

Eco-friendly synthesis of jasminaldehyde by condensation of 1-heptanal with benzaldehyde using hydrotalcite as a solid base catalyst

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Abstract

The catalytic activity of hydrotalcite ($[M(II)_{1-x}M(III)_x(OH)_2]^{n+}(CO_3^{2-})_{x/n} \cdot mH_2O$; where $M(II) = Mg, Ni, Zn$ and $M(III) = Al$) was evaluated for the synthesis of jasminaldehyde by solvent free condensation of 1-heptanal with benzaldehyde. The effect of activation of as-synthesized Mg-Al hydrotalcite samples of varied Mg/Al molar ratio on its catalytic activity was studied and correlated with their basicity as determined from the model test reaction. The effect of reaction parameters such as, amount of catalyst, benzaldehyde to 1-heptanal molar ratio and reaction temperature on conversion of 1-heptanal and selectivity of jasminaldehyde was studied in detail. Maximum selectivity of jasminaldehyde (86%) with 98% conversion of 1-heptanal was observed using as-synthesized Mg-Al hydrotalcite of Mg/Al molar ratio of 3.5 as a catalyst. The kinetics of the reaction was measured and reaction rate and order of reaction were determined under optimum reaction conditions. The catalyst was re-used upto three cycles without significant loss in its activity. The base catalyzed reaction mechanism for condensation of 1-heptanal with benzaldehyde is proposed.

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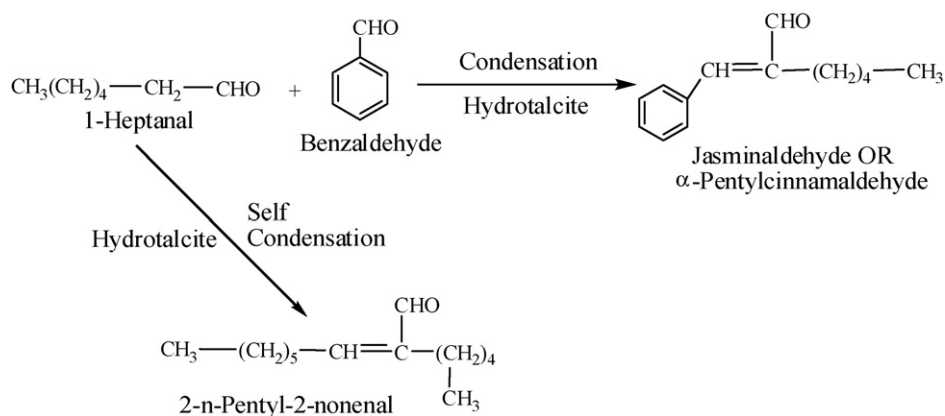
Keywords: Jasminaldehyde; Hydrotalcite; 1-Heptanal; Benzaldehyde; Solid base catalyst

1. Introduction

Jasminaldehyde or α -pentylcinnamaldehyde is a perfumery chemical of commercial interest and is synthesized by the condensation of 1-heptanal with benzaldehyde in the presence of liquid alkali NaOH or KOH taken in more than stoichiometric amounts as a homogeneous catalyst [1]. The main drawbacks of homogeneous process for synthesis of jasminaldehyde include lack of reusability of the catalyst, hazardous nature of liquid base like KOH or NaOH and post reaction work-up of spent liquid bases. Therefore, it is desirable to develop solid base catalysts which would overcome these disadvantages and provide a commercial process having easy handling of the catalyst, easy separation of products, decreased corrosion of the reactor, and possible regeneration and re-use of the catalyst. The applicability of various solid acid and base catalysts has been reported for the

synthesis of jasminaldehyde in the literature [1–8]. Corma and co-workers reported the applicability of large pore HY and beta zeolites, mesoporous MCM-41 aluminosilicates (Al-MCM-41) and amorphous aluminophosphate (ALPO) as solid acid catalysts for the synthesis of jasminaldehyde [2–4]. These processes involve two steps. The heptanal di-methyl acetal is formed in the first step by the reaction of 1-heptanal with excess methanol. In the second step, the methanol is distilled in vacuum and benzaldehyde is added to the heptanal dimethyl acetal and system is heated at the desired temperature for synthesis of jasminaldehyde. With ALPO as a catalyst, 96% conversion of 1-heptanal with 86% selectivity of jasminaldehyde was achieved by varying the benzaldehyde to 1-heptanal molar ratio from 1 to 10 [2–4]. In another study, Al-MCM-41 supported magnesium oxide was used as a solid base catalyst and 31% conversion of 1-heptanal with 40% selectivity of jasminaldehyde was found in 2 h reaction time at 150 °C and benzaldehyde to heptanal molar ratio 10 [5]. Jaenicke et al. reported 90% conversion of 1-heptanal and 50% selectivity of jasminaldehyde for MCM-41 based hybrid materials as catalysts in a batch reactor at 160 °C with benzaldehyde

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Scheme 1. Synthesis of jasminaldehyde.

to 1-heptanal molar ratio 1.5 [6]. The selectivity of jasminaldehyde is very important in the condensation reaction of 1-heptanal with benzaldehyde. 2-*n*-Pentyl-2-nonenal is a major by-product of this reaction, which is also a base catalyzed self-condensation product of 1-heptanal. The selectivity of jasminaldehyde can be enhanced by tuning the acidity/basicity of the catalyst. Therefore, the research efforts are directed to develop a catalytic process, which can produce jasminaldehyde with high selectivity from condensation of 1-heptanal with benzaldehyde using eco-friendly re-usable solid base catalyst (Scheme 1).

