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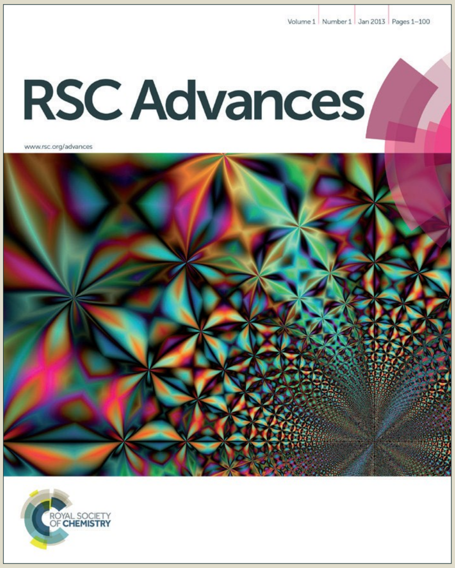

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An elegant synthesis of chitosan grafted hydrotalcite nano-bio composite material and its effective catalysis for solvent-free synthesis of jasminaldehyde

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Abstract

A novel nano-bio composite of chitosan and a layered double hydroxide was elegantly synthesized by co-precipitation method. The nano-bio composite material (CMA) was thoroughly characterized by FTIR, TGA, XRD, SEM and TEM. The composite material CMA had shown efficient catalytic activity for selective synthesis of jasminaldehyde under solvent free conditions by condensation of benzaldehyde and 1-heptanal. In typical employed conditions, 39.5 mmol benzaldehyde, 7.9 mmol 1-heptanal, 100 mg catalyst, 160 °C and 700 rpm, a maximum selectivity of 89% with 99% conversion was obtained. The investigations were performed in detail as a function of amount of the catalyst, temperature and molar ratio of 1-heptanal to benzaldehyde to observe the effect of these reaction parameters on the conversion, selectivity and rate of the formation of the condensation products. All these parameters were found to influence the performance of the catalyst. The initial rate of formation of jasminaldehyde was found to be ~20% more than those of the rates with individual chitosan and hydrotalcite. The rate of formation of 2-pentyl-2-nonenal with CMA was found to be less in comparison of individual catalyst, chitosan and hydrotalcite. The determined activation energy was 16.3 kJ/mol. The catalyst was elegantly separated, washed and dried, and found to be effective for its recycling for six times without any substantial loss in its activity.

1. Introduction

The cross aldol reaction has proved to be an important synthetic tool for C−C bond formation for the synthesis of α, β −unsaturated carbonyl products. Conventionally, this reaction is carried in presence of strong liquid alkali bases like NaOH or KOH taken more than in stoichiometric quantities. The use of these alkalies results in increase in the cost of synthesis, environmental pollution, lack of thermal stability, reusability of catalyst and post reaction work-up. Apart from the conventional bases, several weak bases like amines[1], ammonium salts[2] and amino acids[3] are used in a homogenized system. Later numerous heterogeneous acid and base catalysts like alkaline earth metal oxides[4,5], alumina supported hydroxide[6,7], ion-exchange resins[8,9], zeolites[10], amino group immobilized silica gel[11], amino acid supported gold nanoparticles[12], silica immobilized piperazine[13], amino modified Zr−terephthate MOF[14] and synthetic talc[15] have been used. These catalysts have shown the potential advantages of ease of separation, robustness, long operating life, reusability and environmentally benign nature over the homogeneous catalysts. The heterogeneous catalysts find their importance in the large number of processes in the chemical industries[16].

The incorporation of various active components into the supports that exemplifies an increase in efficiency of catalyst as a result of cooperative effect is investigated in detail[17-19]. The work by climent et al. showed that the amorphous aluminophosphates containing acid-base pairs increases the selectivity without affecting the activity of the catalyst[20,21]. Using this approach, Kadib et al.[22] functionalized chitosan microspheres by inorganic mono metal (lewis acid) oxide clusters for the synthesis of jasminaldehyde wherein the basic –NH_2 sites adjacent to acidic metal center accounts for the increase in the selectivity.

The use of solid base catalysts chitosan[23] and hydrotalcite[24] are reported for the synthesis of jasminaldehyde. These catalyst systems were found to have efficient catalytic activities via an environmental friendly route in which the hazardous liquid base KOH/NaOH was successfully replaced with these green solid base catalysts under solvent free conditions. These two catalysts are individually studied in detail wherein kinetic aspect of chitosan catalyzed reaction is also dictated. Both these catalysts have shown efficient recyclability up to six times. The present study is to have an synergic insight of the composite effect of these two chitosan and hydrotalcite catalytic materials for selective synthesis of jasminaldehyde. The composite material of chitosan and Mg/Al hydrotalcite had been elegantly synthesized by simple co-precipitation route. This nano-bio composite material CMA had been thoroughly characterized and investigated in detail for the synthesis of jasminaldehyde as shown in scheme 1. A kinetic insight is also substantiated in the present work for the synthesis of jasminaldehyde by evaluating the rates of formation of selective major product, jasminaldehyde and minor product, 2-pentyl-2-nonanal. The effects of various parameters namely amount of catalyst, temperature and molar ratio of benzaldehyde to 1-heptanal on the rate of the formation of jasminaldehyde were investigated.

2. Experimental

2.1. Materials

Magnesium nitrate ($Mg(NO_3)_2·6H_2O$; 98.9%), aluminum nitrate ($Al(NO_3)_3·9H_2O$; 99.1%), sodium hydroxide (NaOH; 99.99%) and hydrochloric acid (HCl; 35.4%) were purchased from S. D. Fine Chemicals, India. Low-molecular weight chitosan, 1-heptanal and benzaldehyde were procured from Sigma-Aldrich and used without further purification.

2.2. Synthesis of chitosan-hydrotalcite nano-bio composite

The chitosan-hydrotalcite nano-bio composite was prepared by co-precipitation method. In the typical synthesis of CMA, an aqueous solution (A) of 10 g $Mg(NO_3)_2·6H_2O$ and 4.18 g $Al(NO_3)_3·9H_2O$ was prepared in 100 mL of double distilled millipore water. The solution A was added dropwise into second solution (B) containing low-molecular weight chitosan (5 g) completely dissolved in 0.1 M HCl (325 mL) under vigorous stirring at room temperature for 24 h. The temperature of the bath was slowly raised to 70 °C for 2 h. The pH of the solution was adjusted to 10 by adding 0.2 M NaOH solution whereby the initial pale yellow color solution changed to white precipitates. The content was aged for 16 h without stirring at room temperature and then filtered. After filtration the precipitates formed were washed with excess millipore water until filtrate became neutral. The obtained precipitates were dried at 70 °C and then were powdered by using mortar and pestle. The powdered material was stored in a vial simply under atmospheric conditions.

