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Selective Hydrogenation of Citral Over Noble Metals Intercalated Montmorillonite Catalysts

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Abstract Surfactant stabilized platinum and ruthenium nano particles were intercalated into the interlamellar space of montmorillonite. The XRD patterns of the metal intercalated montmorillonite reveal that there was a significant swelling during the intercalation of surfactant stabilized metal particles without affecting the crystallinity of montmorillonite. The success of the synthesis of nano particles into montmorillonite catalysts was confirmed from the TEM micrographs of the catalytic materials. The TEM micrographs clearly indicated well dispersion of particles and the average diameter (in nm) of the intercalated metal particles were also determined. The catalytic activity and selectivity of these newly developed catalysts towards the selective hydrogenation of citral in liquid phase was found to be appreciable. The conversion levels were found to be 38% and 18% at 30 °C and increased to 61% and 46% at 100 °C over Pt-CTA-MM 2 and Ru-CTA-MM 2 catalysts respectively at 9 bar hydrogen pressure. The best selectivity towards geraniol and nerol was observed to be 61% over Pt-CTA-MM 2 among the catalysts studied. The effect of temperature, hydrogen pressure, amount of catalyst and time on stream on the conversion and selectivity towards geraniol and nerol were also discussed in detail.

Keywords Noble metal catalysts · Intercalation · Selective hydrogenation · Citral

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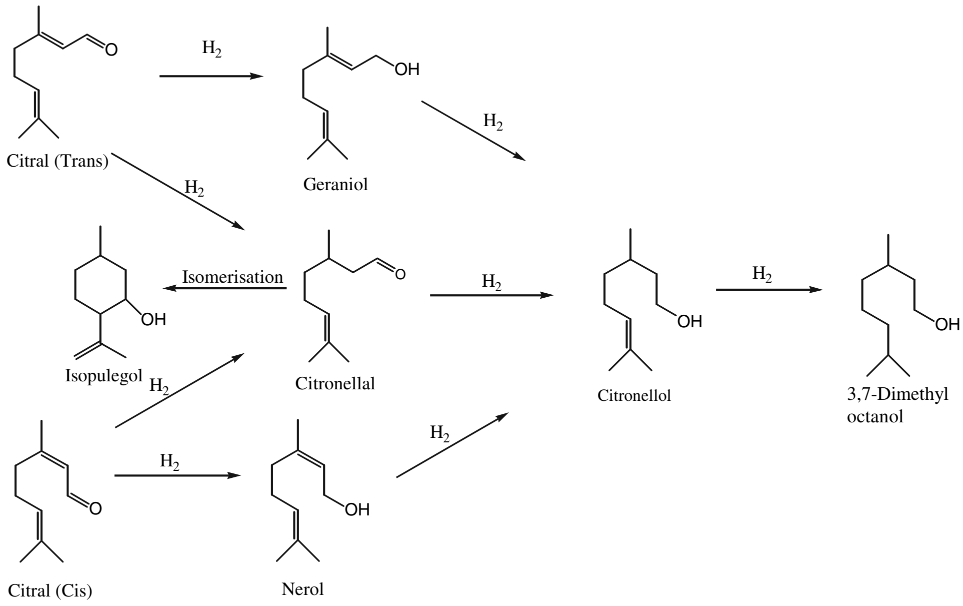
1 Introduction

Selective catalytic hydrogenation of α, β-unsaturated aldehydes is an important step in the preparation of various fine chemicals. The products unsaturated alcohols are important intermediates in several industries such as flavour, fragrance and pharmaceutical industries [1–3]. Crotonaldehyde and cinnamaldehyde are the most widely documented compounds in this respect [4–13]. However, among the unsaturated carbonyl compounds, citral is particularly attractive, because it possesses an isolated C=C bond in addition to the conjugated C=O and C=C bonds [14–20]. Thus obtaining the selective products by overcoming the C=C hydrogenation and the possible isomerisation with another C=C has been a difficult task for decades. Since the reaction pathway is complicated, understanding the properties of the catalysts in the selective hydrogenation of citral is still difficult.

