Simple and efficient synthesis of jasminaldehyde over modified forms of zirconia: Acid-base bifunctional catalysis

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The synthesis of jasminaldehyde over zirconia based acid-base bifunctional catalysts has beem reported. Solid catalysts such as zirconia, ceria and ceria-zirconia have been prepared and characterized for their physico-chemical properties such as surface area, surface acidity, surface basicity, crystalinity, functionality and elemental analysis by using techniques such as BET, NH_3-TPD, CO_2-TPD, PXRD, FT-IR and ICP-AES. The solid catalysts are evaluated in the aldol condensation of benzaldehyde and 1-heptanal to synthesize jasminaldehyde. Reaction conditions such nature of the catalyst, weight of the catalyst, molar ratio of the reactants, reaction temperature and reaction time have been studied to get a set of optimized reaction conditions under which highest possible yield of jasminaldehyde could be obtained. Reactivation and reusability of these solid catalysts is also studied. Ceria-Zirconia mixed oxide is found to be highly active and efficient bifunctional catalyst for the selective synthesis of jasminaldehyde. This catalyst is found to be reusable atleast for 6 reaction cycles without much loss of its catalytic activity.

Jasminaldehyde (α-n-pentylcinnamaldehyde) is an industrially important fine chemical with a plenty of applications in flavor, fragrance as well as in pharmaceuticals. A major drawback in the synthesis of jasminaldehyde is the formation of 2-*n*-pentyl-2-*n*-nonenal as a by-product which reduces the selectivity of jasminaldehyde. Generally, jasminaldehyde is synthesized by the aldol condensation of benzaldehyde with 1-heptanal catalyzed by homogenous bases such as KOH or NaOH[1,2]. Keeping in view the disadvantages associated with homogenous catalysts, a lot of research is going on throughout the world to replace such catalysts with more advantageous heterogenous solid catalysts for fine chemical synthesis. The synthesis of jasminaldehyde *via* aldol condensation could be carried out over acid or base catalysts. A few reports are available in the literature for the synthesis of jasminaldehyde over heterogenous solid acid catalysts such as zeolites, mesoporous aluminophosphates (AlP), amorphous aluminophosphates, silica-alumina as well as solid base catalysts like Mg-organosilicates, Mg-Al mixed oxides, etc[3-6]. It is reported that the selective synthesis of jasminaldehyde could be achieved over base catalysts rather than over acid catalysts[3]. Some reports are also available on the application of an acid-base functional catalysts such as hydrotalcite supported on silica and amorphous AlPs for this reaction wherein acid sites of the catalyst will be utilized to protonate carbonyl group of benzaldehyde and the basic sites are used to generate enolate 1-heptanal intermediate[3,6]. Such bifunctional catalysts were found to produce jasminaldehyde in good yield with high selectivity.

Among various heterogenous catalysts, metal oxides such as zirconia (ZrO_2) and ceria (CeO_2) have played a vital role as either catalyst supports or as catalysts by themselves in the field of organic fine chemical synthesis[7,8]. These oxides are amphoteric in nature i.e., they consist of both acidic as well as basic sites. Further, the acid-base and redox properties of these individual metal oxides can be enhanced by mixing them into a form of mixed oxide i.e., ceria-zirconia[9,10]. Ceria-zirconia is a versatile mixed oxide catalyst which has been used in various industrially important reactions such as condensation of anilines[11], nitration[12], oxidation[13], etc.We have reported the application of ceria-zirconia as a bifunctional catalyst in the synthesis of biodiesel[14]. Even though some work has been reported in the application of ceria-zirconia as a solid acid catalyst, its use as acid-basebifunctional catalyst is less explored.

In the present article, keeping in view the importance of ceria-zirconia based bifunctional catalysts and the importance of jasminaldehyde; the authors have made an attempt to report the research work pertaining to the synthesis of zirconia, ceria and ceria-zirconia as catalysts. These catalysts were characterized for their surface area, surface acidity, surface basicity, crystalinity, functionality and elemental analysis. The catalytic activity of ceria-

zirconia was measured in the aldol condensation of benzaldehyde and 1-heptanal by varying the reactions conditions such as the nature of the catalyst, weight of the catalyst, molar ratio of the reactants, reaction temperature and reaction time. This catalytic material was reactivated and reused at least for 6 reaction cycles.