2.3. Characterization of the catalyst

The structural studies of the catalyst were carried out by Rigaku MINIFLEX-II (FD 41521) powder X-ray Diffractometer. The samples were scanned in the 2θ range of 10–80° using CuKα (λ=1.54178 Å) radiation and a Ni filter. FT-IR spectra of the catalyst were recorded with Perkin-Elmer GX spectrophotometer system using KBr pellets in the wavelength range of 400-4000 cm^{-1}. Thermogravimetric Analysis (TGA) was carried out on a Mettler TGA/DTA 851e instrument at a nitrogen flow rate of 50mL/min. N_2 sorption analysis was carried out at 77.4 K in sorptometer (ASAP 2010, Micromeritics). The sample was degassed at 120 °C for 4 h prior to the sorption analysis. The morphology of the composite was determined using a LEO series 1430

VP scanning electron microscope (SEM). The size and shape of the particles were analyzed using Transmission Electron Microscopy (JEOL JEM 2100 microscope).

2.4. Condensation reaction

The desired amounts of benzaldehyde, 1-heptanal and catalyst were taken into a oven dried double neck round bottom flask with 0.01 g tetradecane as internal standard. One neck of the flask was fitted with refluxing condenser with spiral tube inside and other neck was blocked using a silicon rubber septum. Water at 15 °C was circulated in the spiral tube of the condenser and the flask was kept in an oil bath equipped with temperature controller and magnetic stirring unit. The reaction was carried out under nitrogen atmosphere to inhibit formation of corresponding acids from aldehydes. The reaction was carried out at 125 °C. The product mixture was cooled down to room temperature after the completion of the reaction. The progress of the reaction was monitored in terms of consumption of 1-heptanal by taking aliquots at different time intervals. The conversion was evaluated by considering the subsequent decrease in concentration of 1-heptanal. The analysis of product mixture was carried out by GC (Bruker 450 GC, Japan), and GC-MS (Shimadzu, QP-2010, Japan*)*. The GC has a 5% diphenyl- and 95% dimethyl siloxane universal capillary column and a flame ionization detector (FID). The quantification of the FID response was done by using a standard calibration curve. To ensure the reproducibility of the reaction, repeated experiments were carried out under identical reaction conditions. Selected representative chromatograms are given in the Supporting information (Fig. S1 to S5). The results obtained including conversion and selectivity were found to be in the range of 5% variation. For recyclability studies, the catalyst used after each cycle was separated by Whatman filter paper (Grade 41), washed thrice with methanol, dried and crushed. Thus obtained catalyst was reused under selected identical conditions of 7.9 mmol heptanal, 39.6 mmol benzaldehyde, 125 ^{o}C, 700 rpm for 8 h reaction time.

3. Results and Discussion

3.1. Characterization of the catalyst

The characterization of the catalyst was carried out by N_2 Sorption, FTIR, TGA, XRD, SEM and TEM. The BET surface area of CMA composite was found to be 3.77 m^2/g.

3.1.1. FTIR

The FTIR spectrum of hydrotalcite (HT), pure chitosan powder (CT) and nano-bio composite (CMA) are shown in Fig 1. The typical characteristic bands in the FTIR spectrum of CT powder[23] as well as HT[24] were obtained. The FTIR spectra of CT powder showed a wide OH vibrational stretching peak at 3450 cm^{-1} indicating the hydrogen bonding of hydroxyl groups. The peak at 1602 cm^{-1} indicates the presence of $–NH_2$ group resulting from deacetylation of chitin. The band that appeared at 2886-2929 cm^{-1} is due to the C–H stretching vibration of aliphatic CH groups and that at 1083 cm^{-1} is due to the C–O–C bond stretching vibrations. The band at 1660 cm^{-1} corresponds to amide stretching vibration[25]. The FTIR spectrum of HT showed absorption at 3500-3600 cm^{-1} which is attributed to the H-bonding vibrations in the layers of the LDH material. The characteristic shoulder bands for H_2O and CO_3^{2-} were observed at 1637 and 1450 cm^{-1} respectively. The shoulder due to the interlayer carbonates appeared at 1380 cm^{-1}. The bands obtained at 659 cm^{-1} is attributed to the in plane carbonate bonding in the LDH. For the spectrum of CMA, a broad peak between 3100-3700 cm^{-1} and centered at 3442 cm^{-1} was obtained and attributed to the O–H and N–H stretching vibrations. The hydroxyl groups of the brucite layer overlapped with O–H and N–H of chitosan. The band location at 1602 cm^{-1} and 1560 cm^{-1} changed after the composition. These results indicated strong hydrogen bonding between the N–H groups of chitosan and O–H groups of LDH brucite layer[26]. The bands at 420 and 630 cm^{-1} was due to M–O or O–M–O bonds in CMA.

3.1.2. TGA

The TGA profile (Fig. 2) for the CMA showed three step weight loss. The first weight change (11%) was observed in the range of 40-190 °C due to physically adsorbed water molecules without any change in the structure. The second weight loss (20%) observed in the range of 210-310 °C is attributed to the decomposition of polysaccharide chain in the nano-bio composite. The third weight loss (22%) observed in the range of 320-570 °C is due to the removal of condensed water molecules and carbonate anion entrapped in the residual brucite layer.

3.1.3. XRD

The XRD pattern of HT, CT and CMA are shown in Fig 3. The XRD pattern of HT showed sharp, intense and symmetric peaks at lower diffraction angles (2θ= 10-25°) and a broad asymmetric reflection at higher diffraction angles (2θ= 30-50°) which are characteristic of highly crystalline layered structure[24]. The broad diffraction peaks at 2θ= 10° and 21° for semicrystalline chitosan[27] were present in the XRD pattern of the nano-bio composite. The XRD pattern of CMA showed no significant change in the characteristic planes of HT which indicated retention of the structure. However after the formation of the composite, a slight shift towards lower 2θ values for peaks corresponding to (003) and (006) planes was observed which is due to concurrent decrease of the positive charge of the layers of HT. The XRD pattern was also indicative of a slight intercalation of the biopolymer into the LDH layer as observed by marginal shift of (001) peak relative to parent LDH along with the retention of both the phases (CT and HT).

3.1.4. SEM

The morphology of the CMA nanobiocomposite was investigated by SEM (Fig. 4). The SEM image revealed the grafting of the biopolymeric part over inorganic layered nanoplatelet material. Also it showed that the nanoplatelets are spread over the polymer in the composite.

3.1.5. TEM

The TEM of the CMA composite showed that the polymer is grafted over LDH material (Fig. 5a). The Fig. 5b reveals the presence of an interplanar distance of approximately 1.4 nm indicating some exfoliation of the LDH material. The inset in Fig. 5b shows presence of single LDH layers in the composite sample. The Fig. 5c shows the presence of the small particles of the layered structure whilst the Fig 5d shows the lattice fringes of the LDH material. The inset in Fig 5d shows the electron diffraction pattern of the composite. It confirms the presence of pure composite material.

3.2. Catalytic activity

Catalytic activity of the catalyst was investigated for the synthesis of jasminaldehyde by the condensation of benzaldehyde with 1-heptanal. A 97% conversion of 1-heptanal with 80% selectivity to jasminaldehyde was obtained within 7 h of reaction at 160 °C. On increasing the time to 14 h, a maximum selectivity of 89% was obtained. The effect of reaction parameters like reaction time, temperature, the catalyst amount and the heptanal to benzaldehyde molar ratio on the conversion of 1-heptanal and selectivity to jasminaldehyde has been investigated in detail.