Hydrotalcite (layered double hydroxides) has recently received much attention as solid base catalysts [9]. The basicity of the hydrotalcite could be modified either by changing the divalent to trivalent cations molar ratio [M(II)/M(III)] or intercalation of a suitable anion in the interlayer space. The as-synthesized hydrotalcite is converted into aluminium–magnesium mixed oxide on thermal decomposition at about 450 °C, which is reported to be a potential solid base catalyst for a variety of organic transformations such as condensation, isomerization, anion exchangers and epoxidation reactions [10–19]. The detailed study on applicability of as-synthesized hydrotalcite of varied divalent metal cations [M(II)] and different divalent to trivalent molar ratio [M(II)/Al; M(II) = Mg, Ni, Zn] as solid base catalysts for the synthesis of jasminaldehyde is reported in the present study.

The aim of present study is to evaluate catalytic activity of as-synthesized and activated hydrotalcite of varied divalent metal cations [M(II)] and different divalent to trivalent molar ratio [M(II)/Al; M(II) = Mg, Ni, Zn] for synthesis of jasminaldehyde by solvent free condensation of 1-heptanal with benzaldehyde. The hydrotalcite of varied divalent metal cations and M(II)/Al molar ratio were synthesized, characterized and their catalytic activity was evaluated for condensation of 1-heptanal with benzaldehyde.

2. Experimental

2.1. Materials

Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 98.9%), aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; 99.1%), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot$

$6\text{H}_2\text{O}$; 98%), zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 98%), sodium carbonate (Na_2CO_3 ; 99.9%) and sodium hydroxide (NaOH ; 99.9%) were purchased from s.d. Fine Chemicals, India for the synthesis of hydrotalcite samples. The double distilled milli-pore deionized water was used during the synthesis. β -Isophorone, 1-heptanal and benzaldehyde were purchased from Sigma–Aldrich and used as received.

2.2. Catalyst synthesis

The Mg–Al hydrotalcite samples with Mg/Al molar ratio in the range of 2.0–3.5 were synthesized by co-precipitation method at constant pH [9]. For example, during the synthesis of hydrotalcite of Mg/Al molar ratio 2.5, an aqueous solution (A) of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.22 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.088 mol) was prepared in 200 mL double distilled deionized water. The solution A was added dropwise into a second solution (B) containing NaOH (0.72 mol) and Na_2CO_3 (0.21 mol) in 200 mL double distilled deionized water, in around 2 h under vigorous stirring at room temperature. The content was then transferred into the teflon coated stainless steel autoclave and aged at 70 °C for 14 h under autogenous pressure. After 14 h, the precipitate formed was filtered and washed thoroughly with hot distilled water until pH of the filtrate was 7. The washed precipitate was dried in an oven at 80 °C for 14 h. The hydrotalcite samples with Mg/Al molar ratio varying from 2.0 to 3.5 were synthesized as per above procedure using appropriate amounts of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Similar procedure was followed for the synthesis of Ni–Al and Zn–Al hydrotalcite samples. The activation of as-synthesized Mg–Al hydrotalcite samples was carried out at 450 °C in muffle furnace for 4 h in the presence of air.

2.3. Characterization of the catalysts

Powder X-ray diffraction (P-XRD) patterns of hydrotalcite samples were recorded with powder diffractometer (Philips, X'Pert MPD system) using PW3123/00 curved Cu-filtered $\text{Cu K}\alpha$ ($\lambda = 1.54056 \text{ \AA}$) over a 2θ range of 2–70°. Fourier transform infrared (FT-IR) spectra of the hydrotalcite samples were

recorded with PerkinElmer GX-FTIR system using KBr pellet in the wavelength range of 400–4000 cm^{-1} .

