



Carbon Molecular Sieve Supported Pd Catalyzed Hydrogenation of Cinnamaldehyde in Alkaline Medium

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Synthesis of various fine chemicals and pharmaceuticals are regulated through selective hydrogenation of α,β -unsaturated aldehydes. Hydrocinnamaldehyde is one of the important compounds in perfumery and flavouring industries. It is highly precarious and challenging to control the product selectivity as well as conversion in cinnamaldehyde hydrogenation. In this study, an effective hydrogenation of cinnamaldehyde was attained in presence of aqueous-protic organic medium by utilizing Pd/CMS and other additives of alkali such as K_2CO_3 . The Pd/CMS catalyst along with alkali media catalyzed the hydrogenation of C=C selectively in cinnamaldehyde in order to form hydrocinnamaldehyde with 100% conversion rate. Additionally, the parallel hydrogenation of C=O and C=C bonds in cinnamaldehyde takes place in absence of media. The C=O bond reduction in cinnamaldehyde can be restricted through K_2CO_3 addition to aqueous-protic solution. The active sites of palladium were found to be uniform and analyzed using HRTEM data. Based on the mechanism involved in micropores of carbon molecular sieves, the key role of promoter is associated with hydrogenation of cinnamaldehyde. The catalytic criterion was appropriate with the acquired activity data.

Keywords: Alkali carbonate, Hydrocinnamaldehyde, Cinnamaldehyde, CMS supported Pd catalyst, Hydrogenation.

INTRODUCTION

Synthesis of various fine chemicals and pharmaceuticals are regulated through selective hydrogenation of α,β -unsaturated aldehydes [1-4]. Hydrocinnamaldehyde is one of the important compounds in perfumery and flavouring industries. Additionally, it is known to play as a vital intermediate for anti-viral drugs, specifically protease inhibitors of HIV [5]. Basic hydrogenation of cinnamaldehyde leads to formation of products like hydrocinnamaldehyde, cinnamyl alcohol and hydrocinnamyl alcohol. Therefore, it is considerably challenging to regulate product selectivity along with conversion process in cinnamaldehyde hydrogenation. To overcome this adversity, various metal hydrides such as $LiAlH_4$, $NaBH_4$ are in use as liquid phase to inflexibly hydrogenate C=C bonds in order to generate equivalent saturated forms of aldehydes. Nevertheless, their usage was found to be in stoichiometric quantities

generating huge quantity of salts. Additionally, other hydrogenation reactions have been reported utilizing Ni and Pd as homogenous catalyst and $HCOONa$ and hydrogen as reducing forms both in aqueous and non-aqueous phases [6]. Nonetheless, the system being homogenous, separation of reaction mixture from catalyst becomes difficult and restating of catalyst makes it less economical and has low selectivity. Generally, catalysts like Pd are moderately effective in hydrogenation of α,β -unsaturated aldehydes with higher selectivity towards saturated forms of aldehyde [7]. To improve the hydrogenation activity, organic solvents are used instead of water, however, product selectivity is poor with organic solvents. On the contrary, low selectivity and high activity was documented with Ni catalysts.

The production of hydrocinnamaldehyde by selective hydrogenation of cinnamaldehyde relies on the nature of support material, metal, solvents, promoters and auxiliaries [8]. It was illustrated that the selectivity and conversion of hydrocinnamaldehyde

maldehyde actively depends on chemical nature of solution in catalytic liquid phase of cinnamaldehyde hydrogenation [9,10]. It has been reported by Arterburn *et al.* [9] that alkaline modifiers act as promoters and catalytically deliver cinnamic acid to generate saturated forms of cinnamic acid in high quantities. It was determined by Tin *et al.* [10] that Pd-catalyst complex along with microporous support can be engaged to efficiently carry out hydrogenation of cinnamaldehyde to hydrocinnamaldehyde with 91% yield under alkali media. While, the hydrogenation of the C=C bond is mediated by catalyst, the C=O bond hydrogenation function of catalyst was constrained through inclusion of Na_2CO_3 at pH 12. Likewise, it was also documented that the hydrocinnamaldehyde selectivity was found to be increased by addition of potassium acetate and no increase was observed in the selectivity with rise in K/Pd ratios above 10 [11].

Materials supported by carbon are widely studied for the process of selective hydrogenation of cinnamaldehyde. Additionally, few carbon made materials like carbon nanofibers, nanotubes, aerogels and xerogels have been extensively used in hydrogenation process and also few composite materials such as $\text{CeO}_2\text{-ZrO}_2$ titanate nanotubes modified by silica, zeolitic imidazolate frameworks were applied as per the reports [12-14]. Carbon molecular sieves (CMS) are few of the superior carbon materials mostly used as catalyst as a result of their thermal stability, hydrophobic nature, resistance to alkali, acidic media and morphological features like being amorphous in nature, micro sized structure, geometry of slit pore type in comparison with zeolites. Furthermore, CMS catalyst is found to be highly stable in water phase [15-20]. These kinds of catalysts exhibit different behaviour to that of other traditionally used supports and some compelling results were obtained [13].

