Chitosan as an eco-friendly solid base catalyst for the solvent-free synthesis of jasminaldehyde

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ABSTRACT

Chitosan was modified through the hydrogel synthesis route and its catalytic activity was evaluated for the synthesis of jasminaldehyde by the condensation of 1-heptanal with benzaldehyde under solvent-free conditions. Chitosan being natural product and also the solvent-free synthesis procedure of jasminaldehyde have the advantage of green catalysis. Maximum conversion of >99% and 88% selectivity to jasminaldehyde were obtained at 160 °C. The effect of reaction parameters such as the amount of the catalyst, temperature and the benzaldehyde to 1-heptanal molar ratio on the conversion and selectivity was studied. The catalyst was recycled up to six times without significant loss in its activity and selectivity.

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1. Introduction

In recent years biopolymers [1–4] have gained a great research interest for their use as a support for catalysts. Chitin, the naturally occurring polysaccharide, is one of the principal ingredients of the carapaces, crusts, and shells of crustacea, such as crabs, lobsters, prawns, and shrimps. Chitosan is the second most abundant organic resource on the earth next to cellulose, and the amount of its production is estimated to be several billion tons per year [5]. This natural polymer is nontoxic, biodegradable, and biocompatible. It has been shown to be a reactive and functional polymer which has a wide range of applications in biomedicine, pharmacology and agriculture [6]. Chitosan, which is obtained by alkaline deacetylation of chitin, has been used most widely as a support for catalytic applications [7,8]. Presence of both hydroxyl and amino groups in chitosan (Scheme 1) make it have a potential to work as a catalyst, efficient for base catalyzed reactions [9,10]. The use of such solid base catalysts can provide a commercial process with easy handling of the catalyst, easy separation of products, avoiding the use of alkali bases and regeneration and reusability of the catalyst. Moreover the biopolymers can be used as green catalysts as it avoids the use of metal complexes and

has the advantage of environmental friendly disposal of the spent catalyst.

Jasminaldehyde or α-pentyl cinnamaldehyde is a perfumery chemical of commercial interest and is synthesized by the condensation of 1-heptanal with benzaldehyde (Scheme 2) in the presence of liquid alkali like NaOH and KOH, taken in more than stoichiometric quantities [11]. The main drawbacks of this homogeneous process include lack of reusability of the catalyst, hazardous liquid alkali waste and post-reaction treatment of spent liquid bases. Thus solid base catalysts can be a substitute to overcome these drawbacks. Recently Corma et al. have reported the synthesis of jasminaldehyde using large pore HY and beta zeolites, mesoporous MCM-41 aluminosilicates and amorphous aluminophosphates [12–14] as catalysts. However, this catalytic reaction involves a two-step process, acetalization of 1-heptanal with methanol and then the reaction between acetal with benzaldehyde. During the synthesis of jasminaldehyde, different by-products are also obtained that can reduce selectivity to jasminaldehyde. The major by-product is the base catalyzed self-condensation of 1-heptanal to 2-pentyl-2-nonenal. The self-condensation can be inhibited to some extent by increasing the benzaldehyde to 1-heptanal ratio in the reaction mixture. Abenhaem et al. reported solventless synthesis using solid–liquid phase-transfer catalysis at room temperature giving 82% yield to jasminaldehyde [15]. Solventless synthesis of jasminaldehyde using hydrotalcite and magnesium organosilicate as solid base catalysts has also been reported [16,17]. The selectivity to jasminaldehyde was found to be increased with an increase in the Mg/Al ratio of hydrotalcite giving 86% selectivity with 98%

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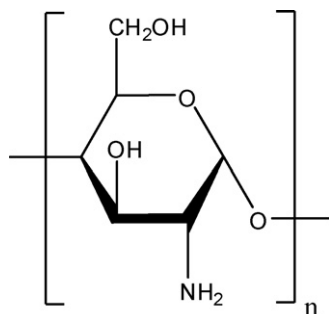
Scheme 1. Structure of chitosan.

conversion for the Mg/Al ratio of 3.5. In the case of magnesium organosilicate the conversion and selectivity were found to be increased with an increase in basicity of the catalyst. In the present investigation, chitosan has been used as catalyst for the synthesis of jasminaldehyde and is found to be an efficient catalyst. The study is one of the very few if any, for using chitosan as catalyst for the synthesis of jasminaldehyde from the condensation of 1-heptanal with benzaldehyde. We report here the detail investigations on the catalytic aspects of the aldol condensation reaction for the synthesis of jasminaldehyde under solvent-free conditions using chitosan as a solid base catalyst.

