



A novel approach for selective cross aldol condensation using reusable NaOH-cationic micellar systems



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ABSTRACT

The efficiency of NaOH-cationic micellar systems was demonstrated for selective cross aldol condensation of benzaldehyde with *n*-heptanal (as model reaction, which involves cross and self condensation reactions) in equimolar amount to synthesize jasminaldehyde (cross product) with high selectivity. In comparison of biphasic reactions in NaOH aqueous solution (in absence of surfactant), the aldol reactions in NaOH-micellar solution were faster and selective to cross product without consumption of NaOH. The reaction rate and jasminaldehyde selectivity was observed to be influenced by surfactant concentration and reaction temperature. The equimolar reaction of both aldehydes in NaOH-cetyltrimethyl ammonium bromide (CTAB: 200 mM) aqueous solution resulted to highest conversion of *n*-heptanal (99%) with 90% selectivity to jasminaldehyde within 4 h. The reusability of NaOH-CTAB system was examined for five reaction cycles.

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1. Introduction

The water being a green solvent has always been the choice of researchers to develop environmental benign route for organic synthesis. There are numerous examples of aqueous organic reactions, in which water promotes the reactions [1]. For instance, water plays crucial role in aqueous organocatalytic aldol reactions, which is one of the most versatile and powerful tool for the construction of new C–C bond [2–10]. It was reported that the water molecules facilitate the aldol reactions by activating the aldehyde molecules transferring a proton through hydrogen bonding to carbonyl oxygen for nucleophilic attack [2,4]. However, the major constrain of water mediated synthesis is the insolubility of most of hydrophobic organic compounds in water [11–15]. Therefore, it is desirable to devise a system having confined hydrophobic environment in water, which can solubilize hydrophobic compounds for catalysis using water soluble catalysts. The surfactant micelles are amphiphilic structures with hydrophobic core and ionic micellar surface, which make the organic substrates compatible with aqueous medium for reactions showing significant enhancement in reaction rate [16]. The use of micelles in catalysis is widespread and has been investigated in detail for different

reactions in aqueous solutions [12,13,16,17]. The micellar systems enable the reactions in aqueous medium by solubilizing the organic compounds (i.e., reactants) and providing a common platform for their interaction with inorganic components (e.g., catalysts). In addition, the localized concentration of reactants and catalytic species, stabilization of ionic intermediates or transition state facilitate the reactions [18]. The micelles also make the reaction selective to desired product by orienting the reactant molecules at interface [19,20]. The surfactant structure and nature (cationic/anionic/nonionic), chain length, head group size, surfactant concentration, electrolytes, organic additives (alcohols), substrate/reactant concentration, substrate structure (hydrophobicity, substituents, etc.), reaction temperature, etc. are the some major factors influencing the micellar catalysis [18].

The homogeneous bases like NaOH, KOH, etc. being highly reactive and less expensive are extensively used in base catalyzed organic reactions [21]. The traditional aldol reactions are generally performed using alkalies like NaOH and KOH in an organic solvent. The basic reagents are good catalysts for the aldol condensation as well as for the side reactions like oxidation and Cannizzaro reaction of aldehydes. Therefore, it is very important to modify the experimental conditions to avoid the competitive reactions [22–25]. The major drawbacks of alkalies as catalyst are their non-recyclability due to either their consumption in reaction (salt formation) or devastation in post reaction workup generating inorganic waste. The efforts making these bases reusable would be highly

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appreciated in order to have environmentally friendly alkali based processes.

