



Amino functionalized chitosan as a catalyst for selective solvent-free self-condensation of linear aldehydes

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ABSTRACT

An aminopropyltrimethoxysilane functionalized chitosan was found to be an efficient solid base catalyst for the self-aldol condensation of linear aldehydes under solvent-free conditions. The modified catalyst was characterized using physical techniques, elemental analysis, FT-IR, and TGA. The modified chitosan was evaluated for the aldol condensation of C₃–C₇ linear aldehydes in which the selective formation was obtained for α,β -unsaturated aldehydes. A decreasing trend in the conversion from propanal to heptanal was observed. Propanal and pentanal were subjected for detail investigations to study the effect of parameters like amount of catalyst and aldehyde, and temperature on the conversion and selectivity. Kinetic performance of the modified chitosan investigated for a representative aldehyde, pentanal showed that the rate was increased with the catalyst amount, pentanal and temperature. The catalyst was reused up to six cycles without significant loss in its activity and selectivity.

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1. Introduction

Aldol condensation is an important reaction in organic synthetic chemistry due to the formation of carbon–carbon bonds during the reaction process. This type of reaction may occur via self-condensation between two of the same aldehyde or ketone molecules or via cross-condensation between two molecules of different aldehydes or ketones [1–3]. Such a reaction usually proceeds over basic or acidic catalysts such as sodium hydroxide or sulfuric acid in the liquid phase. However, the disadvantages of such a process include corrosion, safety hazards, separation procedures, and environmental problems due to the use of sodium hydroxide or sulfuric acid. Therefore, the use of solid bases or acids has drawn increasing interest during the past three decades [4–9]. The solid base catalysts generally used for aldol condensations include MgO [10], hydrotalcites [11,12] and synthetic talc [13].

Self-condensations of aldehydes are important in the view of industrial applications. These products find applications in the fields of pharmaceuticals, fragrances, plasticizers, detergents and cosmetics. The synthesis of 2-ethylhexenal and its hydrogenated product 2-ethylhexanol from self-condensation of butanal find its use in soap, detergent, plasticizers, coatings, adhesives, dioctyl-phthalate and specialty chemical industries [14]. Another

important aldol product is aldol intermediate of pentanal which is commercially important product and finds use in the synthesis of plasticizer and detergent alcohols [15].

The aim of present investigation is to develop a suitable solid base catalyst for aldol condensation of linear aldehydes in solvent-free environment. Chitosan is a polyaminosaccharide, normally obtained by alkaline deacetylation of chitin [16]. Chitosan, even having a large amount of $-\text{NH}_2$ group, is not found to be effective for base catalyzed reactions [17]. The generally used method is to treat with HCl and then to form chitosan beads by adding it into the NaOH solution. It will be a better choice to functionalize the chitosan avoiding the use of acids and alkalis to obtain active base catalyst. Therefore, modified chitosan was synthesized by modification with aminopropyltrimethoxysilane (APTMS), characterized and investigated as solid base catalyst for self-aldol condensation of C₃–C₇ linear aldehydes.

2. Experimental

2.1. Materials

The aldehydes propanal (98%) from Loba chemie, India, butanal (99%) from s.d. Fine Chemicals, India, and pentanal (97%), hexanal (98%), heptanal (95%) from Sigma–Aldrich, USA, were obtained. Toluene (99.5%) was obtained from Fisher Scientific, India. Aminopropyltrimethoxysilane (97%) and chitosan were purchased from Sigma–Aldrich, USA. All the chemicals were used as such.

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2.2. Catalyst synthesis

Amino functionalization of the chitosan was done by treating chitosan with APTMS. In a typical procedure 1.5 g chitosan and 1 g APTMS was taken in 25 ml toluene in a 50 ml round bottom flask (RBF). The RBF was connected with a water condenser and an inert atmosphere was created by nitrogen. The RBF under an inert atmosphere was refluxed in an oil bath at 110 °C. The refluxing was continued for 24 h with stirring at 450 rpm. After 24 h, the flask was cooled to room temperature. The catalyst was filtered, dried at 100 °C and powdered to get the amino functionalized chitosan (CHM).

2.3. Characterization of the catalysts

Fourier transform infrared spectra (FT-IR) were recorded with Perkin-Elmer, GX-FTIR using KBr pellet. Elemental (C, H, N) analysis of chitosan and modified chitosan was carried out with Perkin-Elmer CHNS/O analyzer (Series II, 2400). Thermogravimetric analysis (TGA) was done using Mettler Toledo TGA/SDTA 851e equipment in flowing nitrogen (flow rate, 50 mL/min), at a heating rate of 10 °C/min. N₂ sorption analysis was carried out at 77.4 K in a sorptometer (ASAP 2010, Micromeritics). The sample was degassed at 120 °C for 4 h prior to the sorption analysis.