2. Experimental

2.1. Materials

NaOH and HCl were purchased from S.D. Fine Chemicals, India. The double distilled milli-pore water was used during the synthesis of the catalyst. 1-Heptanal and benzaldehyde were procured from Sigma–Aldrich and used without further purification.

2.2. Catalyst synthesis

The chitosan catalyst was synthesized by the following procedure reported in literature [10,18]. Low-molecular weight chitosan (0.32 g) was dissolved in 0.1 M HCl (20 mL) at room temperature and stirred up to its complete dissolution. The completely dissolved chitosan solution was poured dropwise into 0.1 M NaOH solution (300 mL). The resulting chitosan hydrogel was kept at room temperature for 1 h aging without stirring and then filtered. After filtration chitosan found in the form of hydrogel was washed with excess distilled water until the filtrate became neutral. The neutrality of the filtrate was checked by phenolphthalein. The obtained

hydrogel was dried at 80 °C and then was powdered by using a mortar and pestle.

### 2.3. Characterization of the catalyst

FT-IR spectra of the catalyst were recorded with a Perkin Elmer GX-FT-IR 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 50 mL/min. N_2 sorption analysis was carried out at 77.4 K in a sorptometer (ASAP 2010, Micromeritics). The sample was degassed at 80 °C for 4 h prior to the sorption analysis. Surface morphology was characterized using scanning electron microscopy (Leo Series VP1430).

2.4. Determination of number of accessible amino groups

The number of accessible amino groups on the catalyst was determined by the previously reported method [10]. In a typical experiment, 50 mg of the catalyst was mixed with 3 mL of 0.16 M solution of salicylaldehyde in ethanol with nitrobenzene as gas chromatography (GC) internal standard. The salicylaldehyde forms Schiff base complex with the accessible amino group present on the catalyst. The residual salicylaldehyde was calculated by GC from which the accessible amino groups were determined.