The cross aldol condensation, also known as Claisen Schmidt reaction, is an important class of organic reactions for the synthesis of α,β -unsaturated carbonyls (cross aldol products). The cross aldol condensation between two different carbonyls usually results to formation of significant amount of self aldol product, which reduces the yield of cross aldol product. It is of great interest to establish the synthesis methodology for selective synthesis of cross product in cross aldol reactions. Jasminaldehyde (α -pentylcinnamaldehyde) is an α,β -unsaturated aromatic aldehyde, which finds application in perfumery. The 2-*n*-pentyl-2-nonenal is usually formed as a major by-product during the reaction by self condensation of *n*-heptanal, which reduces the yield of jasminaldehyde. The highest selectivity of jasminaldehyde is usually achieved by using high molar amount of benzaldehyde [26–29]. From the industrial point of view, one of the fundamental challenges and ultimate goals for this reaction is the selective synthesis of jasminaldehyde using equimolar amount of benzaldehyde and *n*-heptanal under ambient conditions. In continuation of our work to maximize the selectivity of cross aldol product in aldol condensation reactions, we studied the effectiveness of CTAB micelles-NaOH catalytic system for selective cross condensation of benzaldehyde and *n*-heptanal to jasminaldehyde (cross aldol product). The inorganic base-cationic micellar system has been used in organic synthesis to promote the reactions [30–34], however, its applications to several synthetically useful reactions have been much less explored. For the first time, we have been able to achieve the highest selectivity (~90%) of jasminaldehyde at equimolar aldol reaction of benzaldehyde and *n*-heptanal in aqueous NaOH-CTAB micellar solution at room temperature. Our novel finding is that the use of cationic micelles with homogeneous base (e.g., NaOH) not only improves the efficiency of catalytic system for selective reaction in aqueous medium but it also makes the homogeneous catalyst reusable. This work also discusses the effects of surfactant concentration on cross aldol condensation.

2. Experimental

2.1. Materials

Benzaldehyde (>99%), *n*-heptanal (98%), sodium hydroxide (NaOH; 97%), ethyl acetate (99%), *n*-hexane (99%), concentrated hydrochloric acid (HCl; 35%) and sodium chloride (NaCl; 99%) were purchased from Merck, India. The quaternary ammonium surfactants (QASs) like decyl trimethyl ammonium bromide (98%) was from Spectrochem, India, dodecyl trimethyl ammonium bromide (98%), tetradecyl trimethyl ammonium bromide (98%) and hexadecyl trimethyl ammonium bromide (98%) were from s.d. Fine Chemicals, India and octadecyl trimethyl ammonium bromide (99%) was procured from Sigma Aldich. All the chemicals were used without any further purification. The milli-pore deionized water was used in all the reactions.

2.2. Procedure for biphasic aldol condensation of benzaldehyde and *n*-heptanal in aqueous NaOH solution

The biphasic aldol reaction of benzaldehyde (**1**) and *n*-heptanal (**2**) was carried out in aqueous NaOH solution (Scheme 1). The 10 mL deionized water was taken in a 50 mL reaction tube of reaction station (12 Place Heated Carousel Reaction Station, RR99030, Radleys Discovery Technologies, UK) and a mixture of benzaldehyde (5 mmol) and *n*-heptanal (5 mmol) was added under stirring (at 700 rpm). The NaOH (5 mmol) was dissolved in the biphasic mixture and the reaction mixture was stirred at 30 °C for the required period of time (4–72 h). After completion of reaction, the reaction

mixture was neutralized with concentrated HCl. The organic phase was extracted with ethyl acetate (10 mL) and was analyzed by gas chromatography (Agilent 7890A) having a HP-5 (60 m, 250 μ m diameter) capillary column with a programmed oven temperature from 50 to 280 °C, at 1 mL min⁻¹ flow rate of N₂ as carrier gas and FID detector. The conversion of *n*-heptanal was calculated on the basis of its weight percent as follows,

$$\text{Conversion (wt.\% of } n\text{-heptanal)} = 100 \times \frac{[\text{Initial wt.\% of } n\text{-heptanal} - \text{Final wt.\% of } n\text{-heptanal}]}{\text{Initial wt.\% of } n\text{-heptanal}}$$

The selectivity of the jasminaldehyde was calculated as below,

$$\text{Selectivity (\% of jasminaldehyde)} = 100 \times \frac{(\text{GC peak area\% of jasminaldehyde})}{\sum \text{Total peak area for all the products}}$$

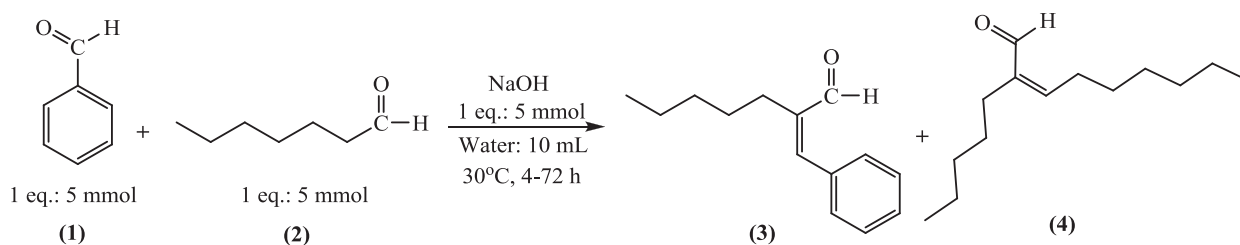
The products formed in the reactions were characterized by GC-MS analysis and the data were matched with those reported in the literature. GC-MS analysis was carried out using gas chromatograph mass spectrometer (Agilent 5975 GC/MSD with 7890A GC system) having HP-5 capillary column of 60 m length and 250 μ m diameter with a programmed oven temperature from 50 to 280 °C, at 1 mL min⁻¹ flow rate of He as carrier gas and ion source at 230 °C.