Experimental Section

The raw materials such as zirconyl nitrate, ceric ammonium nitrate, benzaldehyde and 1-heptanal were obtained from LOBA Chemie India Pvt Limited.

Preparation of catalysts
(a) Preparation of zirconia (ZrO₂) and ceria (CeO₂)]

Known amounts of zirconyl nitrate or ceric ammonium nitrate were mixed with a limited amount of deionized water. The mixture was made into a paste. The resulting paste was dried in an air oven at 120°C for 12 h and calcinated for 5 h at 550°C.

(b)Preparation of ceria-zirconia (30%CeO₂-70%ZrO₂) mixed oxide

Known amount of ceric ammonium nitrate and zirconyl nitrate were mixed with limited amount of deionized water. This mixture was made into a paste. The resulting mixture was dried in an air oven at 120°C for 12 h and calcined for 5 h at 550°C.

These catalysts were abbreviated as; ZrO_2 (Z), CeO_2 (C) and CeO_2-ZrO_2 (CZ).

Characterization of catalysts

All the catalysts were characterized for their surface are, surface acidity, surface basicity, crystalinity and functionality by BET, NH_3–TPD, CO_2-TPD, PXRD and FT-IT techniques respectively. BET surface area of the catalyst samples were recorded on Quanta Chrome Autosorb analyzer.

Surface acidity and surface basicity were obtained by NH_3–TPD, CO_2-TPD methods using Micromeritics instrument. The PXRD patterns were recorded by X-ray powder diffractometer (Philips X'pert) using CuKα radiation (λ=1.5418 A⁰) over graphite crystal monochromator, FT-IR spectrums were obtained from Nicolet IR spectrometer using KBr pellet technique and elemental analysis was carried out by ICP-AES using Thermo-iCAP 6000 analyser.

Catalytic activity studies (in aldol condensation to synthesize jasminaldehyde)

Aldol condensation of benzaldehyde with 1-heptanal (Scheme 1) was carried in a 2 necked 50 mL round bottomed flask fitted with a water cooled condenser. Known amounts of benzaldehyde and the catalyst (ceria or zirconia or ceria-zirconia) taken in RB flask was heated in the temperature ranging from 100-150°C for a stipulate time. 1-Heptanal was added drop wise into the reaction mixture after definite intervals of time.

After the completion of the reaction, the reaction mixture was cooled to room temperature and centrifuged to separate the catalyst. The reaction mixture was then analyzed quantitatively by GC and qualitatively by GC-MS (Hewlett Packard) fitted with a capillary column (HP-624, 30 m × 25 μm × 0.25 μm).

## Results and Discussion
Characterization of catalysts
Surface area

The values of surface area, surface acidity and surface basicity of the solid catalysts determined by BET, NH_3-PD and CO_2-TPD are given in Table 1. The surface area of pure zirconia and pure ceria were found to be lower than ceria-zirconia mixed oxide. It was

Table 1 — Surface area, acidic and basic site distribution of solid catalysts used for the present work

Catalyst	BET surface area (m²/g)	Acid site distribution (mmols/g)			Basic site distribution (mmols/g)		
		Weak	Moderate	*TSA	Weak	Moderate	#TSB
Z	43	0.30	0.09	0.39	0.23	0.09	0.32
C	41	0.23	0.08	0.31	0.38	0.11	0.49
CZ	76	0.11	0.57	0.68	0.13	0.63	0.76