As citral exists in two different isomeric forms namely E and Z forms, the hydrogenation may take place through various pathways resulting in different products such as geraniol and nerol, citronellal or 3, 7-dimethyloctanol as shown in Fig. 1. Apart from these reactions, secondary processes of cyclization or of reaction with the solvent (alcohol) can lead to other by-products like isopulegol or acetals of citronellal. The products namely geraniol, nerol, citronellol and citronellal find many applications individually in industrial sectors like perfume and food processing areas [21].

In general, the selectivity towards the particular product depends on many factors such as width of the d band of the metal chosen, particle size of the metal centers, dispersion level over the support, temperature and pressure of the reaction and also the solvent taken [1, 22, 23]. Earlier studies for the title reaction show that Pd, Rh and Ni are

Fig. 1 Various products possible in the hydrogenation of citral



least selective, Pt and Ru are moderately selective and Ir and Os are highly selective [1]. Vast literature survey is available on the selective hydrogenation of citral catalyzed by different noble metals supported catalysts [24–27]. Bimetallic catalysts are also used in citral hydrogenation to improve selectivity [28–30]. The selectivity towards geraniol and nerol could also be increased by controlling the particle size and dispersion of noble metal by choosing the suitable support material carefully and incorporating the metal of interest by a suitable procedure.

The clay minerals have recently been used to control the size of the metal particles in nm range because of the availability of the interlamellar space in nm range where the metal nano particles could be generated easily [31–34]. The metal nano particles in interlamellar space can produce steric constraints, which orientate the adsorption of the reactant molecules and direct the selectivity of the reaction. Thus, metal clusters (Pt, Rh, Ru) located in the interlamellar space of montmorillonite may lead to the production of unsaturated alcohols. However, only a limited work has been carried out so far over nanoparticles intercalated clay minerals, particularly literature on the selective hydrogenation of citral over clay intercalated noble metal catalysts is scarce.

The use of montmorillonite intercalated metal catalysts for the hydrogenation of citral emphasizes the importance of clay mineral as support in deciding the activity and selectivity of the catalysts in the hydrogenation reactions. In recent years there has been a vast research reported for the easier synthesis of metal particles dispersed clay catalysts [35–41]. The reported literature evidenced that intercalation of metal particles through micelle technique has been one of the best methods to develop nano sized metal intercalated clay catalysts [42, 43]. Our earlier work also proved that through the micelle technique, particles of nanosize with better dispersion over the support could be achieved and also proved their ability as catalysts in certain selective hydrogenations [44, 45].

Thus a study of hydrogenation of citral over Pt and Ru intercalated montmorillonite catalysts could reveal the potential of noble metal intercalated clay catalysts in selective hydrogenation reactions to replace the conventional catalysts. With this view, montmorillonite was chosen as the representative clay mineral in the 2:1 phyllosilicate smectite family, intercalated with nano sized platinum and ruthenium metal particles at very low concentration and made a detailed study on citral hydrogenation at different temperatures and hydrogen pressures.

2 Experimental Techniques

2.1 Materials

Montmorillonite used in this study was purchased from Lancaster (Alfa Aesar) and washed with water several times to remove washable impurities (CEC = 87 meq/100 g). Hexammineruthenium chloride (99.9% purity), hexachloroplatinicacid (99.9% purity), sodium borohydride (95% purity) (Merck Ltd, Mumbai) and the cationic surfactant cetyltrimethyl ammonium bromide (Otto Chemie) were used as received.

2.2 Synthesis

Calculated amount of corresponding metal precursors namely H_2PtCl_6 and $[Ru(NH_3)_6Cl_3]$ for Pt and Ru respectively so as to attain 1 and 2 wt.% of metal concentration over the support was dissolved in aqueous solution of cationic surfactant (cetyltrimethyl ammonium bromide) whose concentration is above its cmc and then reduced by the drop wise addition of ethanolic solution (0.05 g in 10 mL) of $NaBH_4$. This resulted in black coloured colloidal metal sol in which the metal particles were stabilized by the micelles. The colloidal metal sol obtained was allowed to interact with the aqueous suspension containing 3 g of Na-montmorillonite. The ion exchange reaction between Na^+ and CTA^+ resulted in the simultaneous irreversible adsorption of metal particles in the interlamellar space [46, 47]. The surfactant concentration was increased between 10 and 30 times of its cmc and it was found that at 10 times of its cmc, the size of the metal particles formed was controlled in nm range in the colloidal sol and the same has been retained while dispersing them in the interlamellar space of montmorillonite. The excess surfactant molecules were removed by repeated washing using ethanol and toluene.