2.4. Aldol condensation

Weighed amount of aldehyde and catalyst was taken in an oven dried 50 ml double necked round bottom flask. One neck of the flask was fitted with refluxing condenser having spiral tube inside and another neck of the flask was blocked with silicon rubber septum. The top of the refluxing condenser was connected to balloon filled with nitrogen. The entire experimental setup was kept in an oil bath equipped with temperature and agitation speed controlling units. The water at 15 °C was circulated in refluxing condenser throughout the course of reaction from a water chiller at the flow rate of 6 L/min. The reaction was carried out at 100 °C for 8 h. The silicon grease was used in all joints to prevent the vapor loss of reaction mixture and progress of the reaction was monitored in terms of consumption of aldehyde. The analysis of product mixture was carried out by gas chromatography (GC) (Shimadzu 17A, Japan) and GC–MS (mass spectrometer, Shimadzu-QP2010, Japan). The 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 initial column temperature was increased from 40 to 200 °C at the rate of 10 °C/min. Nitrogen gas at a flow rate of 100 mL/min was used as the carrier gas. The temperatures of the injection port and FID were kept constant at 200 °C during the product analysis. The retention times of different compounds were determined by injecting pure compounds under identical GC conditions.

2.5. Kinetics

Kinetic experiments were carried out in an oven dried double necked round bottom flask in which desired amounts of aldehyde and catalyst were taken. The flask was kept in an oil bath having provision for control of temperature and agitation speed. During the course of the reaction aliquots were taken out at different time intervals and the analysis of product mixture was carried out by GC. The kinetics was investigated in detail as a function of temperature and the catalyst amount and aldehyde. To ensure the reproducibility of condensation reaction, repeated experiments were carried out under identical reaction conditions. The results obtained, including conversion and selectivity data were found to be reproducible within 5% variation.

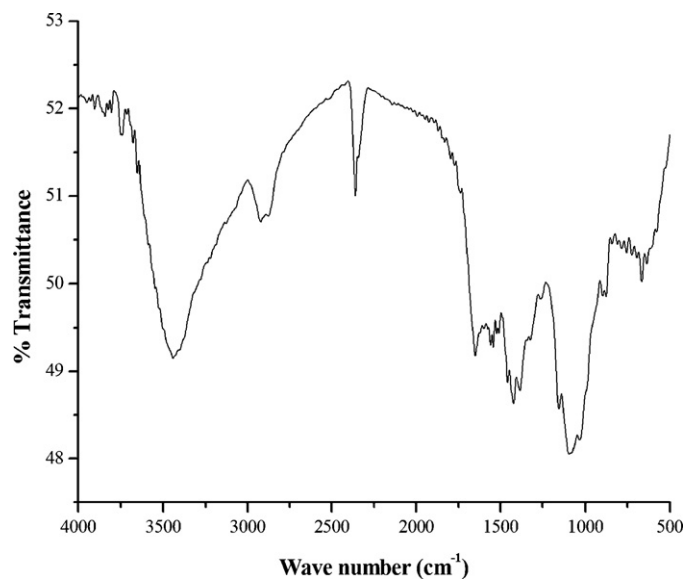


Fig. 1. FT-IR spectrum of CHM.

3. Result and discussion

3.1. Characterization of the catalysts

3.1.1. FT-IR analysis

The FT-IR spectrum of CHM (Fig. 1) showed distinctive absorption band at 1542 cm⁻¹ for –NH₂ bending. The absorption bands at 1154 cm⁻¹ (anti-symmetric stretching of the C–O–C Bridge), 1093 and 1026 cm⁻¹ (skeletal vibration involving the C–O stretching) are characteristics of its saccharide structure [18]. The absorption bands at 3441, 2921 cm⁻¹ are attributed to O–H and methylene (–CH₂) group respectively.

3.1.2. Thermogravimetric analysis

The thermal behavior of CHM is shown in Fig. 2. Chitosan has two main weight losses with one starting at 80 °C and another starting at around 260 °C. The first weight loss of 5% is attributed to the

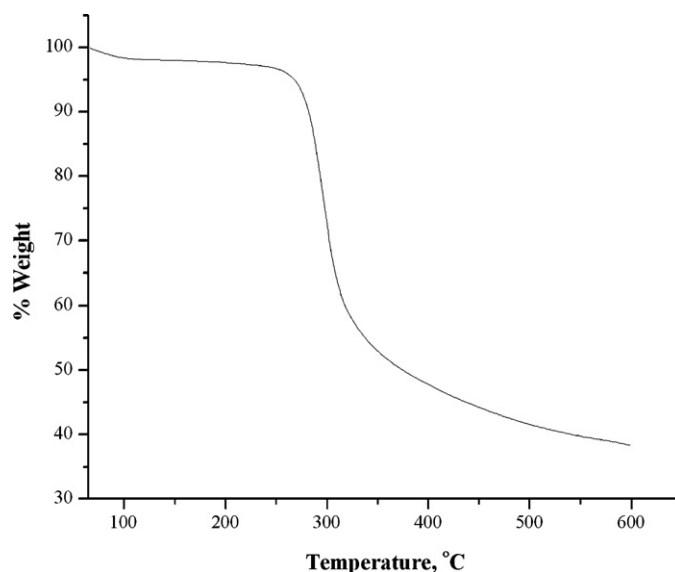
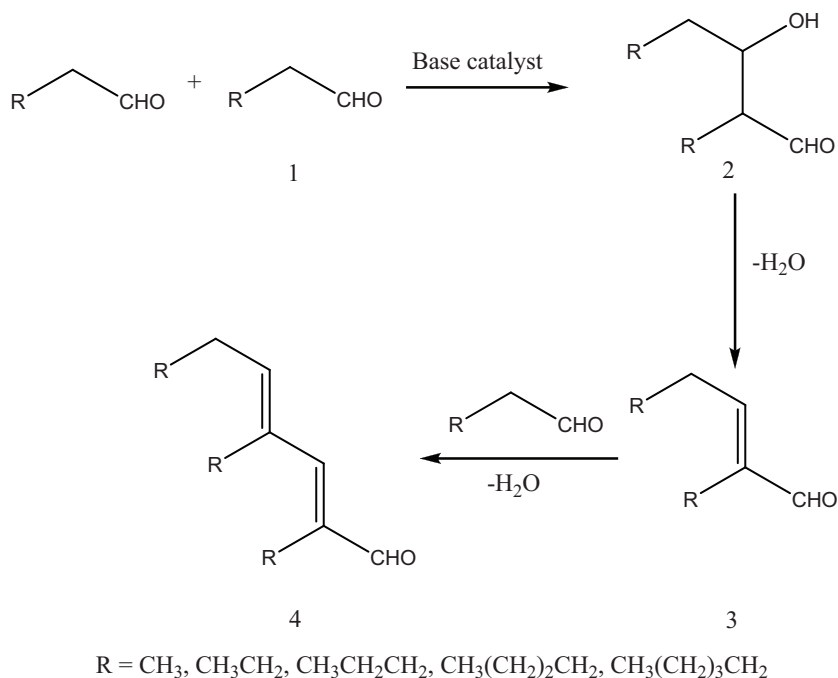