*TSA – Total surface acidity; #TSB – Total surface basicity
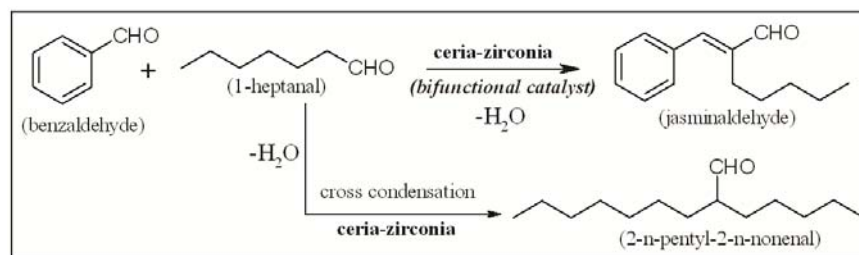
Scheme 1 — Aldol condensation of benzaldehyde with 1-heptanal over ceria-zirconia bifunctional catalyst

observed that the incorporation of ceria into zirconia resulted in an increase in the surface area of the mixed oxide i.e., ceria-zirconia. It is reported that the addition of ceria into zirconia decreases the crystalline size of zirconia by the suppression of particle growth thereby increasing the surface area[13].

Surface acidity and surface basicity

All the solid catalysts used for the present work (Z, C, CZ) were found to be bifunctional because they consist of both acidic as well as basic sites. However, the amount of acidic sites or basic sites was found to be different in these solid catalysts.

Among pure metal oxides, surface acidity of pure zirconia was found to be more than the surface acidity of pure ceria (Table 1). However, when the surface basicity of these oxides was compared, pure ceria was found to be more basic than pure zirconia. But when the acid-base properties of pure metal oxides (zirconia or ceria) were compared with ceria-zirconia mixed oxide, the latter was found to possess more acidity as well as more basicity than its counterparts. The incorporation of Zr^{4+}

into the ceria unit cell or vice-versa modified the surface acid-base sites. It is reported than in ceria-zirconia mixed oxide, Ce^{4+} and Zr^{4+} ions act as acid sites and O^{2-} ions act as basic sites[11]. $M^{+} \!-\!\!-\!\!-\, O^{-}$ (M = Zr or Ce)

The acidic and basic site distribution of Z, C and CZ solid catalysts are also given in Table 1 and the TPD profiles (NH_3-TPD and CO_2-TPD) are given in Fig. 1[A] and 1[B] respectively. It is clear that all these solid catalysts contain 'weak and moderate' acidic/basic sites. But the distribution of acidic or basic sites was found to be different in these oxides. Pure zirconia and pure ceria were found to possess more number of 'weak' acid/base sites than 'moderate' acid/base sites. However, ceria-zirconia mixed oxide consists of more 'moderate' acid/base sites than 'weak' acid/base sites. This indicates that the incorporation of ceria into zirconia or vice versa results not only in an increase in the total surface acidity/basicity of the resulting mixed oxide but also helps in the formation of more number of acid/base sites with 'moderate' strength.

PXRD studies

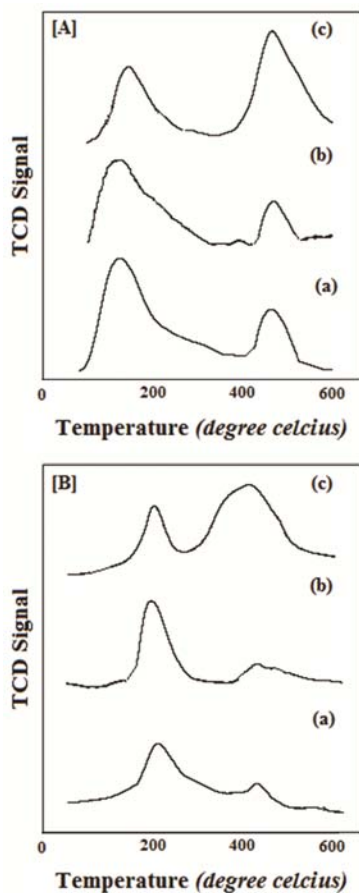The PXRD patterns of Z, C and CZ are shown in Fig. 2[A]. Pure zirconia was found to possess peaks

