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Reconstructed Mg/Al hydrotalcite as a solid base catalyst for synthesis of jasminaldehyde

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ABSTRACT

Reconstructed hydrotalcites (Mg/Al molar ratio = 3.5) of varied reconstruction time were synthesized and used as catalysts for solvent free condensation of 1-heptanal with benzaldehyde. Maximum conversion of 1-heptanal with higher selectivity to jasminaldehyde was obtained using reconstructed hydrotalcites of 8–12 h reconstruction time. Catalytic activity of reconstruction hydrotalcite was compared with as-synthesized and activated hydrotalcite of Mg/Al molar ratio 3.5 and significantly higher conversion of 1-heptanal was observed in case of reconstructed hydrotalcite of 8 h reconstruction time as a catalyst. Similar to the conversion, higher selectivity to jasminaldehyde was also obtained using reconstructed hydrotalcite. Effect of reconstruction time on conversion and selectivity to jasminaldehyde was studied by varying the reconstruction time of hydrotalcite from 0.5 to 72 h. Kinetic experiments were carried out to study the effect of stirring speed, benzaldehyde to 1-heptanal molar ratio, amount of catalyst and reaction temperature on the rate of reaction using reconstructed hydrotalcite as a catalyst.

1. Introduction

Jasminaldehyde is a commercially important chemical in the cosmetic and fragrance industries. Apart from its natural source, jasminaldehyde is also synthesized by condensation of 1-heptanal and benzaldehyde in the presence of liquid sodium hydroxide (NaOH) or potassium hydroxide (KOH) in more than stoichiometric amounts [1]. This homogeneous process has several drawbacks like reusability of catalyst, use of hazardous and corrosive liquid base like KOH or NaOH, separation and disposal of effluent containing NaOH or KOH. Therefore, it is desirable to develop a solid base catalyst to provide a green catalytic route for the synthesis of jasminaldehyde. Catalytic activities of large pore HY and beta zeolites, amorphous aluminophosphate (ALPO), hydrotalcite, synthetic talc and MCM-41 aluminosilicates (Al-MCM-41) based materials have been studied by several researchers for the synthesis of jasminaldehyde [1–10]. Corma and coworkers [2–4] reported a process in which 1-heptanal was heated with excess methanol to obtain heptanal di-methyl acetal in the first step and formed heptanal di-methyl acetal was mixed with benzaldehyde in second step. Then, the mixture was again heated at desired temperature in the presence of a catalyst to obtain jasminaldehyde. In our previous reports [9,10], catalytic activity of amine/diamine functionalized synthetic talc (MOS) and hydrotalcites (as-synthesized and activated) of varied divalent metal cations [M(II)] and divalent to trivalent metal cations molar ratio [M(II)/Al; M(II) = Mg, Ni, Zn] was studied in detail for synthesis of jasminaldehyde by solvent free condensation of 1-heptanal with benzaldehyde. Jasminaldehyde selectivity is a crucial parameter in this reaction because by-product (2-*n*-pentyl-2-nonenal) is also formed by base catalyzed self-condensation of 1-heptanal. Highest selectivity to jasminaldehyde (86%) was obtained using as-synthesized hydrotalcite of Mg/Al molar ratio 3.5 as compared to activated hydrotalcite (75%) of similar molar ratio [10]. No significant difference in the conversion of 1-heptanal was observed on activation of hydrotalcite. The catalyst having Brønsted (OH^- groups) basic sites was observed to be more selective for jasminaldehyde as compared to the catalyst having Lewis (O^{2-}) basic sites [10]. These results indicate that the proper tuning of acidic and basic properties of hydrotalcite can enhance the jasminaldehyde selectivity. The proper combination of acidio-basic properties of hydrotalcite required for the reaction can be achieved by intercalation of hydroxyl groups in a control way by reconstruction process at desired reconstruction time. When calcined hydrotalcite is stirred with water vapours or de-carbonated water under inert atmosphere, a highly active solid base catalyst is obtained by restoration of the original layered structure (memory effect) of hydrotalcite having hydroxyl

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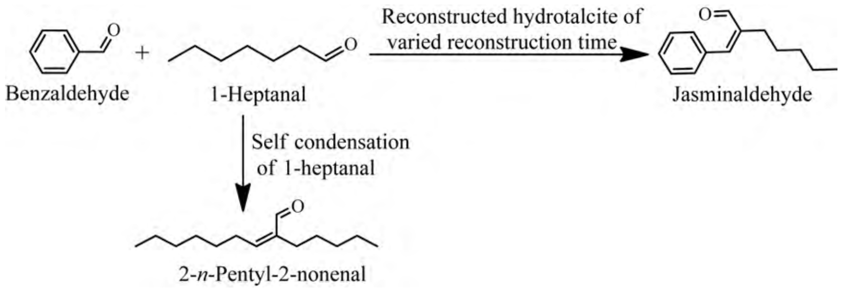

Scheme 1. Synthesis of jasminaldehyde.

groups in major amounts as charge balancing anions in the interlayer space instead of carbonate anions [11]. The Brønsted (OH^-) basic sites formed by reconstruction method are reported to be more active than Lewis (O^{2-}) sites for aldol condensation reactions [12–15]. The reconstruction time and degree of reconstruction have pronounced effect on the structural and catalytic activity of hydrotalcite. Effect of reconstruction time on the structural properties of hydrotalcite is well documented in the literature [16–21]. However, limited literature is available for the effect of reconstruction time on catalytic activity of reconstructed hydrotalcite [12,13].

The present work is taken up with as objective to study the effect of reconstruction time on catalytic activity of reconstructed hydrotalcite of Mg/Al molar ratio 3.5 for the synthesis of jasminaldehyde by condensation of 1-heptanal with benzaldehyde in the solvent free conditions (Scheme 1). The reconstructed hydrotalcite samples of varied reconstruction time were synthesized, characterized to study the structural changes during reconstruction period and used as catalysts for the synthesis of jasminaldehyde. Kinetic experiments were also carried out to study the effect of stirring speed, benzaldehyde to 1-heptanal molar ratio, amount of catalyst and reaction temperature on the rate of condensation reaction using reconstructed hydrotalcite as a catalyst.

2. Experimental

2.1. Materials

Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$; 98.9%), aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$; 99.1%), 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 in the present study. 1-Heptanal and benzaldehyde were purchased from Sigma–Aldrich and used as received.

