Journal of Advances and Scholarly Researches in Allied Education
Vol. 19, Issue No. 5, October-2022, ISSN 2230-7540

Jasminaldehyde production without the use of solvents by employing solid-acid catalysts based on a double metal cyanide

Snehlata[1*], Dr. Pankaj Gupta[2]

[1] Research Scholar, Sunrise University, Alwar, Rajasthan

[2] Professor (Dept. of Chemistry), Sunrise University, Alwar, Rajasthan

Abstract - Solvent-free synthesis of jasminaldehyde via liquid phase condensation of benzaldehyde and 1-heptanal at 433 K is investigated, with a focus on the catalytic activity of Fe-Zn double metal cyanide catalysts. Under ideal reaction circumstances, 1-heptanal is converted to jasminaldehyde with a selectivity of 77%. Condensation is facilitated in Fe-Zn double metal cyanide because to the presence of coordinatively unsaturated Zn^{2+} in the framework of the compound. Selectivity of jasminaldehyde was investigated by varying the complexing and co-complexing agent, catalyst amount, benzaldehyde to 1-heptanal molar ratio, and temperature.

Keywords: Catalysts, Double metal cyanide, Jasminaldehyde, Heptanal, Benzaldehyde, Solid acid catalyst, Aldol condensation.

- X -

INTRODUCTION

By condensing benzaldehyde and 1-heptanal, the valuable fine chemical jasminaldehyde can be produced. Typically, this reaction is conducted at room temperature using a catalyst of sodium or potassium hydroxide. The generation of unwanted byproducts reduces the yield of jasminaldehyde, which is the main constraint of this procedure. As 1-heptanal condenses on itself, it produces the byproduct 2-pentyl-2-nonenal. New methods for the highly selective and efficient production of jasminaldehyde are required to address this bottleneck.

There are many different solid base catalysts that have been described for the production of jasminaldehyde[1], including anionic exchange resins, mixed oxides, and phase transfer catalysts.

As of late, magnesium organosilicates[2] and hydrotalcite[3] have been described as solid base catalysts for the production of jasminaldehyde by Sharma et al. Synthesis of jasminaldehyde also makes use of the solid acids as catalysts. Some solid acid catalysts have been described for the production of jasminaldehyde[4-7]. These include large pore zeolites (HY and Beta), mesoporous aluminosilicates (Al-MCM-41), and amorphous aluminophosphates (ALPO). These studies found that zeolites were less active and selective than mesoporous aluminosilicates (Al-MCM-41)[4-7]. This was attributed to the self-condensation of 1-heptanal within the voids of the microporous materials and the rapid deactivation of the catalyst caused by the confinement effects of the reactants and products within the voids. Studies for the production of jasminaldehyde employing solid acid catalysts are few due to the decreased selectivity often observed when utilising acid catalysts as opposed to bases.

For trans-esterification processes, double metal cyanides have recently been reported as very effective solid acid catalysts[8,9]. For the Prins condensation of -pinene and paraformaldehyde, we have recently identified Fe-Zn double metal cyanide (DMC) as a promising solid acid catalyst[10].

In this work, we report the solvent-free synthesis of jasminaldehyde over Fe-Zn double metal cyanide catalysts with Lewis acidic sites due to the presence of coordinative unsaturated Zn^{2+}.

MATERIALS AND METHODS

Preparation and characterization of catalysts

The catalyst was prepared from potassium ferrocyanide ($K_4[Fe(CN)_6].3H_2O$) purchased from Polypharm Pvt. Ltd., India, and zinc chloride ($ZnCl_2$) purchased from Rankem, India. All of the alcohols used as complexing agents—n-butanol, iso-butanol, and tert-butanol —came from SD.

India's Fine Chemicals Ltd. Benzaldehyde and 1-heptanal were purchased from Sigma-Aldrich, USA, along with Pluronic P123, a triblock copolymer consisting of poly(ethylene glycol) blocks of poly(propylene glycol) and poly(ethylene glycol) (m. wt. = 5800, $EO_{20}PO_{70}EO_{20}$). None of the chemicals were purified before use.