2.4. Synthesis of jasminaldehyde

The desired amounts of benzaldehyde, 1-heptanal (benzaldehyde to 1-heptanal molar ratio = 5) and catalyst were taken with 0.01 g of tetradecane as an internal standard in an oven dried double necked round bottom flask for the condensation of 1-heptanal with benzaldehyde. One neck of flask was fitted with 0.7 m long refluxing condenser with spiral tube inside the condenser and silicon rubber septum was inserted in second neck of flask. The top of the refluxing condenser was closed by a standard size cork. Water at 15 °C was circulated in spiral tube of refluxing condenser continuously during the course of reaction from water chiller at a flow rate of 6 L/min. Flask fitted with refluxing condenser was kept in an oil bath equipped with temperature and agitation speed controlling unit. Reaction was carried out at 125 °C for 8 h. After completion of the reaction, reaction mixture was cooled down to room temperature and was subsequently filtered. The weight of initial reaction mixture and product mixture after reaction was compared to ensure the absence of vapor loss of reaction mixture. This reaction was carried out in the nitrogen atmosphere to avoid oxidation of 1-heptanal and benzaldehyde. Progress of reaction was monitored in terms of consumption of 1-heptanal. Analysis of product mixture was carried out by gas chromatography (GC) (Shimadzu 17A, Japan) and GC-MS (mass spectrometer, Shimadzu-QP2010, Japan). GC has a 5% diphenyl and 95% dimethyl siloxane universal capillary column (60 m length and 0.25 mm diameter) and a flame ionization detector (FID). The retention time of different compounds was determined by injecting pure compounds into GC column under identical GC conditions. The conversion and selectivity data observed in the present study are reproducible within $\pm 5\%$ error. The conversion and selectivity were calculated by the following formula

$$\% \text{Conversion} = \frac{\text{Moles of 1-heptanal reacted}}{\text{Moles of 1-heptanal fed}} \times 100$$

$$\% \text{Selectivity of jasminaldehyde} = \frac{\text{Moles of jasminaldehyde}}{\text{Moles of (jasminaldehyde + 2-n-pentyl-nonanal)}} \times 100$$

2.5. Isomerization of β -isophorone

The isomerization of β -isophorone to α -isophorone was performed as a model test reaction for basicity measurement of as-synthesized and activated hydrotalcite samples [12,14]. 10 mL of isophorone was added into 30 mL heptane as a solvent in a 50 mL oven dried double necked round bottom flask. The nitrogen was purged to remove CO_2 present in the reaction atmosphere and the agitation was started at 35 °C temperature and 1000 rpm. After 2 min, 0.1 g catalyst was added to this mixture from side neck of the round bottom flask and reaction was continued by stirring at 1000 rpm. The analysis of product mixture was

carried out by GC-MS (mass spectrometer, Shimadzu-QP2010, Japan).

3. Results and discussions

3.1. Characterization of the catalysts

P-XRD patterns of as-synthesized Mg-Al, Ni-Al and activated Mg-Al hydrotalcite samples are shown in Fig. 1. P-XRD patterns of as-synthesized hydrotalcite samples showed sharp, intense and symmetric peaks at lower diffraction angles ($2\theta = 10\text{--}25^\circ$) and broad asymmetric reflections at higher diffraction angles ($2\theta = 30\text{--}50^\circ$), which are characteristic of highly crystalline layered structure [9]. Presence of CO_3^{2-} anions in interlayer space of hydrotalcite was confirmed by the characteristic basal spacing $d_{003} = 7.65 \text{ \AA}$. P-XRD patterns of Ni-Al and Zn-Al hydrotalcite were observed to be similar to that of the Mg-Al hydrotalcite. On calcination of hydrotalcite at 450 °C, P-XRD patterns of Mg-Al (3.5)A revealed broad peaks that can be assigned to Mg-Al mixed oxide [Mg(Al)O] phase, with diffraction lines at values similar to that of MgO. The intensity of (003) plane peak, which is related to the crystallinity of Mg-Al hydrotalcite samples was observed to decrease with increase in Mg/Al molar ratio. The decrease in the crystallinity on increasing Mg/Al molar ratio of hydrotalcite samples is due to increase in amount of divalent cation (Mg^{2+}) which have ionic radii 0.65 \AA that favors the formation of brucite by replacing the smaller ionic radii trivalent cations (Al^{3+}) [20]. *d*-Spacing of (003) plane of hydrotalcite was found to increase on increasing Mg/Al molar ratio of hydrotalcite samples (Table 1). Similar to the crystallinity of Mg-Al hydrotalcite, the crystallinity of the Ni-Al and Zn-Al hydrotalcite samples were also observed to decrease on increasing Ni/Al or Zn/Al molar ratio.