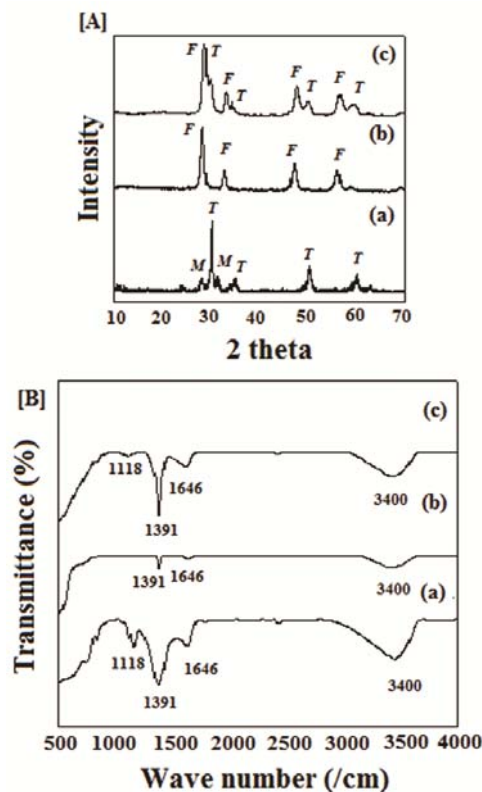Fig. 1 — [A] NH_3-TPD and [B] CO_2-TPD profiles of (a) Z, (b) C and (c) CZ

Fig. 2 — [A] PXRD patterns and [B] FTIR spectra of (a) Z, (b) C and (c) CZ [M – monoclinic phase of zirconia; T – tetragonal phase of zirconia; F – fluorite phase of ceria]

due to both monoclinic (2Θ = 24.5, 28.3, 31.0, 41.5) and tetragonal (2Θ = 30.2, 35.1, 50.4, 60.0) phases.In case of pure ceria, the peaks at 2Θ = 28.5, 33.4, 47.3, 56.2 corresponding to the fluorite structure were observed. However, in case of PXRD pattern of ceria-zirconia mixed oxide peaks pertaining to tetragonal phase of zirconia and fluorite phase of ceria were found. No peaks related to monoclinic phase of zirconia were observed.This indicates the structure stabilization effect of ceria upon zirconia.

FT-IR studies

The FT-IR spectra of Z, C and CZ are given in Fig. 2[B]. The bands at 1391 cm^{-1} and 1118 cm^{-1} can be due to M-OH bending and Zr-O-Zr stretching modes respectively, which confirms the formation of ZrO_2 phases.The bands at 1646 cm^{-1} and 3400 cm^{-1} correspond to bending and stretching modes of –OH groups of water molecules present in all the catalyst samples[12].

ICP-AES studies

The elemental analysis of ceria-zirconia reveals that the percentage of Ce(IV) and Zr(IV) in ceria-zirconia mixed oxide were 32.2 and 67.8 respectively.

Catalytic activity studies (*in aldol condensation to synthesize jasminaldehyde*)

The catalytic activity of solid catalysts (Z, C, CZ) prepared for the present work was evaluated in the synthesis of jasminaldehyde by the aldol condensation of benzaldehyde (BA) and 1-heptanal (HP).When the reactions were carried out in the absence of any catalyst, a very low conversion of 1-heptanal (~19%) was observed. But in presence of solid catalysts the yield of jasminaldehyde was found to increase drastically. Therefore, it can be inferred that the synthesis of jasminaldehyde *via* aldol condensation is a catalytic reaction. After the reaction under a set of reaction conditions, when the reaction mixture was analyzed qualitatively by GC-MS, only two products were confirmed; i.e., jasminaldehyde (JA) and 2-*n*-pentyl-2-*n*-nonenal (PN).

In order to obtain high conversion of with good selectivity towards the desired reaction product i.e., jasminaldehyde, the reaction conditions were optimized by varying the reaction parameters such as nature of the catalyst, weight of the solid catalyst, molar ratio of the reactants, reaction temperature and reaction time.