In this study, a very common impregnation process was employed in order to prepare Pd-CMS catalysts along with Pd loadings. By using BET, HRTEM, XRD, TPR and TPD the characterization of catalyst was done. Activity of the catalyst was determined for selective hydrogenation of cinnamaldehyde to analogous hydrocinnamaldehyde under existence of alkali. The correlation was carried out without alkali media for selectivity and conversion against hydrogenation of C=C bond. The

impact of catalyst structure on selectivity of cinnamaldehyde of cinnamaldehyde and activity was also measured.

EXPERIMENTAL

Preparation of catalyst: The Pd catalysts supported by CMS have been prepared by method of wet impregnation using $\text{Pd}(\text{OAc})_2$ solution (5% Pd wt/vol.) as precursor. The selected catalysts are specified as Pd/CMS, Pd/CMS-2, Pd/CMS-3, Pd/CMS-4, Pd/CMS-5 and Pd/CMS-6 consisting of 0.5, 1, 2, 3, 4 and 5% of palladium. The characterization of catalyst was done using H_2 -TPR, XRD, NH_3 -TPD, BET surface area and HRTEM. The XRD of reduced catalyst Pd/CMS have been recorded on Miniflex X-ray diffractometer by making use of nickel filtered $\text{CuK}\alpha$ radiation. The pore size distribution and BET surface area have been executed on Autosorb 2120 by N_2 adsorption using multipoint method. The TPR studies were carried out on Newchrom TPD/pulse chemisorptions unit using 5% hydrogen in argon mixture. The temperature was increased to about 850 °C at a rate of 10 °C/min and maintained in isothermal state for about 10 min.

Hydrogenation of cinnamaldehyde: All the experiments carried out in presence of catalyst have been conducted in autoclave. Hydrogen to cinnamaldehyde mole ratio was retained in all the experiments. At the beginning, reactor was filled up with needed substrate, catalyst and solvent and then heated to about 50 °C. Once the stabilization of temperature occurred, system was pressurized with hydrogen in order to get desired hydrogen to cinnamaldehyde mole ratio. The final products were collected and investigated by gas chromatography of Varian-450 type and final product quantification was carried out by utilizing a multipoint calibration. At last, the qualitative analysis was carried out by GC/MS (Agilent 6890N) by making use of HP-5 capillaries.

Pore size distribution studies and BET surface area: In Fig. 1a-b, the N_2 adsorption/desorption isotherms of Pd/CMS and pore size distribution studies are shown and the surface area values are found to be within the range of 218-344 m^2/g . The isotherms of nitrogen adsorption of Pd/CMS catalyst displayed intense increase at lower pressure of ($P/P_0 < 0.03$) indicating huge quantity of microporous forms, while a slight

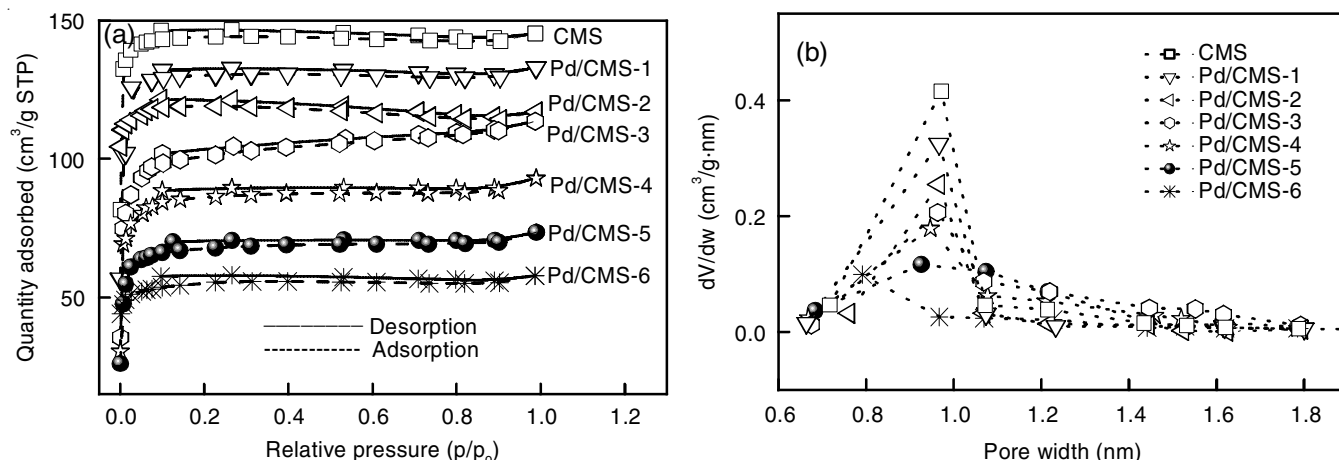


Fig. 1. N_2 adsorption-desorption isotherms of reduced CMS and Pd/CMS (a) and Horvath-Kawazoe graphs for pore size distribution of reduced CMS and Pd/CMS (b)