In order to recover the spent NaOH solution and to examine the reusability in next reaction cycle, the biphasic reaction was carried out in another set under similar condition for 72 h. After the completion of reaction, the stirring was stopped and the reaction mixture was allowed to stand for 10 min for phase separation. The aqueous phase (the bottom phase) was completely separated by using a separating funnel and the obtained spent NaOH solution was reused in next reaction cycle. In the spent NaOH solution, the mixture of benzaldehyde (5 mmol) and *n*-heptanal (5 mmol) was added under stirring (700 rpm) and the reaction was carried out at 30 °C for 72 h to test the reusability. After completion of reaction, the reaction mixture was worked up and analyzed as previously described.

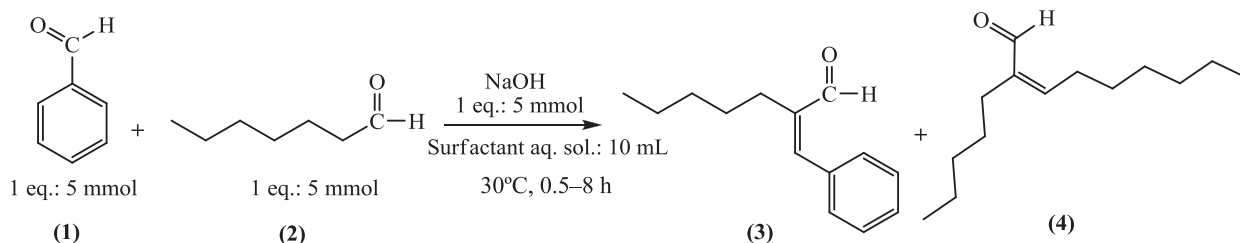
2.3. A typical procedure for aldol condensation of benzaldehyde and *n*-heptanal in NaOH-cationic surfactant micellar solution

The aldol condensation of benzaldehyde (**1**) and *n*-heptanal (**2**) in NaOH-surfactant aqueous solution was carried out under similar reaction condition (Scheme 2). In the reaction tube, 10 mL of surfactant aqueous solution was taken and a mixture of benzaldehyde (5 mmol) and *n*-heptanal (5 mmol) was added in the solution under stirring. The NaOH (5 mmol) was dissolved in the solution and the reaction mixture was stirred at 30 °C for the required period of time (0.5–8 h). After the completion of reaction, the reaction mixture was neutralized with concentrated HCl and excess of saturated NaCl solution was added to reduce the surfactant concentration below the cmc. The organic phase was extracted with ethyl acetate (10 mL) and was analyzed by gas chromatography.

To recover the surfactant-NaOH aqueous solution after the completion of reaction, the stirring of reaction mixture was stopped and the solution was allowed to stand for 10 min for phase separation. The micellar solution (from the bottom) was separated by using a separating funnel and the surfactant-NaOH solution was reused for 1st cycle. In spent surfactant-NaOH solution, the mixture of benzaldehyde (5 mmol) and *n*-heptanal (5 mmol) was added under stirring (700 rpm) and the reaction was further carried out at 30 °C for 4 h. The reaction mixture was worked up as previously described. For 2nd and subsequent reaction cycles, the



Scheme 1. Biphasic aldol condensation of benzaldehyde (1) and *n*-heptanal (2) in aqueous NaOH solution.



Scheme 2. Aldol condensation of benzaldehyde (1) and *n*-heptanal (2) in NaOH-cationic surfactant solution.

spent surfactant–NaOH solution was obtained by phase separation of reaction mixture of previous cycle.