3.2. Catalytic activity

Catalytic activity data for the synthesis of jasminaldehyde carried out by condensation of 1-heptanal with benzaldehyde

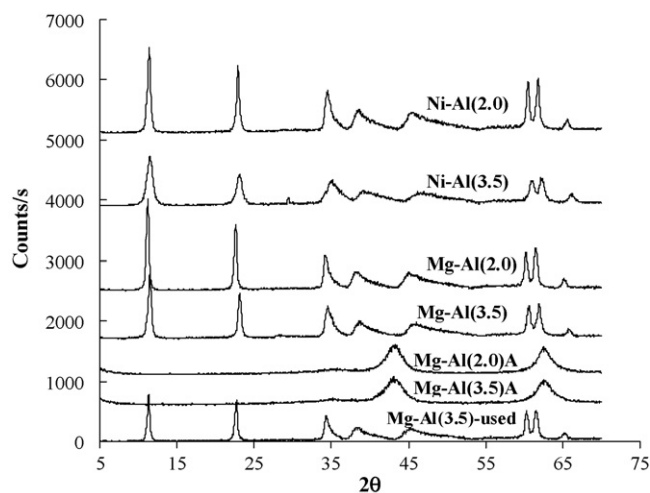


Fig. 1. P-XRD patterns of Ni-Al, Mg-Al hydrotalcite samples and Mg-Al(3.5) used catalyst.

Table 1
Chemical composition and crystallinity of catalysts used

Catalyst samples	Chemical composition	<i>d</i> -Spacing (Å) (0 0 3) plane
Mg-Al(2.0)	[Mg _{0.67} Al _{0.33} (OH) ₂](CO ₃) _{0.165} · <i>m</i> H ₂ O	7.58
Mg-Al(2.5)	[Mg _{0.72} Al _{0.28} (OH) ₂](CO ₃) _{0.14} · <i>m</i> H ₂ O	7.63
Mg-Al(3.0)	[Mg _{0.75} Al _{0.25} (OH) ₂](CO ₃) _{0.125} · <i>m</i> H ₂ O	7.65
Mg-Al(3.5)	[Mg _{0.78} Al _{0.22} (OH) ₂](CO ₃) _{0.11} · <i>m</i> H ₂ O	7.74
Ni-Al(2.0)	[Ni _{0.66} Al _{0.34} (OH) ₂](CO ₃) _{0.17} · <i>m</i> H ₂ O	7.63
Ni-Al(2.5)	[Ni _{0.72} Al _{0.28} (OH) ₂](CO ₃) _{0.14} · <i>m</i> H ₂ O	7.65
Ni-Al(3.0)	[Ni _{0.75} Al _{0.25} (OH) ₂](CO ₃) _{0.125} · <i>m</i> H ₂ O	7.67
Ni-Al(3.5)	[Ni _{0.77} Al _{0.23} (OH) ₂](CO ₃) _{0.11} · <i>m</i> H ₂ O	7.71
Zn-Al(2.0)	[Mg _{0.67} Al _{0.33} (OH) ₂](CO ₃) _{0.165} · <i>m</i> H ₂ O	7.62
Zn-Al(3.5)	[Zn _{0.78} Al _{0.22} (OH) ₂](CO ₃) _{0.11} · <i>m</i> H ₂ O	7.69

using hydrotalcite samples of varied M(II)/Al molar ratio as catalysts are given in Table 2. 1-Heptanal conversion in the range of 96–99% was observed for the studied catalysts. This shows that no significant change in the conversion of 1-heptanal was observed on varying Mg/Al molar ratio of as-synthesized and activated Mg-Al hydrotalcite samples. Selectivity of jasminaldehyde was observed to increase from 83% at Mg/Al molar ratio of hydrotalcite 2.0 to 86% at Mg/Al ratio 3.5. The GC–MS fragmentation data showed standard fragmentation pattern corresponding to 1-heptanal (*m/z*: 114, 70, 55, 44, 41, 29), benzaldehyde (*m/z*: 106, 77, 51), jasminaldehyde (*m/z*: 202, 145, 129, 117, 91) and 2-*n*-pentyl-2-nonenal (*m/z*: 210, 153, 125, 97, 81, 55, 41, 29). On activation of Mg-Al hydrotalcite samples, the selectivity of jasminaldehyde decreased significantly from 86 to 75% (Mg/Al = 3.5). The conversion of 1-heptanal was obtained as 98% with 78% selectivity of jasminaldehyde using MgO as a catalyst. Selectivity of jasminaldehyde decreased to 62% using activated MgO at 450 °C as a catalyst. In view of higher selectivity of jasminaldehyde observed in case of as-synthesized Mg-Al hydrotalcite used as a catalyst, the experiments were conducted using Ni-Al and Zn-Al hydrotalcite samples as catalysts without

activation to observe the effect of divalent cations on their catalytic activity. As-synthesized Ni-Al hydrotalcite showed 97% conversion of 1-heptanal, which is similar to the conversion observed in case of as-synthesized Mg-Al hydrotalcite. The selectivity of jasminaldehyde was observed to increase from 73 to 78% by varying the Ni-Al molar ratio of hydrotalcite from 2.0 to 3.5. The selectivity of jasminaldehyde increased from 78 to 84% by introducing Mg in Ni-Al (3.5) hydrotalcite sample. The selectivity of jasminaldehyde was observed to decrease to 72% on activation of Ni-Mg-Al (3.5) catalyst. 1-Heptanal conversion of 96% with 70% selectivity of jasminaldehyde was observed using Zn-Al hydrotalcite of Zn/Al molar ratio 2.0 which showed small increase in conversion (97%) and selectivity of jasminaldehyde (76%) on increasing the Zn/Al molar ratio 3.5.

