RECORDSOF CHEMICAL SCIENCES

Accepted: 21th June, 2024
Published: 29th June, 2024

Synthesis of Jasminaldehyde (α-pentylcinnamaldehyde) using Cs-AlMCM-41 Nanoparticle as Heterogeneous Solid Base Catalyst

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https://doi.org/10.33003/frscs_2024_0302/07

FRsCS Vol.3 No. 2 (2024)
Official Journal of Dept. of Chemistry, Federal University of Dutsin-Ma, Katsina State.
http://rscsfudma.com

ISSN (Online): 2705-2362
ISSN (Print): 2705-2354

Abstract

In this study, the ultra-small mesoporous Cs-AlMCM-41 nanoparticle materials were obtained with high specific BET surface areas in the range of 426 m^2g^{-1} with 1.97 nm pore size. The pore volume was found to be 0.86 cm3. The material possesses a basic site due to caesium ions (Cs^+) counterbalancing the negative rise by Al in the mesoporous framework. The basicity of the sample was found to be 115.48 mol g^{-1}. The basicity was proven via the condensation reaction of heptanal and benzaldehyde using microwave irradiation with a microwave power of 800 W. The sample (Cs-MCM-41) gave a higher conversion of heptanal (73.8%) with (70.1%) selectivity to jasminaldehyde. The CsMCM-41 can be a promising base catalyst in aldol condensation reaction for the synthesis of jasminaldehyde under autogenous pressure. Hence, the solid catalyst is easily recycled up to five (5) times with minimal loss of activity due to washing.

Keywords: Cs-AlMCM-41, nanoparticle, hydrothermal method, jasminaldehyde, aldol condensation.

Introduction

Jasminaldehyde or α-pentylcinnamaldehyde is a well-known perfume ingredient with an aromatic scent. It is used extensively in perfumery industries. Jasminaldehyde is usually synthesized *via* aldol condensation between benzaldehyde and heptanal catalyzed in both acidic and basic media (Casale et al., 2007 and Sharma et al., 2008). Traditionally, it is prepared using homogeneous bases (i.e. KOH, NaOH) in more than stoichiometry (Climent et al., 2001). Recently, heterogeneous solid bases have the centre stage due to several problems faced by homogeneous catalysis systems such as severe environmental concerns in waste disposal, toxicity, the difficulty of handling and storing corrosive homogeneous catalysts, and difficulty in separation and recycling problems. Many solid base catalysts used to synthesize jasminaldehyde with high selectivity have been reported. Clement et al. observed that in aldol condensation reaction involving benzaldehyde and heptanal recorded low selectivity to jasminaldehyde when using microporous zeolite as a catalyst (Climent et al., 2001 and Martins et al., 2010). The smaller pore size of the zeolite coupled with the larger molecule size of both the reactant and the product cause rapid deactivation of the catalyst due to trapping molecule in a microporous zeolite void (Lutz 2014 and Casale et al., 2007). Therefore, the formation of 2-pentyl-2-nonenal and diphenyl allyl cations takes centre stage as the product of self-aldol condensation of heptanal and benzaldehyde, respectively. On the other hand, the use of mesoporous aluminosilicate (AlMCM-41) gave an excellent catalytic performance and selectivity to jasminaldehyde than using microporous zeolites (Climent et al., 2001).

AlPO-n zeotype catalyst also displayed an excellent performance as a catalyst and appeared as the best catalyst among the catalyst tested (Lagno et al., 2005 and Climent et al., 2001). The whole idea is attributed to the acid-base bi-functional character of the aluminophosphate. Hence, the benzaldehyde molecule was activated by weak acid sites *via* protonation of the carbonyl functional group. This will in turn facilitate the attack of heptanal intermediate (enolate) produced from the weak basic site of the amorphous aluminophosphate catalyst. In the present work, the mesoporous CsMCM-41 catalyst is reported. The catalyst basicity is also fully characterized. The activity and selectivity of CsMCM-41 are examined by studying the effects of different operating parameters in the aldol condensation of benzaldehyde with heptanal. The mechanism for both the cross-aldol condensation and self-aldol condensation reactions is studied. The catalyst is highly selective to the needed product (Jasminaldehyde) and can be recycled.