Effect of nature of the solid catalyst

Aldol condensation reactions of BA with HP were carried out over pure zirconia (Z), pure ceria (C) and ceria-zirconia (CZ) mixed oxide. The activity of these solid catalysts was compared with a 'strong' solid bases such as Ca(II)/ZrO_2 (CaZ) and Ba(II)/ZrO_2 (BaZ)[15]. The results pertaining to the catalytic activity of these solid catalysts are given in Table 2. In general all the catalysts used for the present study were found to be active in the synthesis of jasminaldehyde. However, when the catalytic activity of the solid catalysts was compared, pure zirconia or pure ceria were found to be less active than ceria-zirconia mixed oxide. But pure zirconia or pure ceria were found to be equally selective towards the formation of the reaction products. The low activity of pure oxides can be due to the presence of more number of 'weak' active sites than the active sites with 'moderate' strengths. However, higher activity of ceria-zirconia can be attributed to the presence of more number of 'moderate' active sites on them. This also indicates that the aldol condensation of BA with HP is more facile over the catalysts which bear active sites with 'moderate' strengths than 'weaker' active sites.

Further, when aldol condensation was carried out over strong solid bases such as CaZ or BaZ, though the conversion of HP was reasonably good but the selectivity of JA was found to be lower than PN. Formation of less amount of JA can be attributed to the presence of less number of acid sites which are required to activate BA molecules. It was also observed that when the reactions were carried out over CaZ or BaZ, during the reaction the reaction mixture started turning viscous with a change in color from colorless to grey. This can due to the formation of by-products over these catalysts because of the presence of 'strong' basic sites in them. But over ceria-zirconia, such by-products were not formed and it could be inferred as more selective than 'strong' solid bases like CaZ or BaZ. This also indicates that the 'weak' or 'moderate' basic sites present in ceria-zirconia are more favorable in aldol condensation to synthesize jasminaldehyde.

Table 2 — Catalytic activity of solid catalysts (Z, C, CZ) in the aldol condensation of benzaldehyde (BA) and 1-heptanal (HP)

Solid catalyst	Conversion of HP (%)	Selectivity of JA (%)	Selectivity of PN (%)
No catalyst	19	52	48
ZrO_2 (Z)	32	64	36
CeO_2 (C)	36	67	33
CeO_2-ZrO_2 (CZ)	89	86	14
Ca(II)/ZrO_2 (CaZ)	51	41	59
Ba(II)/ZrO_2 (BaZ)	55	38	62

[Reaction conditions:Molar ratio of HP: BA = 1:4; weight of the solid catalyst = 0.2 g; reaction temperature = 130°C; reaction time = 4 h].

It is reported that for the synthesis of jasminaldehyde *via* aldol condensation of BA with HP, both acid sites as well as basic sites of the catalyst play a vital role, wherein acid sites of the catalyst will be utilized to protonate carbonyl group of benzaldehyde and the basic sites are used to generate enolate 1-heptanal intermediate[3,6]. But for the formation of 2-*n*-pentyl-2-*n*-nonenal, basic sites of the catalyst are more favorable than acid sites[16]. 2-*n*-Pentyl-2-*n*-nonenal (PN) is formed by the self condensation of 1-heptanal where basic sites are utilized to generate enolate from 1-heptanal which further reacts with another 1-heptanol molecule producing PN. As jasminaldehyde is formed over all the catalysts used for

the present work i.e., ZrO_2, CeO_2 and CeO_2-ZrO_2 these solid catalysts could be inferred as *bifunctional* catalysts which have both active acidic as well as basic sites.

By keeping in view these results, for further optimization studies, a *bifunctional* catalyst i.e., ceria-zirconia having balanced number of acidic/basic sites with 'moderate' strength was selected as a catalyst as it showed highest conversion of 1-heptanal with reasonably good selectivity towards jasminaldehyde.