2.3 X-ray Diffraction

Increase in basal spacing of the organoclay was determined with a Philips X'pert X-Ray Diffractometer, Cu–K α radiation ($\lambda = 1.54$ Å) being used at 40 kV and 35 mA. The investigated scattering angle range was between $1° \leq 2\theta \leq 50°$ for the dry clay samples. The basal plane distance d_L was calculated from the first order (001) Bragg reflections.

2.4 Transmission Electron Microscopic Analysis

Particle size was determined from electron micrographs taken on JEOL JEM-2010F transmission electron microscope. One drop of dilute colloidal dispersion in isopropanol was placed on a copper grid and allowed to stand for 40–50 s. After solvent evaporation, electron micrographs were taken of the particles retained on the film. Particle sizes were determined by taking average of 30–40 particles on magnified transmission electron microscope images.

2.5 BET Surface Area Analysis

The specific surface areas of Na Montmorillonite, CTAM, Pt-CTA-MM 1 and Ru-CTA-MM 1 samples were determined by the BET nitrogen method with a Quantachrome Nova 4200 e. The samples in the sorption vessel were pretreated at 343 K under vaccum ($p < 10^{-3}$ Torr) for 2 h.

2.6 Thermo Gravimetric Analysis

TGA thermograms of Na Montmorillonite and CTAM were taken in the temperature range of 323–873 K using Perkin Elmer Diamond TG/DTA analyzer.

2.7 Atomic Absorption Spectroscopic Studies

The active metal content present in all the Pt-CTA-MM and Ru-CTA-MM samples were determined from atomic absorption spectrophotometer using Perkin Elmer 2380 Atomic Absorption Spectrometer and are reported in Table 1.

2.8 Selective Hydrogenation of Citral

The liquid phase hydrogenation reaction of citral was carried out in the hydrogenation reactor made up of SS in which temperature and pressure of the reaction could be controlled and varied for each reaction. Prior to the actual run, the desired amount of catalyst was activated at 373 K and 10 bar hydrogen pressure for about 3 h with minimum amount of ethanol. After 3 h the reactor was cooled down to room temperature and the reaction was carried out with required amount of citral (0.02–0.08 M) and ethanol to bring the total volume of 75 mL with pre activated catalyst of different amounts. After the attainment of the desired temperature, the hydrogen pressure was adjusted to the desired pressure and the reaction was allowed to proceed for about 8 h. The reaction mixture was withdrawn at

Table 1 Structural properties of the synthesized catalysts

Materials	Metal content Wt.% (AAS)	$a^S{}_{BET}$ (m^2/g)	2 θ (Å, XRD)		d spacing (Å)	d_{ave} (nm, TEM)
			d(001)	(111)		
Na-Mont	–	208.7	6.0	–	14.72	–
CTAM	–	90.5	1.5	–	59.23	–
Pt-CTA-MM 1	0.978	128.9	1.5	40.1	59.23	2.3
Pt-CTA-MM 2	1.967	–	1.5	40.1	59.23	9.0
Ru-CTA-MM 1	0.869	112.5	1.5	44.5	59.23	11.2
Ru-CTA-MM 2	1.928	–	1.5	44.5	59.23	21.7

different intervals of time and subjected to GC (Shimadzu 17 A) analysis (using FID detector) to analyze the products formed and also to study the course of the reaction. Product separation was carried out using OV 1 stainless steel column (2 m × 1/8 inch o.d.). Column temperature was programmed from 423 to 493 K at a heating rate of 10 K/min. The injector and the detector temperatures were kept at 523 K and 553 K respectively. The products were identified by comparison with commercial standards and using GC-MS analysis. Analysis of all the samples was repeated at least twice to check the reproducibility and was found to be within ± 2%.

