

Effect of Alkali Carbonate/Bicarbonate on Citral Hydrogenation over Pd/Carbon Molecular Sieves Catalysts in Aqueous Media

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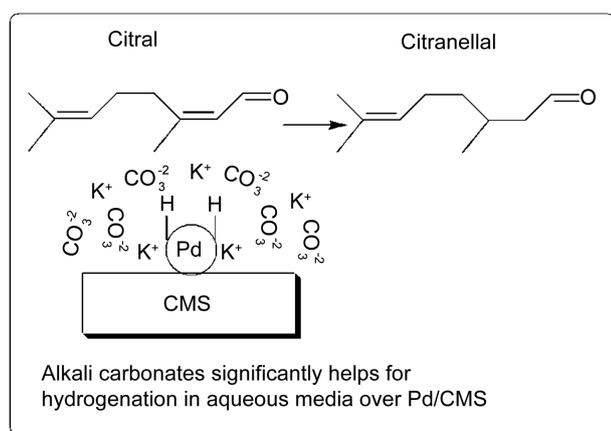
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Abstract

The efficient citral hydrogenation was achieved in aqueous media using Pd/CMS and alkali additives like K_2CO_3 . The alkali concentrations, reaction temperature and the Pd metal content were optimized to enhance the citral hydrogenation under aqueous media. In the absence of alkali, citral hydrogenation was low and addition of alkali promoted to ~92% hydrogenation without reduction in the selectivity to citronellal. The alkali addition appears to be altered the palladium sites. The pore size distribution reveals that the pore size of these catalysts is in the range of 0.96 to 0.7 nm. The palladium active sites are also quite uniform based on the TPR data. The catalytic parameters are correlated well with the activity data.



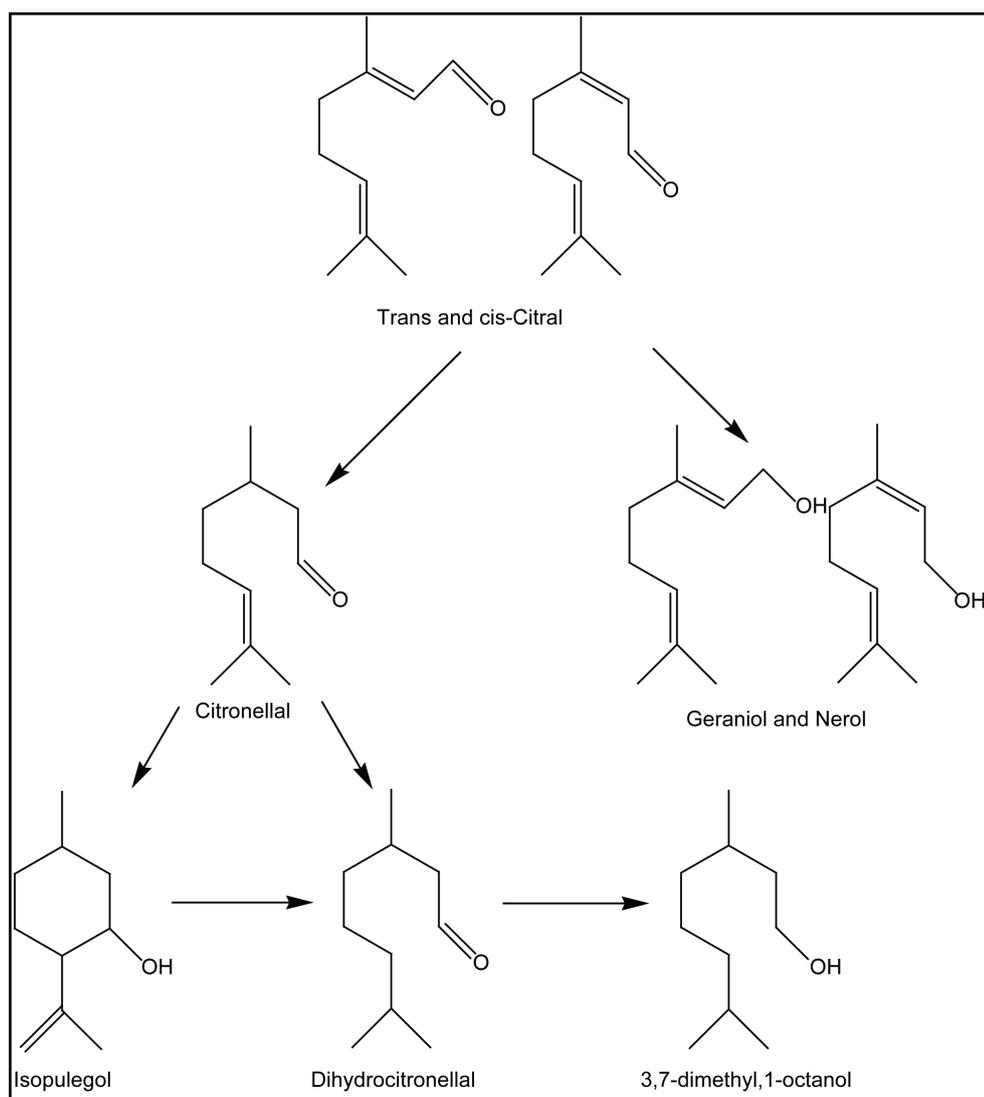
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Keywords