2.5. Condensation reaction

1-Heptanal and benzaldehyde were taken in a 1:5 molar ratio with the desired amount of the catalyst and chitosan, in a two-neck round-bottom flask and 0.01 g tetradecane was added to this mixture as an internal standard. One neck of the flask was connected to a reflux condenser and the other neck was blocked with a silicon rubber septum. Water at 18 °C from a chiller was circulated through the condenser and the flask was then kept in an oil bath equipped with temperature-controller and a magnetic stirring unit. The reaction was done under nitrogen atmosphere to inhibit the formation of corresponding acids from aldehyde. The reaction was carried out at 140 °C. The product mixture was cooled down to room temperature after completion of the reaction and was filtered. The progress of reaction was monitored in terms of the consumption of 1-heptanal by taking the samples at different time intervals. The conversion was evaluated by considering the subsequent decrease in the concentration of 1-heptanal. The analysis of product mixture was carried out by GC (Shimadzu 17A, Japan) and GC–MS (Schimadzu QP-2010, Japan). The GC has a 5% diphenyl- and 95% dimethylsiloxane universal capillary column and a flame ionization detector (FID). To ensure the reproducibility of the reaction,
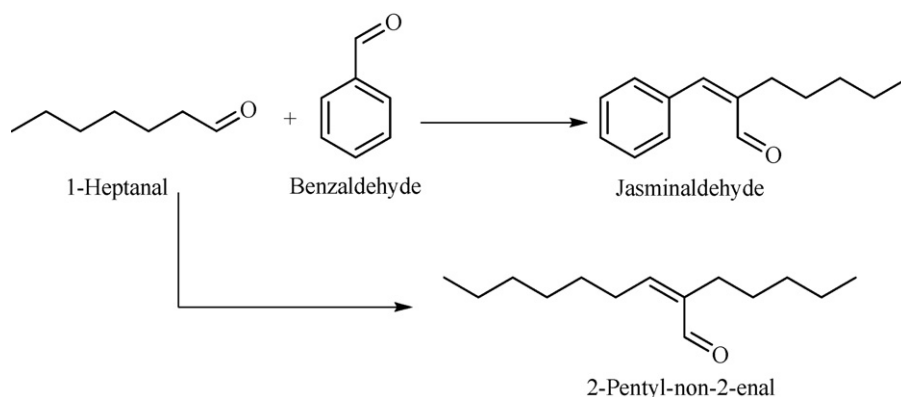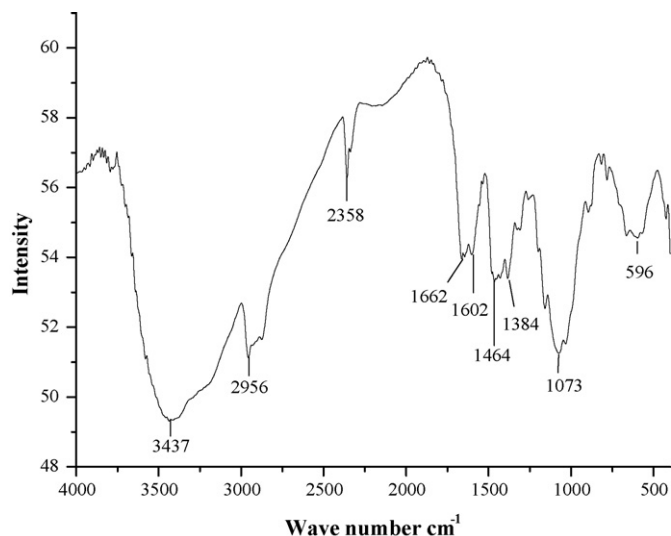

Scheme 2. Synthesis of jasminaldehyde.

Fig. 1. FT-IR spectrum of the chitosan catalyst.

Fig. 3. SEM image of the chitosan catalyst.

repeated experiments were carried out under identical reaction conditions. The results obtained, including conversion and selectivity were found to be in the range of 5% variation.

3. Results and discussions

3.1. Characterization of the catalyst

The FT-IR spectrum for the catalyst is shown in Fig. 1. The peak at 1602 cm^{-1} indicated [19] the presence of –NH$_2$ group resulting from deacetylation of chitin. The band at 3437 cm^{-1} corresponds to the vibrational stretching of the hydroxyl groups [20]. This wide peak also indicated that the hydroxyl groups are hydrogen-bonded. The band that appeared at 2956 cm^{-1} is due to the C–H stretching vibration of aliphatic CH groups and that at 1073 cm^{-1} to the C–O–C bond stretching vibrations [20–22].

The TGA curve of the catalyst shown in Fig. 2 has given weight loss at two stages. The first one in the region of 80–150 °C with 5% weight loss is due to the physically adsorbed water molecules. The second weight loss between 250 and 400 °C is attributed to the decomposition of the polysaccharide chain. Weight loss of 60%
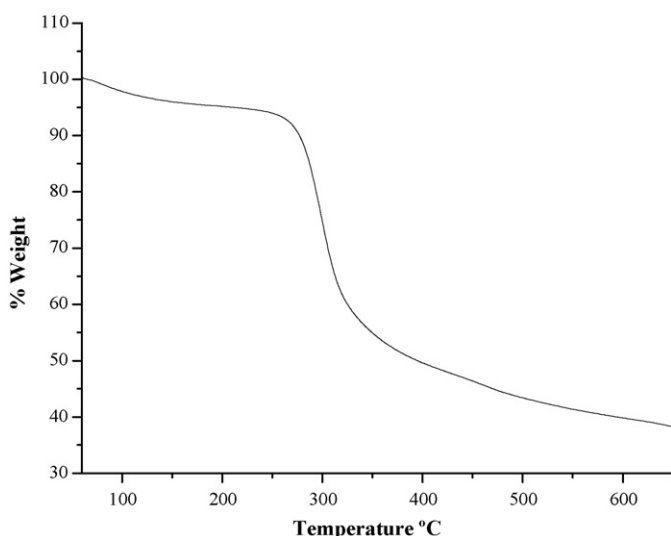