Fig. 2. TGA of CHM.



Scheme 1. Pathways of self-aldol condensation of linear aldehydes.

removal of adsorbed water molecules. The second stage weight loss of 60% is due to the decomposition of polysaccharide chain. Hence the catalyst is thermally stable up to 250 °C.

3.1.3. C, H, N analysis

C, H, N analysis of chitosan and CHM were recorded and found to be: chitosan (C: 39.32, H: 6.55, N: 8.37); CHM (C: 41.04, H: 6.71, N: 10.96). From these results it is clear that the chitosan was functionalized by APTMS.

3.1.4. Surface area and number of accessible amine group

It is known that the chitosan normally has a very low surface area. The surface area was found to be 1.58 m²/g. The number of accessible amino groups on the catalyst was determined by treating 50 mg catalyst. The catalyst (50 mg) was mixed with 3 ml of 0.16 M solution of salicylaldehyde in ethanol with nitrobenzene as GC internal standard. The salicylaldehyde forms salicylidimine Schiff base with the accessible amino group present on the catalyst. The residual salicylaldehyde was calculated by GC from which the accessible amino groups were determined. The percentage amount

of accessible amine group was found to be 32%. The functionalized APTMS and chitosan itself are capable enough to contribute for the observed 32% of accessible amino group. In the modified chitosan, the grafted APTMS will have most of the amino groups exposed on the surface whereas the amino groups of the chitosan itself being in bulk will not have that much exposure. The salicylaldehyde adsorption onto -NH₂ group is done in the presence of ethanol which is a protic solvent. The use of protic solvent ethanol leads to the swelling of polysaccharide framework of chitosan [19,20]. In protic solvents the chitosan swells and the salicylaldehyde can enter into the polymer chain to have access to the bulk amino groups. This resulted in the higher accessible basic sites though the catalyst has lower surface area.

3.2. Catalytic activity

The catalytic activity of CHM was evaluated for self-condensation of linear aldehydes from propanal to heptanal as represented in Scheme 1 and the corresponding results are listed in Table 1. The experiments were carried out in detail with

Table 1
Aldol condensation of linear aldehydes.

Entry	Aldehyde	% conversion with time (h)				% selectivity with time (h)												TOF
						α,β -Unsaturated aldehyde ^a				β -Hydroxy aldehyde ^b				Further aldol product ^c				
		2	4	6	8	2	4	6	8	2	4	6	8	2	4	6	8	
1	Propanal	58 (98)	88	94	98	83 (96)	84	90	94	17 (1)	3	2	–	– (3)	13	8	6	43
2	Butanal	42 (98)	78	90	96	85 (94)	85	92	94	15 (4)	3	–	–	– (2)	12	8	6	39
3	Pentanal	38 (96)	75	89	95	83 (90)	89	94	95	– (7)	–	–	–	17 (3)	11	6	5	39
4	Hexanal	35 (93)	73	88	93	86 (91)	87	92	95	– (5)	–	–	–	14 (4)	13	8	5	37
5	Heptanal	30 (92)	65	82	90	88 (88)	89	93	97	– (7)	–	–	–	12 (5)	11	7	3	33

Reaction conditions: aldehyde = 2.32×10^{-2} mol, catalyst = 50 mg, temperature = 100 °C, rpm = 450. TOF = (mmol of α,β -unsaturated aldehyde/g catalyst/h).

In parenthesis, reaction conditions: aldehyde = 1 g, catalyst = 100 mg, temperature = 100 °C, rpm = 450, time = 1 h.

1 – *2-methyl pentanal, ³3-hydroxy-2-methyl-pentanal, #2,4-dimethyl hepta-2,4-dienal.

2 – *2-ethyl hexenal, ⁵3-hydroxy-2-ethyl-hexenal, #2,4-diethyl octa-2,4-dienal.

3 – *2-propyl heptenal, #2,4-dipropyl nona-2,4-dienal.

4 – *2-butyl octenal, #2,4-dibutyl deca-2,4-dienal.

5 – *2-pentyl nonenal, #2,4-dipentyl undeca-2,4-dienal.

