnamaldehyde (CMD) molecule contains two reducible group, C=C and C=O, in addition to the aromatic ring. Hence, the hydrogenation of CMD is complex in nature. Parallel and consecutive hydrogenations of the reducible functions are possible. Hence, a range of hydrogenated prod-
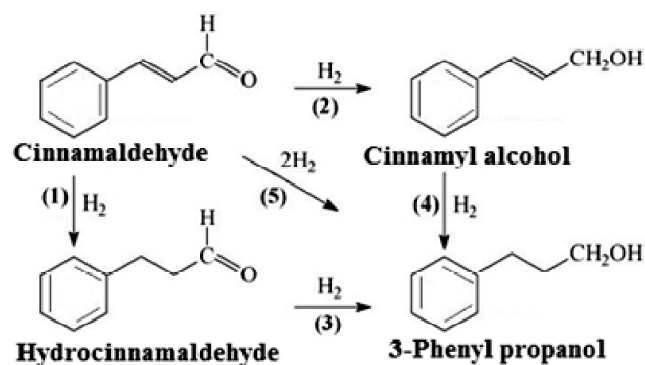

Fig. 1. Reaction pathways in the hydrogenation of cinnamaldehyde.

ucts may form depending on the reaction conditions. Promoters of supported metal catalysts exhibit definite role in shaping product distribution[14]. Under the applied reaction conditions in the present study, only cinnamyl alcohol (CML), hydrocinnamaldehyde (HCMD), and 3-phenyl-1-propanol (PPL) were obtained as products. Possible reaction pathways are shown in Fig. 1[2]. The catalysts (Pt/CX, PtCo/CX, PtZn/CX, PtCoZn/CX) were evaluated in the hydrogenation of CMD at 75°C under 16 bar H_2, taking cyclohexane as solvent and the performances are shown in Table 3. The pristine Pt/CX catalyst was observed to be poor performer. 13 h was taken by this catalyst to achieve 50% conversion of CMD. Selectivities of the products are also poor. Selectivity of both, CML and HCMD, the value added semi-hydrogenation products are lower than 50%. Also, PPL, the fully hydrogenated product was formed to a significant amount. However, CMD hydrogenation activity and CML selectivity were improved greatly over both the Co and Zn promoted, PtCo/CX and PtZn/CX, catalysts. While the monometallic Pt/CX catalyst took 780 min for 50% conversion of CMD, the promoted catalysts PtCo/CX and PtZn/CX took 160 and 300 min, respectively, for the same extent of CMD conversion. At the same time CML selectivity increased to about 75% over the promoted catalysts.

The results clearly indicate that the promoters favour attack at the C=O and suppress the hydrogenation at the C=C function[2]. When both, Co and Zn, were applied together as promoter, CML selectivity augmented further remarkably. Over the PtCoZn/CX catalyst, 50% CMD conversion was achieved in 190 min with 88% CML selectivity. XPS analysis has revealed shifting of Pt[0] binding energy towards lower

Table 3. Performance of the catalysts in the hydrogenation of cinnamaldehyde

Catalyst	Product selectivities (%) at 50% CMD conversion			
	Time required (min)	S_{CML}	S_{HCMD}	S_{PPL}
Pt/CX	780	43	44	13
PtCo/CX	160	75	5	20
PtZn/CX	300	74	7	19
PtCoZn/CX	190	86	6	8

S_X – selectivity of X.

Reaction conditions: 0.300 g catalyst (0.077 mmol Pt), 2.115 g CMD (16 mmol), 100 mL solvent (cyclohexane), 16 bar H_2, 75°C, 1100 rpm.

values in the Co and Zn promoted catalysts compared to the pristine Pt/CX catalyst; this establishes that Pt in the promoted catalysts is electron enriched. Thus, back donation of electron to π*-CO molecular orbital from electron enriched Pt becomes easier in the promoted catalysts. Consequently, the activated CO function of CMD is attacked easily by chemisorbed hydrogen. The result is that the reaction goes faster and at the same time towards CML[2].

CMD conversion and products selectivity profiles with reaction time over the tri-metallic, PtCoZn/CX, catalyst are shown in Fig. 2. CML selectivity practically remained constant over time; and thus was independent of CMD conversion. However, noticeable decline of HCMD selectivity and at the same time increase in PPL selectivity at the higher CMD conversion could be observed clearly. Pertaining to CMD conversion and products selectivity profiles, similar observation can be seen in repeat use of the catalyst.
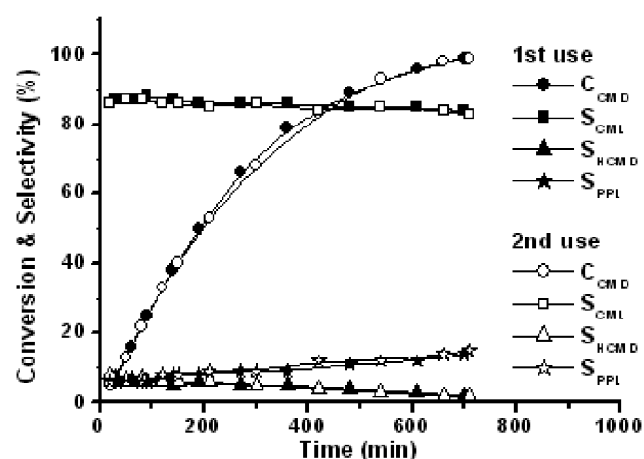

Fig. 2. Cinnamaldehyde conversion and products selectivities over PtCoZn/CX catalyst. C_{CMD} – cinnamaldehyde conversion, S_X – selectivity of X.

The results clearly indicate that PPL mainly formed as a result of the consecutive hydrogenation of HCMD. Also, comparing the CMD conversion and products selectivity profiles between the first and repeat use of catalyst it can be inferred that the tri-metallic, PtCoZn/CX, catalyst can be successfully applied for multiple use.

Conclusions

Carbon xerogel supported Co and Zn promoted Pt catalysts were synthesized. Promoted Pt catalysts, particularly the tri-metallic PtCoZn/CX appeared to be excellent performer in the hydrogenation of cinnamaldehyde selectively to cinnamyl alcohol. Electron enriched Pt sites, depicted by XPS analysis, in the promoted catalyst is believed to be responsible for higher cinnamaldehyde hydrogenation activity and cinnamyl alcohol selectivity.

Acknowledgements

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