2.2. Catalyst synthesis

Hydrotalcite of Mg/Al molar ratio 3.5 was synthesized by co-precipitation method at constant pH [22]. In a typical synthesis procedure, an aqueous solution (A) of $Mg(NO_3)_2 \cdot 6H_2O$ (0.0518 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (0.0149 mol) was prepared in 150 mL double distilled deionized water. Solution A was added drop wise into a second solution (B) containing Na_2CO_3 (0.079 mol) in 150 mL double distilled deionized water, in around 45 min under vigorous stirring at 25 °C. Constant pH (10 ± 0.1) of the mixture was maintained by adding 1 M NaOH solution. The content was then transferred into teflon coated stainless steel autoclave and aged at 60 °C for 16 h under autogenous pressure. Then formed precipitate was cool down to room temperature, filtered and washed thoroughly with hot deionized distill water until pH of the filtrate reached to 7. Washed precipitate was dried in an oven at 80 °C for 14 h and ground to convert it into powder form. Activation of hydrotalcite was carried out at 450 °C in muffle furnace for 4 h in the presence of air and further the material was reconstructed in liquid phase. For the synthesis of reconstructed hydrotalcite samples, freshly activated hydrotalcite (2.5 g) was mixed in 1 M NaOH solution prepared in 100 mL de-carbonated deionized water under nitrogen atmosphere. Suspension was stirred at 800 rpm for desired reconstruction time under N_2 atmosphere at 30 °C. Then, the suspension was filtered in vacuum and obtained solid cake was washed thoroughly to remove sodium ion. Finally, solid cake was dried at 80 °C for 14 h, ground and store in vacuum.

2.3. Characterization of the catalyst

Powder X-ray diffraction (P-XRD) patterns of hydrotalcite samples were recorded on a Philips X'Pert MPD system equipped with XRK 900 reaction chamber, using Ni-filtered Cu-K_α radiation (λ = 1.54056 Å) over a 2θ range of 5–70°. Crystallinity of hydrotalcite samples was calculated by the summation of integral intensities of (0 0 3) and (0 0 6) planes. Fourier transform infra red (FT-IR) spectra of hydrotalcite samples were recorded with a Perkin-Elmer Spectrum GX-Fourier transform infrared spectrometer (FT-IR) system in the region of 400–4000 cm^{-1} using KBr pellets. Thermogravimetric analysis (TGA) of hydrotalcite samples was carried out using a Mettler Toledo TGA/SDTA 851e equipment in flowing nitrogen (flow rate = 50 mL/min) at a heating rate of 10 °C/min. Surface area measurements of hydrotalcite samples were carried out using ASAP 2010 Micromeritics, USA. Samples were activated at 130 °C for 4 h under vacuum (5×10^{-2} mm Hg) prior to N_2 adsorption measurements.

2.4. Synthesis of jasminaldehyde

Desired amount of catalyst, benzaldehyde and 1-heptanal was taken in an oven dried double-necked round bottom flask with 0.01 g tetradecane as an internal standard. One neck of flask was fitted with refluxing condenser having spiral tube inside for cold water circulation (6 L/min) at 10 °C. The nitrogen was purge into flask from top of the refluxing condenser to avoid oxidation of 1-heptanal and benzaldehyde. A silicon rubber septum was inserted in second neck of flask to withdraw samples at different time interval for GC analysis. Flask fitted with refluxing condenser was kept in an oil bath equipped with temperature and agitation speed controllers. Reaction mixture was analyzed by gas chromatography (GC) (Shimadzu 17A, Japan) and GC–MS (mass spectrometer, Shimadzu-QP2010, Japan). GC has a 5% diphenyl and 95% di-methyl siloxane universal capillary column (60 m length and 0.25 mm diameter) and a flame ionization detector (FID). Conversion of 1-heptanal and selectivity to jasminaldehyde were calculated by the following formula:

$$\% \text{ Conversion} = \left(\frac{\text{moles of 1-heptanal reacted}}{\text{moles of 1-heptanal fed}}\right) \times 100$$

$$\% \text{ Selectivity of jasminaldehyde} = \left(\frac{\text{moles of jasminaldehyde}}{\text{moles of (jasminaldehyde} + \text{2-}n\text{-pentyl-2-nonenal}}\right) \times 100$$

2.5. *Kinetic analysis and reproducibility*

Reaction parameters which might have pronounced effect on the rate of condensation of 1-heptanal with benzaldehyde include, degree of reconstruction of hydrotalcite, stirring speed, benzaldehyde to 1-heptanal molar ratio, amount of catalyst and reaction temperature. Therefore, kinetic experiments were carried out by varying these parameters. Sample (0.1 mL) was taken using glass syringe at different time interval and change in concentration of 1-heptanal with respect to time was determined by gas chromatography in each case. Total reaction mass loss due to sampling for kinetic analysis was not more than 2% during the course of reaction. Initial rate of reaction was calculated in the lower conversion (~10%) range of 1-heptanal by the method reported in literature [23]. The mass transfer resistance was analyzed by performing experiments at varied amount of catalyst and stirring speed. To ensure reproducibility of the reaction, repeated experiments were carried out under identical reaction conditions. Obtained results including rate of reaction, conversion and selectivity were found to be reproducible within ±2.5% variation.

3. Results and discussions

3.1. *Characterization of catalyst*

P-XRD patterns of as-synthesized, calcined and reconstructed hydrotalcite at varied reconstruction time are shown in Fig. 1. P-XRD pattern of as-synthesized hydrotalcite sample was obtained similar to the pure hydrotalcite [21]. Basal spacing of 0 0 3 plane $d_{spacing} = 0.765$ nm confirmed the presence of carbonate anions in the interlayer space of hydrotalcite. Calcination of hydrotalcite at 450 °C gave a uniform mixed oxide phase Mg(Al)O_x, with diffraction lines very similar to that of MgO. As-synthesized hydrotalcite structure was recovered via reconstruction of calcined hydrotalcite in liquid phase using de-carbonated water under inert atmosphere. All characteristic peaks of as-synthesized hydrotalcite were observed in the XRD of reconstructed hydrotalcite sample within 1 h reconstruction time which showed that the magnesium and aluminum coordination modes were restored to the original octahedral hydrotalcite structure [17]. Peaks intensities and sharpness of (0 0 3) and (0 0 6) planes, which are directly proportional to the crystallinity of material, were observed to increase on increasing the reconstruction time of hydrotalcite. The degree of reconstruction (α) was calculated by comparing the peak intensities of (0 0 3) and (0 0 6) planes of each sample with the peak intensities of sample at 72 h reconstruction time. The 72 h sample was assumed as a reconstructed hydrotalcite of highest crystallinity. Degree of reconstruction was observed to increase almost linearly up to 12 h (Fig. 2). Slow increase in the degree of reconstruction was observed on further increase in the reconstruction time from 12 to 72 h.