Catalysts are prepared and characterised

Solution 1 was made by dissolving 0.01 mol of potassium ferrocyanide, $K_4[Fe(CN)_6].3H_2O$, in 40 mL of double-distilled water, as part of a standard method for synthesising DMC-1 catalyst. To make solution 2, 0.1 mol of $ZnCl_2$ was dissolved in 100 mL of distilled water and 20 mL of n-butanol in a separate beaker (complexing agent). Solution 3 was made by dissolving the tri-block copolymer (15 g, co-complexing agent) in 2 mL of distilled water and 40 mL of n-butanol in a third beaker. At 323 K and a vigorous stirring speed, solution 2 was added to solution 1 over the course of an hour. After a stirring period of 1 hour, solution 3 was added to the stirred reaction mixture within 5-10 min. To remove any uncomplexed ions, we filtered the reaction mixture and washed the resulting solids in double-distilled water. DMC-1 was determined after the filter cake was dried at 298 K for 8 hours. DMC-5 and DMC-6 catalysts were prepared using iso-butanol and tert-butanol as complexing agents and tri-block copolymer as co-complexing agents8-11, and the effect of complexing agents on catalytic activity was studied. As shown in Table 1, n-butanol, iso-butanol, and tert-butanol were used alone as complexing agents in the synthesis of catalysts DMC-2, DMC-4, and DMC-7, while no complexing or co-complexing agents were used in the synthesis of DMC-3.

DRIFT spectroscopic studies of adsorbed pyridine were performed on a Thermoelectron Corporation (Nicolet 6700) FT-IR instrument with the selector DRIFT accessory, which included an environmental chamber (EC) assembly and an automatic temperature controller, to determine the Lewis acidity of DMC samples. Some samples of the catalyst were heated to 120 degrees Celsius for 4 hours before being subjected to pyridine vapours to begin the activation process. Five millilitres of dry pyridine and two-tenths of a gramme of samples were stored under vacuum for twenty-four hours in a desiccator. The samples were then evacuated at room temperature (10-2 Torr) for 30 minutes to desorb the physisorbed pyridine. Automatic temperature controller linked to the EC was used to heat the DMC samples on-site to 100, 200, 300, and 400 °C at atmospheric pressure and at a heating rate of 10 °C/min. For 30 minutes, the sample was kept at the optimal temperature for pyridine desorption prior to spectrum recording. Pyridine vapours were extracted from a diluted HCl solution after being desorbed. Scans were typically co-added at a resolution of 4 cm-1, with 300 scans being the norm. KBr pellet FT-IR spectra were acquired on a Perkin-Elmer GX-FTIR spectrometer.

Table 1– Characterization data of the studied double metal cyanide based catalysts

Catalysts	Fe(II)precursor	Zn(II)precursor	Complexingagent	Co-complexingagent
DMC-1	$K_4Fe(CN)_6.3H_2O$	$ZnCl_2$	*n*-butanol	EO20PO70EO20
DMC-2	$K_4Fe(CN)_6.3H_2O$	$ZnCl_2$	*n*-butanol	nil
DMC-3	$K_4Fe(CN)_6.3H_2O$	$ZnCl_2$	nil	nil
DMC-4	$K_4Fe(CN)_6.3H_2O$	$ZnCl_2$	*iso*-butanol	nil
DMC-5	$K_4Fe(CN)_6.3H_2O$	$ZnCl_2$	*iso*-butanol	EO20PO70EO20
DMC-6	$K_4Fe(CN)_6.3H_2O$	$ZnCl_2$	*tert*-butanol	EO20PO70EO20
DMC-7	$K_4Fe(CN)_6.3H_2O$	$ZnCl_2$	*tert*-butanol	nil

Jasminaldehyde synthesis

Reactions typically involve taking 0.1 g of n-decane as an internal GC standard, combining it with 0.1 g of 1-heptanal and benzaldehyde (mole ratio = 1:5) in an oven-dried double-necked round-bottom flask, and then performing the reaction. A 2.25-foot-long refluxing condenser with a spiral tube inside was attached to one of the flask's necks, while the other was sealed off with a silicon rubber septum. A regular cork was used to seal off the top of the condenser, preventing the reflux from escaping. During the reaction, water from a water chiller was pumped at a rate of 6 L/min into the refluxing condenser to keep the temperature there constant at 288 K. The entire apparatus for the experiment was stored in an oil bath with temperature and agitation speed controls. The flask was charged with the calculated amount of DMC catalyst, and the reaction was run at 433 K for 12 hours. After the reaction mixture was brought down to room temperature, it was filtered and put through a gas chromatograph (Shimadzu 17A, Japan) and a mass spectrometer (GC-MS) (mass spectrometer, Shimadzu QP2010, Japan).