3. Results and discussion

3.1. Biphasic reaction of benzaldehyde and *n*-heptanal in aq. NaOH solution

The biphasic aldol condensation of benzaldehyde and *n*-heptanal in aq. NaOH solution (pH: 13.7) took 72 h to achieve 92% conversion of *n*-heptanal into cross (3; 90%) and self (4; 2%) aldol products (Table 1). The benzoic acid and *n*-heptanoic acid were the byproducts in this reaction, which were probably formed by oxidation of benzaldehyde and *n*-heptanal, respectively. The pH of spent NaOH solution was found to be decreased from 13.7 to 13.3 and this may be due to neutralization of some fraction of NaOH with organic acids forming their respective salts. The reaction with spent NaOH solution (entry 5) gave almost similar conversion, but reduced the selectivity of cross product (3; 69%), and substantial amount of acids (14% benzoic acid and 15% *n*-heptanoic acid) was found in the reaction mixture. The pH of spent NaOH solution was also dropped from 13.3 to 13. The results of biphasic aldol reaction in aq. NaOH indicated that the reaction was slow but selective toward cross condensation, but with progress of reaction, formation of acid byproducts reduced the cross product selectivity and strength, and therefore activity of spent NaOH solution.

Table 1
Conversion and products selectivity in biphasic aldol condensation of benzaldehyde and *n*-heptanal in aq. NaOH.^a

Entry	Reaction time (h)	<i>n</i> -heptanal conv. (wt.%)	Selectivity (%) of		
			(3)	(4)	Others
1	4	53	94	6	–
2	24	82	91	2	1 ^b , 6 ^c
3	48	87	91	2	1 ^b , 6 ^c
4	72	92	90	2	2 ^b , 6 ^c
5 (reuse)	72	91	69	2	14 ^b , 15 ^c

^a 5 mmol (0.53 g) benzaldehyde, 5 mmol (0.57 g) *n*-heptanal, 5 mmol (0.2 g) NaOH, 10 mL water, 30 °C.

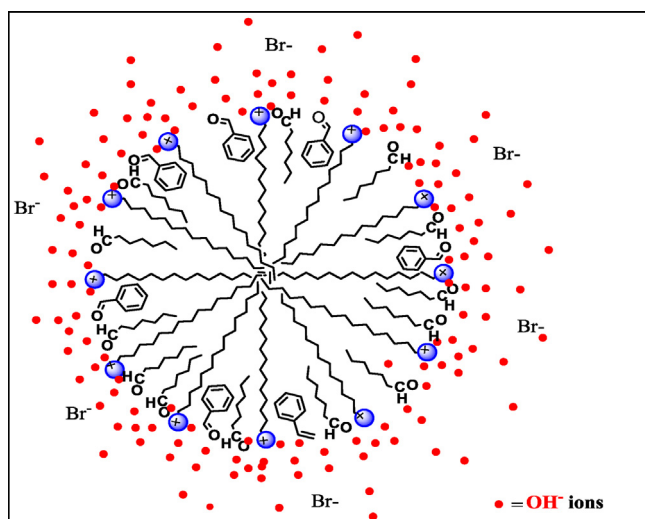
^b Benzoic acid.

^c Heptanoic acid.

The slow reaction in biphasic system may be attributed to less interfacial area (water-organic phase) available for interaction between reactants (1 and 2) and catalyst (OH^-) taking long reaction time to achieve highest conversion. The benzaldehyde being more polar than *n*-heptanal will be significantly available at interface as compared to *n*-heptanal, therefore the probability of interaction of carbanions of *n*-heptanal, produced at the interface, with benzaldehyde molecules will be more giving high selectivity of cross product (i.e., jasminaldehyde). The less availability of *n*-heptanal at water–oil interface will produce less carbanions for reaction with benzaldehyde slowing down the reaction rate. The biphasic system favors the cross condensation giving high selectivity of cross product in aldol reaction, but the slow reaction rate, formation of acid byproducts and reduced activity or non-reusability of spent NaOH solution are the major drawbacks of the biphasic aldol reaction. Therefore, it would be promising to fabricate the aqueous system compatible for aldehyde reactants facilitating the reactions selectively with faster rate and avoiding the side reactions (i.e., oxidation of aldehydes) to have a reusable catalytic system.