rise of high pressures less than or equal to 1 associate to adsorption over the outer region. The isotherm plot was constant till a pressure of ($P/P_0 < 0.8$) for all CMS backed up with palladium catalyst, indicating the presence of porous structure. From the plots obtained by differential pore volume, it can be assessed that in CMS-Pd catalyst size distributions of pores fall within the range of supermicropores which usually range from 0.7-2.0 nm (Fig. 1a). However, it was found that adsorption of N_2 has come down slowly along with rising Pd content from 0.5-5%. It was attributed to reduction in volume of pore. With the rise in Pd content, width of pore reduced to 0.79 and pore volume has reduced constantly (Table-1).

Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore width (nm)
CMS	344	0.0415	0.97
Pd/CMS-1	322	0.0324	0.96
Pd/CMS-2	317	0.0224	0.96
Pd/CMS-3	280	0.0206	0.96
Pd/CMS-4	257	0.0198	0.94
Pd/CMS-5	227	0.0116	0.92
Pd/CMS-6	218	0.0089	0.79

Temperature programmed reduction studies: With Pd/CMS catalyst, the TPR patterns displayed a pointed negative peak around 90 °C (T_{max}) in CMS and intensity of Pd/CMS catalyst was found to vary widely (Fig. 2). This particular peak belongs to H_2 elution through β -PdH_x decomposition. It was observed that the β -PdH_x disintegration peak intensities were rising with addition of Pd, attributed to particle size of Pd [21]. With 475-700 °C of temperature, a very wide peak was noticed, which correlates to consumption of H_2 along with evasion of carbon deposits [22]. Nevertheless, consumption of H_2 ascribed to the phenomenon of spill-over in catalyst with CMS. The results of TPR were matched with carbon-Pd catalysts as obtained earlier [23]. By TPR experiments, one can analyze that Pd/CMS catalyst is comprised of particles of Pd with variable sizes and greater quantity of molecules for Pd/CMS-6.

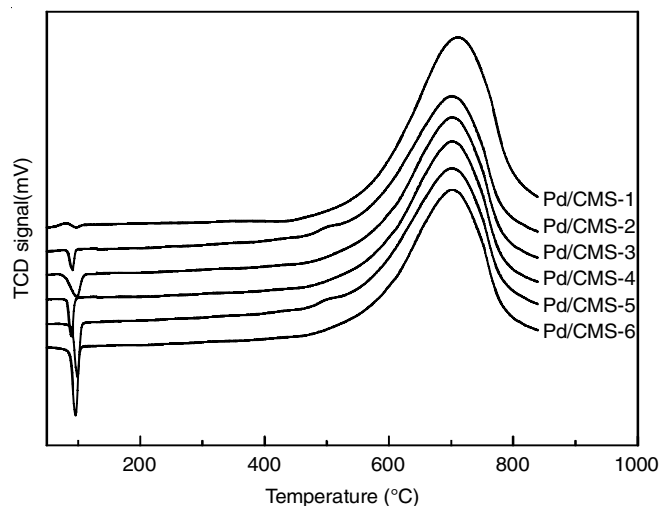


Fig. 2. TPR pattern of calcined Pd/CMS catalysts

Temperature programmed desorption studies: Strength and quantity of acidic sites are the main factors on which catalyst performance relies on. To determine the catalyst's acidic strength, experiments like NH_3 -TPD have been performed for Pd/CMS catalyst and also CMS within the temperature range of 40-750 °C (Fig. 3). All of the Pd/CMS catalyst displayed only one peak within 375-450 °C in the experiments of NH_3 -TPD.