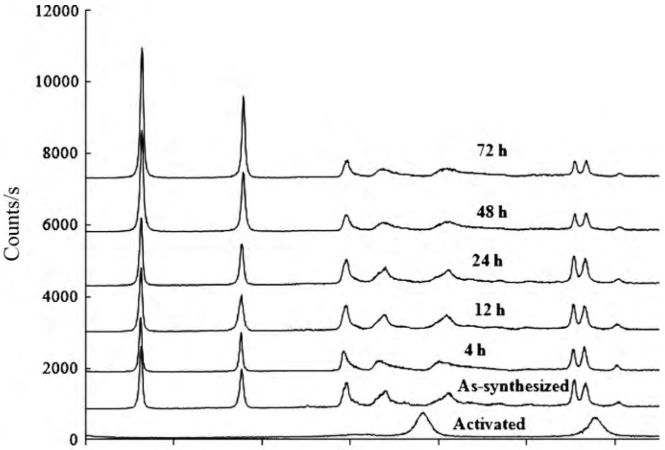

Fig. 1. P-XRD patterns of as-synthesized, calcined and reconstructed hydrotalcite at different reconstruction time.

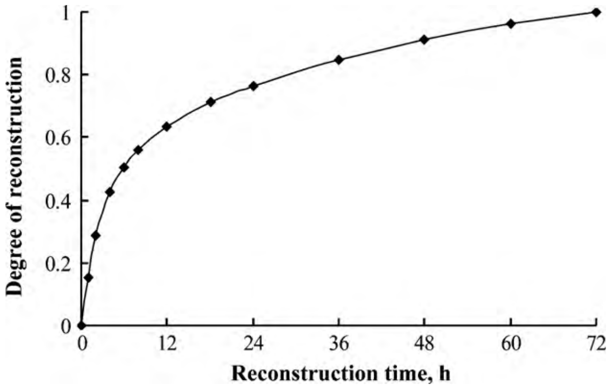

Fig. 2. Degree of reconstruction of hydrotalcite with respect to time.

FT-IR spectra of as-synthesized, calcined and reconstructed hydrotalcite at different reconstruction time are shown in Fig. 3. Absorption bands at about 3465–3497 cm^{-1} were attributed to the stretching vibrations of structural hydroxyl groups in the brucite-like layer. Hydrogen bonding between water molecules and interlayer CO_3^{2-} anions was confirmed by the presence of a shoulder at 3000 cm^{-1}. The bands at around 1640 and 1370 cm^{-1} showed the presence of interlayer water molecules and carbonate anions, respectively. The band appeared at about 555 cm^{-1} was ascribed to the translation mode of hydroxyl groups mainly influenced by the aluminum cations [16,19]. Disappearance of peaks at around 1640 cm^{-1} (water bending vibrations) and 3000 cm^{-1} (interaction of H_2O–CO_3^{2-} in the interlayer) was observed in the IR spectrum of calcined hydrotalcite due to removal of water molecules. Intensity of the bands at around 3497 and 1370 cm^{-1} also decreased significantly. Reconstruction of calcined hydrotalcite in the de-carbonated water induced a recovery of pristine hydrotalcite structure. Presence of structural hydroxyl groups in the brucite-like layer was confirmed by the appearance of band at around 3468 cm^{-1} in all reconstructed hydrotalcite samples. The appearance of strong bands at about 3000 and 1640 cm^{-1} also confirmed the presence of water molecules in reconstructed hydrotalcite. On increasing the reconstruction time, the intensity and broadening of bands at around 3468 and 3000 cm^{-1} were observed to increase which shows that the amount of water/hydroxyl groups increased on increasing reconstruction time. Translation modes of hydroxyl groups, mainly influenced by the aluminum and magnesium cations, were observed in the FT-IR spectra of reconstructed hydrotalcite. The peak at about 1370 cm^{-1} indicated that the carbonate ions are still present after reconstruction. Similar observations on the presence of carbonate anions were reported in the literature also [16].

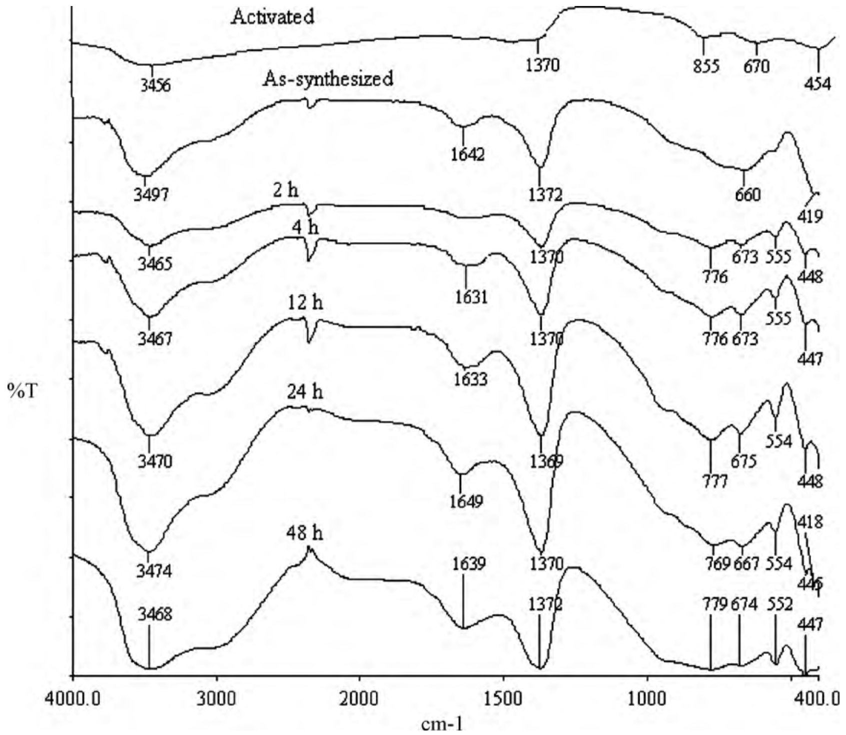

Fig. 3. FT-IR spectra of as-synthesized, activated and reconstructed hydrotalcite at different reconstruction time.

Two steps weight loss, similar to that of as-synthesized hydrotalcite at respective temperatures, was observed in the thermogravimetric analysis (TGA) of reconstructed hydrotalcite samples (Table 1). Weight loss in first step was attributed the loss of physically adsorbed water molecules with relatively smaller amount of condensed water molecules and CO_2 without collapse of the hydrotalcite structure in the temperature range of 115–125 °C. The weight loss in second step was observed due to removal of condensed water molecules and carbon dioxide from the carbonate anions present in the interlayer space of hydrotalcite in the temperature range of 405–410 °C. Weight loss in the reconstructed hydrotalcite sample was observed to increase on increasing the reconstruction time. For example, 18% total weight loss in the reconstructed hydrotalcite sample was calculated for 0.5 h reconstruction time, which increased to 32% for 4 h and finally 51% for the 72 h reconstruction time. Increment in the weight loss on increasing reconstruction time of the hydrotalcite sample is due to increased amount of hydroxyl groups/water molecules present in the reconstructed hydrotalcite samples, which is further supported by the broadening of peak intensity at around 3468 cm^{-1} in the FT-IR spectra of reconstructed hydrotalcite samples.