3.2. Aldol condensation of benzaldehyde and *n*-heptanal in NaOH-surfactant micellar solutions

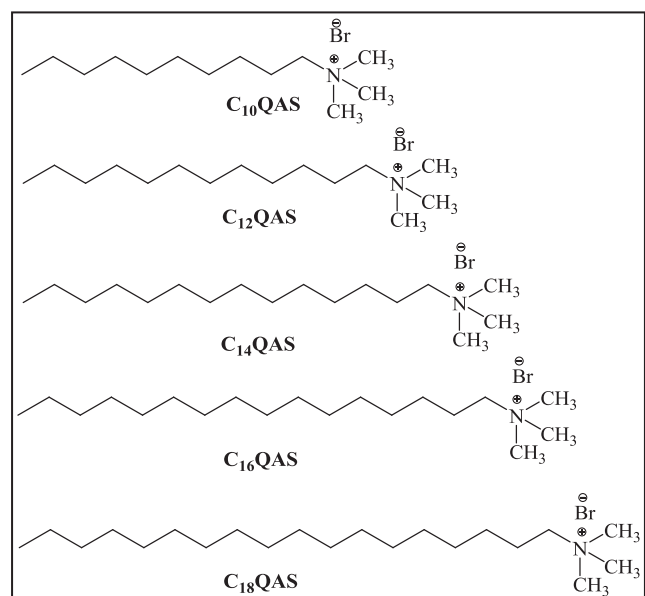
The attractive features, particularly amphiphilic nature, of surfactant micelles were utilized to carry out the cross aldol reaction in water with faster rate and high cross product selectivity. As the reaction involves the participation of OH^- ions, the quaternary ammonium surfactants (QASs; cationic surfactants) were employed to have positively charged micelles in water. The QASs are positively charged (independent of the pH of their solution) polyatomic ions of the structure NR_4^+ , having an R as long chain alkyl group and with an anion (usually a halide). The QASs in aqueous solution will produce positively charged micelles, which can solubilize the reactants within the micelles and concentrate the OH^- ions on positively charged micellar surface (Scheme 3). As the surfactant chain length and concentration are the major parameters influencing the catalytic property of micellar systems [18], the chain length of alkyl group (i.e., hydrophobicity) and concentration of QASs were varied to study their effect on catalytic activity of the QAS–NaOH system.



Scheme 3. Positively charged micelles of QASs having solubilized reactants within the micelles and surface OH⁻ ions.

3.2.1. Aldol condensation of benzaldehyde and *n*-heptanal in different QASs micellar solutions

The QASs (given in Scheme 4) like decyl trimethyl ammonium bromide (C₁₀QAS), dodecyl trimethyl ammonium bromide (C₁₂QAS), tetradecyl trimethyl ammonium bromide (C₁₄QAS), hexadecyl trimethyl ammonium bromide (C₁₆QAS) and octadecyl trimethyl ammonium bromide (C₁₈QAS) were studied to evaluate the potential of NaOH-QASs micellar systems for equimolar aldol reaction of benzaldehyde and *n*-heptanal in water. The reactions were carried out in 15 mM QASs solution in water. The reaction of benzaldehyde and *n*-heptanal in aqueous solution of NaOH-QASs (Fig. 1) gave remarkably higher conversion of *n*-heptanal (97–98% after 4 h) than biphasic reaction (53% conversion), however the selectivity for cross product was lesser (78–84%) than biphasic reaction (94%). The exciting observation was that with NaOH-QASs the same conversion and jasminaldehyde selectivity could be achieved in 3 h instead of 72 h reaction in biphasic condition. Furthermore, unlike biphasic reaction no acid byproducts were formed



Scheme 4. QASs used in aldol reaction of benzaldehyde and *n*-heptanal in NaOH-QASs micellar solutions.

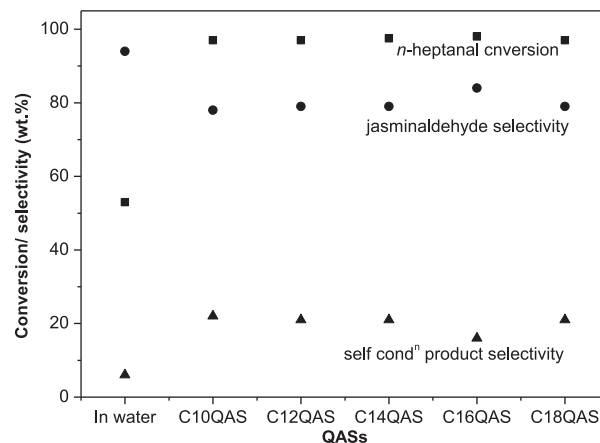


Fig. 1. *n*-heptanal conversion and products selectivity in aldol condensation of benzaldehyde and *n*-heptanal in NaOH-QASs micellar solutions of different QASs [5 mmol (0.53 g) benzaldehyde, 5 mmol (0.57 g) *n*-heptanal, 5 mmol (0.2 g) NaOH, 10 mL QASs aqueous solution (15 mM), 30 °C, 4 h].