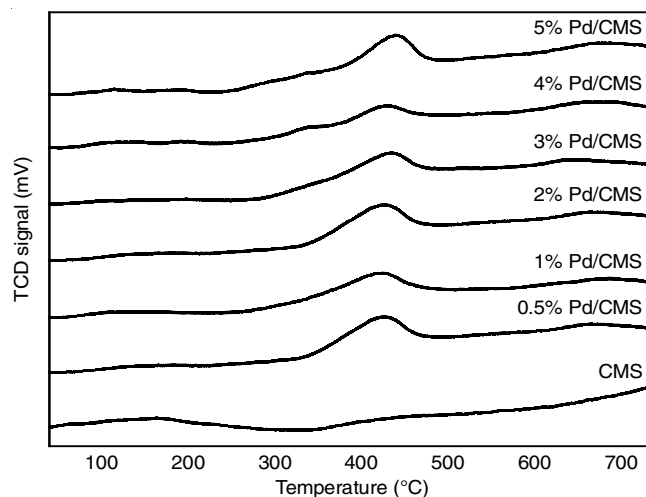


Fig. 3. NH_3 -TPD pattern of calcined Pd/CMS catalysts

X-ray diffraction studies: Patterns of XRD of CMS-Pd catalyst and reduced CMS are presented in Fig. 4. It was observed that CMS is found to be amorphous in nature while the patterns of Pd/CMS catalyst are crystalline in form. The signals of diffraction at $2\theta = 38.18^\circ$, 34° and 45° correlate with the FCC standard peaks of Pd metal (crystalline) (JCPDS 87-037). The intensities of the peaks were found to be rising with Pd content under catalyst of Pd/CMS. The data obtained from XRD were in good compliance with TPR observations of Pd/CMS catalysts.

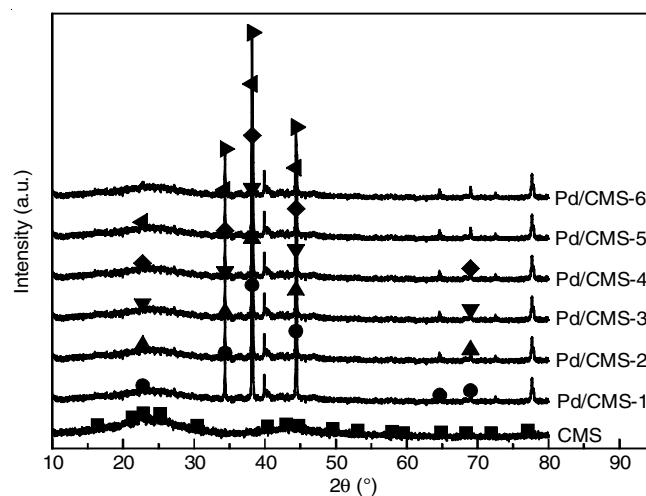


Fig. 4. XRD pattern of reduced CMS and Pd/CMS

HRTEM studies: From TEM images, the average particle size of the metals and metallic dispersions were analyzed. The TEM images of Pd/CMS-2, Pd/CMS-1, Pd/CMS-5, Pd/CMS-3, Pd/CMS-6 and Pd/CMS-4 are presented in Fig. 5. The