The catalytic activity of hydrotalcite depends upon its basicity which in case of as-synthesized hydrotalcite is mainly due to their hydroxyl groups which act as Bronsted basic sites for condensation of 1-heptanal with benzaldehyde. Higher selectivity of jasminaldehyde observed in case of as-synthesized hydrotalcite as a catalyst confirmed that the material having

Table 2
Condensation of 1-heptanal with benzaldehyde using solid base catalysts

Run	Catalyst		% Conversion ^a	% Selectivity	
				Jasminaldehyde	2- <i>n</i> -Pentyl-2-nonenal
1	Mg-Al(3.5)	Without activation	98	86	14
2	Mg-Al(3.0)	Without activation	98	84	16
3	Mg-Al(2.5)	Without activation	98	82	18
4	Mg-Al(2.0)	Without activation	97	83	17
5	Mg-Al(3.5)A	Activated at 450 °C/4 h	98	75	25
6	Mg-Al(3.0)A	Activated at 450 °C/4 h	99	75	25
7	Mg-Al(2.5)A	Activated at 450 °C/4 h	99	74	26
8	Mg-Al(2.0)A	Activated at 450 °C/4 h	99	72	28
9	MgO	Without activation	98	78	22
10	MgO	Activated at 450 °C/4 h	99	62	38
11	Ni-Al(3.5)	Without activation	97	78	22
12	Ni-Al(3.0)	Without activation	97	77	23
13	Ni-Al(2.5)	Without activation	97	74	26
14	Ni-Al(2.0)	Without activation	96	73	27
15	Ni-Mg-Al	Without activation	96	84	16
16	Ni-Mg-Al	Activated at 450 °C/4 h	98	72	28
17	Zn-Al(3.5)	Without activation	97	76	24
18	Zn-Al(2.0)	Without activation	96	70	30

^a Reaction conditions: benzaldehyde = 39.6 mmol, heptanal = 7.9 mmol, catalyst = 75 mg, temperature = 125 °C, time = 8 h.

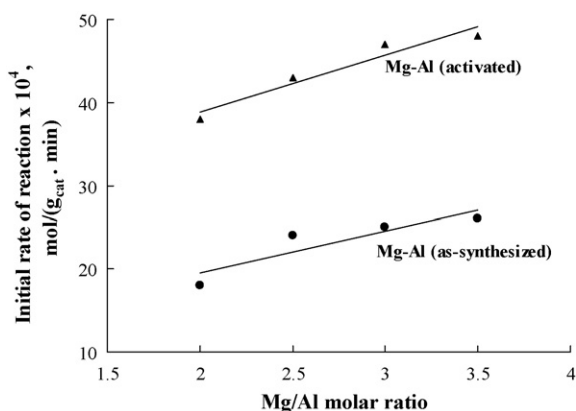


Fig. 2. Initial rate of reaction for the isomerization of β -isophorone to α -isophorone as a model reaction to test the basicity of as-synthesized and activated Mg-Al hydrotalcite samples.

weakly basic sites (hydroxyl groups) is appropriate for this reaction. Decrease in the selectivity of jasminaldehyde on activation of as-synthesized hydrotalcite shows that the catalyst having strong basic sites are not suitable for selective synthesis of jasminaldehyde. This was also confirmed by the data obtained on performing the reaction using MgO as a catalyst, which is known to be a strong base catalyst. The basicity of as-synthesized and activated hydrotalcite samples of Mg/Al ratio 2.0, 2.5, 3.0 and 3.5 were evaluated by isomerization of β -isophorone to α -isophorone as a model test reaction reported for basicity measurement to support our observations in the present study [12,14]. The initial rate of reaction was observed to increase significantly on activation of as-synthesized hydrotalcite samples of different Mg/Al molar ratio (Fig. 2). The initial rate of reaction for as-synthesized hydrotalcite of Mg/Al molar ratio 2.0 was calculated as 18×10^{-4} mol/(g_{cat} s) which increased to 38×10^{-4} mol/(g_{cat} s) for activated hydrotalcite of Mg/Al molar ratio 2.0. For as-synthesized hydrotalcite of Mg/Al molar ratio 3.5, the initial rate of reaction was calculated as 26×10^{-4} mol/(g_{cat} s) and increased to 48×10^{-4} mol/(g_{cat} s) with activated hydrotalcite sample. The isomerization of β -isophorone to α -isophorone is zero order reaction; hence, the value of initial rate of reaction is equal to the rate constant. The value of rate constant for isophorone isomerization is reported to be directly proportional to the number of basic sites [12,14]. The higher values of initial rate of reaction obtained on activation of hydrotalcite indicate that the number of basic sites increased sig-

nificantly on the activation of catalyst. From these results, it is clear that the activated hydrotalcite samples have higher number of basic sites as compared to as-synthesized hydrotalcite samples. However, the initial rate of reaction is also observed to increase on increasing the Mg/Al molar ratio of as-synthesized and activated hydrotalcite. But the extent of increase in initial rate of reaction at varied Mg/Al molar ratio of as-synthesized hydrotalcite is significantly less compared to the difference in the initial rate of reaction of activated hydrotalcite.