in NaOH-QASs system showing that the micellar system avoids the oxidation of aldehydes during aldol reaction. The presence of QASs micelles made the reaction faster showing enhanced interaction of *n*-heptanal molecules with OH⁻ ions by increasing the interfacial area. The positively charged micelles will attract the OH⁻ ions increasing the pH of the micellar surface than the bulk solution [35]. The micelles will also concentrate the reactants by solubilizing in micelles in required orientation. The high pH at micellar surface will enhance OH⁻ ions availability at interface to produce more carbanions from *n*-heptanal to react with benzaldehyde. It was found that the C₁₆QAS micelles (i.e., cetyl trimethyl ammonium bromide: CTAB) gave slightly higher cross product selectivity; therefore the detail study was carried out with CTAB micellar solutions.

3.2.2. Aldol condensation of benzaldehyde and *n*-heptanal in NaOH-CTAB micellar solutions

The reactions in NaOH-CTAB micellar solutions of different CTAB concentrations (cmc to 300 mM) resulted to 74–98% conversion of *n*-heptanal with 76–90% selectivity to cross product within 4 h (Table 2). In comparison of reaction in water, the significant enhancement in *n*-heptanal conversion was observed at cmc and above cmc, i.e., at 10 mM concentration of CTAB. It indicates that by increasing the number of micelles (i.e., with increasing CTAB concentration), the reaction becomes faster due to increasing interfacial area. The CTAB concentration also influenced the cross product selectivity. With increasing the CTAB concentration

Table 2
n-heptanal conversion and products selectivity in aldol condensation of benzaldehyde and *n*-heptanal in NaOH-CTAB micellar solutions of different CTAB concentrations.^a

CTAB conc. (mM)	Conv. of <i>n</i> -heptanal (wt.%)	Selectivity (%) of	
		3	4
In water	53	94	6
1 (i.e. cmc)	74	74	26
10	96	76	24
15	98	84	16
25	98	84	16
50	98	86	14
100	98	86	14
150	98	87	13
200	99	90	10
250	98	88	12
300	96	82	18

^a 5 mmol (0.53 g) benzaldehyde, 5 mmol (0.57 g) *n*-heptanal, 5 mmol (0.2 g) NaOH, 10 mL aqueous CTAB solution, 30 °C, 4 h.

Table 3
Effect of reaction temperature on cross aldol condensation of benzaldehyde and *n*-heptanal in aq. CTAB micellar medium.^a

Reaction temperature (°C)	15 mM CTAB			200 mM CTAB		
	<i>n</i> -heptanal conv. (wt.%)	Selectivity (%)		<i>n</i> -heptanal conv. (wt.%)	Selectivity (%)	
		3	4		3	4
10	96	85	15	99	90	10
20	96	84	16	99	90	10
30	98	84	16	99	90	10
60	97	75	25	99	85	15

^a 5 mmol (0.53 g) benzaldehyde, 5 mmol (0.57 g) *n*-heptanal, 5 mmol (0.2 g) NaOH, 10 mL aqueous CTAB solution, 4 h.

Table 4
Comparison of reaction conditions and catalytic activity of NaOH-CTAB micellar system and other catalyst systems for cross aldol condensation of benzaldehyde and *n*-heptanal.

Sr. no.	Catalyst	Reaction conditions			% conversion	Jasmin-aldehyde % selectivity	Ref.
		Benzaldehyde/ <i>n</i> -heptanal molar ratio	Temp. (°C)	Time (h)			
1	Sulfated zinc ferrite	5	150	12	95	68	[37]
2	TBD	4	60	2	97	84	[38]
3	Mg Organosilicate	10	125	8	99	80	[27]
		7			99	79	
4	HT (Mg/Al = 3.5)	10	125	8	98	86	[28]
		7			98	85	
5	Chitosan	10	140	8	95	85	[29]
		7			86	86	
6	Natural talc	5	125	8	58	56	[27]
7	ALPO	5	125	3	96	86	[26]
8	Zeolite HY-100	5	125	16	53	52	[26]
9	TiO ₂ /Chitosan aerogels	5	80	4	98	86	[39]
10	DBU-H ₂ O	4.4	60	6	71	31	[38]
11	Reconstructed HT	10	130	4	98	87	[40]
		7			98	84	
12	Na-ALPO	5	125	22	71	67	[26]
13	Al-MCM-41	5	125	10	99	56	[26]
14	Zeolite H-Beta	5	125	6	93	21	[26]
15	SFS	6	100	2	84	92	[41]
16	NaOH-CTAB micellar system	1	Room temp.	4	99	90	Present work ^a