3.2.1. Effect of catalyst amount

The effect of the catalyst amount on condensation of benzaldehyde and 1-heptanal was studied by varying the catalyst amount from 10 to 300 mg and the corresponding results are tabulated in Table 1. On increasing the catalyst amount from 10 to 100 mg conversion and selectivity both increased from 40 to >99% and 76 to 86% respectively. Further increase in catalyst amount to 200 mg gave no significant change in conversion and selectivity. On increasing the amount of catalyst to 300 mg, conversion of 1-heptanal started declining with increase in selectivity towards jasminaldehyde. As the reaction proceeds the conversion increase with decrease in the amount of 1-heptanal. As the concentration of 1-heptanal decreases, benzaldehyde competes with 1-heptanal to favor the selectivity towards jasminaldehyde.

3.2.2. Effect of reaction temperature

The effect of temperature on the condensation reaction was studied by selecting the temperature in a range of 80 to 180 °C (Table 2) maintaining other reaction parameters under identical conditions. The conversion of 1-heptanal and selectivity to jasminaldehyde were determined at different time intervals i.e. 3, 7 and 14 h and the results are listed in Table 2. The conversion of 1-heptanal and selectivity to jasminaldehyde both increased with an increase in the temperature from 80 °C to 160 °C. Further increase of temperature resulted in a decrease in the selectivity. A 95% conversion with 76% selectivity towards jasminaldehyde was observed at 100 °C (Entry 2) which increased to >99% with 86% selectivity with increase in the temperature to 125 °C (Entry 3). A maximum selectivity with >99% conversion of 1-heptanal was observed at 160 °C which decreased to 85% on increasing temperature to 180 °C without any change in conversion.

3.2.3. Effect of 1-heptanal to benzaldehyde molar ratio

In the effect of molar ratio of 1-heptanal to benzaldehyde, the study performed in the range of the molar ratio of 1:1 to 1:10, it was observed that the conversion increased with time and reached up to 99% at 14 h and remained the same for the molar ratios of 1:1 to 1:5 (Entries 1-5). Further increase in the molar ratio resulted in a decrease in conversion (Entries 6 and 7). A drop in the conversion was observed from 99% for the molar ratio of 1:5 to 89% for the molar ratio of 1:10. The increase in molar ratio hinders the active sites on the catalyst thus reducing the conversion. A 59% selectivity to jasminaldehyde at 1:1 molar ratio of 1-heptanal to benzaldehyde increase to 66% selectivity on increasing the molar ratio to 1:2. The selectivity was increased till molar ratio of 1:4 and then remained the same i.e. 86% for higher molar ratio. The self-condensation of 1-heptanal befits lower selectivity to jasminaldehyde at lower heptanal to benzaldehyde ratios. Thus the optimum molar ratio of heptanal to benzaldehyde was 1:5 giving >99% conversion with 86% selectivity.

3.2.4. Kinetic studies

The condensation between benzaldehyde and 1-heptanal using CMA as catalyst was carried out with respect to reaction time and the kinetic profile (Fig. 6) was obtained in terms of consumption of 1-heptanal and formation of the aldol products, jasminaldehyde and 2-pentyl-2-nonenal. There was a decrease in amount of 1-heptanal with increase in formation of cross aldol product, jasminaldehyde for entire time of the reaction. The decrease in the amount of 1-heptanal and formation of jasminaldehyde were almost linear upto initial 4 h of the reaction and major conversion (~75%) occurred. After that the conversion became slow. The formation of self-condensation product 2-pentyl-2-nonenal was increased upto 2 h and gave a slow decreasing trend with time. It is of interest to have an insight in this decreasing trend of the selectivity of 2-pentyl-2-nonenal with CMA composite in comparison of the performance of the individual components, CT[23] and HT[24], used as catalysts for this reaction. In case of the reported individual CT system for aldol condensation of 1-heptanal and benzaldehyde, the rate of formation of the self-condensed product, 2-pentyl-2-nonenal was observed to be continuously increasing along with the desired cross aldol product, jasminaldehyde with respect to time. In case of individual HT catalyzed system, the rate of formation of 2-pentyl-2-nonenal gave an initial increase followed by decrease in the trend with respect to time. Contrary to these systems, for the present composite system, the rate of formation of 2-pentyl-2-nonenal is observed to decrease (Fig. 6) continuously with respect to time after 2 h, unlike the trend followed by the individual component systems. It is believed that the composite system facilitates the suppression of the undesired self-aldol condensation which may be due to the dominant competency of the benzaldehyde in comparison to 1-heptanal present in the system. Also, this byproduct molecule being branched may have comparatively less possibility for its egress with respect to the linear product, jasminaldehyde. It is quite possible that unlike the individual catalyst systems, the composite system may possess some space constraint as a result of the compactness of the composite structure. The initial rates of formation of jasminaldehyde (equation 1) and 2-pentyl-

2-nonenal (equation 2) were calculated from the plots of Fig. 6, from their increasing concentration from early linear portion of the plots upto 4 h. The initial rate of consumption of 1-heptanal (equation 3) was calculated from its decreasing concentration.

$$v_1 = \frac{\mathrm{d[jasminaldehyde]}}{\mathrm{dt}} \qquad (1)$$

$$v_2 = \frac{\mathrm{d[2-pentyl-2-nonenal]}}{\mathrm{dt}} \qquad (2)$$

$$v = \frac{-d[\mathrm{1-heptanal}]}{dt} \qquad (3)$$

The rates v_1, v_2 and v were divided by the employed amount of the catalyst and expressed in terms of mmol of product per unit time per gram of the catalyst[28]. The determined rates (mmol/h/g_{cat}) v, v_1 and v_2 were found to be 14.65, 13.25 and 1.25 repectively. The summation of the rates v_1+v_2 (14.50) was found to be almost identical to v (14.65) indicating a fine rate balance between amount of the consumption of 1-heptanal and formation of the aldol products.