The trend observed in present study shows that the strong solid base catalysts such as MgO, activated hydrotalcite gave higher conversion of 1-heptanal but poor selectivity of jasminaldehyde. Similar observations are also reported in the literature [7,8]. The reason for lower selectivity of jasminaldehyde is the competitive side reaction, i.e., self-condensation of 1-heptanal to 2-*n*-pentyl-2-nonenal catalyzed by strong base catalyst such as activated hydrotalcite. Activation of as-synthesized hydrotalcite at 450 °C gives a well-dispersed mixture of magnesium and aluminum mixed oxides having strong Lewis (isolated O²⁻ anions) and weaker Bronsted (hydroxide groups) basic sites [21]. The numbers of stronger Lewis O²⁻ sites are higher as compared to weaker Bronsted OH⁻ on the surface of activated hydrotalcite. Therefore, activated hydrotalcite is a strong basic catalyst compared to as-synthesized hydrotalcite, both in terms of basic strength and number of basic sites [22]. Keeping in view of the higher conversion and selectivity of jasminaldehyde values observed for Mg as a divalent cation of as-synthesized hydrotalcite, further experiments were carried out using Mg-Al as-synthesized hydrotalcite of Mg/Al molar ratio 3.5 [Mg-Al(3.5)] as a catalyst.

3.3. Effect of benzaldehyde to 1-heptanal molar ratio

The effect of benzaldehyde to 1-heptanal molar ratio was studied by varying their molar ratio from 1 to 10 at constant amount of the catalyst [Mg-Al(3.5)] (Table 3). At benzaldehyde to 1-heptanal molar ratio 1, 94% conversion with 56% selectivity of jasminaldehyde was observed. Conversion of 1-heptanal was found to increase upto 96% with 74% selectivity of jasminaldehyde on increasing this ratio to 3. The jasminaldehyde selectivity was observed to increase upto 86 with 98% conversion of 1-heptanal at benzaldehyde to 1-heptanal molar ratio of 5. No significant effect on conversion and selectivity data were observed on further increase in the ratio, which indi-

Table 3
Effect of benzaldehyde to 1-heptanal molar ratio on selectivity of jasminaldehyde

Run	Benzaldehyde/1-heptanal molar ratio	% Conversion ^a	% Selectivity	
			Jasminaldehyde	2- <i>n</i> -Pentyl-2-nonenal
1	1	94	56	44
2	2	96	67	33
3	3	96	74	26
4	5	98	86	14
5	7	98	85	15
6	10	98	86	14

^a Reaction conditions: catalyst [Mg-Al (3.5)] = 75 mg, temperature = 125 °C, reaction time = 8 h.

Table 4
Effect of reaction temperature on selectivity of jasminaldehyde

Run	Temperature (°C)	% Conversion ^a	% Selectivity	
			Jasminaldehyde	2- <i>n</i> -Pentyl-2-nonenal
1	60	38	88	12
2	80	57	87	13
3	100	80	86	14
4	125	98	86	14
5	140	100	84	16
6	170	100	81	19

^a Reaction conditions: benzaldehyde = 39.6 mmol, heptanal = 7.9 mmol, catalyst [Mg-Al(3.5)] = 75 mg, reaction time = 8 h.

cates that the optimum benzaldehyde to 1-heptanal molar ratio is 5 under the studied experimental conditions. Probability of faster adsorption of carbanions of 1-heptanal is higher as compared to that of benzaldehyde on active sites of catalysts at lower benzaldehyde to 1-heptanal molar ratio. This could result into the higher selectivity of 2-*n*-pentyl-2-nonenal, which is a base catalyzed self-condensation product of 1-heptanal. However, at higher benzaldehyde to 1-heptanal molar ratio, the concentration of benzaldehyde will be higher which leads to increased interaction probability of benzaldehyde rather than 1-heptanal molecules with the active sites of catalyst. Similar observations were reported by Corma and co-workers for higher benzaldehyde to 1-heptanal molar ratio [3].