TBD: Triazabicyclodecene (1,5,7-triazabicyclo[4.4.0]dec-5-ene); HT: Hydrotalcite; ALPO: Amorphous aluminophosphate; DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene; SFS: Silica functionalized with sulfonic acid.

^a 5 mmol (0.53 g) benzaldehyde, 5 mmol (0.57 g) *n*-heptanal, 5 mmol (0.2 g) catalyst, CTAB aq. Solution (200 mM) room temp. (30 °C), 4 h.

from cmc to 200 mM, the selectivity of cross product gradually increased from 76% to 90% and above 200 mM (i.e., at 250 mM and 300 mM), the cross product selectivity was slightly reduced (88% and 82%, respectively). The successive increase in cross product selectivity with increasing CTAB concentration may be attributed to decrease in the number of *n*-heptanal molecules in the micelles due to increasing number of micelles in unit volume. This will reduce the probability of self condensation reaction of *n*-heptanal in the micelles increasing the selectivity toward cross product. The surface OH⁻ ions concentration may be reduced at higher CTAB concentration (above 250 mM), which seems to be responsible for decrease in the cross product selectivity at higher CTAB concentration. This was observed that on reducing the NaOH amount in the micellar aldol reactions at a particular concentration of CTAB (15 mM or 200 mM), the conversion and cross product selectivity decreases (see ESI Table S2). The effect of reaction temperature on micellar mediated reaction was studied in the temperature range of 10–60 °C at 15 mM or 200 mM concentration of CTAB (Table 3). The conversion of *n*-heptanal remained unchanged with temperature from 10 °C to 60 °C giving 96–99% conversion, while the selectivity of cross product decreased at 60 °C. This indicates that high temperature promotes self condensation. It is usually observed that the selectivity of cross product decreases at high temperature [27,28,36], which has been explained to be attributed to lower activation energy of cross condensation than that of self condensation in aldol reaction of benzaldehyde and *n*-heptanal with HMS supported Mg–Al mixed oxide [36].

The conversion and jasminaldehyde selectivity reported with various catalysts are listed in Table 4. It shows that with all reported catalysts the highest selectivity of jasminaldehyde could be achieved by using excess of benzaldehyde (4–10 times more molar quantity of benzaldehyde) and at high temperature (60–150 °C). It is evident from the table that NaOH-CTAB micellar catalytic system gave highest selectivity of jasminaldehyde (90%) using equimolar ratio of reactants at room temperature showing the potential of NaOH-CTAB micellar systems for cross condensation reactions.

3.3. Reuse study of spent NaOH-CTAB micellar solution

It was observed that in the reactions, which were carried out using 15 mM or <15 mM CTAB solution, the products completely separate out at the top of solution after completion of reaction giving transparent aqueous phase (Fig. 2). But the reaction mixture containing higher CTAB amount (above 15 mM), the products remained dissolved in micellar solution and therefore, the products were isolated from reaction mixture by diluting with water followed by extraction with ethyl acetate. It would be desirable to have the reaction system with easier product separation from the reaction mixture and to reuse the spent alkali-micellar solution; therefore, the reuse study was performed with 15 mM CTAB solution. The spent NaOH-CTAB solution was used for consecutive five reaction cycles under similar reaction condition. The product mixture separated out at the top of solution was removed by the use of syringe/micropipette and the remaining aqueous solution was used