Table 2
Effect of catalyst amount on the condensation of propanal.

Entry	Catalyst amount (mg)	% conversion with time (h)		% selectivity with time (h)						TOF
		4	8	2-Methyl pentenal		3-Hydroxy-2-methyl-pentalal		2,4-Dimethyl hepta-2,4-dienal		
				4	8	4	8	4	8	
1	25	6 (27)	25	36 (39)	45	64 (57)	53	– (4)	2	4
2	50	42 (72)	82	49 (78)	96	50 (19)	2	1 (3)	2	19
3	75	51 (100)	93	64 (86)	83	30 (6)	5	6 (8)	12	20
4	100	78 (100)	95	98 (93)	80	2 (–)	4	– (7)	16	35

Reaction conditions: propanal = 2 g, temperature = 100 °C, rpm = 450.

In parenthesis, reaction conditions: propanal = 1 g, temperature = 100 °C, rpm = 450, time = 2 h. TOF = (mmol of α,β -unsaturated aldehyde/g catalyst/h).

2.32×10^{-2} mol of aldehyde and 50 mg catalyst with time. No reaction was observed when chitosan as such was used. The modified chitosan was found to be an efficient catalyst for the self-aldol condensation with appreciable conversion and selectivity to major formation of α,β -unsaturated aldehyde with a small formation of β -hydroxy aldehyde and further aldol products. A decreasing trend in the conversion from propanal to heptanal was observed. As the reaction time increased to 8 h the conversion reached up to 98% for propanal. It is decreased to 90% for heptanal. The reason for decrease in the conversion with increase in chain length is the larger chain length in which the removal of H^+ ion by the basic catalyst becomes difficult due to the +I effect of alkyl group.

In order to see the effect of lower time and higher catalyst amount, 100 mg catalyst was used for the condensation of 1 g aldehydes for 1 and 2 h reaction times. In 1 h time both the conversion and selectivity to α,β -unsaturated aldehyde were increased (Table 1). On increasing the time for 2 h, the conversion was increased to 100% for all the aldehydes and selectivities for α,β -unsaturated aldehyde for propanal, butanal, pentanal, hexanal and heptanal were 93, 90, 88, 84 and 85% respectively. A comparison of the results of conversion, selectivity and time associated with 100 and 50 mg of the catalyst indicated that both conversion and selectivity were more for 100 mg catalyst in less time. The TOF was calculated in terms of the product α,β -unsaturated aldehyde (mmol of product/g catalyst/h) at 4 h of reaction time. A decreasing trend in the TOF was observed on increasing the chain length. The TOF for propanal was 43 mmol/(g_{cat} h) and dropped to 33 mmol/(g_{cat} h) for heptanal. Propanal and pentanal were investigated in detail to observe the effects of the catalyst amount and aldehyde, and temperature on conversion and selectivity.

3.3. Effect of catalyst amount

The effect of catalyst amount on conversion of propanal and selectivity of 2-methylpentenal was studied by varying the amount of catalyst from 25 to 100 mg at two different amounts of propanal (1 and 2 g) and at 100 °C (Table 2). The conversion was increased with increase in the catalyst amount. The conversion (Entry 1, 8 h) at the low catalyst amount (25 mg) was 25%. The selectivity (Entry

1, 8 h) to 2-methylpentenal and 3-hydroxy-2-methyl-pentalal was 45 and 53% respectively with minor formation (2%) of 2,4-dimethyl hepta-2,4-dienal. The conversion (82%) and selectivity to 2-methylpentenal (96%) were increased (Entry 2, 8 h) with 50 mg catalyst.

On further increasing the amount (Entry 3 and 4, 8 h), the conversion was increased but the selectivity got decreased. The decrease in the selectivity of 2-methylpentenal at higher catalyst amount may be mainly due to the condensation of 2-methylpentenal with propanal to higher condensation product. At lower amount (1 g) of propanal higher conversions were obtained at lower time of 2 h. The conversion (Entry 1) at the low catalyst amount (25 mg) was 27% for 1 g of propanal. The selectivity (Entry 1) to 2-methylpentenal and 3-hydroxy-2-methyl-pentalal was 39 and 57% respectively with minor formation (4%) of 2,4-dimethyl hepta-2,4-dienal. On further increasing the catalyst amount the conversion became 100% and selectivity to 2-methylpentenal was obtained up to 93% with 100 mg (Entry 4) catalyst.

In the studied effect of the catalyst amount on the self-condensation of two different amounts of pentanal (1 and 2 g) given in Table 3, for 1 g pentanal, 51% conversion was obtained with 25 mg (Entry 1) catalyst, which increased up to 100% on increasing the amount of catalyst to 75 mg (Entry 3) at 2 h. For the higher amount of pentanal of 2 g, 80% conversion of pentanal was obtained at 25 mg (Entry 1) catalyst, which increased up to 95% on increasing the amount of catalyst to 50 mg (Entry 2) at 8 h. The TOF showed an increasing trend with the catalyst amount for propanal. For pentanal TOF was initially increased and then got decreased.

The self-condensation is catalyzed by the active basic sites available on the surface of catalyst. As the amount of catalyst decreases, the amount of active basic sites available for condensation reaction on the surface of catalyst also decreases and hence lower conversion was observed at lower catalyst amount. Another possible reason for lower activity of the catalyst is strong adsorption of reactant molecules (or slow diffusion) on the surface of CHM at lower amount of catalyst, which could block the active basic sites present on the surface of catalyst. On increasing the amount the number of the active basic sites increases significantly.