BET surface area of as-synthesized and activated hydrotalcite samples was obtained as 106 and 214 m^2/g, respectively (Table 1) while surface area of reconstructed hydrotalcite sample of 1 h reconstruction time increased to 231 m^2/g. Increase in the surface area of reconstructed hydrotalcite sample in the liquid phase has also been reported by other researchers [16,24]. The observed higher surface area of reconstructed hydrotalcite may be due to the effect of mechanical stirring during the reconstruction process that can break and exfoliate the hydrotalcite-like platelets. Further increase in the reconstruction time led to the significant decrease in surface area of samples.

3.2. Catalytic activity for the synthesis of jasminaldehyde

Effect of reconstruction time on the catalytic activity of reconstructed hydrotalcite for synthesis of jasminaldehyde was investigated at 130 °C and benzaldehyde to 1-heptanal molar ratio 5 (Fig. 4). Hydrotalcite of Mg/Al molar ratio 3.5 gave maximum

Table 1
Weight loss and BET surface area of as-synthesized, activated and reconstructed hydrotalcite at different reconstruction time.

Reconstruction time (h)	T_1 (°C)	T_2 (°C)	W_1 (%)	W_2 (%)	Total weight loss (%)	BET surface area (m^2/g)
As-synthesized	125	400	10	26	36	106
Activated		450–550	0	4	4	214
0.5	115	410	6	12	18	226
1	115	410	7	18	25	231
2	115	405	9	20	29	187
4	120	405	10	22	32	162
8	125	405	12	22	34	131
12	125	410	12	26	38	118
24	120	405	14	29	43	110
48	125	405	13	33	46	101
72	125	410	16	35	51	97

W_1 = first stage weight loss at temperature T_1.
W_2 = second stage weight loss at temperature T_2.

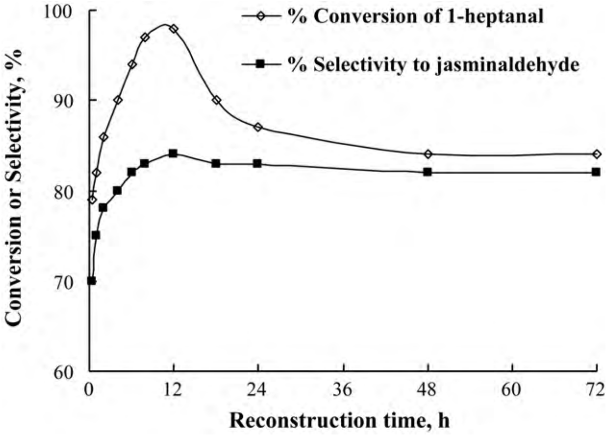

Fig. 4. Effect of reconstruction time of hydrotalcite on conversion and selectivity for the synthesis of jasminaldehyde. Reaction conditions: 1-heptanal = 8.05 mmol, benzaldehyde = 40.25 mmol, catalyst = 0.09 g, T = 130 °C, t = 3 h at 800 rpm.

selectivity to jasminaldehyde in our earlier reports [10] therefore, hydrotalcite of 3.5 Mg/Al molar ratio was taken as a precursor for reconstruction experiments in the present study and reconstruction time was varied from 0.5 to 72 h. Both, conversion of 1-heptanal and selectivity to jasminaldehyde were observed to increase on increasing the reconstruction time from 0.5 to 12 h. At 0.5 h reconstruction time, 79% conversion of 1-heptanal was achieved with 70% selectivity to jasminaldehyde in 180 min reaction time. Conversion of 1-heptanal increased to 94% with 82% selectivity to jasminaldehyde on increasing the reconstruction time of hydrotalcite to 6 h. On further increasing the reconstruction time to 12 h, conversion reached to 98%. Slight increase in the conversion of 1-heptanal was observed in the range of 8–12 h reconstruction time. Conversion of 1-heptanal decreased to 87 and 84% for reconstructed hydrotalcite having reconstruction time of 24 and 72 h, respectively. Selectivity to jasminaldehyde was also observed to increase on increasing the reconstruction time of hydrotalcite up to 12 h. However, no significant increase in the selectivity to jasminaldehyde was observed on further increasing the reconstruction time of hydrotalcite to 72 h. These results clearly showed that the reconstructed hydrotalcite of 8–12 h reconstruction time gave highest conversion of 1-heptanal and maximum selectivity to jasminaldehyde, therefore, effect of other reaction parameters such as, stirring speed, amount of catalyst, benzaldehyde to 1-heptanal molar ratio and reaction temperature on conversion of 1-heptanal and selectivity to jasminaldehyde was studied by taking reconstructed hydrotalcite of 8 h reconstruction time as a catalyst. Kinetic study was also carried out in detail to study the effect of above parameters on the rate of reaction.

To understand the effect of reconstruction of hydrotalcite on the activity of catalyst, experiments were performed under identical reaction conditions using as-synthesized, calcined and reconstructed hydrotalcite samples as catalysts. Higher conversion of 1-heptanal in shorter reaction time was observed using reconstructed hydrotalcite of 8 h reconstruction time as a catalyst (Fig. 5). 87% conversion of 1-heptanal was achieved in 60 min reaction time using reconstructed hydrotalcite, while 30% and 43% conversion of 1-heptanal were achieved using as-synthesized and calcined hydrotalcite, respectively as catalysts. In case of the reconstructed hydrotalcite, conversion of 1-heptanal reached 96% within 120 min, however, 51 and 60% conversion was obtained using as-synthesized and calcined hydrotalcites, respectively. Reconstructed hydrotalcite showed higher selectivity to jasminaldehyde as compared to the as-synthesized and calcined hydrotalcite samples. For example, 68% selectivity to jasminaldehyde was found in 120 min reaction time using as-synthesized hydrotalcite, which increased to 81% in case of reconstructed hydrotalcite. Calcined hydrotalcite showed poor selectivity to jasminaldehyde (56%) due to presence of Lewis basic sites, which assist faster self-condensation of 1-heptanal to 2-*n*-pentyl-2-nonenal. Time on stream data for the variation in conversion of 1-heptanal and selectivity to main products, i.e. jasminaldehyde and 2-*n*-pentyl-2-nonenal is shown in Fig. 6 using reconstructed hydrotalcite of 8 h reconstruction time as a catalyst.