Effect of weight of the solid catalyst (ceria-zirconia)

The weight of the solid catalyst i.e., ceria-zirconia (CZ) was varied from 0.05 g to 0.3 g and the results are given in Fig. 3. An increase in the conversion of HP was
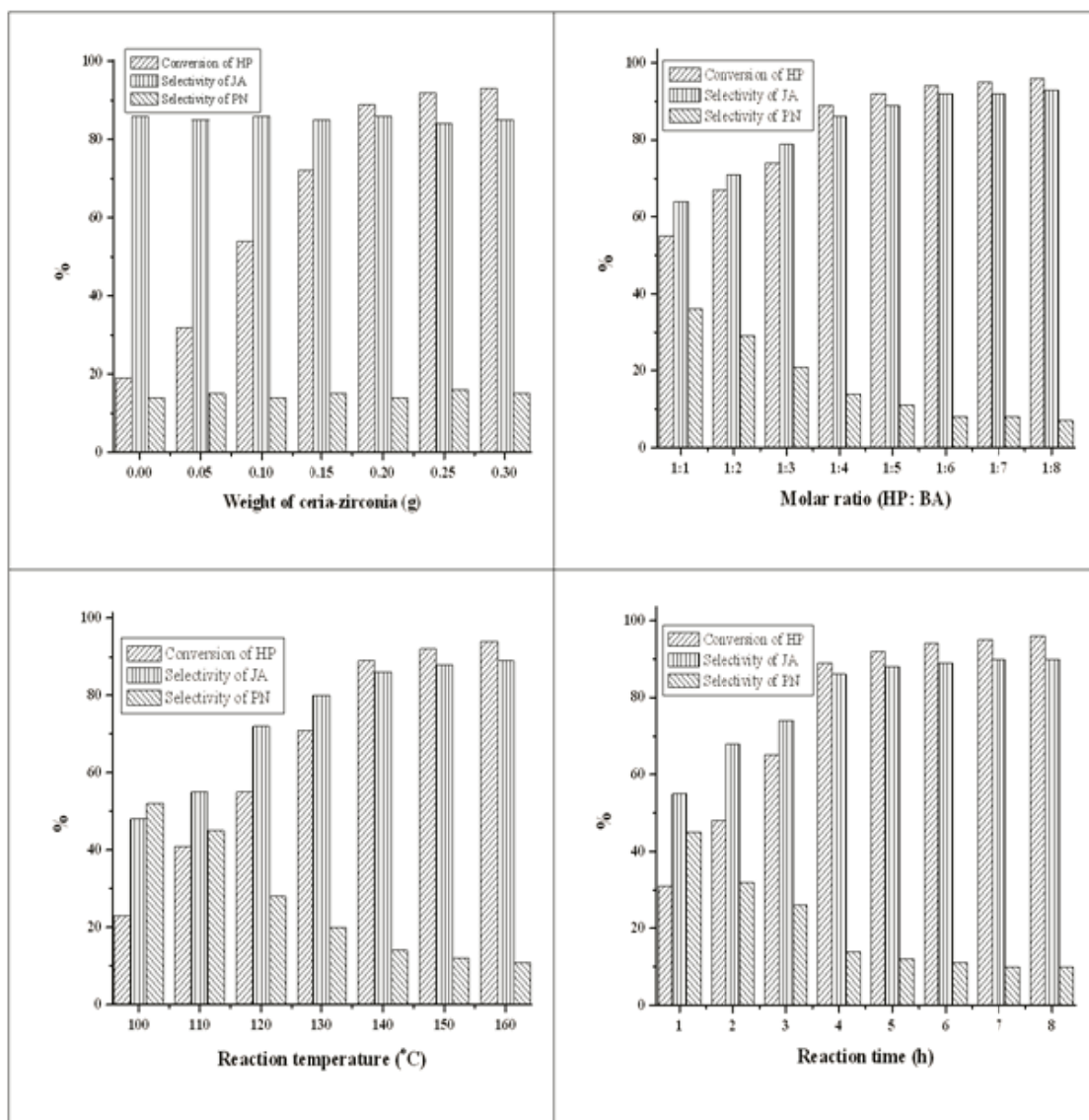

Fig. 3 — Effect of weight of the catalyst, molar ratio of the reactants, reaction temperature and reaction time on the conversion of HP and selectivity of the products [Reaction conditions:Molar ratio of HP: BA = 1:4; reaction temperature = 140°C; reaction time = 4 h; weight of the catalyst 0.2 g].

observed when the amount of catalyst was increased from 0.05 till 0.2 g. Further increase in the weight of the catalyst beyond 0.2 g did not result in any substantial increase in the conversion of HP but stabilization could be observed. But no change in the selectivity of either JA or PN was observed. Therefore, for further studies the weight of the catalyst was chosen as 0.2 g.