The variation of rate of aldol condensation with respect to catalyst amount ranging from 10 to 200 mg is shown in Fig.7. The rate of formation of jasminaldehyde linearly increased upto 100 mg of the catalyst and on further increasing the amount of the catalyst, the rates started to attain saturation. This represented the first order dependence with respect to catalyst towards its lower amounts. The rate of the formation of the self-condensed product increased upto 50 mg of the catalyst followed by decrease in the rate. In the individual CT[23] catalyzed synthesis of jasminaldehyde, the rate of formation of 2-pentyl-2-nonenal was observed to increase on increasing the catalyst amount. Thus the CMA composite catalyzed reaction here dictated its more influence in suppressing the rate of formation of 2-pentyl-2-nonenal as shown in Fig.7 in comparison of CT catalyzed reaction, thereby showing its potential advantage to contribute better towards the selectivity of jasminaldehyde. The effect of rate on the temperature between 80 and 180 °C is shown in Fig. 8. On increasing the temperature the rate of formation of jasminaldehyde increased upto 125 °C and further increase in temperature could not influence the rate. The rate of formation of 2-pentyl-2-nonenal was increased from 80 to 100 °C and after that a decreasing trend was observed on increasing the temperature. The temperature dependence performances with individual catalysts, CT[23] and HT[24] for the aldol condensation of 1-heptanal and benzaldehyde reported are observed to be different particularly for the selectivity of the self-condensation product, 2-pentyl-2-nonenal. With individual CT catalyzed reaction[23], the rate of formation of both the aldol products were almost linearly increased with temperature in the range of 80-180 °C with higher rate of jasminaldehyde than 2-pentyl-2-nonenal. Like the individual CT, similar trend of increase in selectivity with temperature was observed in individual HT catalyzed[24] reaction also, however the selectivity of jasminaldehyde was not much influenced. Thus CMA composite catalyzed reaction had demonstrated a potential over both the individual CT and HT catalyzed systems wherein the rate of 2-pentyl-2-nonenal was decreased with temperature (Fig. 8). It is of interest to mention here that the rates v_1 were 13.25, 10.3 and 10.1 for CMA, HT (calculated from ref. 24) and CT[23] catalyzed aldol reaction respectively whereas the rate V_2 were 1.25, 1.80 and 2.80 for these respective catalysts. This indicated that the composite based catalyst CMA afforded >20% enhancement in the rate of formation of jasminaldehyde in comparison of the individual components, HT and CT. Also, the rate of formation of 2-pentyl-2-nonenal was slower with CMA than that of HT/CT. The activation energy determined from the temperature dependence from the Arrhenius plot was found to be 16.3 kJ/mol. The reported activation energy for this reaction with individual CT[23] catalyst is 20.1 kJ/mol, which is greater than that for CMA catalyzed reaction. The lower activation energy with CMA is again in the line of the higher reaction rate with this composite catalyst. The effect of rate on benzaldehyde was studied with benzaldehyde amounts ranging from 7.9 and 79 mmol (Fig. 9). With increase in the amount of the benzaldehyde the rate of formation of jasminaldehyde increased giving the highest rate for 1-heptanal to benzaldehyde ratio of 1:5. On further increasing the amount of the benzaldehyde the rate of formations were remained almost uninfluenced.

3.3. Catalyst recycling

The condensation reaction was performed at two different times for 3 h and 14 h in order to observe the recyclability of the catalyst (Table 4). For the fresh catalyst, a 64% conversion with 74% was observed in 3 h of the reaction. The conversion increased to >99% along with 86% selectivity on increasing the time to 14 h. The fresh catalyst separated by filtration was washed thrice with methanol and dried. The catalyst was reused under identical conditions. A decrease in the conversion from 64% to 61% for 3 h recycling was observed in the first cycle (Entries 1 and 2). The conversion and selectivity both remained almost constant up to the fourth recycle. A similar trend was observed for the recycling of the catalyst for 14 h. The catalyst was effectively recycled up to six cycles without much loss in its activity and selectivity.

4. Conclusion

The chitosan-hydrotalcite nano-bio composite (CMA), synthesized, thoroughly characterized and investigated for the aldol condensation of 1-heptanal with benzaldehyde was found to be efficient catalyst for the selective synthesis of jasminaldehyde. The catalyst is operative under solvent-free conditions, giving the highest selectivity to jasminaldehyde 89%, with >99% conversion with 100 mg catalyst at 160 °C under optimized reaction conditions. The reaction investigated as a function of catalyst amount, temperature and the 1-heptanal to benzaldehyde ratio was found to influence the conversion, selectivity and rate of the reaction. On increasing the catalyst amount the rate of formation of jasminaldehyde was effectively increased while that of 2-pentyl-2-nonenal, increased first and then showed a decreasing trend. On increasing the temperature the rate of formation of jasminaldehyde increased while the rate of formation of 2-pentyl-2-nonenal tended to decrease. The initial rates of the formation of jasminaldehyde (v_1) were found to be more while the rate of formation of 2-pentyl-2-nonenal (v_2) were less with CMA as compared to the individual catalysts, CT and HT. The activation energy (16.3 kJ/mol) with CMA was found to be less than that of the reported (20.1 kJ/mol) with the individual CT catalyst.

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Scheme 1. Synthesis of jasminaldehyde.

Fig. 1. FTIR Spectra of HT, CT, and CMA.

Fig. 2. TGA profile of CMA.

Fig. 3. XRD pattern of HT, CT, and CMA.

Fig. 4. SEM images of CMA.

Fig. 5. TEM images of CMA.

Fig. 6. Kinetic profile: catalyst = 100 mg, heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol, temperature = 125 °C and 700 rpm.

Fig. 7. Dependence of rate on the amount of catalyst: heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol, temperature = 125 °C and 700 rpm.

Fig. 8. Dependence of rate on the temperature: catalyst =100 mg, heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol and 700 rpm

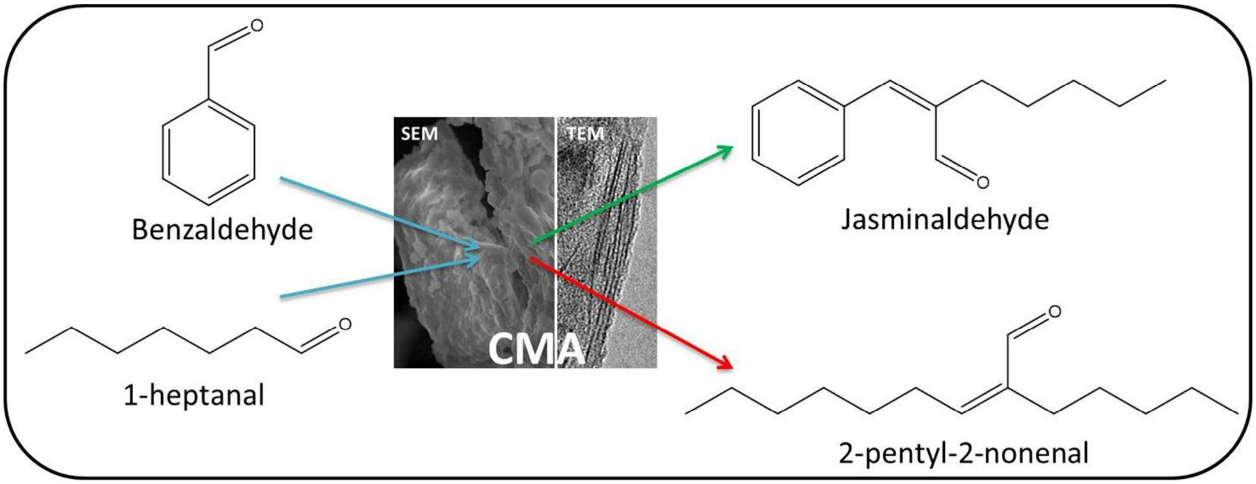
Fig. 9. Dependence of rate on the benzaldehyde: catalyst =100 mg, heptanal = 7.9 mmol, temperature = 125 °C and 700 rpm.