Experimental

Materials

Ludox AS-40, aluminum isoproxide (98%) and caesium hydroxide monohydrate ($CsOH.H_2O$, 99.5%) were purchased from Sigma-Aldrich chemical company. Cetyltrimethylammonium bromide (CTAB, 98%) was purchased from Merck. All the chemicals were used as received except the distilled water which was prepared in the laboratory using a distiller.

Synthesis of CsMCM-41 nanoparticles

The Synthesis of CsMCM-41 nanoparticles was described as follows: 4.3880 g of CTAB was dissolved in 80.7416 g of distilled water under vigorous stirring (Solution-1). Then, 3.9627g of $CsOH.H_2O$ was mixed and stirred with 7.0300 g LUDOX AS-40 colloidal silica. The mixture was labelled as Solution-2. Then, Solution-2 was added to Solution-1 drop-wise under continuous stirring. Then some amounts of aluminium isoproxide (0.4810g) were added into the resulting solution to obtain gel mixtures with a molar composition of $4SiO_2$: $0.2Al_2O_3$: 1CTAB: $1Cs_2O$: $400H_2O$. The SiO_2/Al_2O_3 ratios from the compositions were 20, and the samples were denoted as CsAlMCM-41, the samples were placed in an oven at 100°C for 24 h. Then, the pH of the mixture was adjusted to 10.0 with 5wt% acetic acid. The samples were further heated for 24 hrs. The pH adjustment to 10.0 and reheating were repeated three times before the product was filtered, washed until pH 7, and dried at 60°C overnight. The sample was calcined in a furnace under air condition with a temperature ramp of 1°C/min at 550 °C for 6 h to remove the organic template.

Characterization

The XRD patterns of calcined samples were collected using an X-ray diffractometer operated at 40 kV and 10 mA with nickel-filtered CuKα radiation (K= 1.54060 Å). N_2 adsorption-desorption isotherms were obtained at -196 °C. Initially, the samples were degassed at 250 °C under vacuum. The surface areas were calculated using the BET equation. The pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) model applied to the adsorption branch of the isotherm. The total pore volumes were determined from the nitrogen adsorbed volume at $P/P_o = 0.98$. The chemical composition of the solids was also determined using a Philips PW2404 X-ray fluorescence spectrometer (XRF). The basicity property of the solid sample was determined by using the back titration method. Typically, 0.200 g of dried solid sample was suspended in 10 mL of distilled water. The solution was magnetically stirred for 24 hours before it was centrifuged (10000 rpm, 10 min). The separated solution was then mixed with 5 mL of 0.05 M HCl. The resulting solution was titrated with 0.02M NaOH solution while phenolphthalein was used as the indicator. The endpoint was noted when the colourless solution turned to pink. The readings were performed in triplicate for each sample

Catalytic study

The catalytic activity of the CsAlMCM-41sample ratios was studied in the liquid-phase aldol condensation reaction of heptanal with benzaldehyde using a microwave reactor (Anton Paar, Monowave (400) with microwave power 800 W. In a typical experiment, 0.500 g of solid catalyst was activated at 300 °C and added to the reactant mixture of heptanal and benzaldehyde with a molar ratio of 1:5.The reaction was conducted at various temperatures (150-180 °C) and times (0-60 min). The liquid products were separated and analyzed periodically on a gas chromatograph. The products were also identified using a GC–MS (Perkin-Elmer Clarus 600 Gas Chromatograph) analyzer.