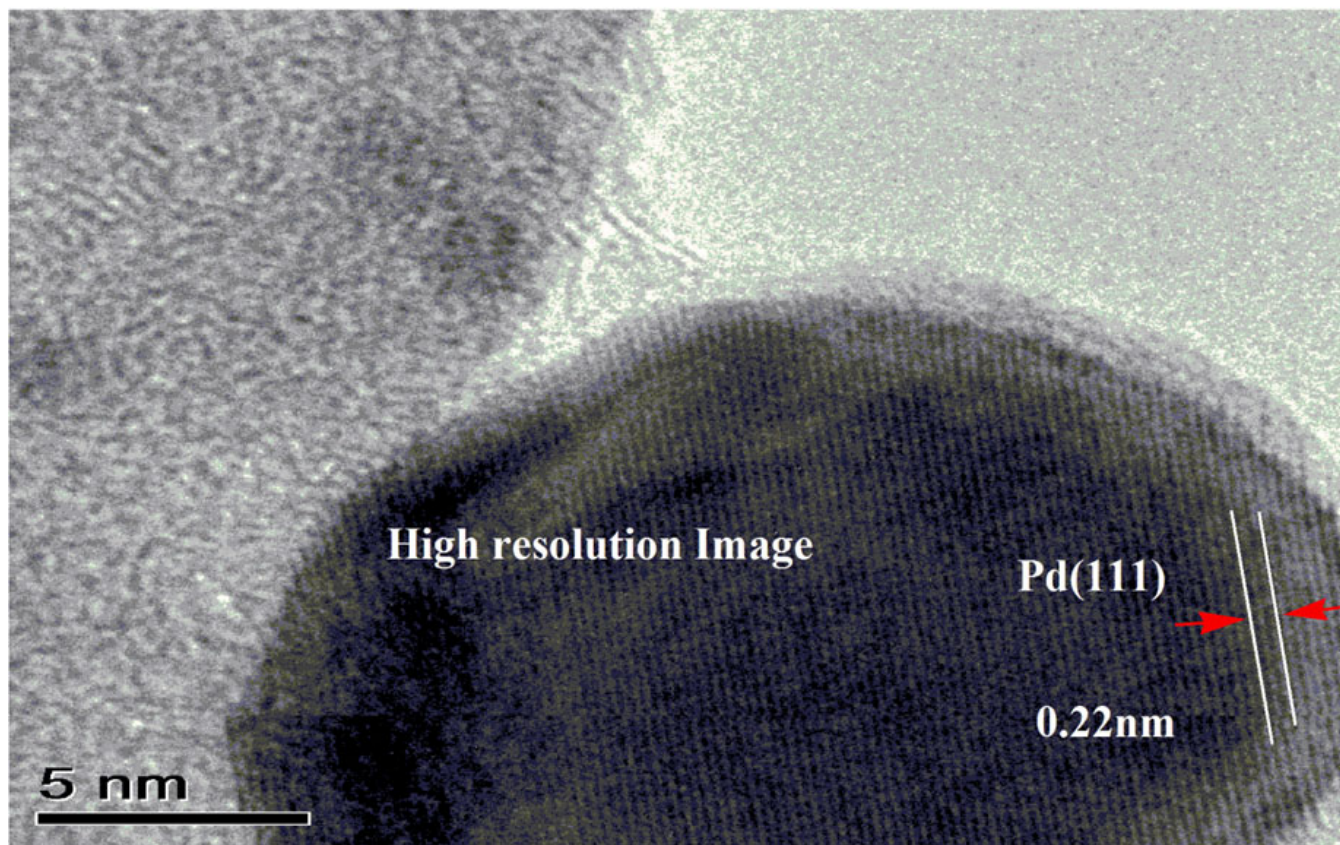
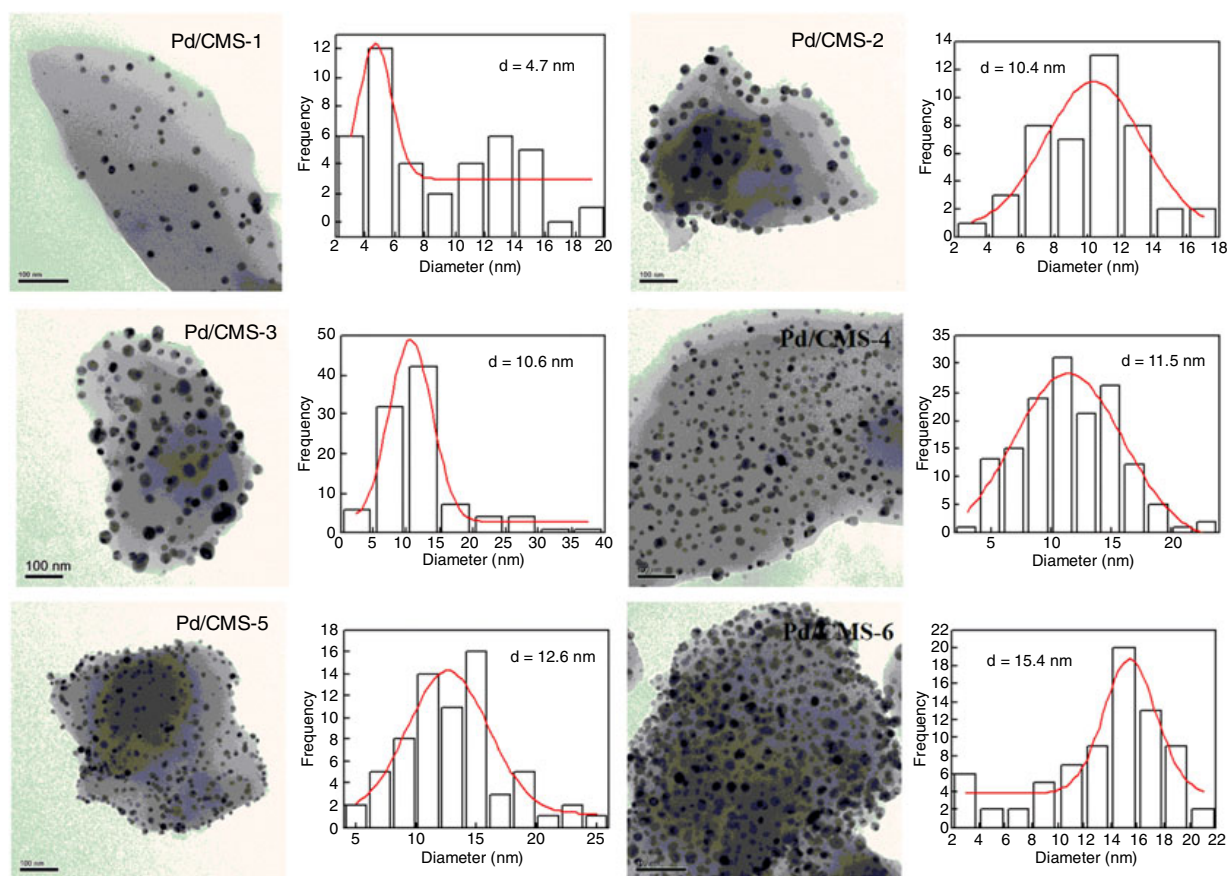
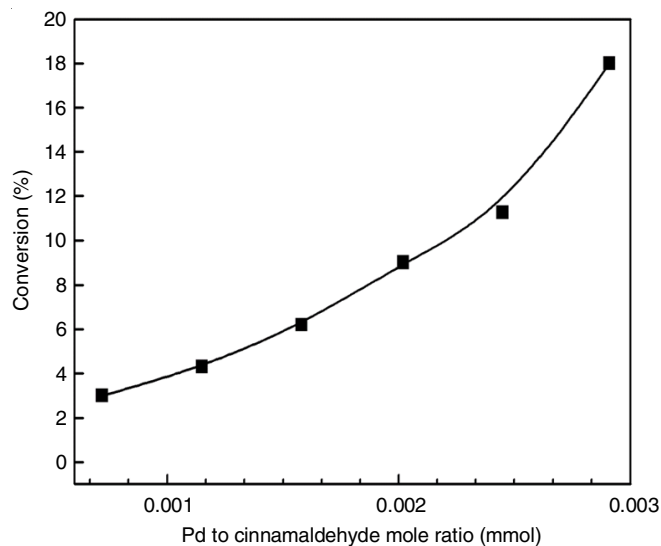