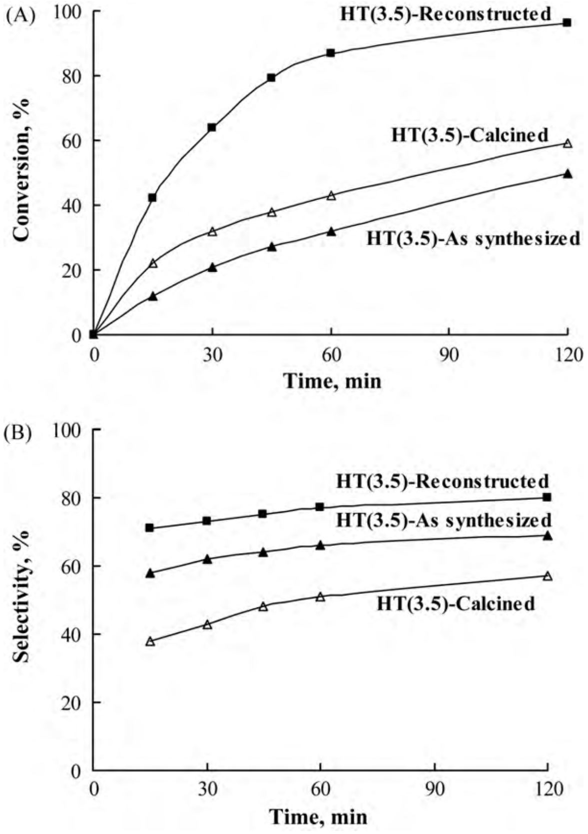

Fig. 5. Conversion of 1-heptanal (A) and selectivity to jasminaldehyde (B) using as-synthesized, activated and reconstructed hydrotalcite (reconstruction time = 8 h) as catalysts for the synthesis of jasminaldehyde. Reaction conditions: 1-heptanal = 8.05 mmol, benzaldehyde = 40.25 mmol, catalyst = 0.09 g, T = 130 °C at 800 rpm.

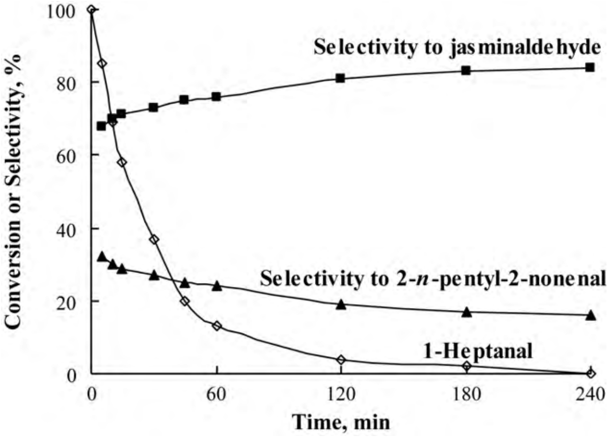

Fig. 6. Variation of the conversion of 1-heptanal and selectivity to the main products (i.e. jasminaldehyde and 2-*n*-pentyl-2-nonenal) with time on stream. Reaction conditions: 1-heptanal = 8.05 mmol, benzaldehyde = 40.25 mmol, catalyst = 0.09 g, T = 130 °C at 800 rpm.

Higher catalytic activity of reconstructed hydrotalcite as compared to as-synthesized hydrotalcite is due to the presence of higher number of Brønsted basic sites (OH^- ions) either on the surface or near the edges of platelets. When calcined hydrotalcite is stirred in de-carbonated water under inert atmosphere, Lewis basic sites of higher basic strength are converted into Brønsted basic sites of low/medium basic strength resulting into a highly active solid base catalyst for condensation reactions. Basic accessible sites (OH^-) detected by the CO_2 molecules were found to be higher in case of liquid phase reconstructed hydrotalcite samples [16] and are probably located near the edges of platelets [16,25]. These sites can also be controlled by modifying the defects in the structural framework of hydrotalcite. The hydroxyl groups, likely to be bonded to low coordination sites (hydrotalcite obtained by reconstruction method), result into more number of basic sites as compared to those present in well ordered hydrotalcite structure obtained by ion-exchange process. Observed higher activity of reconstructed hydrotalcite as compared to activated and as-synthesized hydrotalcite concludes that the hydrotalcite structure of irregular aggregates containing more hydroxyl anions has sufficient basic capacity to catalyze faster condensation of 1-heptanal with benzaldehyde.

3.2.1. *Effect of stirring speed*

To ensure pure kinetic regime and negligence of mass transfer resistance for kinetic study, the reaction was carried out first by varying the stirring speed and amount of catalyst. The stirring speed was varied from 0 to 1000 rpm at benzaldehyde to 1-heptanal molar ratio 5 (Fig. 7). In all cases 93–96% conversion of 1-heptanal was reached within 120 min reaction time at 130 °C temperature (Fig. 7A). However, significant difference in conversion was observed in lower reaction time. Without stirring, 68% conversion of 1-heptanal was observed in 60 min that increased to 75% on increasing the stirring speed to 300 rpm in similar reaction time. On further increase in the agitation speed to 1000 rpm, no significant effect on conversion was observed in 60 min. However, reaction time and stirring speed have significant effect on the selectivity to jasminaldehyde in the studied reaction conditions (Fig. 7B). For example, selectivity to jasminaldehyde increased from 66% in 5 min reaction time to 78% in 240 min at 300 rpm. The selectivity to jasminaldehyde was increased up to 82% in 240 min on increasing the stirring speed to 500 rpm.

Initial rate of reaction was found to increase up to 500 rpm (Fig. 7C), after that significant effect of stirring speed on rate of reaction was not observed. Increase in the rate of reaction up to 500 rpm is due to the combined effect of the mass transfer resistance. However, effect of mass transfer resistance is not prominent after 500 rpm and reaction moved into pure kinetic regime. Absence of mass transfer resistance was further confirmed by studying the effect of catalyst amount on initial rate of reaction.

3.2.2. *Effect of catalyst amount*

Conversion of 1-heptanal was significantly increased on increasing the catalyst amount from 12 to 90 mg (Fig. 8A). Lower conversion of 1-heptanal with higher selectivity to jasminaldehyde was obtained at lower amount of catalyst. At 12 mg catalyst amount, only 37% conversion of 1-heptanal with 81% selectivity to jasminaldehyde was observed in 60 min reaction time. Conversion of 1-heptanal increased to 75 and 87% at 45 and 90 mg catalyst amount, respectively in 60 min. On further increase in the amount of catalyst from 90 to 250 mg, no significant difference in the conversion of 1-heptanal was observed. Selectivity to jasminaldehyde was observed to decrease significantly from 80 to 66% on increasing amount of catalyst from 12 to 250 mg within 60 min reaction time (Fig. 8B). Decrease in the selectivity to jasminaldehyde at higher amount of catalyst is due to availability of higher number of basic site which aids faster self-condensation of 1-heptanal to 2-*n*-pentyl-2-nonenal, which is also a base catalyzed reaction.