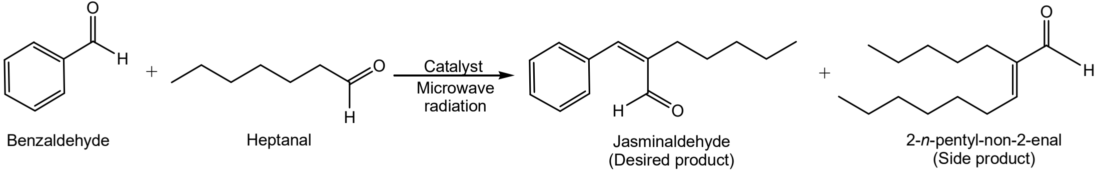

Fig.1. Aldol condensation of benzaldehyde with heptanal.

Result and Discussion

The samples were calcined to remove the organic template and to open the porosity of the solid. The XRD patterns of calcined CsMCM-41 showed a very strong and well-resolved peak at $2\theta = 2.20°$ which was assigned to the (100) plane (Fig. 2). Two weak peaks were observed at $2\theta = 4.00°$ and 4.65°, which were corresponding to the (110) and (200) planes, respectively. The intense reflection line of the (100) plane is a characteristic of the hexagonal structure of MCM-41 and the presence of the reflection lines (110) and (200) planes confirmed the highly ordered hexagonal pore geometry of the mesoporous molecular sieve (La-Salvia et al. 2017, Chen et al. 2018, and ALOthman 2012).

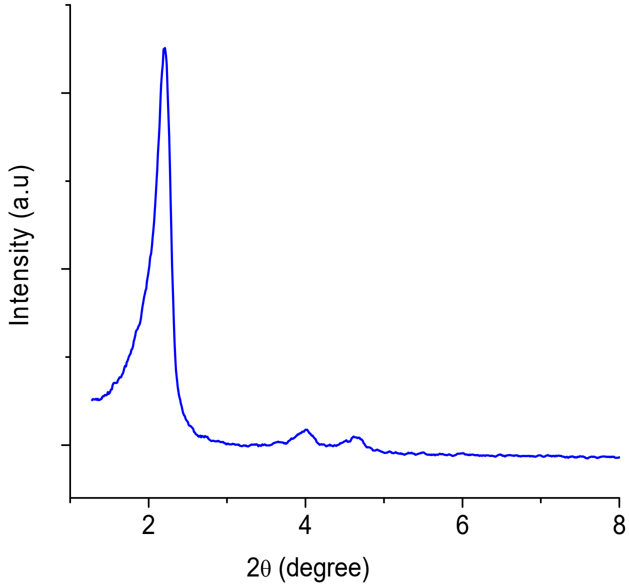

Fig 2: XRD patterns of calcine of CsMCM-□□

The N_2 adsorption-desorption isotherms were recorded at 77 K. The profiles of the sample were of type IV isotherms according to the IUPAC classification, which was typical of the MCM-41 mesoporous molecular sieves (Fig 3). The CsMCM-41 showed the highest specific BET surface area of 425 m^2 g^{-1}. The pore size also is within the mesoporous range, which is 19.68 Å. The isotherm at $p/p_o < 0.3$ represented the monolayer adsorption of N_2 on the wall of the mesopore while that of $p/p_o > 0.4$ represented multilayer adsorption on the surface of the particle (Rath et al. 2014, Abu-Zied et al 2019, Morris & Huddersman 1999). The point at which the inflection started was corresponding to the capillary condensation within the mesopore and its diameter. However, there was a slight shift in the inflection step toward higher $p/p_o < 0.9$ on the insertion of Al in the MCM-41 framework. The chemical composition of the solids was determined using XRF spectroscopy. The elemental composition of the sample is shown in table 1. It revealed that Al, Si, Cs and O were the main elements made up of the mesoporous material. The experimental Si/Al ratio of CsMCM-41 mesoporous samples was determined to be 13.3. Cs content was found in the framework due to Al^{+3} ion incorporated in the siliceous framework. the Cs^+ ion counterbalances the negative charge raised by Al ions to counterbalance the negative charge and electrostatically hold the extra-framework Cs^+ cations $(Si{-}O^-)Cs^+$. This is the reason for the framework's basicity.