Table 3
Effect of catalyst amount on the condensation of pentanal.

Entry	Catalyst amount (mg)	% conversion with time (h)				% selectivity with time (h)								TOF
		2	4	6	8	2-Propyl heptenal				2,4-Dipropylnona-2,4-dienal				
						2	4	6	8	2	4	6	8	
1	25	18 (51)	30	60	80	92 (82) ^a	94	96	97	8 (1)	6	4	3	34
2	50	38 (91)	75	89	95	83 (86) ^b	89	94	95	17 (5)	11	6	5	41
3	75	49 (100)	80	95	97	85 (85) ^c	94	95	96	15 (10)	6	5	4	31
4	100	59 (100)	92	95	98	94 (84) ^d	97	98	97	6 (11)	3	2	3	27

Reaction conditions: pentanal = 2 g, temperature = 100 °C, rpm = 450.

In parenthesis, reaction conditions: pentanal = 1 g, temperature = 100 °C, rpm = 450, time = 2 h, 3-hydroxy-2-propyl-heptanal was also obtained with ^a17%, ^b9%, ^c5% and ^d5% selectivity.

Table 4
Effect of amount of propanal.

Entry	Amount of propanal (g)	Catalyst/propanal ratio (w/w)	% conversion with time (h)		% selectivity with time (h)						TOF
			4	8	2-Methyl pentanal		3-Hydroxy-2-methyl-pentanal		2,4-Dimethyl hepta-2,4-dienal		
					4	8	4	8	4	8	
1	1	0.050	92	100	93	97	5	–	2	3	40
2	1.5	0.033	81	98	92	99	2	1	6	–	52
3	2	0.025	42	82	49	96	50	2	1	2	19
4	2.5	0.020	47	77	44	95	56	2	–	3	24
5	3	0.017	17	55	46	90	54	10	–	–	11
6	4	0.013	9	14	43	86	57	14	–	–	7

Reaction conditions: catalyst = 50 mg, temperature = 100 °C, rpm = 450.

Table 5
Effect of amount of pentanal.

Entry	Amount of pentanal	Catalyst/pentanal ratio (w/w)	% conversion with time (h)				% selectivity with time (h)								TOF	
			2	4	6	8	2-Propyl heptenal				2,4-Dipropylnona-2,4-dienal					
							2	4	6	8	2	4	6	8		
1	1	0.050	91	95	95	97	86 ^a	96	98	97	97	5	4	2	3	28
2	2	0.025	38	75	89	95	83	89	94	95	95	17	11	6	5	41
3	3	0.017	12	25	34	44	72	69	72	79	79	28	31	28	21	16
4	4	0.013	13	22	31	42	63	71	71	74	74	37	29	29	26	19

Reaction conditions: catalyst = 50 mg, temperature = 100 °C, rpm = 450.

^a 9% 3-hydroxy 2-propylheptanal.

Table 6
Effect of temperature on the condensation of propanal.

Entry	Temperature (°C)	% conversion with time (h)		% selectivity with time (h)						TOF
				2-Methyl pentenal		3-Hydroxy-2-methyl-pentanal		2,4-Dimethyl hepta-2,4-dienal		
		4	8	4	8	4	8	4	8	
1	25	15	28	26	38	74	62	–	–	4
2	60	32	56	34	74	66	26	–	–	10
3	100	42	82	49	96	50	2	1	2	19
4	140	47	89	52	94	45	–	3	6	23
5	160	56	94	55	90	42	–	3	8	29

Reaction conditions: catalyst = 50 mg, propanal = 2 g, rpm = 450.

Table 7
Effect of temperature on the condensation of pentanal.

Entry	Temperature (°C)	% conversion with time (h)				% selectivity with time (h)								TOF
						2-Propyl heptenal				2,4-Dipropylnona-2,4-dienal				
		2	4	6	8	2	4	6	8	2	4	6	8	
1	25	6	8	10	11	89	77	85	87	11	23	15	13	4
2	60	14	41	60	77	81	95	98	98	19	5	2	2	24
3	100	38	75	89	95	83	89	94	95	17	11	6	5	41
4	140	47	92	95	97	91	92	94	94	9	8	6	6	52
5	160	64	96	98	98	92	94	96	97	8	6	4	3	55

Reaction conditions: catalyst = 50 mg, pentanal = 2 g, rpm = 450.

3.4. Effect of amount of aldehyde

Amount of aldehyde has significant effect on the aldol condensation. The results of the variation of the amounts of propanal and pentanal are given in Tables 4 and 5 respectively. At lower amount of propanal (Table 4, Entry 1, 1 g, 8 h) conversion was 100% with 97% selectivity of 2-methylpentenal. On increasing the amount of propanal (Entry 3, 2 g), both conversion (82%) and selectivity of 2-methylpentenal (86%) were decreased following similar decreasing trend on further increasing the amount to 4 g. The conversion and selectivity got increased on increasing the catalyst/propanal ratio. The highest selectivity (99%) was found at the catalyst/propanal ratio of 0.033 (Table 4, Entry 2, 8 h).