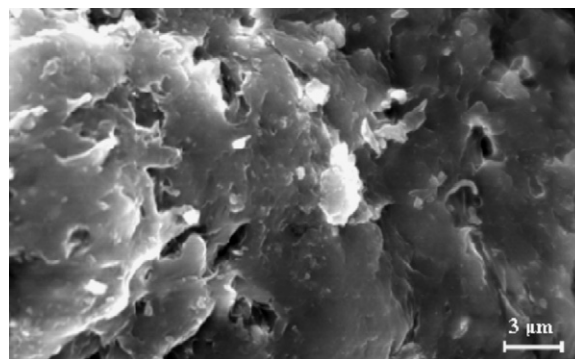**Fig. 2.** TGA profile of the chitosan catalyst.

was observed in the second stage and a stability of the catalyst was observed up to 250 °C. The surface morphology of the catalyst is shown in Fig. 3. From the SEM image it is clear that the catalyst surface has a layered structure with lower surface area which is confirmed by the N$_2$ sorption studies. The BET surface area was found to be 1.04 m^2/g with a pore diameter of 128 Å. The accessible amine group was found to be 45%. The higher percentage of accessible amine group even with lower surface area was due to swelling of the chitosan catalyst. The protic solvent like ethanol acts as a good swelling agent for polysaccharide framework of chitosan [9]. The catalyst swelling leads to availability of more accessible basic sites, i.e., amine in higher percentages. Similar observation was reported by Valentin et al. for chitosan of surface area ≤1 m^2/g and an accessible amine of 27% [9].

3.2. Catalytic activity

Catalytic activity of the catalyst, chitosan, was evaluated for the synthesis of jasminaldehyde by the condensation of 1-heptanal with benzaldehyde. The conversion of 97% with 85% selectivity to jasminaldehyde was obtained within 4 h of reaction at 160 °C. Maximum selectivity of 88% was obtained when the reaction time increased to 8 h. The effect of reaction parameters like 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 conversion and selectivity was studied by varying the catalyst amount from 10 to 400 mg (Table 1). The conversion of heptanal was observed to be 25% with 63% selectivity to jasminaldehyde for a 10 mg amount of the catalyst. The conversion increased to 99% at a 100 mg of the catalyst amount with 84% selectivity to jasminaldehyde. No significant change in the conversion and selectivity was observed on a further increase in the catalyst amount to 200 mg. However a decrease in the conversion of 1-heptanal and selectivity to jasminaldehyde was observed with an increase in the amount of the catalyst to 400 mg. The selectivity to jasminaldehyde was increased with increasing conversion. The conversion is in terms of consumption of 1-heptanal. With increasing conversion the available amount of 1-heptanal will be decreasing. This could be explained on the basis that when the concentration of 1-heptanal is decreased, benzaldehyde competes with 1-heptanal for adsorption, in such a way that it would be possible that the cross-condensation would be favored thereby increasing the selectivity to jasminaldehyde. It can be seen from the time-dependent conversion and selectivity to the products that at shorter time when the conversion was lower (1-heptanal concentration was higher) the selectivity to the self-condensation products was relatively high due to more availability

Table 1
Effect of catalyst amount on the selectivity to jasminaldehyde.

Entry	Catalyst amount (mg)	% conversion			% selectivity					
					Jasminaldehyde			2-Pentyl-non-2-enal		
		2 h	4 h	8 h	2 h	4 h	8 h	2 h	4 h	8 h
1	10	8	13	25	47	54	63	53	46	37
2	30	11	22	40	50	59	64	50	41	36
3	50	22	45	74	70	76	80	30	24	20
4	100	51	79	99	75	78	84	25	22	16
5	150	75	94	100	77	83	87	23	17	13
6	200	82	96	100	79	84	87	21	16	13
7	400	35	63	92	63	74	77	37	26	23

Reaction conditions: heptanal = 7.9 mmol, benzaldehyde = 39.6 mmol, temperature = 140 °C.