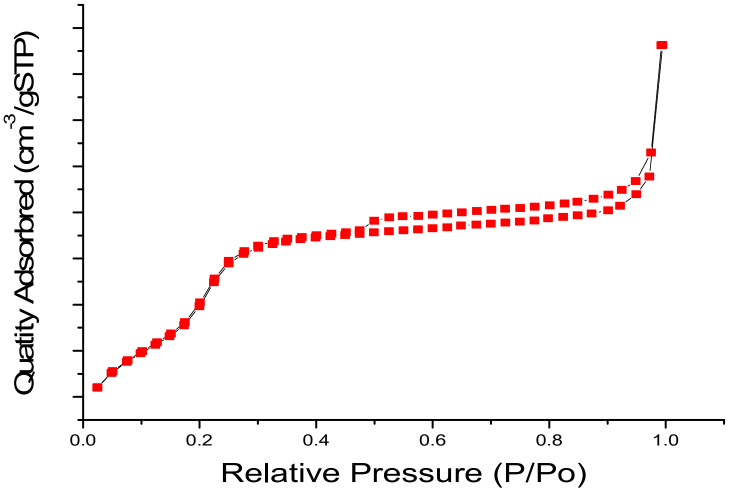

Fig 3: N_2 adsorption (close symbol) and desorption (open symbol) isotherms of calcined CsMCM-41,

Table 1: Chemical elemental and basicity analyses of CsMCM-41 solids

sample	**Weight (%)**				**Si/Al ration**	**Basicity**
	O	**Al**	**Si**	**Cs**		**(μmol g^{-1})**
CsMCM-41	50.87	2.43	34.86	11.84	13.3	101.57

Effect of temperature

The effect of temperature on aldol condensation reaction of heptanal and benzaldehyde over CsM-20 catalyst was studied at different temperatures (150, 160, 170 and 180ºC) and various reaction times (10 to 60 min) (Fig.4). At 150ºC, 56.5%of heptanal conversion with 53.1% selectivity to jasminaldehyde was achieved at 60 min. As predicted, the conversion rate increased steadily as the temperature was elevated from 150 to 180ºC. At 180ºC for 60 min, a heptanal conversion of 76.8% with 72.3% selectivity to jasminaldehyde was recorded. Also, higher temperatures under microwave heating led to higher selectivity for jasminaldehyde (Ganga et al., 2016 and Patil et al., 2013). Based on the obtained results, the optimum catalytic performance (highest conversion, highest selectivity to jasminaldehyde) was achieved at 180ºC for 60 min.

Effect of catalyst loading

The catalytic performance can be influenced by the catalyst amount. In the present study, the CsM-20 amount was varied within the range of 0 – 1.00 g. The catalytic reaction results are shown in Fig.5. The results showed that the reactant conversion increased with an increase in catalyst amount. This can be explained by an increase in the number of active basic sites (Sudheesh, et al. 2010 and Sharma et al. 2008). Beyond 0.500 g of CsM-20 catalyst, a slight increase in the conversion of heptanal with a decline in selectivity to jasminaldehyde, however, was observed. This is due high viscosity of the reacting mixture which resulted in poor stirring efficiency. Hence, the optimal catalyst loading in this work was 0.500 g (76.8%, conversion of heptanal with 72.3% selective to jasminaldehyde).

Effect of heptanal to benzaldehyde molar ratio

The molar ratio of heptanal to benzaldehyde was altered from 1:1 to 1:13 with 0.500 g of catalyst at 180 ºC and 80 min of reaction was used. The study revealed that the heptanal conversion was enhanced with an increase in the benzaldehyde concentration (Fig.6). The conversion increment thus indicated a positive reaction order concerning benzaldehyde (Sharma et al., 2010). The higher its concentration, the higher the chance for benzaldehyde to react with heptanal in the presence of CsM-20 catalyst to yield the jasminaldehyde product (Prabhu et al., 2013). An increase in the molar ratio of heptanal: benzaldehyde from 1:7 to 1:11, however, led to a decrease in the conversion and selectivity to the desired product (jasminaldehyde). Hence, the optimal heptanal: benzaldehyde molar ratio in this study was 1:5 (76.8% conversion and 72.3% selectivity to jasminaldehyde).