3.4. Effect of the reaction temperature

The effect of reaction temperature on selectivity of jasminaldehyde was studied in the temperature range of 60–170 °C at constant benzaldehyde to 1-heptanal molar ratio 5 and 75 mg catalyst amount. Lower conversion of 1-heptanal was found at lower reaction temperature (Table 4). The conversion of 1-heptanal was observed to increase from 38 to 98% by increasing the reaction temperature from 60 to 125 °C. On further increase in the temperature to 140 °C, the conversion increased to 100%. Higher selectivity of jasminaldehyde was observed at lower reaction temperature. The selectivity of jasminaldehyde was observed to decrease from 88 to 81% on increasing the reaction temperature from 60 to 170 °C.

3.5. Reaction kinetics and re-usability of the catalyst [Mg-Al(3.5)]

The effect of reaction time on conversion of 1-heptanal and selectivity of jasminaldehyde was studied at optimum reaction conditions, i.e., 75 mg catalyst, benzaldehyde/1-heptanal molar ratio = 5 and reaction temperature = 125 °C. 1-Heptanal conversion and selectivity of jasminaldehyde with respect to reaction time are shown in Fig. 3. The conversion of 1-heptanal was observed to increase on increasing the reaction time. For example, 62% conversion of 1-heptanal was observed at 2 h reaction time and increased to 80% in 4 h. Finally the conversion of 1-heptanal reached to 98% at 8 h reaction time. The selectivity of jasminaldehyde was observed to increase on

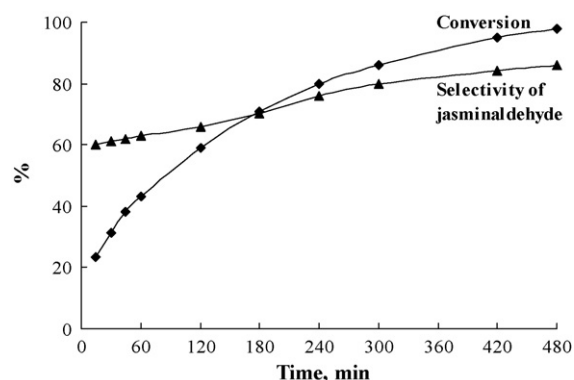


Fig. 3. Kinetic profile with respect to time using Mg-Al(3.5) as a catalyst.

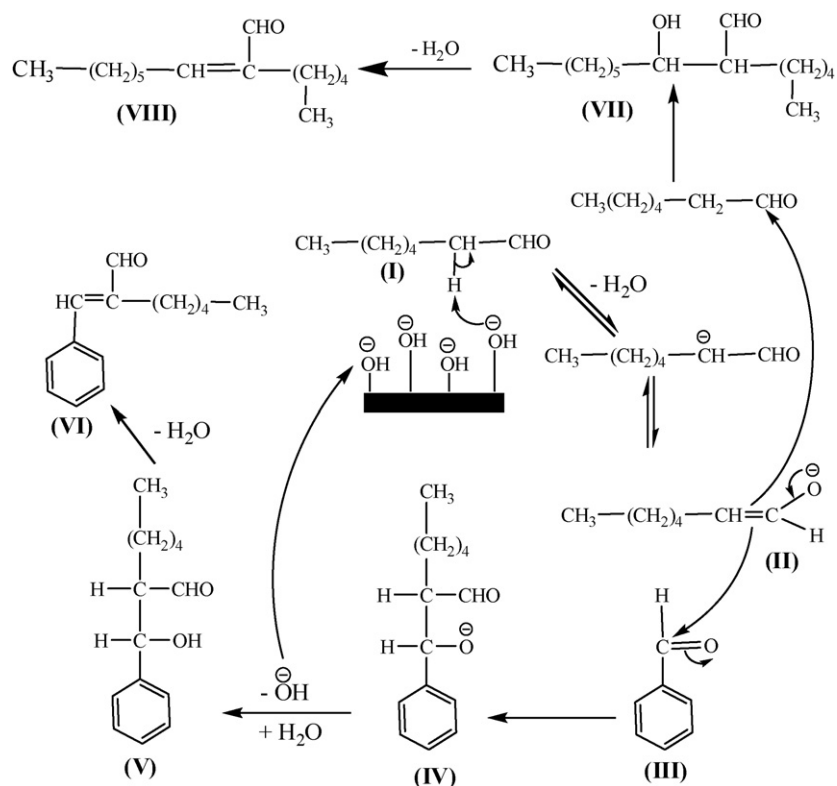
increasing the reaction time. The order of reaction was calculated from the kinetic data and found to be second order reaction with respect to reactant. The rate of reaction was calculated as 11.6×10^{-4} mol/(g_{cat} min) in the lower conversion range (<20%).