The conversion and selectivity were calculated by the following equations:

$$\%\text{Conv. of heptanal} = \frac{\text{moles of 1-heptanal reacted}}{\text{moles of 1-heptanal fed}} \times 100$$

$$\%\text{ Sel. to jasminaldehyde} = \frac{\text{moles of jasminaldehyde}}{\text{moles of (jasminaldehyde} + \text{2-pentyl-2-nonenal)}} \times 100$$

RESULTS AND CONCLUSIONS

Characterization of double metalcyanidecomplex catalysts

Identifying the building blocks of $K_4[Fe(CN)_6]$, a precursor chemical to the Fe-Zn double metal cyanide catalyst. P-XRD, FT-IR, diffuse reflectance UV-vis, SEM, and TGA analysis of $3H_2O$ and $ZnCl_2$ are reviewed in detail elsewhere10.

The IR range of 1450–1700 cm-1 displays bands of pyridine vibration. The bands at 1612 and 1450 cm^{-1}

originate from pyridine's coordination to Lewis acid sites[12-15]. Fig. 1(a) and (b) show the DRIFT spectra acquired at different temperatures following pyridine adsorption for DMC-6 and DMC-7, respectively. The existence of the Lewis acid Zn^{2+} cations on the edge of the catalyst is confirmed by the appearance of the pyridine vibration bands at 1450 and 1612 cm^{-1} in DMC-6. Bands at at 1450, 1490, and 1612 cm^{-1} in the FT-IR spectrum of DMC-7 are assigned to pyridine bound to acid sites (Lpy + Bpy + Hpy[16,17]).

Effect of complexing and co-complexing agents on the catalytic activity

With selectivity to jasminaldehyde in the range of 73–77%, the Fe-Zn double metal cyanide catalysts converted between 82% and 93% of 1-heptanal.In the course of the reaction, 2-pentyl-2-nonenal was produced. The products were confirmed to have formed using GC-MS analysis of the reaction mixture. We saw the expected fragmentation spectra for jasminaldehyde (m/z = 202, 173,145, 129, 117, 91, 65) and 2-pentyl-2-nonenal (m/z = 210, 181,153, 125, 97, 81, 69). It was also shown that 82% conversion and 77% selectivity for jasminaldehyde were achieved with catalysts synthesised without complexing and co-complexing agents (DMC-3). 1-Heptanal conversions of 84% to 89% were achieved by catalysts produced with complexing and co-complexing agents, with selectivities of 73% to 75% for jasminaldehyde (DMC-1, DMC-5, DMC-6). The selectivity of the catalysts for the conversion of 1-heptanal to jasminaldehyde was in the range of 75–77%, and the conversion rate was 90–93% when using only the complexing agent (DMC-2, DMC-4, DMC-7).

This evidence demonstrates that the complexing agents improved the DMC catalysts' performance. When complexing and co-complexing agents were used to create DMC catalysts, the catalysts' activity dropped marginally. The co-complexing agent can be partially blocking the active sites, leading to the reduced activity. Without the catalyst, there was no detectable selectivity for jasminaldehyde. The maximum catalytic activity for jasminaldehyde production was observed for DMC-7, hence it was chosen as a representative catalyst for further investigation.

Effect of varying reaction parameters

The impact of the reaction temperature was investigated between 373K and 443K. At greater temperatures, the condensation process sped up. At 373 K, 1-heptanal was converted with 65% selectivity to jasminaldehyde, and at 393 K, 50% selectivity was achieved. When the temperature was raised to 433K, 1-heptanal was converted to jasminaldehyde with a selectivity of 77%. Even when the reaction temperature is raised to 443K, there is no change in the selectivity for the formation of jasminaldehyde or the efficiency with which 1-heptanal is converted.An increase in the molar ratio of 1-heptanal to benzaldehyde from 1:1 to 1:5 was shown to result in a greater rate of 1-heptanal conversion. At a molar ratio of 1:1, about 73% of 1-heptanal was converted into benzaldehyde; at a molar ratio of 1:5, nearly 93% of 1-heptanal was converted into benzaldehyde. Inadequate amounts of benzaldehyde cause 1-heptanal conversion to be poorer at lower molar ratios. Increasing the molar ratio of 1-heptanal to benzaldehyde also resulted in a notable improvement in selectivity toward jasminaldehyde.