Catalyst recycling test

The catalyst reusability was studied by successive running the reaction five times over CsM-20 and the results were presented in Fig.7. The conversion slightly decreased after multiple cycles of reaction due to the loss of catalyst during separation and washing. In addition, the selectivity to jasminaldehyde showed nearly the same in all five cycles. Hence, the catalyst was stable, and it can be recycled several times.

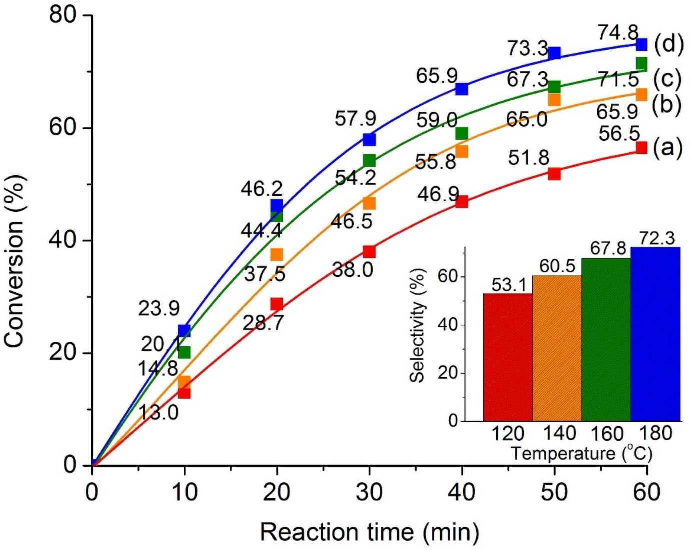

Fig.4. Effect of temperature and reaction time on heptanal conversion over CsM-20 nanocatalyst at (a) 120 °C, (b) 140 °C, (c) 160 °C and (d) 180 °C. Inset: The selectivity to jasminaldehyde at 180 °C after 60 min of reaction.

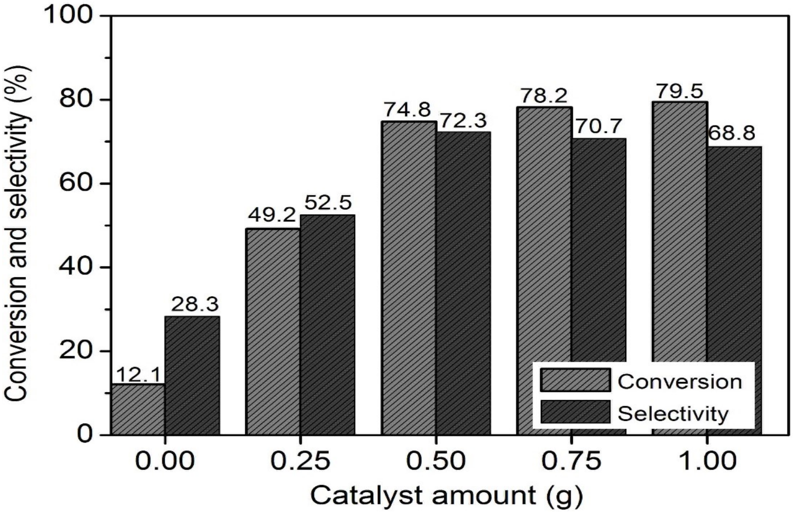

Fig 5: Conversion of heptanal and selectivity of jasminaldehyde catalyzed using different amounts of catalyst. Catalyst: CsM-20, heptanal : benzaldehyde feed ratio = 1:5, temperature = 180 °C, microwave exposure time = 60 min; microwave power = 800 W.