With 1 g of pentanal (Table 5, Entry 1), 97% conversion was achieved. On further increasing the amount of pentanal, conversion and selectivity of 2-propylheptenal were decreased. The lower conversion at higher amount of aldehyde is due to the less availability of the active basic sites of the catalyst. On decreasing the ratio of the catalyst/aldehyde the TOF for the substrates propanal and pentanal were firstly increased. On further decreasing the ratio the TOF was decreased.

3.5. Effect of temperature

The effect of temperature was studied in the range of 25–160 °C for the self-condensation of propanal and the results are given in Table 6. With an increase in the temperature the conversion and selectivity to 2-methylpentenal were increased where as the selectivity to 3-hydroxy-2-methyl-pentanal was decreased. At 25 °C (Entry 1) conversion was 28%, on increasing the temperature to 60 °C (Entry 2) conversion increased to 56%. On further increasing the temperature (Entry 4) conversion increased to 94% at 160 °C but selectivity to 2-methylpentenal was decreased. The condensation of lower aldehydes having low boiling points will not get much affected by increasing the temperature which is much above their boiling points. The temperature was much effective only towards the lower temperature of 25–100 °C for propanal. The conversion for 8 h was doubled from 25 (Table 6, Entry 1, 28%) to 60 °C (Table 6, Entry 2, 56%) and became 82% at 100 °C after that on further increasing the temperature the conversion could reach to 94% at 160 °C, indicating that higher temperature is not much influential. On increasing the temperature TOF was increased.

The results of the effect of temperature on the self-condensation of pentanal are given in Table 7. The conversion (Entry 1) of pentanal was increased from 11 to 95% on increasing the temperature from at 25 to 100 °C. The selectivity of 2-propylheptenal was increased up to 100 °C (98%) and after that started decreasing.

3.6. Kinetic studies

In order to have an insight into the kinetic performance of the CHM catalyzed aldol condensation reactions a representative aldehyde, pentanal was subjected for detailed kinetic investigations as the function of temperature, catalyst amount and pentanal. While varying a parameter, other parameters were kept constant under identical conditions. The effects were evaluated in terms of the rates of the decreasing amount of pentanal with time during the reaction. Kinetic profile for the pentanal condensation reaction is shown in Fig. 3. The consumption of pentanal was 55×10^{-4} mol in 1st h and after 1st h to 6th h a regular decrease was observed in which 151×10^{-4} mol was consumed in the next 5 h indicating that the initial rate of consumption was faster. The aldol condensation product 2-propylheptenal, was increased with time and further aldol product 2,4-dipropylnona-2,4-dienal was observed in very low amounts. The rates of condensation were calculated from the consumption of pentanal in moles with time (Fig. 4) from the

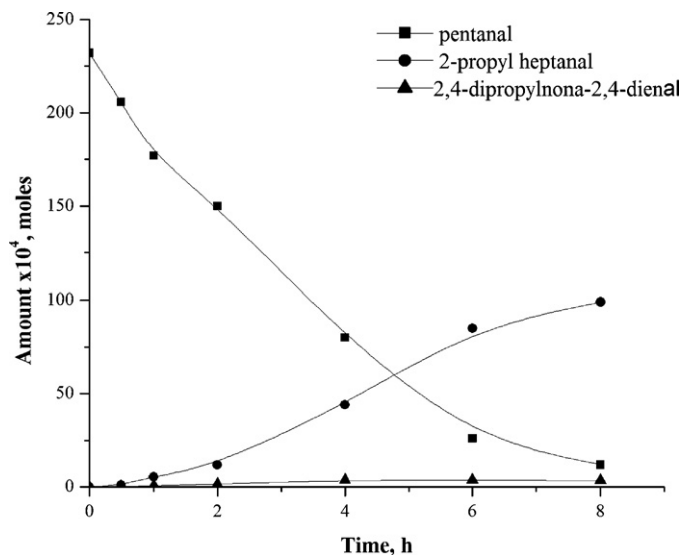


Fig. 3. Kinetic profile for pentanal condensation reaction; pentanal = 2.32×10^{-2} mol, catalyst amount = 50 mg, temperature = 140 °C.

slope of the early linear portion of the decrease in the amount of pentanal. Variation of the catalyst amount (Fig. 5) showed that as the catalyst amount increased, rates were increased, and at higher catalyst amount the reaction rate tended to approach saturation.

The effect of amount of pentanal varied in the range of $1.7\text{--}4.6 \times 10^2$ mol (Fig. 6) indicated that the rates were increased on increasing the amount of pentanal. The effect of reaction temperature shown in Fig. 7 showed that rate was increased with temperature. The rate, 11×10^{-4} mol/min/g_{cat} at 60 °C increased to 20×10^{-4} mol/min/g_{cat} at 100 °C. The rate was increased to 40×10^{-4} mol/min/g_{cat} at 140 °C. The low activity of the catalyst for aldol condensation of pentanal at lower temperature may be due to the strong adsorption of pentanal molecules on the surface of chitosan. Therefore, high temperature is required to avoid this undesirable adsorption which leads to decreased catalytic activity.