Effect of molar ratio of the reactants (BA: HP)

In order to evaluate the effect of molar ratio on the conversion of HP and selectivity of JA, the reactions were conducted in presence of ceria-zirconia mixed oxide by varying molar ratio of HP: BA was varied from 1:1 to 1:8 and the results are shown in the form of a column graph (Fig. 3). It could be seen that the conversion of HP gradually increased when the molar ratio was increased from 1:1 till 1:4 and remained constant when the molar ratio was increased beyond 1:4. It was also observed that the selectivity of the products (JA or PN) was also affected by molar ratio. The selectivity of JA was found to increase when the molar ratio was increased from 1:1 to 1:4. Higher selectivity of JA at lower molar ratio i.e., below 1:4 can be attributed to the presence of BA in higher concentrations wherein the formation of PN seems to get suppressed which forms due to self condensation of HP molecules. At lower molar ratios the formation of PN is favored and at higher molar ratios formation of JA is more favorable. This also indicates that at lower molar ratios the rate of self condensation of HP leading to the formation of PN is higher than the rate of condensation of HP with BA leading to the formation of JA. Therefore, for further studies molar ratio of 1:4 was selected as an optimum molar ratio.

Effect of reaction temperature

The effect of reaction temperature on the conversion of HP and selectivity of the products was studied by varying the temperature from 100°C to 160°C and the results are presented in Fig. 3. As the reaction temperature was increased the conversion of HA as well as the selectivity of JA were found to increase till the reaction temperature of 140°C, beyond which not much change in the conversion of HA and selectivity of JA were observed. Hence reaction temperature of 140°C was fixed as the optimum temperature at which reasonably good conversion of HP with high selectivity of the desired product, JA was observed.

Effect of reaction time

The reaction time was varied from 1 h to 12 h and the obtained results are shown in Fig. 3. The conversion of HP as well as selectivity of JA were found to increase with an increase in the reaction time from 1 h till 4 h. Increase in the reaction time beyond 4 h did not result in an increase ineither the conversion of HP or selectivity of JA. At lower reaction times the higher selectivity of PN can be due to availability of active sites to the reaction mixture in which adsorption of HP may be faster than the adsorption of BA leading to the formation of PN through self condensation of HP. With the progress of the reaction when the reaction time is increased, the concentration of HP decreases and the interaction of BA with the active sites may be higher leading to the cross condensation of the reactants to produce JA.

Effect of reactivation and reusability of solid catalyst (ceria-zirconia)

The solid acid catalyst (ceria-zirconia) used in the first reaction cycle was filtered from the reaction mixture, washed with methanol, dried in an air oven for 2 h at 120°C and finally calcined for 1 h in a furnace at 550°C. Thus reactivated catalyst was used in the second reaction cycle of aldol condensation under a set of optimized reaction conditions. After every use the used catalyst was reactivated and reused for 6 reaction cycles and the data related to the conversion of HP and selectivity of the products is given in Table 3. The table indicates that the bifunctional solid catalyst (ceria-zirconia) has a tremendous reusability atleast for 6 reaction cycles. Not much decrease in either conversion of HP or selectivity towards any reaction product was observed. A negligible decrease in the activity can be due to the loss of the catalyst during filtration.