Fig. 5. HRTEM characterization of reduced Pd/CMS catalysts

dark spots on C background are formed due to the presence of metal particles of Pd. As in Fig. 5, the particles of Pd were dispersed uniformly in carbon frame of Pd/CMS catalysts. The particles of Pd displayed confined distribution which usually range in between 4.7-15.4 nm in correlation with the metal loading of 0.5-5% Pd on CMS. The existence of bigger Pd particles are due to deposition of particles of Pd over the surface of CMS micropores with Pd/CMS-6 catalyst in the impregnation step, that actually gets buried by accumulation of carbon layers over the surface of CMS support. Balanced collection of Pd particles was noticed in the case of Pd/CMS-6 catalyst. The crystal nature of particles was disclosed by well-defined lattices of crystals in HRTEM images with a spacing of 0.22 nm analogous to the Pd plane. The TEM images for Pd/CMS catalysts presented amorphous forms of CMS micropore and the data of XRD and TPR was found to be in correlation with the rise in Pd content, Pd particle size and H_2 [21,23]. Nevertheless, the particles of Pd are visible on Pd/CMS in consonance with results of XRD and TPR.

RESULTS AND DISCUSSION

Impact of Pd to cinnamaldehyde mole ratio: The impact of Pd on cinnamaldehyde mole ratio was investigated over a range starting from 0.00072-0.00291 in acetonitrile solution by using Pd-CMS-2 catalyst (Fig. 6). With decreased mole ratio, the process of hydrogenation was less around 3% and with increased mole ratios, hydrogenation process expanded to an extent of 18% with 0.00291 acetonitrile solution. The activity of hydrogenation was found to be raised from around 3-15% with rise in mole ratio from 0.00072 to 0.00291. Under provided conditions, all of the Pd-cinnamaldehyde mole ratios displayed selectivity towards hydrocinnamaldehyde. It was observed that the impact of Pd-cinnamaldehyde ratio was not a compelling factor for product selectivity in the presence of acetonitrile. Yet, the Pd-cinnamaldehyde mole ratio displayed



Reaction condition: H_2 pressure = 0 bar, acetonitrile, cinnamaldehyde/ H_2 mole ratio = 12, reaction temperature = 25 °C, reaction time = 2 h, Pd/cinnamaldehyde mole ratio = 0.00072 to 0.00291

Fig. 6. Effect of Pd to cinnamaldehyde mole ratio in millimoles

critical influence on cinnamaldehyde conversion. Identical results have been documented on hydrogenation of α,β -unsaturated aldehydes in ethanol and Pd/zeolite catalyst [24]. Additional experiments were conducted with average mole ratio around 0.00202.

Impact of Pd content: The impact of Pd on the alteration of cinnamaldehyde was investigated by altering concentration from 0.5-5% (Fig. 7). The results reveal that with decreased Pd content, activity of cinnamaldehyde was low around 5% and this may occur due to the filling up of the micropore volume ($0.0415 \text{ cm}^3/\text{g}$) with Pd particles and only fewer cinnamaldehyde molecules being collaborated with the pores. On facilitating an increase in 5% Pd content, the values raised significantly to 24%. It shows that external surface of catalyst micropore and the particle size of the Pd molecule impedes a serious effect on cinnamaldehyde activity. The data obtained through XRD, TEM and TPR prove that as Pd content increases, Pd particle size and uptake of hydrogen was raised [21-23]. Initially, the hydrogenation of cinnamaldehyde to hydrocinnamaldehyde occurs and then it gets desorbed to solution from Pd crystals and larger Pd particles promoted desorption of hydrocinnamaldehyde from surface of catalyst [13].