3 Results and Discussion

3.1 X-ray Diffraction Analysis

The XRD patterns of Na-montmorillonite, Pt-CTA-MM 1, Pt-CTA-MM 2, Ru-CTA-MM 1 and Ru-CTA-MM 2 are shown in Figs. 2 and 3. The basal spacing for Na montmorilllonite was determined to be 14.72 Å (Fig. 2a), which increased to 59.23 Å for Pt incorporated CTAM catalysts (Fig. 2c). This increase in basal spacing is attributed to exchange of Na$^+$ with the CTA$^+$. Pt-CTA-MM and Ru-CTA-MM catalysts showed d (111) reflections at 2θ 40.1° and 44.5° respectively. The shifting of (001) reflection from 14.72 to 59.23 Å and appearance of peaks (111) at 40.1 and 44.5° for Pt-CTA-MM and Ru-CTA-MM catalysts confirm the swelling of montmorillonite and the intercalation of Pt or Ru particles into the interlamellar space respectively. The XRD patterns also indicated that the intensity of the peak of d (111) reflection of the metal particles increased as the metal loading was increased.

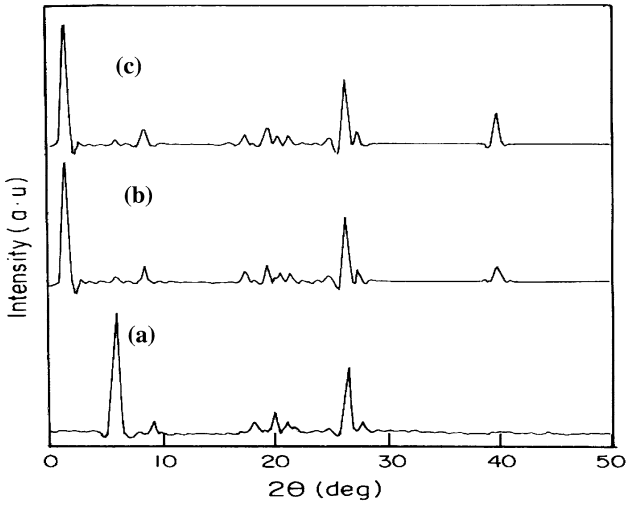


Fig. 2 X-ray diffraction patterns of Na-Mont, Pt-CTA-MM 1 and Pt-CTA-MM 2

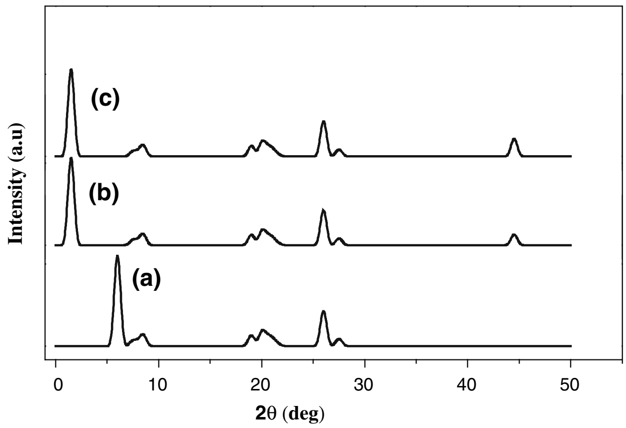


Fig. 3 X-ray diffraction patterns of Na-Mont, Ru-CTA-MM 1 and Ru-CTA-MM 2

3.2 Transmission Electron Microscopic Analysis

The synthesized catalysts were subjected to TEM analysis for the measurement of the size of the particles formed and the level of dispersion. TEM micrographs of Pt-CTA-MM 1, Pt-CTA-MM 2, Ru-CTA-MM 1 and Ru-CTA-MM 2 catalysts were shown in Fig. 4. The micrographs show that the particles were well dispersed and the average particles size calculated was in nm range and the data are reported in Table 1. As the particle size was in nm range in all the catalysts, there was a very good dispersion of Pt and Ru particles in montmorillonite.

3.3 BET Surface Area Analysis

The BET surface area of Na montmorillonite, CTAM, Pt-CTA-MM 1 and Ru-CTA-MM 1 was also reported in Table 1. The surface area of the metal loaded montmorillonite was found to be higher than that of CTAM and lower than that of Na-montmorillonite. The low specific surface area of the metal loaded montmorillonite catalysts when compared to Na-montmorillonite suggests that the structure of organo clay is quite different from the structure of Na-montmorillonite i.e. for dry organoclay samples the internal surface sites are not accessible to the nitrogen molecules [48].