Table 1 Effect of catalyst amount on the selectivity of jasminaldehyde

Table 2 Effect of reaction temperature on the selectivity of jasminaldehyde

Table 3 Effect of 1-heptanal (H) to Benzaldehyde (B) ratio on the selectivity of jasminaldehyde

Table 4 Reusability of the catalyst



Scheme 1. Synthesis of jasminaldehyde

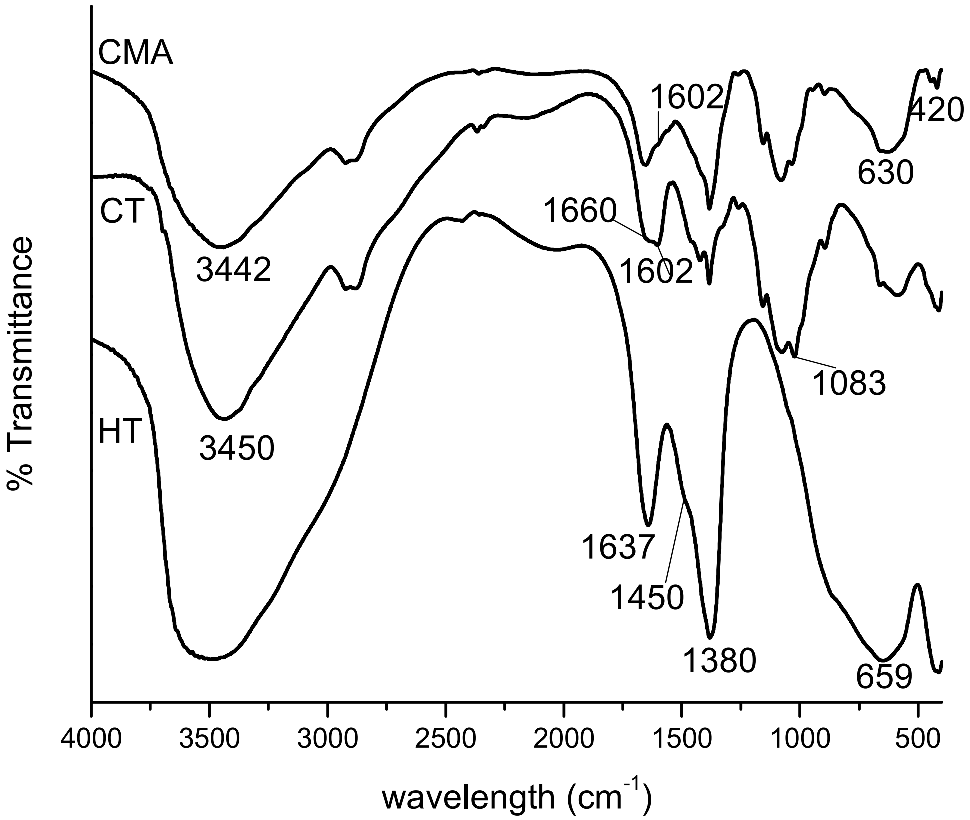


Fig. 1. FTIR Spectra of HT, CT and CMA.

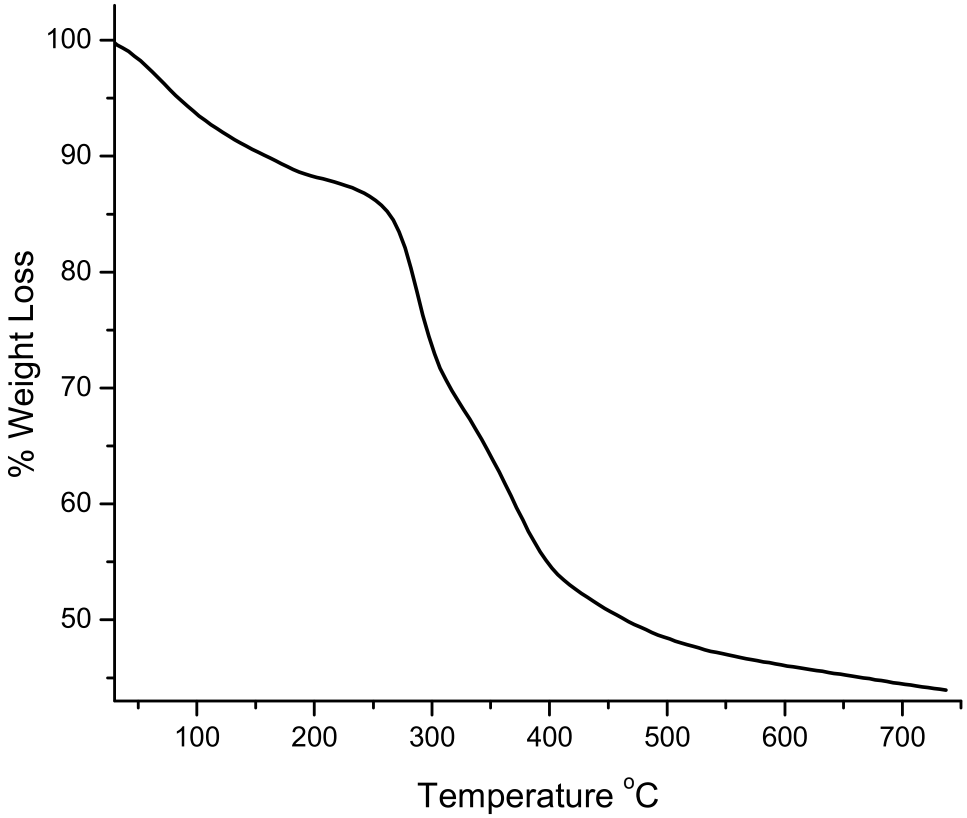


Fig. 2. TGA profile of CMA.

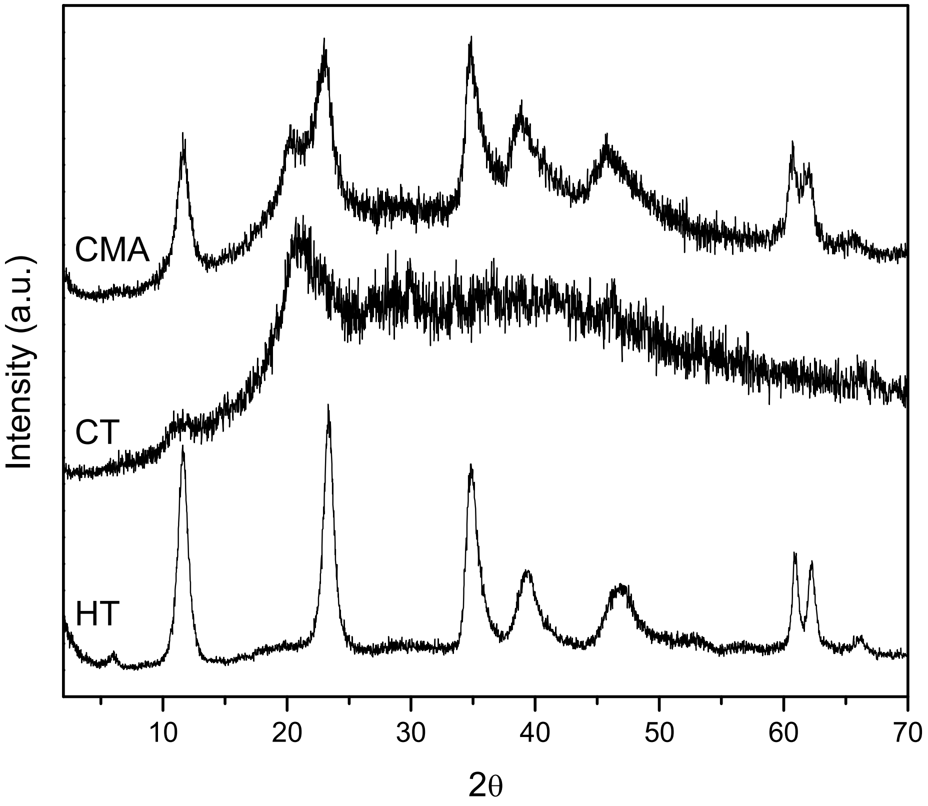


Fig. 3. XRD pattern of HT, CT and CMA.