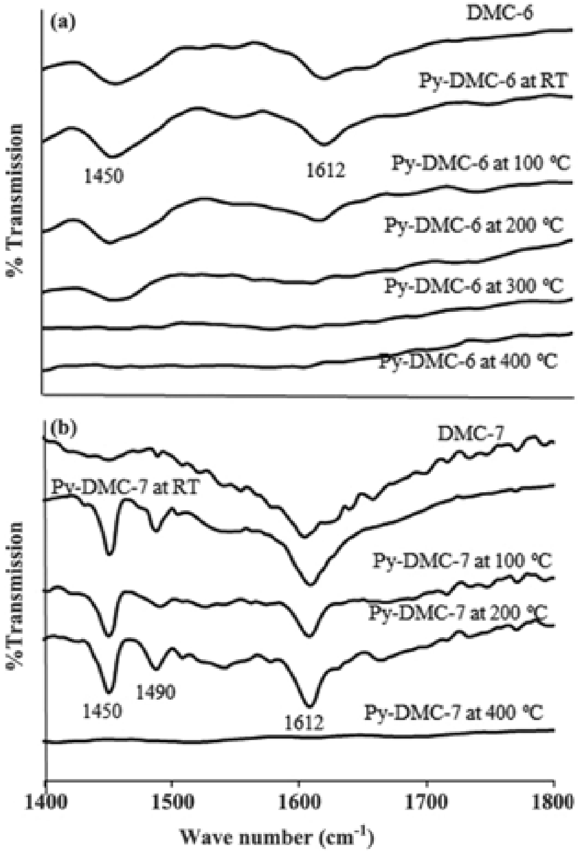


Figure 1–DRIFTspectraofDMCcatalysts.[(a)DMC-6;(b)DMC-7].

In one experiment, changing the molar ratio of 1-heptanal to benzaldehyde from 1:1 to 1:4 boosted selectivity to jasminaldehyde from 62 percent to 77 percent. But even when the ratio was increased to 1:5, the selectivity for jasminaldehyde remained same. The selectivity for the self-condensation product 2-pentyl-2-nonenal from 1-heptanal was also found to diminish with increasing 1-heptanal: benzaldehyde molar ratios. This shows that at larger 1-heptanal concentrations, self-condensation occurs more quickly than cross-condensation with benzaldehyde[3].

Initial 1-heptanal self-condensation rates are higher than those for 1-heptanal cross-condensation with benzaldehyde. In a 1-hour reaction time, 61% selectivity was achieved in the conversion of 1-heptanal to jasminaldehyde. Conversion of 1-heptanal went up to 71% with 70% selectivity for jasminaldehyde when the reaction period was extended from 1 to 5 hours. The conversion rate of 1-heptanal increased to 93% with a selectivity for jasminaldehyde of 77% when the reaction period was extended to 12 hours.

Each reaction competes with the other, therefore it is necessary that the active sites be either acidic or basic. The self-condensation product of 1-heptanal is formed when all the catalytic active sites are first exposed to the reaction mixture, where adsorption of 1-heptanal would be much faster than adsorption of benzaldehyde. As the reaction goes on, less and less 1-heptanal is present in the combination. At lower concentrations of 1-heptanal, benzaldehyde would have a greater chance of adsorbing to and interacting with active sites. For this reason, extending the duration of the reaction improves selectivity toward jasminaldehyde. As the 1-heptanal concentration was increased, a linear increase in the rate of 2-pentyl-2-nonenal production was observed[18].