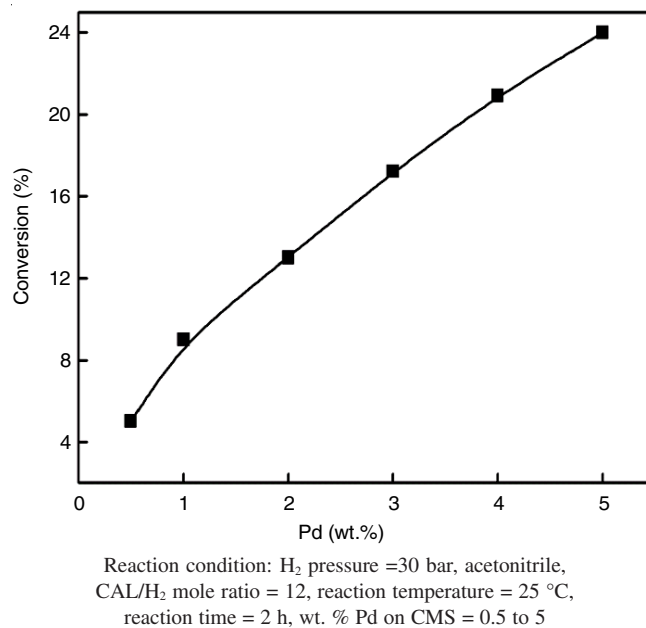


Fig. 7. Effect of Pd content on hydrogenation of cinnamaldehyde (CAL)

Impact of alkali additive: Under fluid phase reactions, K_2CO_3 performs a key role in the hydrogenation of C=C activity with Pd catalyst. In the presence of electrolyte solution, addition of alkali improves hydrogenation of cinnamaldehyde activity when compared to other media solvents like water, ethanol and acetonitrile at temperatures 100, 70 and 25 °C. Though the addition of alkali did not exhibit any impact on product selectivity at room temperature and only hydrocinnamaldehyde was determined as hydrogenated product in ethanol/aqueous electrolyte solution apart from acetonitrile-electrolyte solution. Also, the addition of alkali regulated hydrogenation to a maximum value by affecting selectivity of other products from

temperatures 25-100 °C. The results given in Table-2 indicate increased solubility of substrate based on temperature. The obtained results acknowledge that generated hydrocinnamaldehyde could have been re-adsorbed into the pores of CMS through the C=O bond, which depleted after the hydrogenation of C=C bond forming cinnamyl alcohol and hydrocinnamyl alcohol. Additionally, conditions with optimized reactions are given in Table-2 for 100% cinnamaldehyde conversion with 100% hydrocinnamaldehyde selectivity. The obtained results agreed with the studies of Krishna *et al.* [7], where it was determined that the Pd/CMS catalysts having microporous nature can be effectively implemented to carry out selective hydrogenation of compound citral to citronellal with 92% yield under the presence of alkali. The hydrogenation function of C=O bond has been repressed by K₂CO₃ addition [7]. On inclusion of alkali, the activity of hydrogenation was impacted by two key factors like solubility of hydrogen and cinnamaldehyde. The alkali present could interact with substrate of cinnamaldehyde and dissolve them in aqueous solution, while in contrast, it could also reduce hydrogen solubility [25] and the latter might have the ability to donate electrons of K cation to active sites of Pd. Identical observations have been documented by addition of potassium acetate to the hydrogenation reaction of cinnamaldehyde which accelerated hydrocinnamaldehyde formation and blocked its hydrogenation. It is popularly known that alkali metal on platinum group catalyst is efficiently oxidized by means of contributing electrons to the metal catalyst and promotes desorption and adsorption process of reactants by reducing confining strength between the catalyst and reactant which ultimately results in elevated yield of product or rate enhancement [11].

Mechanism of cinnamaldehyde hydrogenation with Pd/CMS catalyst in the presence and absence of alkali media: The method of hydrogenation of cinnamaldehyde in the presence and absence of alkali K₂CO₃ medium is given in

Figs. 8 and 9. It is hypothesized that while the reactants cinnamaldehyde and hydrogen disseminates through the microporous structure of Pd/CMS catalyst they endured more resistance to diffusion in absence of alkali as a result of abundant catalyst micropores. On the contrary, they go through less resistance towards diffusion in the presence of alkali. Because of additives like alkali, it may get deeply penetrated to catalyst micropores. After the synthesis of hydrocinnamaldehyde occurs in presence of alkali, its desorption takes place from palladium crystal into solution and thereby easily distribute towards exterior of the pore. All these circumstances show up that the occupied potassium metal might trigger interruption of cinnamaldehyde conversion. Nevertheless, if the reaction happens to occur inside micropores in alkali absence, hydrocinnamaldehyde may have stayed back in order to promote hydrogenation to hydrocinnamyl alcohol and cinnamyl alcohol causing limitations in diffusion process. Identical effect occurs due to electron transfer from doped metals to the active forms, thus raising density of electrons at active sites of the metal and reducing contingency of hydrogenation of -C=C- bond by reducing rate