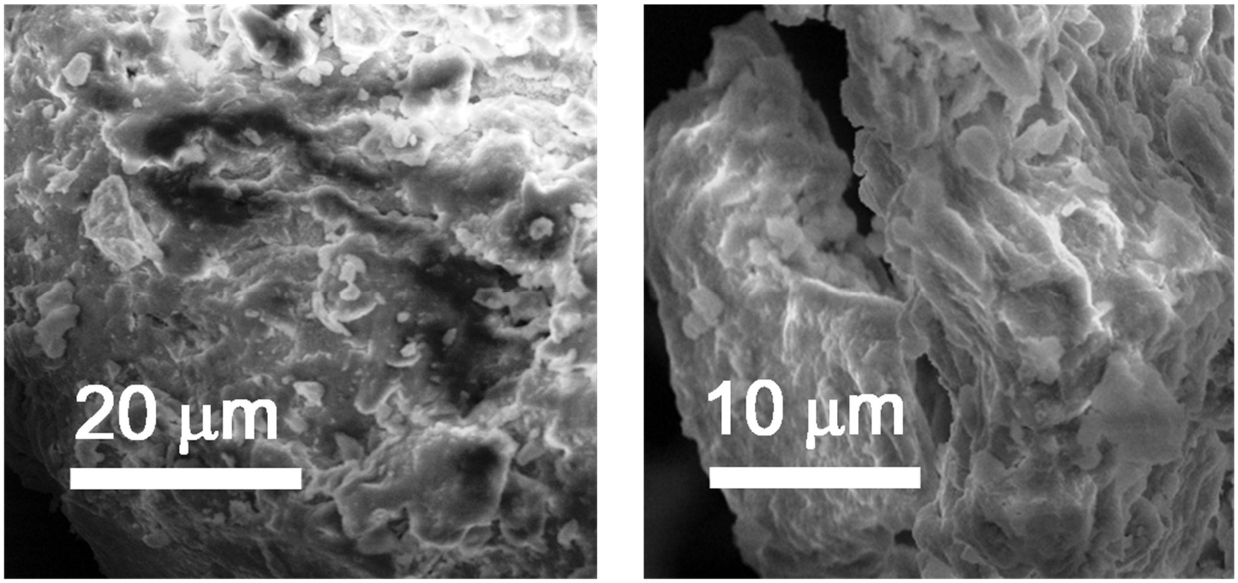


Fig. 4. SEM images of CMA.

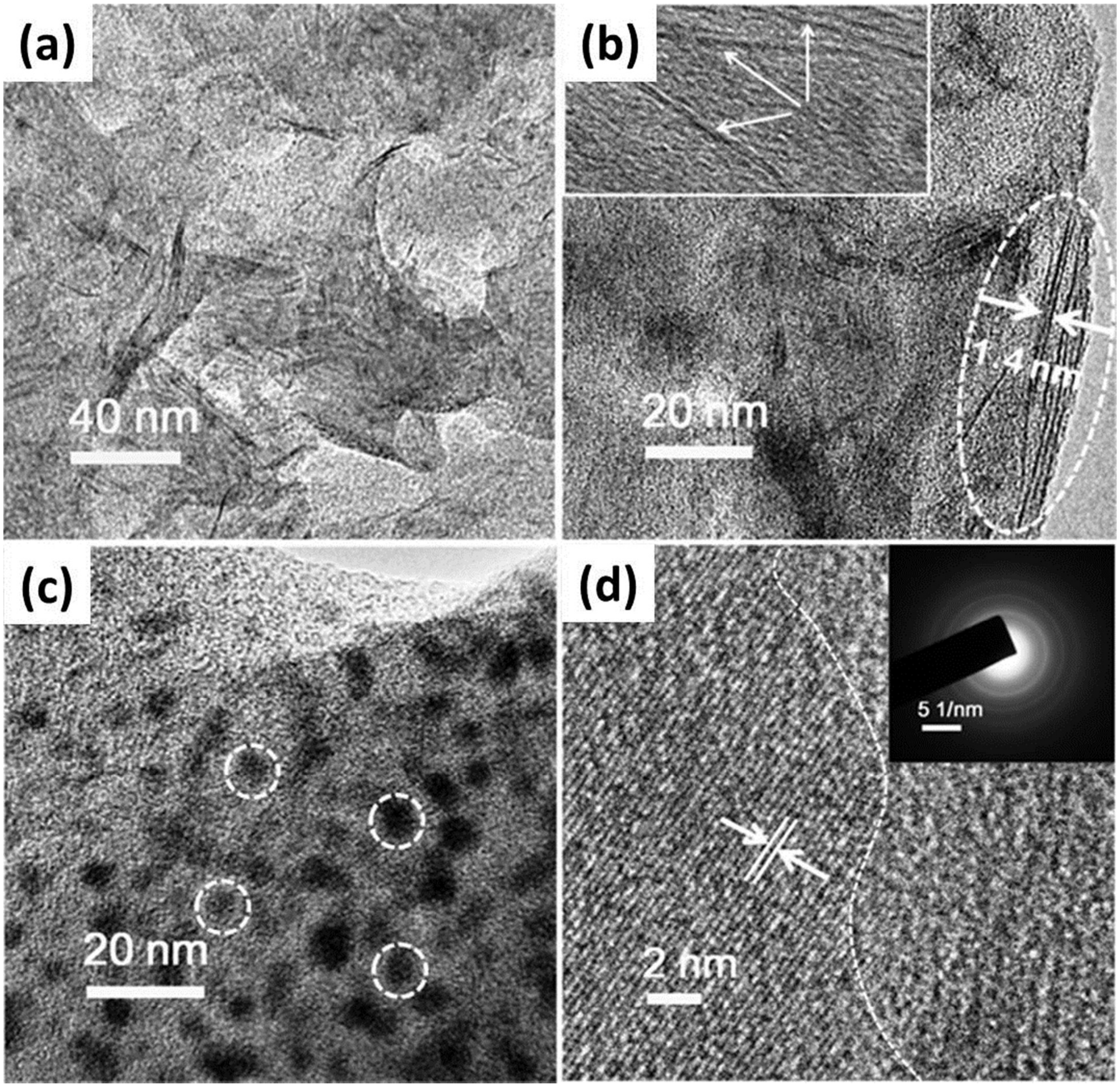


Fig. 5. TEM images of CMA.