3.4 Thermo Gravimetric Analysis

The thermogram of Na Montmorillonite and surfactant exchanged montmorillonite (CTA-MM) are shown in Fig. 5. From the thermograms it was observed that the surfactant molecule started to decompose at 453 K. This indicates that the metal particles may aggregate when the

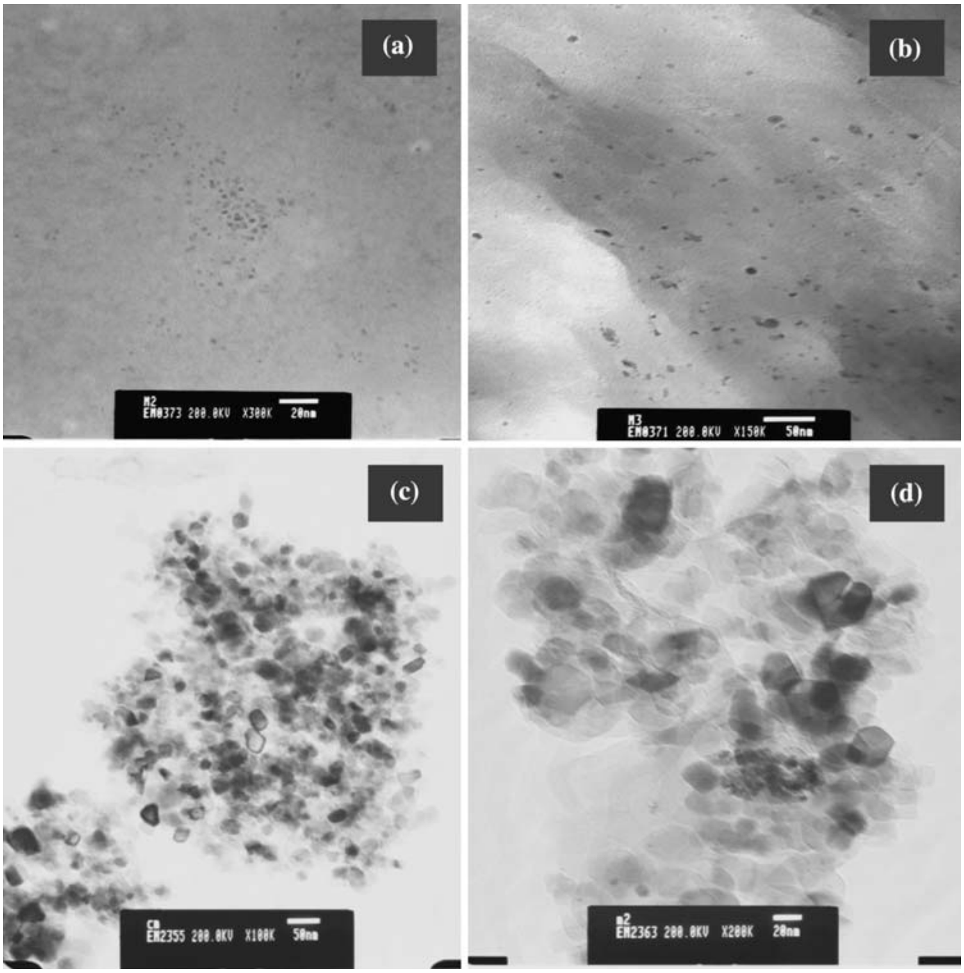


Fig. 4 Transmission electron micrograph of (**a**) Pt-CTA-MM 1, (**b**) Pt-CTA-MM 2, (**c**) Ru-CTA-MM 1, (**d**) Ru-CTA-MM 2

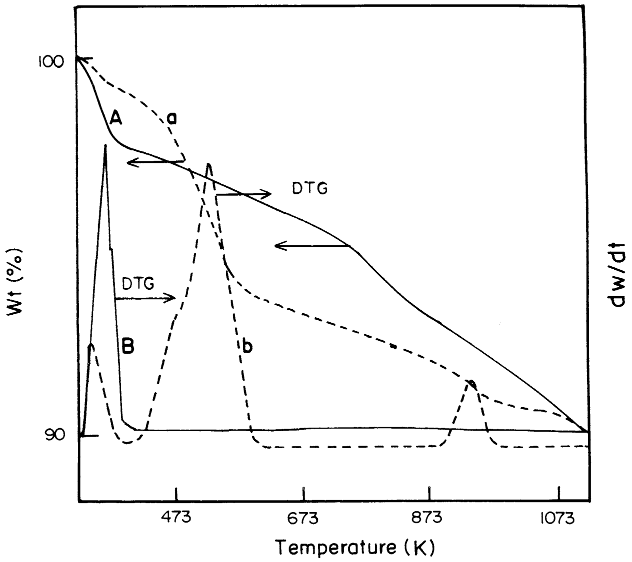


Fig. 5 TG thermogram of (A) Na-MM and (a) CTA-MM DTG thermogram of (B) Na-MM and (b) CTA-MM