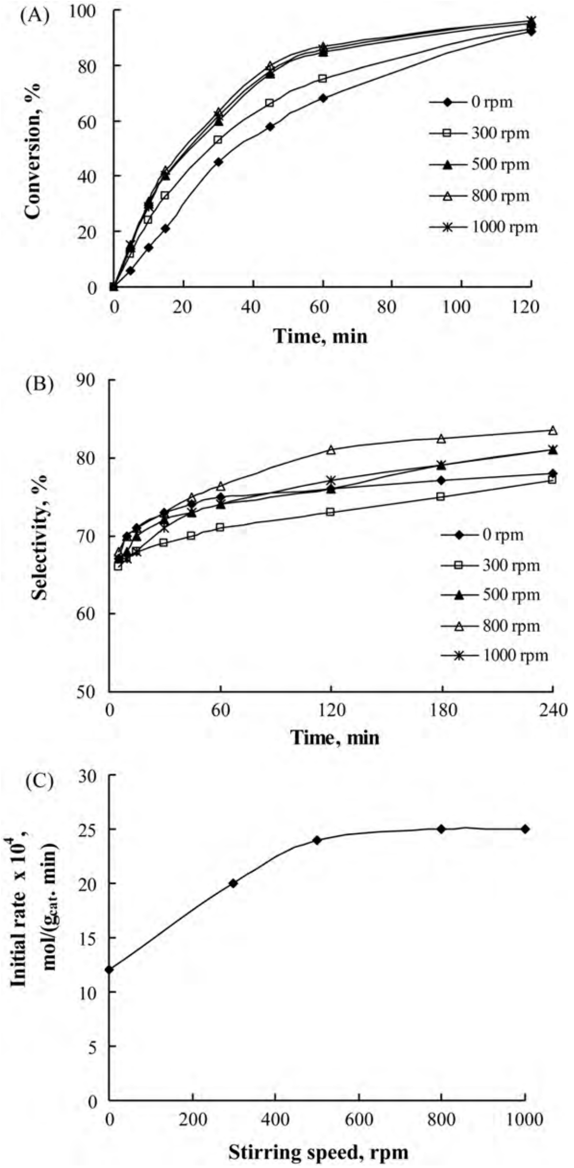

Fig. 7. Effect of stirring speed on conversion of 1-heptanal (A), selectivity to jasminaldehyde (B) and initial rate of reaction (C) using reconstructed hydrotalcite as a catalyst for the synthesis of jasminaldehyde. Reaction conditions: 1-heptanal = 8.05 mmol, benzaldehyde = 40.25 mmol, catalyst = 0.09 g, T = 130 °C.

Initial rate of reaction calculated from 1-heptanal consumption data is shown in Fig. 8C. Initial rate of reaction was observed to increase linearly up to 45 mg catalyst amount and thereafter, slow increase in the rate of reaction was found up to 90 mg catalyst amount. Significant effect on initial rate of reaction was not observed in the range of catalyst amount from 90 to 250 mg, which again confirmed the absence of mass transfer resistance. Therefore, 90 mg amount of catalyst at 800 rpm stirring speed was used for further experiments to ensure pure kinetic regime.

3.2.3. *Effect of benzaldehyde to 1-heptanal molar ratio*

Benzaldehyde to 1-heptanal molar ratio has significant effect not only on rate of reaction but also on the conversion and selectivity to jasminaldehyde (Fig. 9). Higher conversion of 1-heptanal with lower selectivity to jasminaldehyde was observed at lower benzaldehyde to 1-heptanal ratio due to faster self-condensation

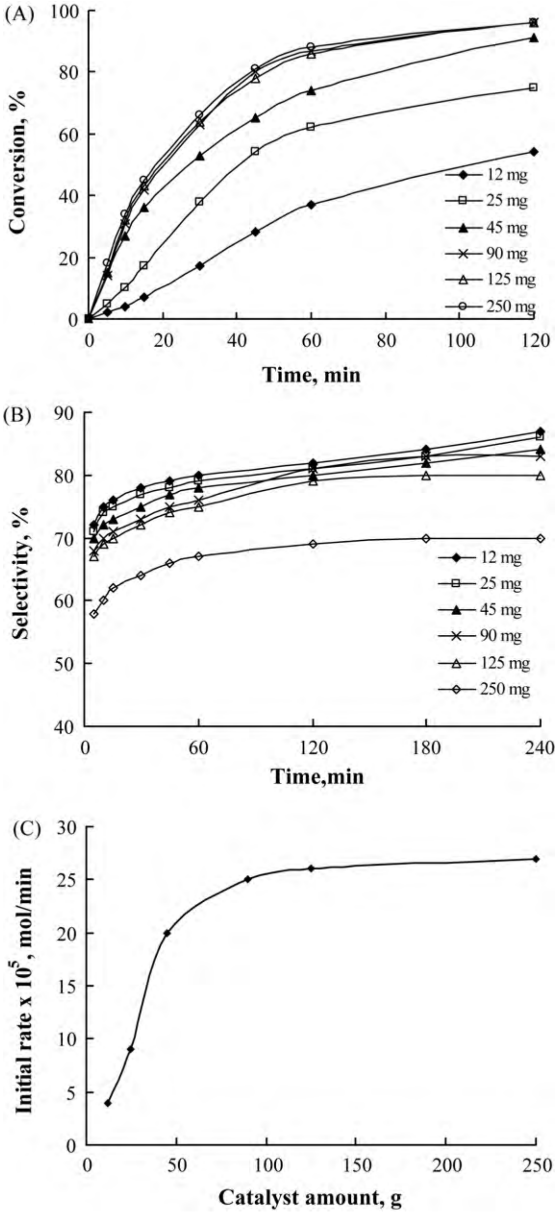

Fig. 8. Effect of catalyst amount on conversion of 1-heptanal (A), selectivity to jasminaldehyde (B) and initial rate of reaction (C) using reconstructed hydrotalcite as a catalyst for the synthesis of jasminaldehyde. Reaction conditions: 1-heptanal = 8.05 mmol, benzaldehyde = 40.25 mmol, T = 130 °C at 800 rpm.