Alkali Carbonates, Citral, Hydrogenation, CMS Supported Pd Catalyst

1. Introduction

Selective hydrogenation of α - β -unsaturated aldehydes was widely used for the synthesis of fine chemicals and pharmaceutical industries [1]-[4]. Citronellal was an essential compound in flavoring and perfumery industries. Simple hydrogenation of citral results (Scheme 1) [5] is in the formation of various products, such as citronellal, citronellol, geraniol, nerol, 3,7-dimethyl-1-octanal and isopulegol, menthol. Hence, it is particularly challenging to control the product selectivity as well as the conversion in the citral hydrogenation. In order to circumvent this difficulty, several metal hydrides (LiAlH_4 , NaBH_4 ...) were employed in the liquid phase for selectively hydrogenate the C=C bond to produce the corresponding saturated aldehyde. However, they are used in stoichiometric amounts which will produce large quantity of salts as by products. Alternative catalytic hydrogenations were reported using Pd, Ni complexes as homogeneous catalysts by using hydrogen or HCOONa as reducing



Scheme 1. Consecutive reaction scheme of citral hydrogenation.

agents in aqueous as well as non-aqueous solvents [6]. However, the homogeneous system suffers from the separation of the catalyst from reaction mixture and reusability of the catalyst besides low selectivity makes less economic process. In general, Pd catalysts were exhibits moderate efficiency in the hydrogenation of α - β -unsaturated aldehyde with high selectivity to saturated aldehyde. On the other hand, high activity, with low selectivity, was reported for nickel catalysts. Citronellal production was through selective hydrogenation of citral which, depends on the nature of metal, support material, promoters, solvents and the auxiliaries [7]-[13]. It was described that the conversion and selectivity of citronellal strongly depend on the basicity of the solution in liquid phase catalytic hydrogenations of citral [14] [15]. Salminen *et al.* were achieved 74% selectivity towards citronellal by addition of an alkaline modifier into ionic-liquid [14]. Recently, the Pd-TMG/GO catalyst in ethanol was reported high efficiency for the selective hydrogenation of citral to citronellal [15]. It was also reported that the selectivity to saturated aldehyde increased with the addition of potassium acetate whereas, at the K/Pd ratio of 10 did not increase the selectivity [16].

On the other hand, carbon supported materials have been the most studied in the selective hydrogenation of citral. However, non-traditional carbon materials such as carbon nanotubes, carbon nano-fibers, carbon xerogel and aerogels were widely studied for hydrogenation application, and few reports were also available on use of composite materials like carbon-TiO₂ in the literature for this application [17]. The CMS were very superior carbon materials, especially as catalyst supports due to their thermal stability, resistance to strong acidic or alkali media, hydrophobic nature, and their morphology properties such as micro-structure, amorphous nature, slit pore geometry, compared to zeolites. Moreover, CMS supports were much more stable in aqueous phase [18]-[23].