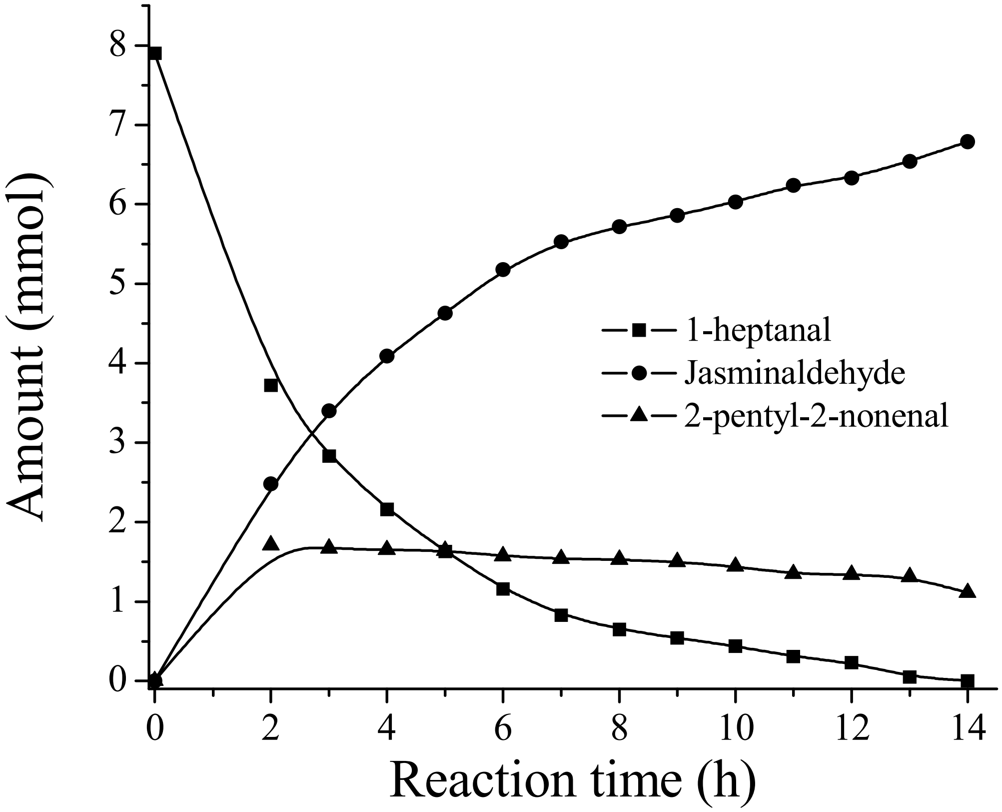


Fig. 6. Kinetic profile: catalyst = 100 mg, heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol, temperature = 125 °C and 700 rpm.

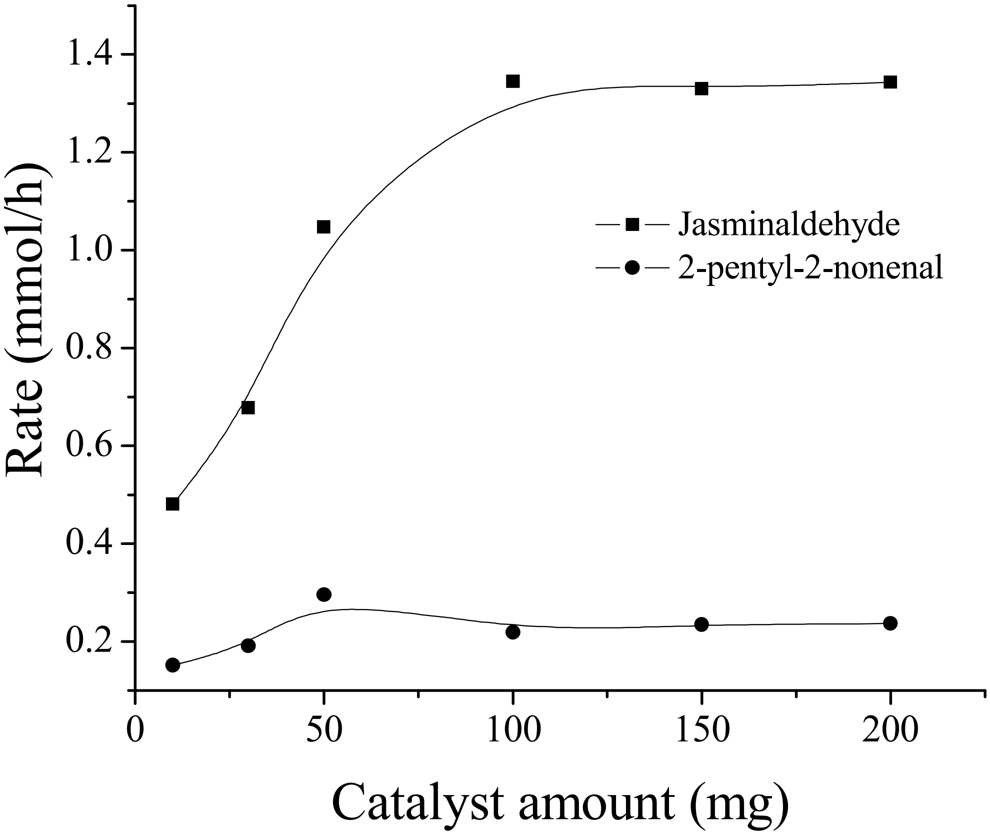


Fig. 7. Dependence of rate on the amount of catalyst: heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol, temperature = 125 °C and 700 rpm.

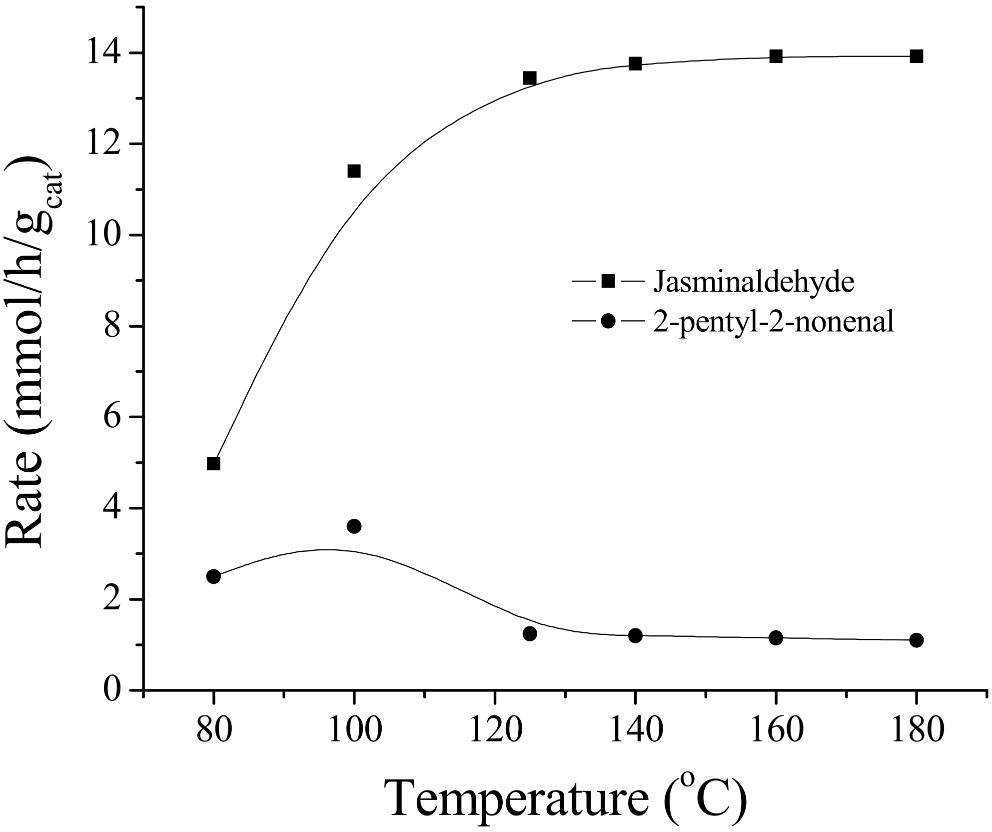


Fig. 8. Dependence of rate on the temperature: catalyst =100 mg, heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol and 700 rpm