Table 2
Effect of reaction temperature on the selectivity to jasminaldehyde.

Entry	Temp (°C)	% conversion			% selectivity					
					Jasminaldehyde			2-Pentyl-non-2-enal		
		2 h	4 h	8 h	2 h	4 h	8 h	2 h	4 h	8 h
1	80	2	3	3	–	–	–	100	100	100
2	100	13	37	72	56	71	78	44	29	22
3	125	43	69	94	72	75	82	28	25	18
4	140	51	79	99	75	78	84	25	22	16
5	160	78	97	>99	80	85	88	20	15	12
6	180	88	98	>99	79	83	85	21	17	15

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

of 1-heptanal, which seems to compete relatively with benzaldehyde.

3.2.2. Effect of reaction temperature

The effect of temperature was investigated in a wide range from 80 to 180 °C by maintaining identical conditions of the other reaction parameters. Both conversion and selectivity were determined with respect to time at 2, 4 and 8 h and the results are listed in Table 2. It was observed that both the conversion of 1-heptanal and selectivity to jasminaldehyde were increased with an increase in the reaction time and temperature. There was an increase up to 160 °C and further increasing the temperature resulted in a decrease in the selectivity. The conversion reached 72% with 78% selectivity to jasminaldehyde at 100 °C (Entry 2) and increased to 94% with 82% selectivity when the temperature was increased to 125 °C (Entry 3). The maximum selectivity was observed at 160 °C with >99% conversion of 1-heptanal. Further increase in temperature to 180 °C, made the selectivity to jasminaldehyde decrease to 85% without change in conversion.

3.2.3. Effect of 1-heptanal to benzaldehyde molar ratio

The effect of the molar ratio of 1-heptanal to benzaldehyde on the conversion and selectivity of the reaction has been investigated in the range of 1:1 to 1:10 at 140 °C and the results are listed in

Table 3. The conversion was found to be increased with time and the conversion reached up to 99% at 8 h and remained the same for the ratios of 1:1 to 1:5 (Entries 1–5). Further increasing the ratio resulted in a decrease in conversion (Entries 6 and 7). The conversion dropped from 99% for the molar ratio of 1:5 to 86% for the molar ratio of 1:10. The increase in benzaldehyde in the reaction mixture will make it difficult for 1-heptanal to find the active sites on the catalyst, which can reduce the conversion at higher benzaldehyde concentration. The 1:1 molar ratio of 1-heptanal to benzaldehyde gave 54% selectivity to jasminaldehyde and increasing the ratio to 1:2 gave 70% selectivity. The selectivity was found to increase by increasing the ratio; the 1:10 ratio gave 86% selectivity. The lower selectivity to jasminaldehyde at lower heptanal to benzaldehyde ratios is due to the self-condensation of heptanal. Therefore the optimum heptanal to benzaldehyde ratio was 1:5, which gave 99% conversion with 84% selectivity.

3.3. Catalyst recycling

In order to observe the recyclability of the catalyst the condensation reaction was performed with 100 mg of the catalyst at 140 °C with two different times 2 and 8 h and the results are given in Table 4. For the fresh catalyst the conversion and selectivity to

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

Entry	H:B	% conversion			% selectivity					
					Jasminaldehyde			2-Pentyl-non-2-enal		
		2 h	4 h	8 h	2 h	4 h	8 h	2 h	4 h	8 h
1	1:1	63	89	99	34	46	54	66	54	46
2	1:2	61	88	99	50	61	70	50	39	30
3	1:3	60	85	99	57	60	76	43	40	24
4	1:4	55	81	99	58	64	78	42	36	22
5	1:5	51	79	99	75	78	84	25	22	16
6	1:7	32	58	95	60	72	85	40	28	15
7	1:10	21	40	86	58	73	86	42	27	14

Reaction conditions: 1-heptanal = 7.9 mmol, catalyst = 100 mg, temperature = 140 °C.