Organic solvents were commonly employed for this transformation; however, to develop a more environmentally friendly process, the use of water as solvent is highly desirable. One of the drawbacks relies on the insolubility of the substrate in water. This problem could be circumvented by performing the hydrogenation in the presence of alkali additive. Indeed, these additives are well known to play a positive role in a large number of reactions in aqueous media. In fact, alkali additive with varying concentrations can interact with reactant substrate and solubilise them in aqueous media [24]. Further, it was found that alkali additives can interact with catalysts by adsorbing at the surface of metal sites favoring the electron donating ability of alkali cation to metal active sites [25].

Present study focused on the selective hydrogenation of citral using Pd/CMS catalysts in water with the objective of establishing the influence of alkali additive with varying concentration.

2. Experimental

2.1. Catalyst Preparation and Characterization

The CMS supported Pd catalysts were prepared by wet impregnation method using Pd(OAc)₂ solution (5% Pd wt/Vol) as the precursor. The catalyst's detailed preparation method was described in earlier studies for carbon supported palladium catalysts [26]. The catalysts were designated as Pd/CMS-1, Pd/CMS-2, Pd/CMS-3 Pd/CMS-4, Pd/CMS-5 and Pd/CMS-6 containing 0.5%, 1%, 2%, 3%, 4%, and 5% of Pd, respectively.

The catalysts were characterized using XRD, H₂-TPR and BET surface area. XRD of reduced Pd/CMS catalysts were recorded on a Miniflex (M/s. Rigaku Corporation) X-ray diffractometer using Ni filtered Cu K _{α} radiation. The BET surface area and pore size distribution were performed on Autosorb 2120 by nitrogen adsorption using multipoint method. The temperature programmed reduction (TPR) studies conducted on Newchrom TPD/Pulse chemisorptions unit using 5% H₂ in Ar the mixture. The temperature was raised to 850°C at a rate of 10°C/min and kept at isothermal for 10 min.

2.2. Reaction Conditions

All the catalytic experiments were conducted in an autoclave (M/s. Micron engineers). In all the experiments, the hydrogen to the citral mole ratio was maintained at 6. Initially, the reactor was charged with the required amount of catalyst, substrate and solvent. The reactor was heated to 50°C after stabilization of the temperature, the system was pressurized with H₂ to get required H₂ to the citral mole ratio. The products were collected and analyzed by a Varian-450 Gas Chromatograph (FID), and the quantification of the products was done using a multi-point calibration for each product. The qualitative analysis was done by GC/MS (Agilent 6890N) using an HP-5 capillary column.

2.3. BET Surface Area and Pore Size Distribution Studies

Adsorption/desorption isotherms and pore size distributions of Pd/CMS catalysts were displayed in (Figure 1(a) & Figure 1(b)), and all catalyst's surface area values are within the range of 344 to 218 m²/g. The nitrogen adsorption isotherms of all Pd/CMS catalysts exhibit a steep rise at a low relative-pressure ($P/P_0 < 0.03$), reflecting the abundance of micro pores structure, while a very slight rise at high relative-pressure ($P/P_0 \leq 1$) attributed to adsorption on the outer surface. In all CMS supported Pd catalysts, the intermediate hysteresis loop was constant up to relative pressure ($P/P_0 < 0.8$) which indicates the micro porous structures. From the differential pore volume plots, it was observed that the pore size distributions of CMS supported Pd catalysts were fall in range of the supermicropores (0.7 to 2 nm) region (Figure 1(b)). However, it was observed that, the nitrogen adsorption gradually decreased with increasing from 0.5% to 5% Pd content. It was ascribed to decrease of pore volume. With an increase of Pd contents, the pore widths were led to fall below 0.9 nm range and pore volumes also decreased gradually.