By changing the 1-heptanal:catalyst ratio from 10-20, we were able to observe how the amount of catalyst affected the 1-heptanal conversion and selectivity to jasminaldehyde. Increasing the amount of catalyst enhanced the rate of 1-heptanal conversion. The 1-heptanal:catalyst weight ratio of 10 resulted in the highest conversion (93%) and highest selectivity (77% to jasminaldehyde). One study found that a 20:1 weight ratio of 1-heptanal to catalyst resulted in a 59% conversion of 1-heptanal and an 86% selectivity for jasminaldehyde. Having fewer active Zn^{2+} sites in the reaction mixture is what causes the conversion of 1-heptanal to drop from 93% to 59% as the amount of catalyst used decreases. Since the self-condensation of 1-heptanal can also be catalysed by the active acidic sites accessible on the surface of catalyst, it was shown that a higher amount of catalyst favoured the self-condensation of 1-heptanal to 2-pentyl-2-nonenal.

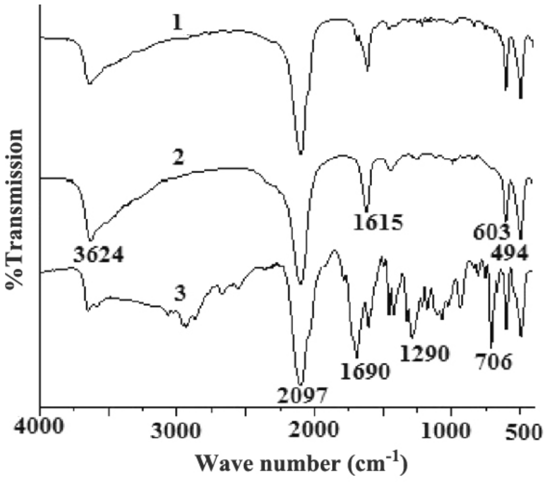


Figure 2– FT-IRspectraofDMC-7catalyst.[1,spentcatalystafterwash;2, fresh catalyst;3, spentcatalyst without wash].

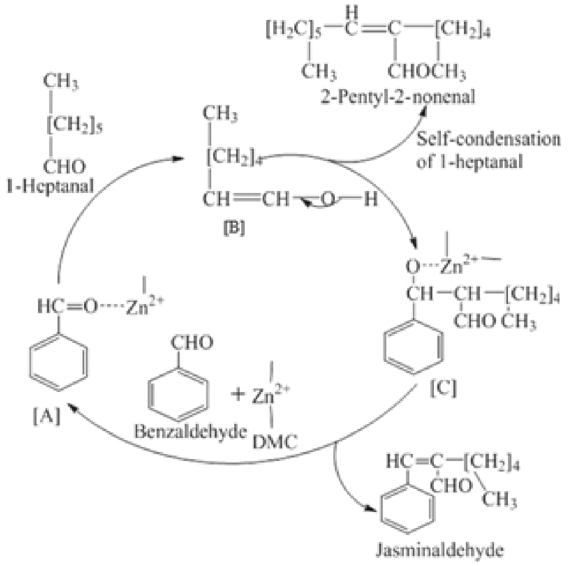
We may anticipate a dramatic rise in the number of active acidic sites when the concentration of catalyst is raised. Since 1-heptanal is more readily adsorbed to the active acidic sites of the catalyst than is benzaldehyde, the self-condensation of 1-heptanal to 2-pentyl-2-nonenal occurs more quickly as the amount of catalyst increases, resulting in less selectivity to jasminaldehyde. At higher amounts of catalyst6, it has been found that 1-heptanal self-condenses at a faster rate than 1-heptanal condenses with benzaldehyde. Since more selectivity to jasminaldehyde and 1-heptanal conversion were obtained with a weight ratio of 10, further optimization tests were conducted with this ratio.

Recycling of the catalyst

The solid catalyst (DMC-7) was washed with methanol three times and dried at 373 K for four hours before being reused in experiments. According to the findings, the catalyst can be reused multiple times with just a minor loss in catalytic activity between cycles. For instance, 1-heptanal was converted by a whopping 93 percent using a new DMC-7 catalyst, with a selectivity of 77 percent yielding jasminaldehyde. By the third cycle, the conversion had dropped to 82%, with jasminaldehyde selectivity at 84%. FT-IR spectroscopy of spent catalyst indicated that adsorption of substrates or products on the catalyst surface was likely the cause of the activity decline rather than handling loss. FT-IR spectroscopy of used catalyst shows evidence of aromatic chemicals as bands between 1200 and 1400 cm^{-1} (Fig. 2).