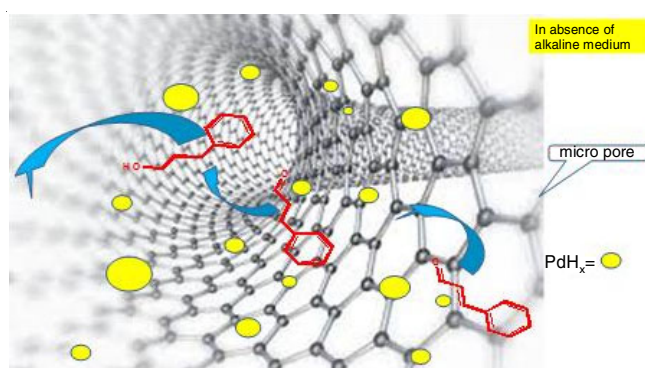


Fig. 8. Process of hydrogenation of cinnamaldehyde over the catalyst in micropore structure in absence of alkali media

TABLE-2
EFFECT OF ALKALI ADDITIVE IN SOLVENT MEDIA

Entry	Reaction media	Temp. (°C)	Conversion (%)	Selectivity (%)		
				Hydrocinnamaldehyde	Hydrocinnamyl alcohol	Cinnamyl alcohol
1	Water	25	12	100	0	0
2	[K ₂ CO ₃] in water	25	30	100	0	0
3	Water	70	20	65	32	3
4	[K ₂ CO ₃] in water	70	40	100	0	0
5	Water	100	32	59	36	5
6	[K ₂ CO ₃] in water	100	90	96	4	0
7	Ethanol	25	16	100	0	0
8	[K ₂ CO ₃] in ethanol	25	46	100	0	0
9	Ethanol	70	43	68	22	10
10	[K ₂ CO ₃] in ethanol	70	100	100	0	0
11	Ethanol	100	68	72	24	4
12	[K ₂ CO ₃] in ethanol	100	100	100	0	0
13	Acetonitrile	25	24	82	18	0
14	[K ₂ CO ₃] in acetonitrile	25	37	92	8	0
15	Acetonitrile	70	55	83	11	6
16	[K ₂ CO ₃] in acetonitrile	70	100	91	9	0
17	Acetonitrile	100	68	72	24	4
18	[K ₂ CO ₃] in acetonitrile	100	100	96	4	0

Reaction conditions: Pd/CMS-6, H₂ = 30 bar, CAL/H₂ mole ratio = 12, Pd/CAL mole ratio = 0.01011, reaction time = 2 h.

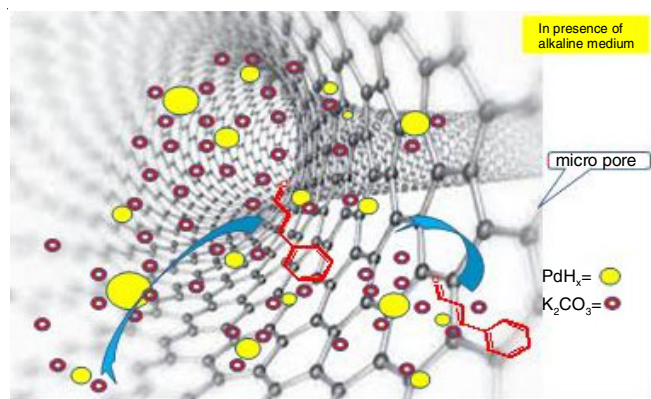


Fig. 9. Process of hydrogenation of cinnamaldehyde over the catalyst in micro-pore structure in presence of alkali media

of synergy between the metal and C=C bond [26–28]. Nonetheless, with palladium metals, the synergy of C=C will be corrected and the extent of hydrogenation is improved in presence of K⁺ cations. Hence, a comprehensive study is recommended to study these effects in order to yield preliminary ideas.

Conclusion

In this article, promising applications of Pd/CMS catalysts have been demonstrated and found to be potentially crucial for hydrogenation of α,β -unsaturated carbonyls, stable towards alkali medium and definitive to cinnamaldehyde. Lower C=C bond hydrogenation rate in cinnamaldehyde can be due to lower solubility in water (0.14g/100g at 25 °C). Through the addition of K₂CO₃, properties of aqueous phase were not only altered, but they also alter the environment surrounding Pd atoms. Hence, through higher selectivity of C=C hydrogenation in cinnamaldehyde molecule can be accomplished by selecting the right reaction conditions under K₂CO₃ that usually resides in carbon molecular sieves support.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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