Table 4
Reusability of the catalyst.

Entry	Catalyst recycle	% conversion		% selectivity			
				Jasminaldehyde		2-Pentyl-non-2-enal	
		2 h	8 h	2 h	8 h	2 h	8 h
1	Fresh	51	99	75	84	25	16
2	First recycle	49	98	72	83	28	17
3	Second recycle	48	98	72	83	28	17
4	Third recycle	48	97	71	82	29	18
5	Fourth recycle	47	97	71	80	29	20
6	Fifth recycle	45	95	68	80	32	20

Reaction conditions: heptanal = 7.9 mmol, benzaldehyde = 39.6 mmol, catalyst = 100 mg, temperature = 140 °C.

Table 5
Comparison of the chitosan catalyst with closely related catalyst systems.

Entry	Catalyst	% conversion	Time (h)	Temp (°C)	% selectivity		Ref.
					Jasminaldehyde	2-Pentyl-non-2-enal	
1	Chitosan	94	8	125	82	18	Present work
2	H-Beta	93[a]	6	125	21	43	[13]
3	HY-100	53[a]	16	125	52	28	[13]
4	Al-MCM-41	99[a]	10	125	56	35	[13]
5	ALPO	96	3	125	86	14	[13]
6	Na-ALPO	71	22	125	67	33	[13]
7	Natural talc	58	8	125	56	44	[17]
8	Magnesium organo silicate	99	8	125	80	20	[17]
9	Hydrotalcite [Mg–Al (3.5)][b]	98	8	125	86	14	[16]

[a] Other products are also formed (Ref. [13]).
[b] Hydrotalcite as such.

jasminaldehyde were 51% and 75% respectively for 2 h, and 99% and 84% respectively for 8 h (Entry 1). The fresh catalyst separated by filtration was washed and dried. The catalyst was reused under identical conditions. For 2 h recycling there was a decrease in conversion from 51% to 49% in the first recycle (Entries 1 and 2). The conversion was remained almost the same up to the fourth recycle. The selectivity to jasminaldehyde also remained almost constant up to the fourth recycle. A similar trend was observed for the recycling of the catalyst for 8 h. The catalyst was effectively recycled up to six cycles without much loss in its activity and selectivity.

3.4. Comparison with closely related catalysts for synthesis of jasminaldehyde

It is of interest to have comparative insights into the performance of chitosan as the catalyst for the synthesis of jasminaldehyde with closely related reported catalysts. The present study compared with other catalyst systems (Table 5) indicated that chitosan has a promising potential to catalyze the synthesis of jasminaldehyde. H-Beta and Al-MCM-41 was active with the conversion level higher but was not selective to jasminaldehyde. ALPO and HT-based catalysts were found to achieve the maximum in terms of conversion and selectivity of >96% and 86% respectively. The ALPO catalyst was active and completed the reaction in 3 h. The present chitosan catalyst was comparable with the ALPO and HT-based catalyst, showing 94% conversion and 82% selectivity at 125 °C. Moreover the green nature of the catalyst has the advantage over other catalyst systems and further improvements in the catalyst through green routes are preferable to obtain a green aldol catalyst.

4. Conclusions

The chitosan catalyst has been found to be efficient for the selective synthesis of jasminaldehyde by the condensation of 1-heptanal with benzaldehyde. The catalyst is operative under solvent-free

conditions, giving the highest selectivity to jasminaldehyde 88%, with >99% conversion with the catalyst of 100 mg at 160 °C under optimized reaction conditions. The effect of parameters such as the catalyst amount, temperature, and the 1-heptanal to benzaldehyde ratio has been investigated; the variation of the catalyst amount and temperature have significantly influenced the conversion. Selectivity to jasminaldehyde was enhanced by increasing the catalyst amount and 1-heptanal to benzaldehyde ratio. The catalyst was elegantly separated and effectively reused up to six times. The performance of chitosan catalyst was comparable with the reported systems and the green nature of catalyst had the advantage over those systems.

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