catalysts are tested above 453 K. Therefore the hydrogenation reactions were restricted in the temperature range of 303–373 K.

3.5 Selective Hydrogenation of Citral

The following optimization studies were carried out for the better conversion and selectivity towards geraniol and nerol over the synthesized catalysts and the results are discussed.

3.5.1 Effect of Temperature

The optimisation of reaction temperature for the hydrogenation of citral is essential as the reaction is temperature sensitive leading to the formation of a variety of hydrogenated products (Fig. 6). The reaction temperature was varied between 303 and 373 K at 9 bar hydrogen pressure with 0.3 g of catalyst and the reaction was continued for 8 h. Figure 9 indicates that as the temperature increased the reaction between the substrate molecule and the adsorbed hydrogen increased which resulted in increased conversion of citral similar to them observed by Singh and Vannice [22]. The transfer of hydrogen from the catalytic site to the unsaturated C=C or C=O bond is facilitated by

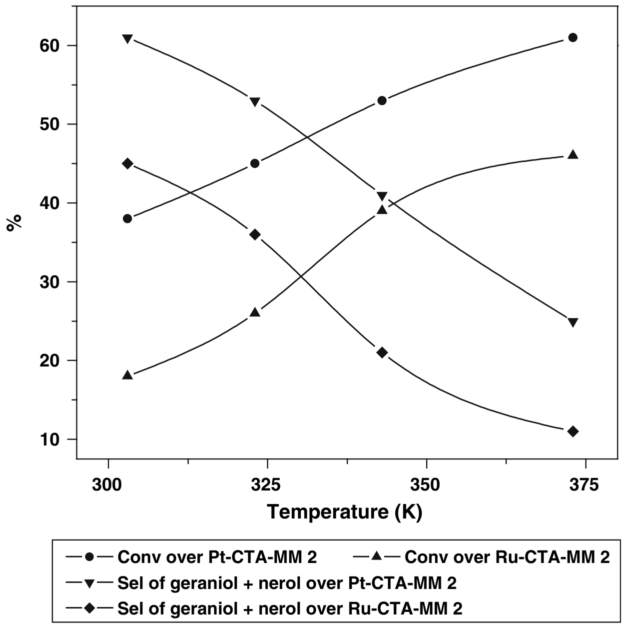


Fig. 6 Effect of temperature on conversion of citral and selectivity on geraniol + nerol

the reaction temperature. Higher the temperature of the reaction system, greater is the transfer of hydrogen leading to higher conversion. Samples collected at the 8 h show that both Pt-CTA-MM 2 and Ru-CTA-MM 2 catalysts are active even at room temperature (303 K). The conversion levels were found to be 38% and 18% at 303 K and increased to 61% and 46% at 373 K over Pt-CTA-MM 2 and Ru-CTA-MM 2 catalysts respectively which is comparatively better than the conversion obtained at 8th h over 3.5% Pt/SiO_2 at 373 K and 20 bar [25].

In citral hydrogenation, temperature of the reaction is one of the major deciding factors which determines the selectivity of the desired product namely geraniol and nerol. As citral exists in two isomeric forms, two unsaturated alcohols namely geraniol and nerol could be formed and the selectivity was calculated by taking the total percentage of geraniol and nerol formed. It is evident from Fig. 9 that selectivity towards geraniol and nerol decreased with increase in temperature of the reaction (Table 2). This decrease in selectivity is due to consecutive hydrogenation of geraniol or nerol and isomerisation which are more favourable at higher temperatures. The decrease in selectivity may also be due to the possibility of cyclisation and acetalisation reactions which can occur at higher temperatures as the solvent used is ethanol [26].