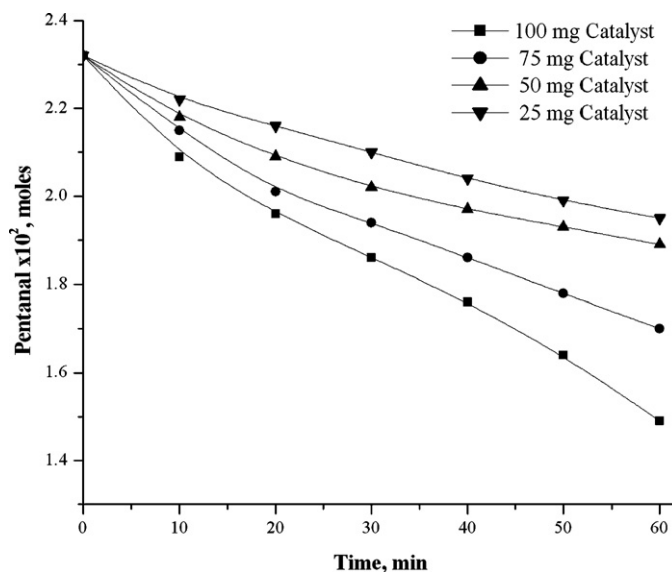


Fig. 4. Plot of decreasing amount of pentanal with time for the variation of catalyst amount; pentanal = 2.32×10^{-2} mol, temperature = 100 °C.

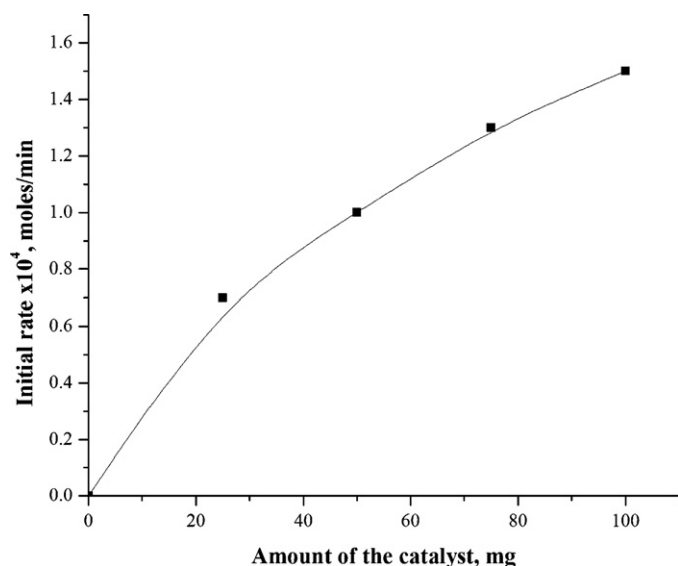


Fig. 5. Dependence of rate on catalyst amount; pentanal = 2.32×10^{-2} mol, temperature = 100°C .

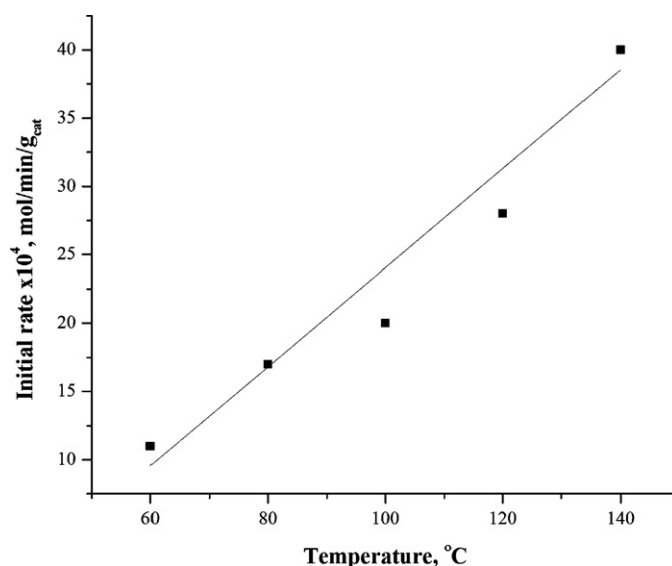


Fig. 7. Dependence of rate on temperature; pentanal = 2.32×10^{-2} mol, catalyst amount = 50 mg.

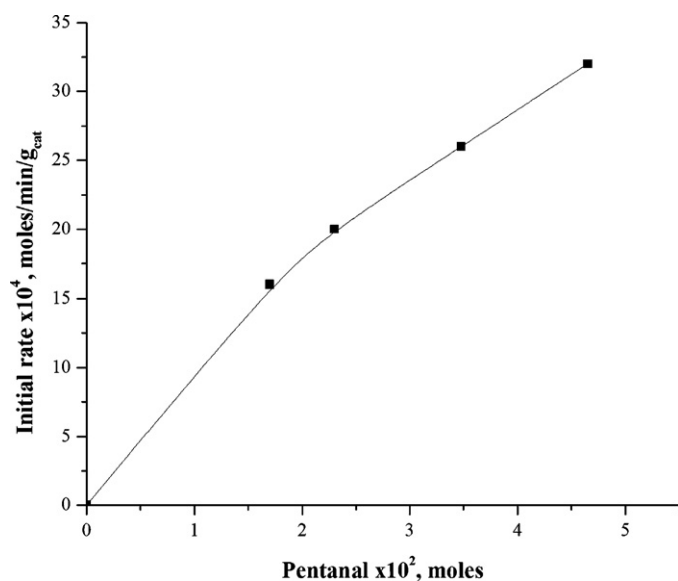


Fig. 6. Dependence of rate on amount of pentanal; catalyst amount = 50 mg, temperature = 100°C .