The spent catalyst [Mg-Al(3.5)] obtained after completion of reaction was washed with 100 mL methanol and dried at 100 °C for 6 h in an oven. The dried material was used as a catalyst for re-usability experiments under similar reaction conditions (Table 2; Run 1) as that of fresh catalyst. The catalyst was recycled upto three cycles without significant losses in the conversion and selectivity of jasminaldehyde (Table 5). After that the conversion and selectivity data was observed to decrease significantly. Spent catalyst was analyzed by P-XRD (Fig. 1) and FT-IR spectroscopy (Fig. 4) to observe the structural changes of

Table 5
Re-usability of catalyst

Cycles	% Conversion ^a	% Selectivity	
		Jasminaldehyde	2- <i>n</i> -Pentyl-2-nonenal
1	98	86	14
2	98	85	15
3	97	83	17
4	94	77	27
5	92	71	29
6	81	70	30

^a Reaction conditions: benzaldehyde = 39.6 mmol, heptanal = 7.9 mmol, temperature = 125 °C, reaction time = 8 h.



Scheme 2. Proposed reaction mechanism for the synthesis of jasminaldehyde using solid base catalyst.

spent catalyst. P-XRD of the spent catalyst showed all the characteristic peaks of pure hydrotalcite. The crystallinity of spent catalyst was observed to decrease significantly. Any new peak was not observed in the FT-IR spectrum of spent catalyst after first cycle. FT-IR data of the spent catalyst after 6th cycle shows the absorption of jasminaldehyde intermediates (skeletal vibrations of phenyl rings) on the catalyst as evident from the peaks observed at 1606 and 1563 cm^{-1} . This could result into the decrease in the relative concentration of jasminaldehyde in the reaction mixture as determined by GC analysis. Therefore, the observed selectivities after 3rd cycle of catalyst re-usability are apparent selectivities.

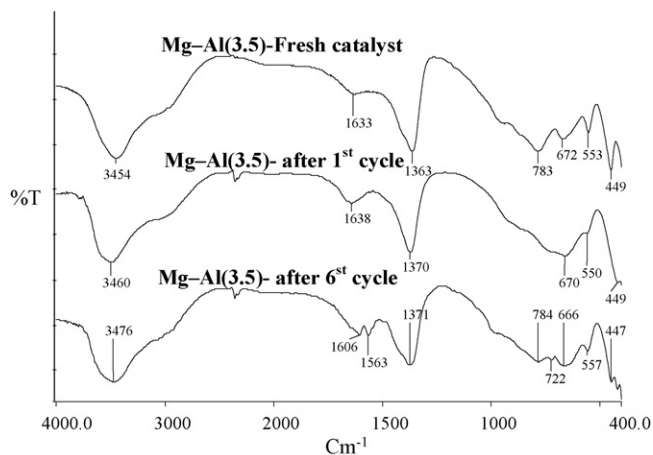


Fig. 4. FT-IR spectra of Mg-Al(3.5) – fresh catalyst, Mg-Al(3.5) – after 1st cycle and Mg-Al(3.5) – after 6th cycle during re-usability study.

3.6. Reaction mechanism

Proposed reaction mechanism for the synthesis of jasminaldehyde by condensation of 1-heptanal with benzaldehyde using solid base catalyst is given in Scheme 2. The reaction is initiated by activation of 1-heptanal (I) molecule to form a stabilized carbanion (II) on the OH^- sites of catalyst by abstracting an acidic proton from α -carbon of (I). Nucleophilic addition of α -carbon of enolate anion (II) to carbonyl carbon of benzaldehyde (III) takes place in the next step to form the intermediate species (IV). The species (IV) abstracts a proton from the in situ generated water molecules to form condensation product (V). In this step, the OH^- sites of catalyst are recycled for the further reaction. Jasminaldehyde (VI) is formed by the dehydration of specie (V). The self-condensation of (I) also follows the similar pathway. The formation of (VII) takes place by nucleophilic addition of α -carbon of enolate anion to the carbonyl group of another (I) molecule and the resulting anion reacts with water to form the product of aldol addition (VII). Dehydration of species (VII) gives the self-condensation product of 1-heptanal, i.e., 2-*n*-pentyl-2-nonenal.

4. Conclusions

The selectivity of jasminaldehyde was observed to increase on increasing the M(II)/Al molar ratio of as-synthesized as well as activated hydrotalcite. The maximum selectivity of jasminaldehyde (86%) with 98% conversion of 1-heptanal was observed using as-synthesized Mg-Al hydrotalcite of Mg/Al

molar ratio of 3.5 as a catalyst. The activated hydrotalcite was found to be more active for self-condensation of 1-heptanal as compared to the condensation of 1-heptanal with benzaldehyde. The conversion of 1-heptanal was observed to increase from 70 to 100% with decrease in selectivity of jasminaldehyde from 86 to 70% on increasing the amount of Mg-Al (3.5) as a catalyst from 20 to 500 mg. Benzaldehyde to 1-heptanal molar ratio was observed to influence the selectivity of jasminaldehyde. The rate of reaction was calculated as 11.6×10^{-4} mol/(g_{cat} min) at optimum reaction conditions. The significant losses in the conversion of 1-heptanal and selectivity of jasminaldehyde were not observed upto three cycles, which shows the re-usability of the catalyst.

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