2.4. Temperature Programmed Reduction Studies

The TPR patterns (Figure 2) of Pd/CMS catalysts; a sharp negative peak centred at 90°C (T_{max}) was observed in the CMS Pd/CMS catalysts with varying in the intensity. This peak corresponds to elution of hydrogen by decomposition of β -PdH_x [26] [27]. The peak intensities of β -PdH_x decomposition were increasing with the Pd content, which is ascribed to the Pd crystallite size [26]. A broad positive peak with onset temperature of 475°C centred at 700°C was observed, which corresponds to the hydrogen consumption together elution of carbonaceous deposits [27]. However, this hydrogen consumption was attributed to the spill-over phenomenon in CMS supported catalysts. The TPR results were in line with the earlier reported for carbon supported palladium catalysts [28].

2.5. X-Ray Diffraction Studies

The XRD patterns of reduced CMS and CMS supported Pd catalysts depicted in Figure 3. The CMS support found to be X-ray amorphous whereas the XRD patterns of Pd/CMS (reduced) catalysts observed to be crystalline in nature. The diffraction signals at $2\theta = 34^\circ$, 38.18° and 45° matches with the standard peaks of face centered cubic (FCC) crystalline Pd metal (JCPDS 87-037). The peak intensities of Pd metal were increasing with the Pd content in Pd/CMS catalysts. The XRD data was also in good agreement with the observations of TPR results for Pd/CMS catalysts.

3. Results and Discussions

3.1. Effect of Solvents

The effect of solvents was studied using the acetonitrile, ethanol, hexane, water and the results were summarized

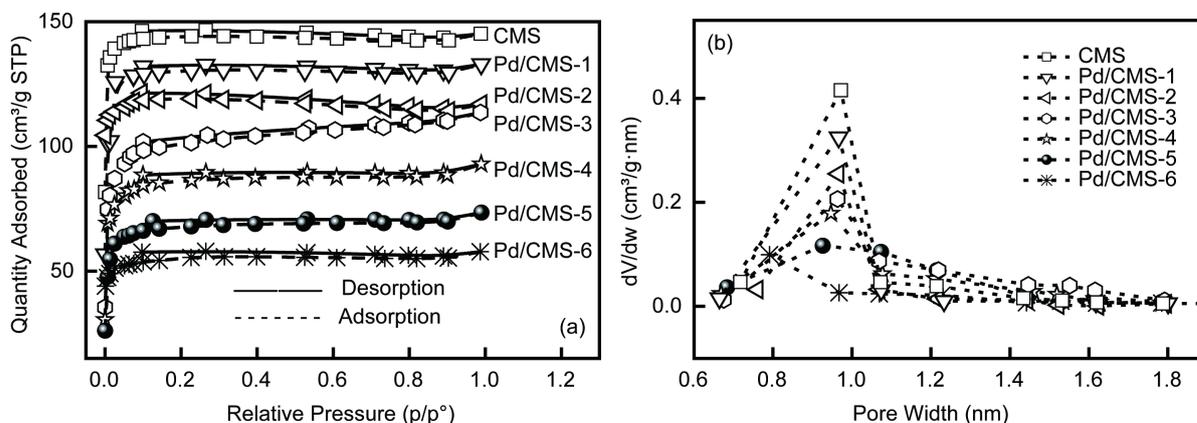


Figure 1. (a) N₂ adsorption-desorption isotherms of reduced CMS and Pd/CMS. (b) Horvath-Kawazoe graphs for pore size distribution of reduced CMS and Pd/CMS.