3.7. Comparison with closely related catalyst systems

It is of interest to have a comparative insight into the performance of the modified chitosan as catalyst with closely related solid base catalyst systems for self-condensation. Table 8 lists the performance of the solid base catalyst systems for self-condensation of propanal, butanal and hexanal. For propanal with CHM, 100% conversion (Entry 1) was achieved in 2 h. In terms of conversion and time the performance of CHM was found to be better than other catalyst systems for propanal (Entries 2–5). For catalyst systems (Entries 2–5) the conversions were less than 100% and also the time taken was 10 h. Among other catalysts (Entries 2–5) hydrotalcite (3.5) activated at 450°C for 4 h was found to be better in terms of conversion (97%) and selectivity (99%) in 10 h. For butanal (Entries 6–8) CHM showed 100% conversion in 2 h at 100°C . The results with $\gamma\text{-Al}_2\text{O}_3$ (Entry 8) is shown at lower temperature 50°C but the conversion is very low (33%) in 2 h. The fixed bed catalyst system $\text{Nb}_2\text{O}_5/\text{SiO}_2$ (Entry 8) showed 51.3% conversion at 150°C . The comparison of CHM (Entry 9) and $\text{NH}_2\text{-FSM}$ (Entry 10) for hexanal showed that 100% conversion was achieved in 2 h by CHM where as $\text{NH}_2\text{-FSM}$ could give 86% conversion at higher temperature 110°C with very long time of 20 h.

Table 8
Comparison of some closely related catalyst systems for aldol condensation.

Entry	Catalyst	Substrate	Time (h)	Temp. ($^\circ\text{C}$)	% conv.	% selectivity		Ref.
						α,β -Unsaturated aldehyde	β -Hydroxy aldehyde	
1	CHM	Propanal	8 (2)	100 (100)	98 (100)	94 (93)	–	Present work
2	Hydrotalcite (3.5) without activation	Propanal	10	100	83	86	9	[21]
3	Hydrotalcite (3.5) activated at $450^\circ\text{C}/4\text{h}$	Propanal	10	100	97	99	0	[21]
4	Magnesium organo silicate	Propanal	10	100	70	82	14	[13]
5	Natural talc	Propanal	10	100	32	99	0	[13]
6	CHM	Butanal	2	100	100	90	2	Present work
7	5.9% $\text{Nb}_2\text{O}_5/\text{SiO}_2$ co-precipitated	Butanal	–	150	51.3	98.5	–	[22]
8	$\gamma\text{-Al}_2\text{O}_3$	Butanal	2	50	33	19.4	58.8	[23]
9	CHM	Hexanal	2	100	100	84	5	Present work
10	$\text{NH}_2\text{-FSM}^a$	Hexanal	20	110	86	70 ^b	–	[3]

^a APTMS functionalized FSM-16.

^b % yield.

Table 9
Reusability of the catalyst.

Run	% conversion	% selectivity		
		2-Methyl pentanal	3-Hydroxy-2-methyl-pentanal	2,4-Dimethyl hepta-2,4-dienal
Fresh catalyst	82	96	2	2
First recycle	82	96	2	2
Second recycle	80	95	3	2
Third recycle	78	94	2	4
Fourth recycle	77	95	2	3
Fifth recycle	75	93	6	1

Reaction conditions: catalyst = 50 mg, propanal = 2 g, temperature = 100 °C, rpm = 450.

3.8. Reusability of catalyst

The spent catalyst was regenerated by washing with toluene. It is then filtered and dried at 100 °C. The regenerated catalyst was again used for the aldol condensation of the propanal under similar conditions. From the data on conversion of propanal and selectivity of 2-methylpentanal given in Table 9 it is observed that the catalyst was reproducible up to six cycles without significant loss in its activity for aldol condensation of propanal. Further more the recycled catalyst was checked for elemental analysis to study the leaching of the APTMS, if any. The obtained results were %C: 43.78, %H: 6.82, %N: 10.59. This confirms the stable functionalization of the CHM and the increase in %C may be attributed to the presence of unreacted adsorbed aldehydes and products. The FT-IR spectrum of recycled catalyst also gave an intense stretch at 1649 cm⁻¹ corresponding to the imine formed by the aldehyde during aldol condensation.

To check for any loss of APTMS from the system the fresh catalyst (CHM) was mixed in toluene and the supernatant solution was separated. In the separated supernatant solution salicylaldehyde was added and the solution was checked by UV–vis spectroscopy in which no peak characteristic to imine was observed indicating that there is no loss of APTMS.

4. Conclusions

Chitosan has been modified using APTMS avoiding the use of HCl and NaOH. The modified chitosan was found to be an efficient catalyst for the self-aldol condensation for linear aldehydes under solvent-free conditions. All the aldehydes selectively gave the desired dehydrated aldol formation as major product. The catalyst evaluated for C₃–C₇ linear aldehydes indicated a decreasing trend in the conversion from propanal to 1-heptanal. The conversions were found to be increased with time. As the reaction time increased to 8 h the conversion reached up to 98% for propanal and 90% for heptanal. With the amount of catalyst of 100 mg and aldehyde 1 g, the conversion was 100% for all aldehydes within 2 h. Kinetic performance of the catalyst investigated for a represen-

tative aldehyde, pentanal significantly depended on the catalyst amount, pentanal and temperature. The catalyst was separated and effectively used up to six cycles under identical employed conditions.

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