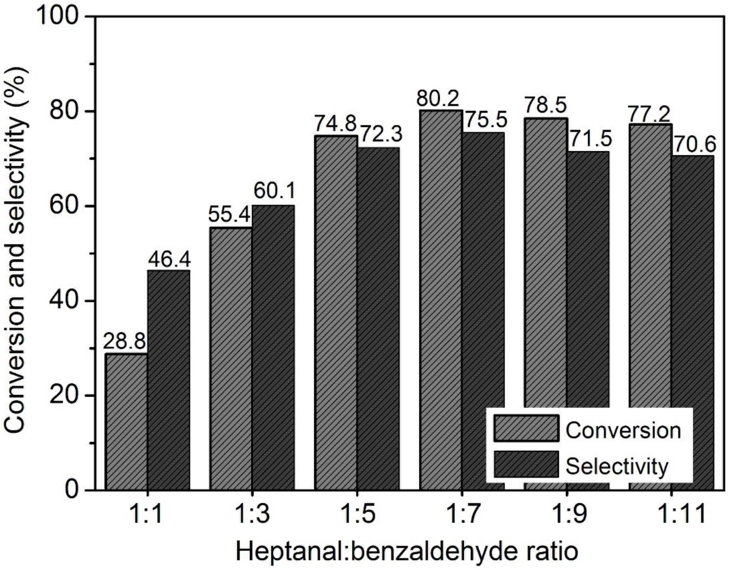

Fig 6: Conversion of heptanal and selectivity of jasminaldehyde using different heptanal: benzaldehyde molar ratios. Catalyst: CsM-20, catalyst loading = 0.5 g, temperature = 180 °C, time = 80 min; microwave power = 800 W.

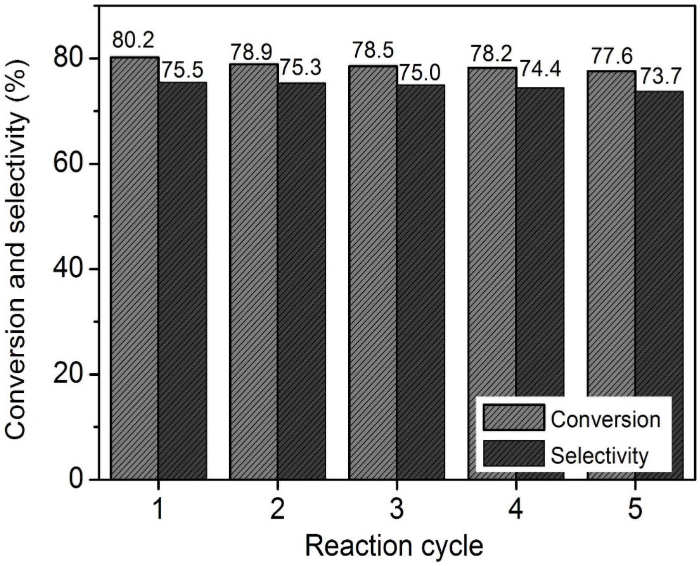

Fig.7. Recycling test of Cs-AlMCM-41 mesoporous nanocatalyst in Aldol condensation reaction.

Conclusion

In conclusion, Al-CsMCM-41 materials obtained had high specific BET surface areas which lie in the range of 400-450 m^2g^{-1}. The number of basicity was found to be 101.57 mol g^{-1}. The basicity was proven via the aldol condensation reaction of heptanal and benzaldehyde using microwave irradiation with a microwave power of 800 W. 74.8% conversion was archived with 72.3% selectivity to jasminaldehyde. The CsMCM-41 can be a promising base catalyst in aldol condensation reaction for the synthesis of jasminaldehyde under autogenous pressure. Hence, the solid catalyst is easily recycled up to five (5) times with minimal loss of activity due to washing.

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