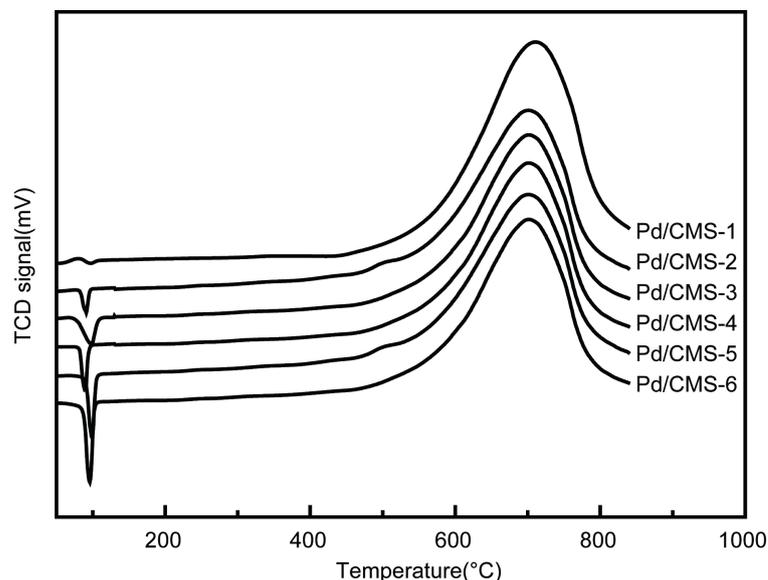


Figure 2. TPR pattern of calcined Pd/CMS catalysts.

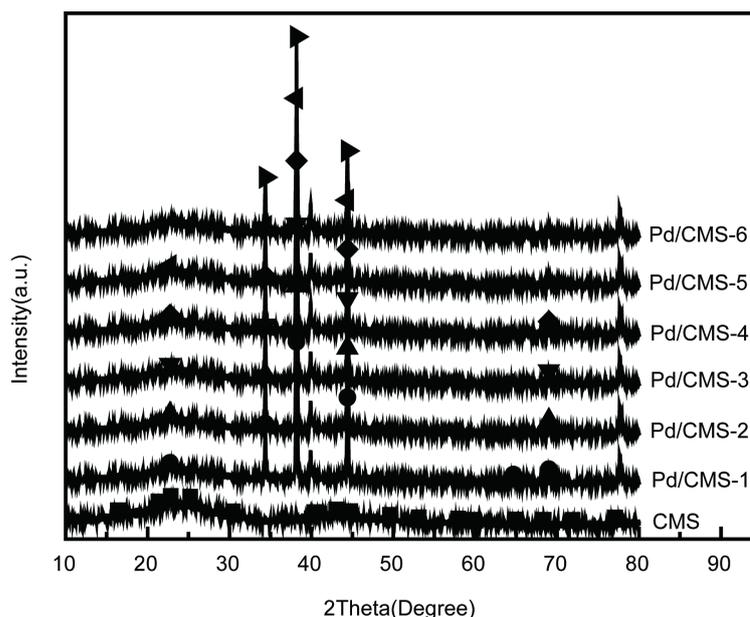


Figure 3. XRD pattern of reduced CMS and Pd/CMS.

in **Table 1**. When acetonitrile employed as solvent the citronellal, dihydrocitronellal, 3,7 dimethyl 1-octanol was observed as products and the corresponding selectivity was 65%, 17%, and 18%, with the conversion level of 39%. Indeed, the citronellal formed could be re-adsorbed in the micro-pores of the CMS support via the C=O bond, thus, leading to the formation of the 3,7 dimethyl 1-octanol. The solubility of hydrogen and citral in acetonitrile appears to be high, and the extended hydrogenation was predominant [29], whereas, in presence of hexane, ethanol and water as solvents, the conversion level of 30%, 13%, and 9% respectively. However, it is interesting to observe that the hydrogenation of citral in presence of aqueous media over Pd/CMS-2 is selective towards citronellal. On the other hand, the results (**Table 1**) clearly show that the hydrogenation activity was significantly reduced in aqueous media. As the hydrogenation in aqueous media is economically as well as environmentally attractive, hence further the efforts were directed to enhance the hydrogenation activity by addition of alkali carbonates/bicarbonates to the aqueous media to increase the hydrogenation activity.

3.2. Effect of Pd Content

The effect of Pd on the conversion of citral was examined by varying the Pd loading from 0.5% to 5% (Figure 4). The results reveal that at lower Pd content, the citral activity was very low (7%), which may be attributed to the Pd particles have been filled in the micro-pore volume ($0.0415 \text{ cm}^3/\text{g}$), and fewer amounts Pd may be available for citral molecules to interacted with this active sites. Further increase in Pd content, the conversion values significantly raised to 22% at 5% Pd. It appears that the Pd particle size and active site density have significant effect on the citral activity. The TPR and XRD data supports the observations that with the Pd content the Pd particle/crystallite size and hydrogen uptake were also increased [26]-[28]. The citral was first getting hydrogenated to citronellal, and then it can be easily desorbed from Pd active sites to solution. The larger palladium particles are facilitating the desorption of citronellal from the catalyst surface [17].