3.5.2 *Effect of Hydrogen Pressure*

To study the effect of hydrogen pressure on conversion and selectivity, citral hydrogenation was carried out over Pt-CTA-MM 2 and Ru-CTA-MM 2 catalysts at different pressures of hydrogen (3–9 bar) at room temperature (Fig. 7). The conversion was found to be maximum at very high pressure of hydrogen (9 bar) and showed a linear dependence with hydrogen pressure for both platinum and ruthenium intercalated montmorillonite catalysts. As far as selectivity was concerned, there was no appreciable change in selectivity towards geraniol and nerol with respect to change in pressure as observed by Singh et al. [50].

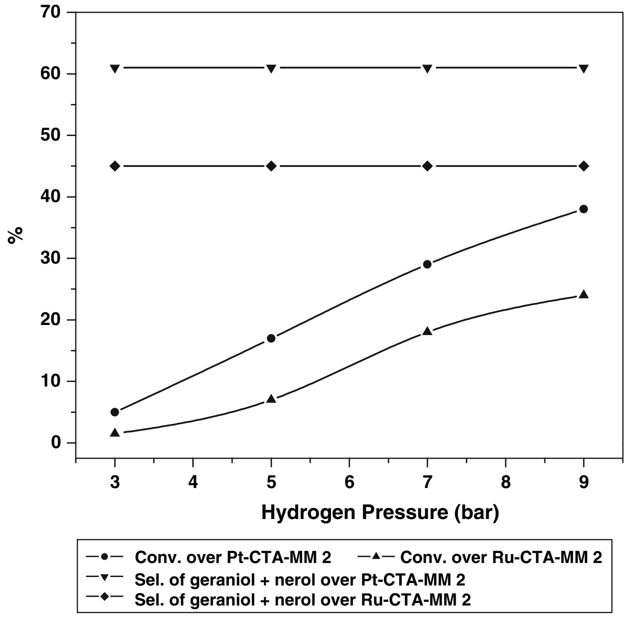


Fig. 7 Effect of hydrogen pressure on conversion of citral and selectivity on geraniol + nerol

Table 2 Conversion of citral and % distribution of products over different catalysts

Catalyst	% Conversion		% Selectivity							
			Geraniol + Nerol		Citronellal		Citronellol		Others	
Temperature (K)	303	373	303	373	303	373	303	373	303	373
Pt-CTA-MM 1	21	43	57	21	26	41	7	19	10	19
Pt-CTA-MM 2	38	61	61	25	19	53	9	17	11	5
Ru-CTA-MM 1	10	16	43	11	31	37	10	41	16	11
Ru-CTA-MM 2	18	46	45	11	29	43	14	39	12	7

Catalyst: 0.3 g. H_2 Pressure: 9 bar

3.5.3 Effect of Initial Concentration of Citral

The hydrogenation reaction was carried out with different concentrations of citral (0.02–0.08 M) over 0.3 g of Pt-CTA-MM 2 catalyst at room temperature and at 9 bar hydrogen pressure to know the conversion and selectivity with respect to different initial concentrations of citral. The conversion increased with increase in the concentration of citral up to a certain level only and thereafter it reached a steady state. The increase in conversion with increase in the concentration of citral was up to 0.06 M. This is due to the large excess of adsorbed hydrogen on catalytic sites to react with citral molecule but when the amount of citral increased beyond 0.06 M, the catalytic sites were saturated.

3.5.4 Effect of Weight of Catalyst

The weight of catalyst was varied from 0.1 to 0.5 g and the reaction was carried out at room temperature and at 9 bar hydrogen pressure. It was found that conversion increased with the weight of catalyst. Maximum conversion of about 54% was obtained with 0.5 g of Pt-CTA-MM 2 catalyst (Fig. 8). This is because of the increase in number of active sites available for the substrate molecule. However, the increase in weight of catalyst has no effect on the selectivity of products as around 60% of selectivity towards geraniol and nerol was obtained in all the reactions carried out over different amounts of catalysts.