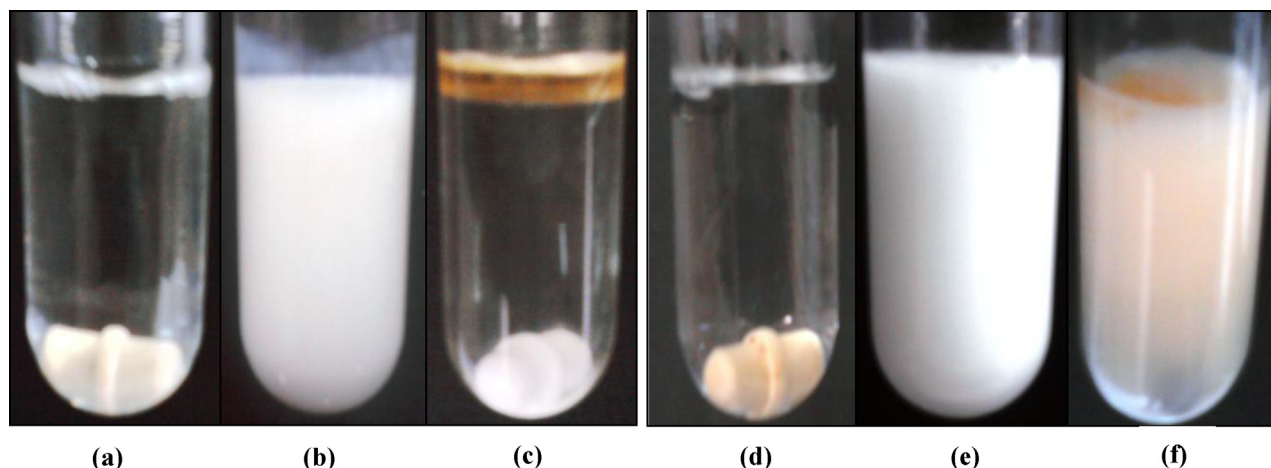


Fig. 2. (a) 15 mM CTAB aq. micellar solution before addition of reactants, (b) 15 mM CTAB aq. micellar solution after addition of reactants, (c) 15 mM CTAB aq. micellar solution after reaction (products separate out at the top after reaction), (d) 200 mM CTAB aq. micellar solution before addition of reactants, (e) 200 mM CTAB aq. micellar solution after addition of reactants and (f) 200 mM CTAB aq. micellar solution after reaction (products do not separate out after reaction).

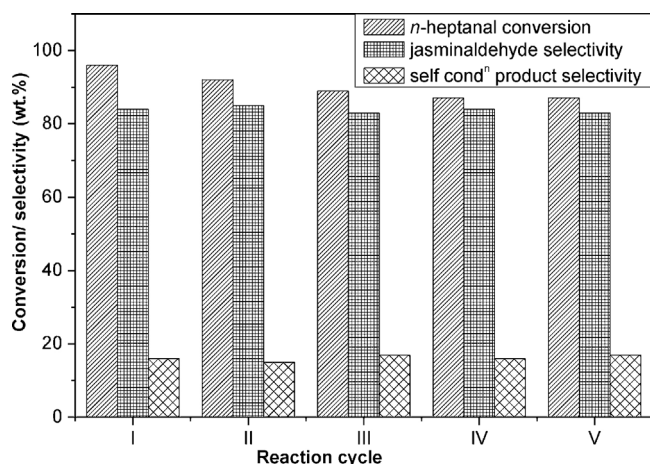


Fig. 3. Recycle of spent NaOH-CTAB micellar solution [5 mmol (0.53 g) benzaldehyde, 5 mmol (0.57 g) *n*-heptanal, 5 mmol (0.2 g), NaOH 10 mL aq. CTAB solution (15 mM), room temp. (30 °C), 4 h].

for next cycle. There was gradual decrease in conversion from 96% to 87% while the selectivity of jasminaldehyde remained unaffected showing no byproducts formation with time (Fig. 3). The possible reason for the decreasing conversion of *n*-heptanal may be due to either presence of unreacted reactants from previous reaction or loss of some NaOH/surfactant amount during product separation. However, the final pH of the solution was not much changed indicating the stability of NaOH-CTAB micellar system and no oxidation of aldehydes to acids.

4. Conclusions

The NaOH-cationic micellar solutions are effective catalytic systems for selective cross aldol condensation of benzaldehyde with *n*-heptanal in equimolar amount to synthesize jasminaldehyde (cross product) with high selectivity. The aldol reactions in NaOH-micellar solution are faster and selective to cross product without consumption of NaOH and formation of acid byproducts. The aldol reactions in NaOH-cationic micellar solutions are influenced by surfactants concentration and reaction temperature. The reusability of NaOH-CTAB system is possible. The significant features of this methodology include faster rate of conversion with high selectivity to cross product, ease of product separation, ambient reaction

conditions for reactions and reusability of catalytic system. The use of micellar system could be explored for carrying out fast and selective organic synthesis using greener route.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2013.06.015>.

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