3.3. Effect of Pressure

The hydrogen pressure was varied from 10 bar to 30 bar at 50°C in aqueous media by using Pd/CMS-6 catalyst. The results reveal that (Table 2), the citral conversions were increased from 22% to 43% as the H_2 pressure raised from 10 bar to 30 bar. Thus the H_2 solubility increased by pressure, and no extended hydrogenations were noticed in aqueous media. It appears that the effect of pressure was also insignificant in product selectivity under aqueous media. However, the effect of pressure has significant influence on the conversion of citral.

3.4. Effect of NaHCO_3 , Na_2CO_3 , and K_2CO_3 Concentration

The effect of alkali additive with varying concentrations on hydrogenation of citral has been investigated (Figure 5 and Figure 6). The effect was investigated by NaHCO_3 (relatively weaker base) as alkali additive for the reaction

Table 1. Effect of solvents.

Solvent	% Conversion	% Selectivity		
		Citronellal	Dihydrocitronellal	3,7-Dimethyl-1-octanol
Acetonitrile	~40	65	17	~18
Hexane	30	100	0	0
Ethanol	13	100	0	0
Water	~9	100	0	0

Reaction conditions: $\text{H}_2 = 10$ bar, water/citral mole ratio = 65, $\text{H}_2/\text{citral} = 6$, reaction temperature = 50°C , reaction time = 2 hours, Pd/citral mole ratio = 0.006, Pd/CMS-2 catalyst.

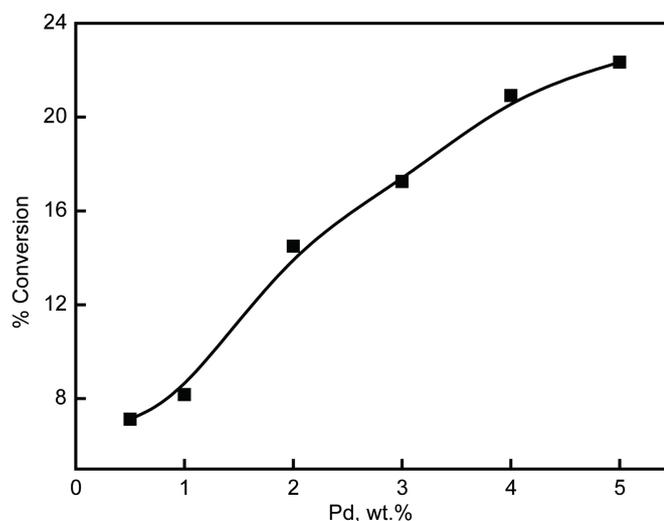


Figure 4. Effect of Pd content on Pd/CMS catalysts. Reaction conditions: H_2 pressure = 10 bar, water/citral mole ratio = 65, $\text{H}_2/\text{citral} = 6$, reaction temperature = 50°C , reaction time = 2 hours.

Table 2. Effect of pressure.

Entry	H ₂ in Bars	% Conversion	% Selectivity		
			Citronellal	Dihydrocitronellal	3,7-Dimethyl-1-octanol
1	10	22	100	0	0
2	20	36	100	0	0
3	30	43	100	0	0

Reaction conditions: H₂ = 10, 20, 30 bar, water/citral mole ratio = 65, H₂/citral = 6, 12, 18 reaction temperature = 50°C, reaction time = 2 hours, Pd/citral mole ratio = 0.033, Pd/CMS-6 catalyst.