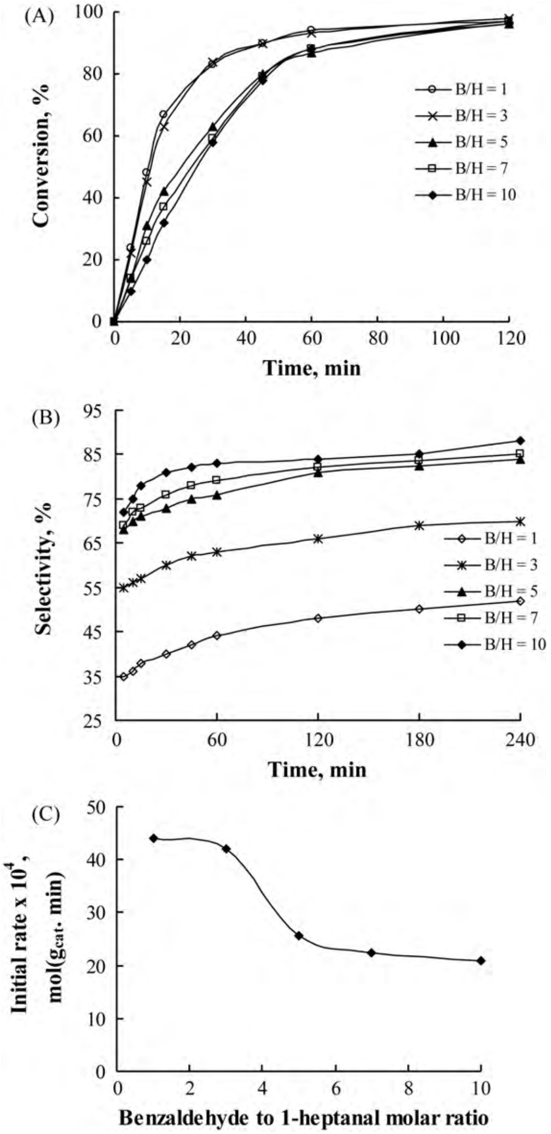

Fig. 9. Effect of benzaldehyde to 1-heptanal molar ratio on conversion of 1-heptanal (A), selectivity to jasminaldehyde (B) and initial rate of reaction (C) using reconstructed hydrotalcite as a catalyst for the synthesis of jasminaldehyde. Reaction conditions: 1-heptanal = 8.05 mmol, catalyst = 0.09 g, T = 130 °C at 800 rpm.

of 1-heptanal. Almost 94% conversion of 1-heptanal was achieved at benzaldehyde to 1-heptanal molar ratio in the range of 1–3 in 60 min reaction time (Fig. 9A). The conversion of 1-heptanal decreased to 87% on increasing this ratio to 5 in similar reaction time. Significant effect on the conversion within 60 min reaction time was not observed in the range of benzaldehyde to 1-heptanal molar ratio 5–10; however, some differences were observed in lower reaction time (less than 30 min). Selectivity to jasminaldehyde was also observed to increase on increasing the benzaldehyde to 1-heptanal molar ratio (Fig. 9B). At lower ratio (1), 44% selectivity to jasminaldehyde was obtained that increased to 63% on increasing the benzaldehyde to 1-heptanal molar ratio 3 in 60 min. For benzaldehyde to 1-heptanal molar ratio 10, 83% selectivity to jasminaldehyde was observed in 60 min reaction time which increased to 88% at 240 min. Present data shows that the conversion of 1-heptanal and selectivity to jasminaldehyde increases with the reaction time. Faster addition of the α-carbon of enolate anion (carbanion of 1-heptanal) to the carbonyl group of another 1-heptanal molecule is the most probable reason for higher selectivity of 2-*n*-pentyl-2-nonenal at lower benzaldehyde to 1-heptanal molar ratio. At higher benzaldehyde to 1-heptanal molar ratio, the concentration of benzaldehyde is higher which leads to increased interaction probability of carbanions of 1-heptanal with activated benzaldehyde molecules on the active sites of catalyst.

Initial rate of reaction was observed to decrease on increasing the benzaldehyde to 1-heptanal molar ratio (Fig. 9C). At lower molar ratio, for example 1, higher rate of reaction [45×10^{-4} mol/(g$_{cat}$ min)] was calculated due to faster self-condensation of 1-heptanal. The rate of reaction was found to decrease to 42×10^{-4} mol/(g$_{cat}$ min) on increasing the molar ratio to 3. On further increase in the benzaldehyde to 1-heptanal molar ratio to 5, initial rate of reaction decreased rapidly to 25×10^{-4} mol/(g$_{cat}$ min). Similar observation was also reported in the literature for condensation of benzaldehyde with acetone due to competitive adsorption of reactants [13]. Slow decrease in the rate of reaction was observed in the benzaldehyde to 1-heptanal molar ratio range of 5–10.

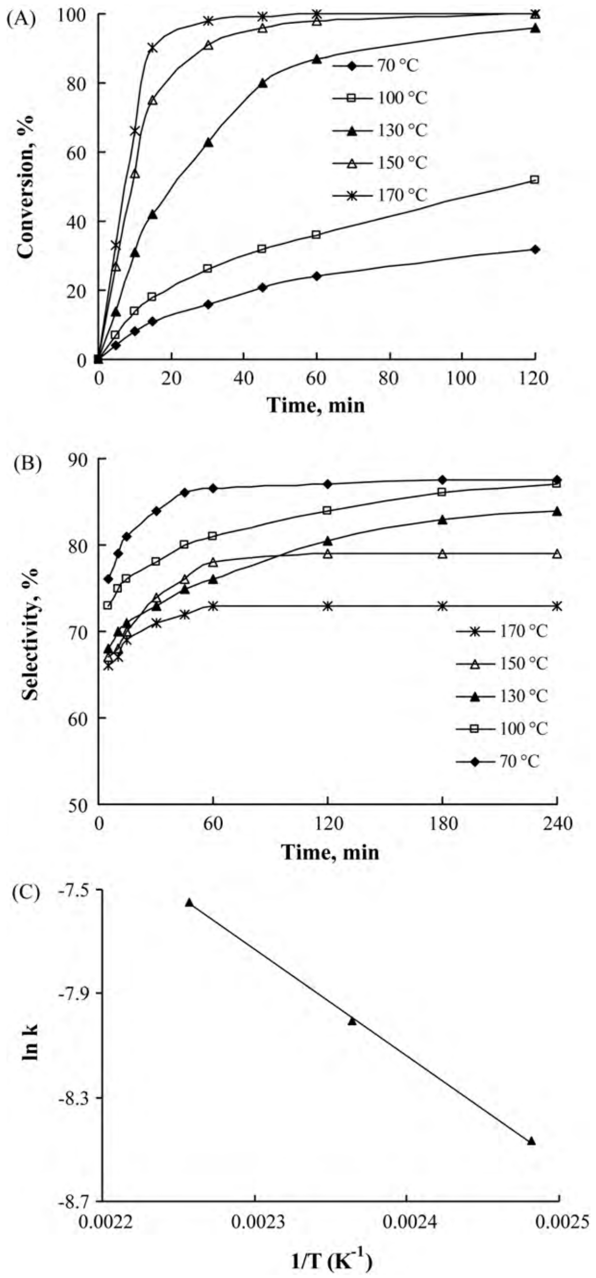

Fig. 10. Effect of reaction temperature on conversion of 1-heptanal (A) and selectivity to jasminaldehyde (B) using reconstructed hydrotalcite as a catalyst for the synthesis of jasminaldehyde; Arrhenius plot (C). Reaction conditions: 1-heptanal = 8.05 mmol, benzaldehyde = 40.25 mmol, catalyst = 0.09 g at 800 rpm.