Reaction mechanism

Scheme 1 depicts a possible chemical pathway for jasminaldehyde production over Fe-Zn double metal cyanide. Weak acidic sites enhance polarisation of the carbonyl group in the benzaldehyde molecule by attacking the Zn^{2+} ions on the carbonyl group[12]. Understanding the mechanism of the cyanide-catalyzed reaction between iron and zinc It has previously been reported[8,9,13] that -pinene can be condensed by the Prins reaction, that dimethylcarbonate can be trans-esterified, and that propylene oxide can be polymerized via ring opening.



Tentativereactionmechanism for synthesis ofjasminaldehydeusingFe^{2+}-Zn^{2+}doublemetalcyanidecomplexesascatalyst.[A]=Zn^{2+}coordinatedbenzaldehyde,

[B]= enolate of1–heptanal,[C]= intermediatespecies

It is anticipated that a similar reaction pathway will occur in the present investigation, with the co-ordinatively unsaturated Zn^{2+} cations in the structure of Fe-Zn double metal cyanide serving as the likely active sites for the formation of species [A], which involves the activation of benzaldehyde via the polarisation of the carbonyl group on the acid sites. After forming, the carbanion reacts with the 1-heptanal enolate produced locally to form the [C] species, which, upon dehydration, yields the, α,β-unsaturated aldehyde (i.e. jasminaldehyde).

CONCLUSIONS

In the current study, researchers report using double metal cyanide (DMC) as a highly active solid base catalyst for the solvent-free synthesis of jasminaldehyde by condensation of 1-heptanal with benzaldehyde. The production of jasminaldehyde is enhanced by catalysts that include Fe^{2+}-Zn^{2+} and complexing agents. Zn^{2+} cations (Lewis acidic sites) on the catalyst's surface may serve as active sites for the condensation reaction.

REFERENCES

1. AbenhaemD,SonCPN,LoupyA&HeipNB,*SynCommun,*24(1994)1199.
2. SharmaSK,PatelHA&JasraRV,*JMolCatalA:Chem,*280(2008)61.
3. SharmaSK,ParikhPA&JasraRV,*JMolCatalA:Chem,*286(2008)55.
4. ChuahGK,JaenickeS,LiuSH&HuXC,*ApplSurfSci,*169(2001)253.
5. ClimentMJ,CormaA,LopezRG,IborraS&PrimoJ,*JCatal,*175(1998) 70.
6. ClimentMJ,CormaA,GarciaH,LopezRG,IborraS&FornésV,*JCatal,*197(2001)385.
7. ClimentMJ,CromaA,FornésV,LopezRG&IborraS,*AdvSynthCatal,*344(2002)1090.
8. SrivastavaR,SrinivasD&RatnasamyP,*JCatal,*241(2006)34.
9. SreeprasanthPS,SrivastavaR,SrinivasD&RatnasamyP,*ApplCatal A:Gen,*314(2006)148.
10. PatilMV,YadavMK&JasraRV,*JMolCatalA:Chem,*273(2007)39.
11. KimI,AhnJT,LeeSH,HaCS&ParkDW,*CatalToday,*
12. 93-95 (2004)511.
13. SaravanamuruganS,PalanichamyM,HartmannM&MurugesanV,*ApplCatalA:Gen,*298(2006)8.
14. KimI,AhnJT,HaCS,YangCS&ParkI,*Polymer,*44(2003)3417.
15. 14CormaA, *ChemRev,*95 (1995)559.
16. BarzettiT,SelliE,MoscottiD& ForniL,*JChemSocFaradayTrans,*92(1996) 1401.
17. ChevalierS,FranckR,Suquet H,LambertJF&BarthomeufD,*JChemSocFaradayTrans,*90 (1994)667.
18. YadavM K&JasraRV, *Catal Commun,*7 (2006)889.
19. SudheeshN,SharmaSK,KhokharMD&ShuklaRS,*JMolCatalA: Chem*, 339(2011)86.

Corresponding Author

Snehlata*

Research Scholar, Sunrise University, Alwar, Rajasthan