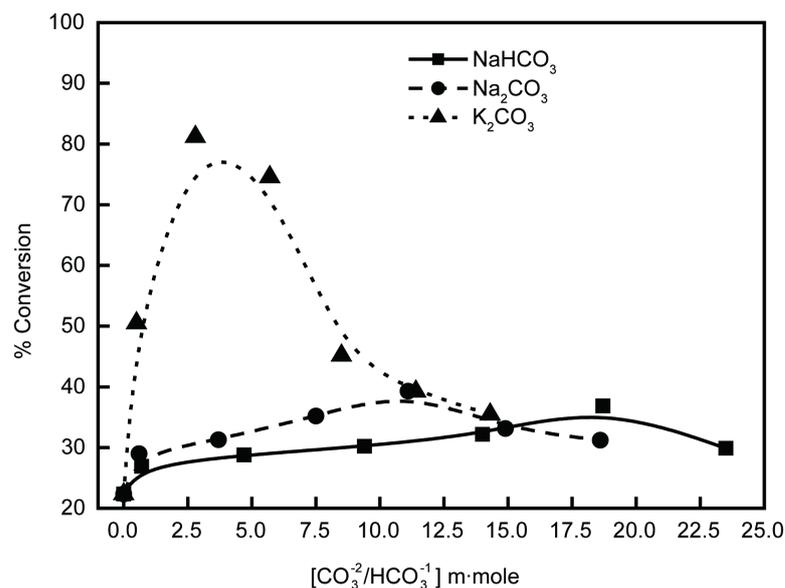


Figure 5. Effect of alkali carbonate/bicarbonate concentration in reaction media on Pd/CMS-6. Reaction conditions: H₂ = 10 bar, water/citral mole ratio = 65, H₂/citral = 6, reaction temperature = 50°C, reaction time = 2 hours, Pd/citral mole ratio = 0.033.

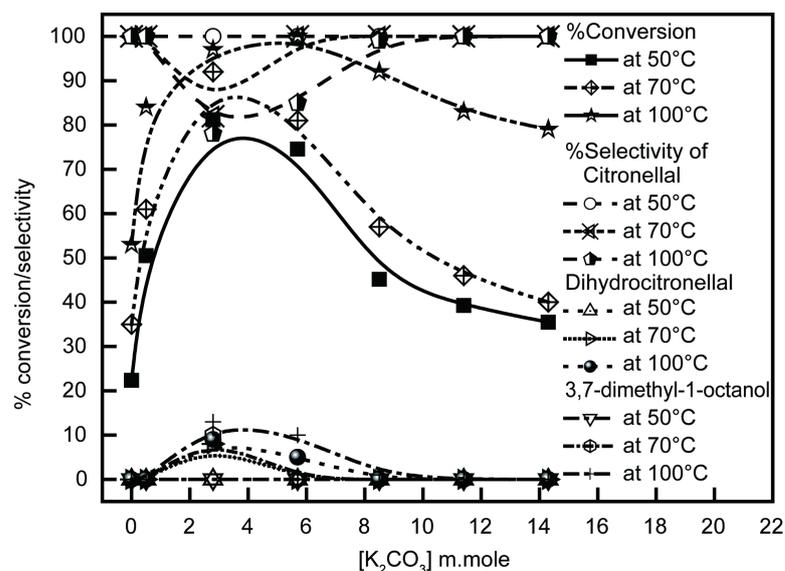


Figure 6. Effect of K₂CO₃ concentration in reaction media on Pd/CMS-6. Reaction conditions: H₂ = 10 bar, water/citral mole ratio = 65, H₂/citral = 6, reaction temperature = 50°C, 70°C, 100°C, reaction time = 2 hours, Pd/citral mole ratio = 0.033.