3.2.4. *Effect of reaction temperature*

Reaction temperature has significant effect on the conversion of 1-heptanal, selectivity to jasminaldehyde and initial rate of reaction (Fig. 10). Two regions can be seen clearly from Fig. 10A; one is the temperature below 100 °C and another region is the above 100 °C. Maximum conversion of 1-heptanal (32%) was observed at 70 °C that increased to 52% on increasing the reaction temperature to 100 °C in 120 min. On further increasing the temperature to 130 °C, 87% conversion was achieved within 60 min and 96% in 120 min reaction time. 90% conversion of 1-heptanal was observed within 15 min at 170 °C that increased to 98% in 30 min reaction time at similar reaction temperature. Higher conversion of 1-heptanal at higher temperature is due to faster consumption of 1-heptanal either for jasminaldehyde or 2-*n*-pentyl-2-nonenal. Selectivity data clearly shows that the higher temperature favors the formation of 2-*n*-pentyl-2-nonenal (Fig. 10B). Higher selectivity to jasminaldehyde (87%) was observed at 70 °C in 60 min reaction time. On increasing the temperature to 100 °C, similar selectivity to jasminaldehyde was obtained in 240 min. Significant decrease in the selectivity to jasminaldehyde was observed at 170 °C. Decrease in the selectivity to jasminaldehyde on increasing reaction temperature is due to the faster self-condensation of 1-heptanal to 2-*n*-pentyl-2-nonenal as compared to the condensation of 1-heptanal with benzaldehyde.

Initial rate of reaction was observed to increase on increasing the reaction temperature. Activation energy was calculated by plotting ln *k* versus 1/*T* in the temperature range of 130–170 °C (Arrhenius plot; Fig. 10C) and found to be 37.6 kJ/mol. The calculated activation energy in the present study again confirmed that the reaction is far away from the diffusional or mass transfer limitations.

4. Conclusions

Reconstruction of hydrotalcite was carried out by stirring a calcined hydrotalcite sample in de-carbonated water under inert atmosphere which results in the restoration of original layered structure containing OH^- anions as major compensating anions in the interlayer space. Reconstruction of hydrotalcite yielded a highly active solid base catalyst for synthesis of jasminaldehyde. Reconstructed hydrotalcite of 8 h reconstruction time showed 96% conversion of 1-heptanal within 120 min as compared to 51 and 60% conversion using as-synthesized and calcined hydrotalcite, respectively under identical reaction conditions. Higher conversion of 1-heptanal with lower selectivity to jasminaldehyde was observed at lower benzaldehyde to 1-heptanal ratio. 88% selectivity to jasminaldehyde was obtained in 4 h reaction time using 12 mg reconstructed hydrotalcite of 8 h reconstruction time as a catalyst at 8.05 mmol 1-heptanal and 40.25 mmol benzaldehyde concentrations. Kinetic data showed that the initial rate of reaction increased linearly up to 45 mg catalyst amount, thereafter, slow increase in the rate of reaction was observed up to 90 mg catalyst amount. Higher reaction temperature and catalyst amount favored the faster self-condensation of 1-heptanal which results into lower selectivity to jasminaldehyde. The activation energy was calculated by Arrhenius plot and found to be 37.6 kJ/mol.

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References

[1] L.S. Payne, EP Patent, 0392579 A2 (1990) to Unilever.
[2] M.J. Climent, A. Corma, V. Fornes, R.G. Lopez, S. Ibora, Adv. Synth. Catal. 344 (2002) 1090–1096.
[3] M.J. Climent, A. Corma, H. Garcia, R.G. Lopez, S. Ibora, V. Fornes, J. Catal. 197 (2001) 385–393.
[4] M.J. Climent, A. Corma, R.G. Lopez, S. Ibora, J. Primo, J. Catal. 175 (1998) 70–79.
[5] J.I. Yu, Y. Shiau, A.N. Ko, Catal. Lett. 77 (2001) 165–169.
[6] S. Jaenicke, G.K. Chuah, X.H. Lin, X.C. Hu, Micropor. Mesopor. Mater. 35–36 (2000) 143–153.
[7] J.I. Yu, Y. Shiau, A.N. Ko, React. Kinet. Catal. Lett. 72 (2001) 365–372.
[8] M.J. Climent, A. Corma, S. Ibora, A. Velty, J. Mol. Catal. A: Chem. 182–183 (2002) 327–342.
[9] S.K. Sharma, H.A. Patel, R.V. Jasra, J. Mol. Catal. A: Chem. 280 (2008) 61–67.
[10] S.K. Sharma, P.A. Parikh, R.V. Jasra, J. Mol. Catal. A: Chem. 286 (2008) 55–62.
[11] S. Miyata, Clays Clay Miner. 28 (1980) 50–56.
[12] D. Tichit, M. Naciri Bennani, F. Figueras, R. Tessier, J. Kervennal, Appl. Clay Sci. 13 (1998) 401–415.
[13] K.K. Rao, M. Gravelle, J. Sanchez Valente, F. Figueras, J. Catal. 173 (1998) 115–121.
[14] D. Tichit, D. Lutic, B. Coq, R. Durand, R. Teissier, J. Catal. 219 (2003) 167–175; D. Tichit, B. Coq, Cattech 7 (2003) 206–217.
[15] D. Tichit, B. Coq, S. Cerneaux, R. Durand, Catal. Today 75 (2002) 197–202.

[16] S. Abello, F. Medina, D. Tichit, J.P. Ramirez, J.C. Groen, J.E. Sueiras, P. Salagre, Y. Cesteros, Chem. Eur. J. 11 (2005) 728–739.
[17] J.A. van Bokhoven, J.C.A.A. Roelofs, K.P. de Jong, D.C. Koningsberger, Chem. Eur. J. 7 (2001) 1258–1265.
[18] J.P. Ramirez, S. Abello, N.M. van der Pers, Chem. Eur. J. 13 (2007) 870–878.
[19] F. Millange, R.I. Walton, D. O'Hare, J. Mater. Chem. 10 (2000) 1713–1720.
[20] A.I. Khan, D. O'Hare, J. Mater. Chem. 12 (2002) 3191–3198 (and reference cited therein).
[21] F. Delorme, A. Seron, M. Bizi, V.J. Prost, D. Martineau, J. Mater. Sci. 41 (2006) 4876–4882.
[22] F. Cavani, F. Trifiro, A. Vaccari, Catal. Today 11 (1991) 173–301.
[23] H.S. Fogler, Elements of Chemical Reaction Engineering, 4th edition, Prentice Hall International Series, USA, 2006.
[24] S. Abello, F. Medina, D. Tichit, J. Perez-Ramirez, Y. Cesteros, P. Salagre, J.E. Sueiras, Chem. Commun. (2005) 1453–1455.
[25] J.C.A.A. Roelofs, D.J. Lensveld, A.J. van Dillen, K.P. de Jong, J. Catal. 203 (2001) 184–191.