Mechanism of aldol condensation of benzaldehyde and 1-heptanal over a bifunctional catalyst
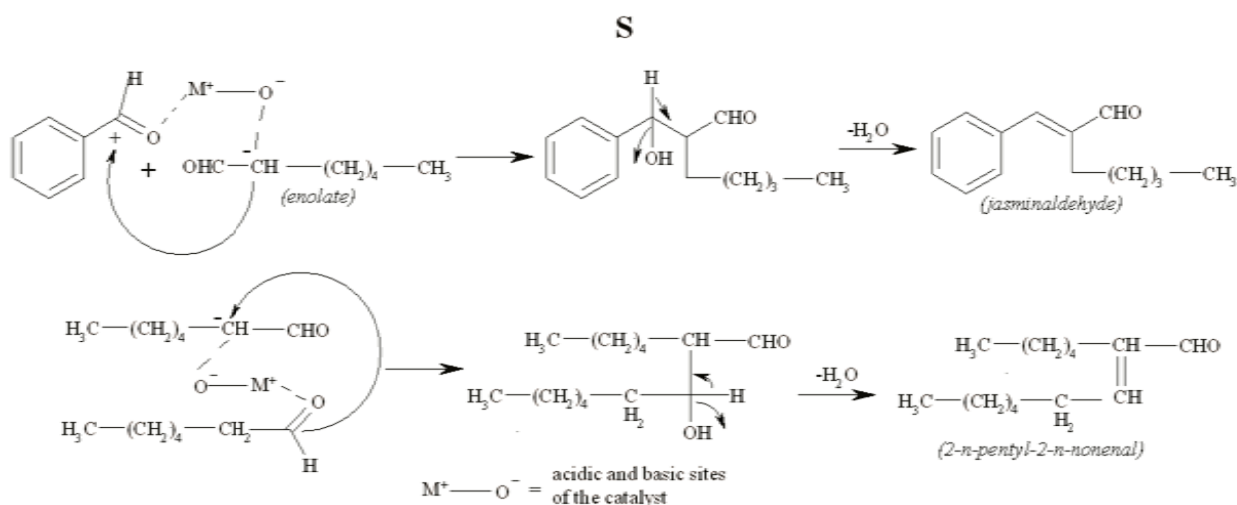
A possible mechanism for the formation of jasminaldehyde over a bifunctional catalyst (over acidic and basic sites) is given in Scheme 2. In the first step, HP is activated by the deprotonation process with the help of moderate basic sites (O⁻) of the catalyst to

Table 3 — Reusability of solid catalyst (ceria-zirconia) in the aldol condensation of benzaldehyde (BA) and 1-heptanal (HP)

Reaction cycle (no.)	Conversion of HP (%)	Selectivity of JA (%)	Selectivity of PN (%)
1 (Fresh)	89	86	14
2	89	86	14
3	88	86	14
4	88	85	15
5	87	86	14
6	86	86	14

[Reaction conditions: Molar ratio of HP: BA = 1:4; weight of the ceria-zirconia = 0.2 g; reaction temperature = 130°C; reaction time = 4 h].

Scheme 2 — Plausible mechanism for the formation of jasminaldehyde and 2-n-pentyl-2-n-nonenal *via* aldol condensation of benzaldehyde with 1-heptanal over a bifunctional catalyst

produce carbanion (enolate). Simultaneously, BA interacts with adjacent moderate acidic site (M^+) of the catalyst. In the second step the enolate reacts with polarized BA to produce an alkoxide intermediate followed by dehydration to yield jasminaldehyde.

Formation of 2-n-pentyl-2-n-nonenal over a bifunctional catalyst is also shown in Scheme 2. HP being aliphatic is more reactive than BA. Therefore, weak active sites are enough for the reaction to take place. The mechanism involves the interaction of two HP molecules over adjacent weakly acidic and weakly basic sites of the catalyst resulting in the formation of 2-*n*-pentyl-2-*n*-nonenal.

Conclusion

The solid catalyst such as zirconia, ceria and ceria-zirconia is an excellent bifunctional catalyst for the synthesis of jasminaldehyde *via* aldol condensation. Specifically, ceria-zirconia mixed oxide could be used as an efficient, economical and ecofriendly catalyst in organic transformations which require acid-base bifunctional active sites. Higher activity of ceria-zirconia can be due to the presence of balanced number of acidic and basic sites with 'moderate' strength which were desirable for the synthesis of jasminaldehyde. However, 2-*n*-pentyl-2-*n*-nonenal may be formed on the 'weak' acidic-basic sites.

Acknowledgement

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