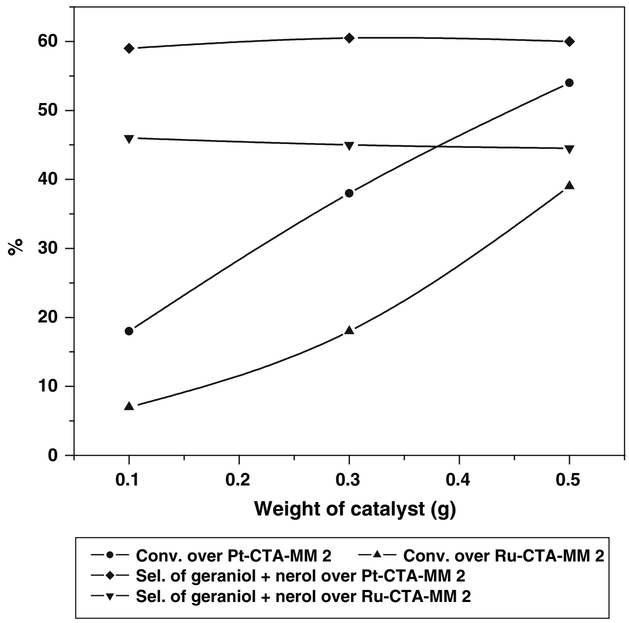


Fig. 8 Effect of weight of catalyst on conversion of citral and selectivity on geraniol + nerol

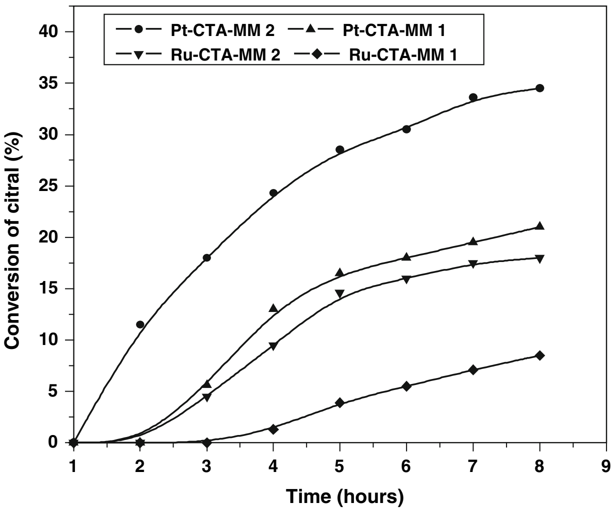


Fig. 9 Effect of reaction time on conversion of citral

3.5.5 Effect of Reaction Time

The effect of reaction time on citral hydrogenation was also carried out to investigate the course of the reaction and the product formation over all the catalysts namely Pt-CTA-MM 1, Pt-CTA-MM 2, Ru-CTA-MM 1 and Ru-CTA-MM 2 (Fig. 9). The reaction was carried out at room temperature and at 9 bar hydrogen pressure for about 8 h and the product withdrawn every one hour interval was subjected to GC analysis. It was found that the conversion increased for all the catalysts with time and found to be maximum (38%) at the end of eight hours with Pt-CTA-MM 2. After the same reaction time the other catalysts such as Pt-CTA-MM 1, Ru-CTA-MM 2 and Ru-CTA-MM 1 showed the conversion of 20, 18 & 8.5% respectively.

It was also noticed from the Fig. 9 that increase in conversion was rapid up to 5 h and levels off thereafter. This may be due to the decarbonylation reaction that occurs at metal surface which prevents the catalytic sites for the adsorption as found by Singh et al. and Singh and Vannice [23] over Pt/SiO_2 catalyst. This study also revealed that there was no inhibition period for all the catalysts. The selectivity of nerol and geraniol decreased slightly with increase in time of reaction because these products formed in the early hours get further hydrogenated to citronellol and other products [50].

4 Conclusion

Platinum and ruthenium intercalated montmorillonite catalysts prepared through the micelle technique show better conversion and selectivity towards geraniol and nerol even at low level loading of active metal. TEM micrograph and XRD study of the catalysts proved that the particles are well dispersed and in nano size. Temperature of the reaction played a major role in determining the conversion and selectivity towards geraniol and nerol. Increase in hydrogen pressure from 3 bar to 9 bar had effect only on the conversion and not on selectivity. Among all the catalysts synthesized, Pt-CTA-MM 2 showed high conversion i.e. 38% at room temperature and 61% at 373 K which is also comparatively better than the earlier reports and selectivity of 61% and 25% at room temperature and at 373 K respectively.

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