mixture. With an increase in the NaHCO_3 concentration, the citral hydrogenation activity increased marginally up to 18.7 m·mol of NaHCO_3 , and further raised the concentration. The hydrogenation activity was slightly declined. On the other hand, the addition of Na_2CO_3 (relatively weak base) the effect of alkali on citral conversion was marginal. With an increase in Na_2CO_3 concentration, the hydrogenation activity slightly increased and goes through a maximum at 11.1 m·mol. It was interesting to observe that when K_2CO_3 (stronger base) used as alkali additive (0.5 to 14.2 m·mol) to the reaction mixture, the conversion levels were increased notably at 0.5 m·mol gave more than 50% hydrogenation activity and attained 82% at 2.8 m·mol. Further, increase in content of K_2CO_3 , the citral hydrogenation goes through a maximum at 2.8 m·mol. The influence of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ was on citral hydrogenation activity was insignificant compared to that of K_2CO_3 . The addition of alkali carbonate/bicarbonate has not been influencing any product selectivity; only citronellal was observed as a hydrogenated product under employed conditions. On the other hand, the addition of K_2CO_3 has governs the hydrogenation activity to 100% with influencing other products selectivity with respects to the temperature from 50°C to 100°C; this tendency might be due to a substrate solubility was increased with respects to temperature. These results revealed that, the citronellal formed could be re-adsorbed in the micro pores of CMS support via the C=O bond, which was weakened after the C=C bond hydrogenation, thus, leading to the formation of the dihydrocitronellal and 3,7-dimethyl-1-octanol upon addition of K_2CO_3 (strong base), the hydrogenation activity was influencing in the following two key factors, *i.e.* 1) solubility of hydrogen, citral, 2) electron donating ability of potassium cation to Pd active sites.

1) The alkali additive can interact with citral substrate and solubilise them in an aqueous medium, in contrast; it may reduce the solubility of the hydrogen [24]. 2) Potassium (K^+) ions may modify the reducibility of Pd active sites, similar observation was reported by addition of potassium acetate to cinnamaldehyde hydrogenation reaction, which promoted notably the formation of hydrocinnamaldehyde and prevented its further hydrogenation. It is well known that alkali metal located on the platinum group metal catalysts is easily oxidized by donating electrons to the catalyst metal, and facilitates the adsorption and desorption process of reactant molecules by decreasing the binding strength between reactant molecule and catalyst metal, which results in rate enhancement or increased product yields [16].

In the case of Pt catalysts, it has been suggested [30]-[32] that a similar effect is caused by electron transfer from the doped metal to the active metals, thereby increasing the electron density at the active metal site and decreasing the probability of -C=C- bond hydrogenation by lowering the interaction between -C=C- bonds and the metal.

However, in the case of Pd metals, the interaction of -C=C- will be optimized and the rate of hydrogenation enhanced by the presence of potassium cations.

At lower alkali amounts, the effect of alkali on H_2 solubility is insignificant, on the other hand; the citral solubility is increased; hence the hydrogenation activity was considerably increased up to 8.5 m·mol. A further increase in the alkali content it appears that the alkali addition is significantly influencing the both solubility of H_2 as well as blocking or poisoning of the catalytic sites, which reduce the hydrogenation activity. The results reveal that the addition of alkali additives like K_2CO_3 , increases the activity up to an optimum concentration, further increase may reduce the hydrogenation due to deactivation of Pd active sites. It was opined that the palladium catalysts; the effect of alkali may cause mainly by poisoning the activity of the catalyst, which leads to the further hydrogenation of hydrocinnamaldehyde. However, a detailed study of these effects is required to shed light on these exploratory ideas.

4. Conclusion

In conclusion, the citral hydrogenation activity was significant in acetonitrile as a solvent over Pd/CMS like ~40% with 65% selectivity to citronellal. In the aqueous media, these catalysts exhibited the ~9% activity with 100% selectivity to citronellal. However, the activity in aqueous media is lower compared to that of organic solvents. The Pd/CMS prepared by simple impregnation method also provided good activity and compared to the literature reported carbon catalysts. The addition of optimum potassium carbonates to the aqueous media clearly demonstrates that cost-effective way of increasing the yields of citronellal. On the other hand, the Pd/CMS catalysts are found to be promising for the hydrogenation of α , β -unsaturated carbonyls and specific to the citral and stable in alkali carbonated aqueous media.

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Research Highlights

- The alkali additives like K_2CO_3 , effective in enhancing the selective hydrogenation of $-C=C-$ in aqueous media for α - β unsaturated carbonyls.
- Selective hydrogenation can be achieved in the aqueous media for α - β unsaturated carbonyls.

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