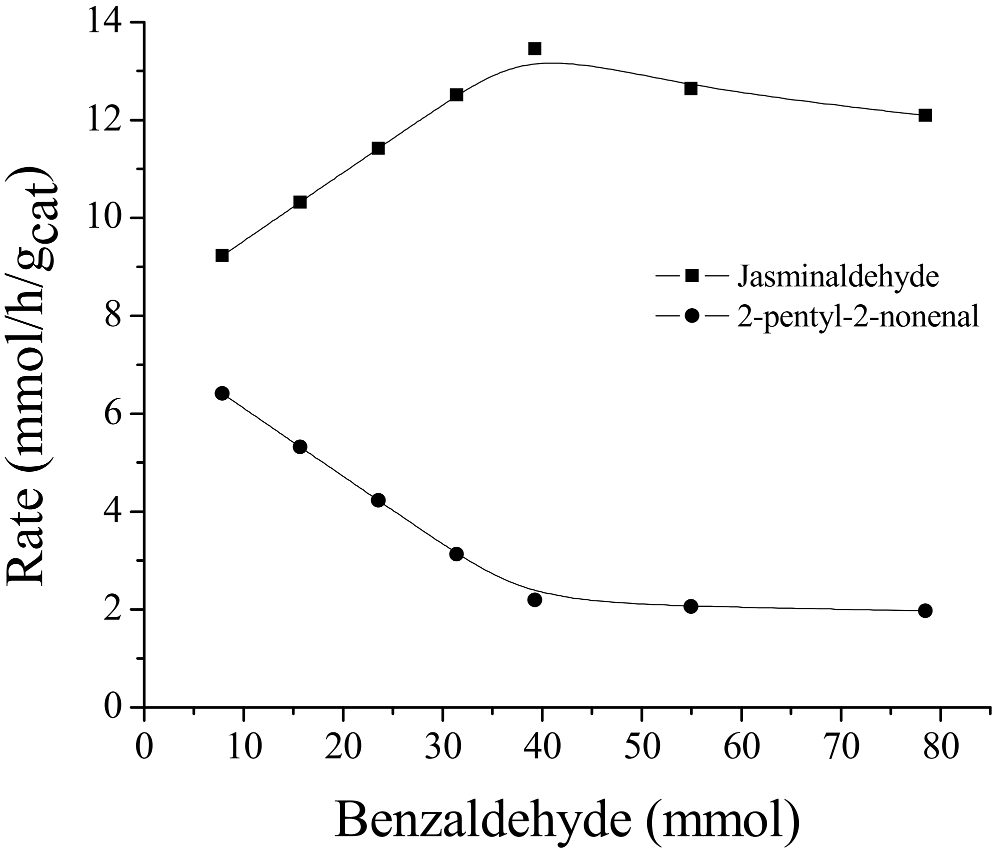


Fig. 9. Dependence of rate on the benzaldehyde: catalyst =100 mg, heptanal = 7.9 mmol, temperature = 125 °C and 700 rpm.

Table 1 Effect of catalyst amount on the selectivity of jasminaldehyde

Entry	Catalyst amount (mg)	Conversion (%)			Selectivity (%)					
					Jasminaldehyde			2-pentyl-non-2-enal		
		3 h	7 h	14 h	3 h	7 h	14 h	3 h	7 h	14 h
1	10	20	27	40	52	68	76	48	32	24
2	30	22	34	55	61	72	78	39	28	22
3	50	47	60	85	68	71	78	32	29	22
4	100	64	85	>99	74	78	86	26	23	14
5	150	80	92	>99	75	78	85	25	22	15
6	200	84	95	100	78	79	85	22	21	15
7	300	85	97	100	65	71	79	35	29	21

Reaction conditions: heptanal=7.9 mmol, benzaldehyde=39.6 mmol, temperature=125 ^{o}C

Table 2 Effect of reaction temperature on the selectivity of jasminaldehyde

Entry	Temp. (°C)	Conversion (%)			Selectivity (%)					
					Jasminaldehyde			2-pentyl-non-2-enal		
		3 h	7 h	14 h	3 h	7 h	14 h	3 h	7 h	14 h
1	80	53	77	90	0	29	35	100	71	65
2	100	56	80	95	54	67	76	46	33	24
3	125	64	85	>99	74	78	86	26	23	14
4	140	68	90	>99	76	79	88	24	21	12
5	160	80	97	>99	77	80	89	23	20	11
6	180	90	98	>99	83	85	85	17	15	15

Reaction conditions: heptanal=7.9 mmol, benzaldehyde=39.6 mmol, catalyst=100 mg

Table 3 Effect of 1-heptanal (H) to Benzaldehyde (B) ratio on the selectivity of jasminaldehyde

Entry	H:B	Conversion (%)			Selectivity (%)					
					Jasminaldehyde			2-pentyl-non-2-enal		
		3 h	7 h	14 h	3 h	7 h	14 h	3 h	7 h	14 h
1	1:1	78	95	99	43	54	59	57	46	41
2	1:2	84	97	99	55	61	66	45	39	34
3	1:3	80	97	99	57	72	73	43	28	27
4	1:4	75	88	99	71	74	80	29	26	20
5	1:5	64	85	>99	74	78	86	26	23	14
6	1:7	46	76	93	69	72	86	31	28	14
7	1:10	34	59	89	68	71	86	32	29	14

Reaction conditions: heptanal=7.9 mmol, catalyst= 100 mg, temperature=125 ^{o}C

Table 4 Reusability of the catalyst

Entry	Catalyst recycle	Conversion (%)		Selectivity (%)			
				Jasminaldehyde		2-pentyl-non-2-enal	
		3 h	14 h	3 h	14 h	3 h	14 h
1	Fresh	64	>99	74	86	26	14
2	First recycle	61	99	72	85	28	15
3	Second recycle	59	95	70	85	30	15
4	Third recycle	58	92	67	83	33	17
5	Fourth recycle	58	89	67	80	33	20
6	Fifth recycle	56	85	65	78	35	22

Reaction conditions: heptanal=7.9 mmol, benzaldehyde=39.6 mmol, temperature=125 ^{o}C