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APPLYING DIFFERENT HEATING METHOD IN-SYNTHESISE OF JASMINALDEHYDE *VIA* ALDOL CONDENSATION REACTION USING HETEROGENEOUS SOLID BASE CSMCM-41

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ABSTRACT

Cesium in-cooperated in Mobile Composite Matter Number 41 (CsMCM-41) was synthesized via hydrothermal synthesis. The material used involve Ludox AS-40 as silica (SiO_2) source, aluminum isoproxide as alumina (Al_2O_3) source, Cesium hydroxide (CeOH) as mineralizer. CsMCM-41 was characterized using X-ray diffraction (XRD), N_2 adsorption-desorption isotherms and X-ray fluorescence (XRF) spectroscopy. The sample shows a high surface area (685 m^2 g^{-1}), large pore volume (0.99 m^{2}g^{-1}), and 20.7 A^o as its pore size. The basicity of the sample was determine using back titration to obtained 101.57 μmol g^{-1}. CsMCM-41 was used as heterogeneous solid base catalyst which is more environmentally friendly to synthesize jasminaldehyde via an aldol condensation reaction between benzaldehyde and heptanal at different temperature and reaction time. This replace the homogeneous base (NaOH, KOH) catalyst that produce corrosive bases as a waste. Four different heating methods were studied. Microwave, non-microwave instant heating, oven and refluxing method. The microwave heating method gave higher conversion (78.2%) and higher selectivity (70.2%) to jasminaldehyde at 180^{o}C in 45 min. as a result of minimized heat loss displayed by the apparatus. Oven synthesis method gave lower conversion (29.4%) and lower selectivity (53.1%), at 180^{o}C at a longer reaction time (24 hours), which resulted due to heat loss to the surrounding. Microwave irradiation was found to be the best heating method for jasminaldehyde synthesis. The catalyst (Cs-MCM-41) is environmentally friendly and can be recycled number of times (up to 5 times), without catalyst deactivation at the same time no waste generated.

Keywords: Jasminaldehyde, Aldol condensation, Mesoporous, Heterogeneous, Aromatic

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 (Fan et al., 2019). Traditionally, it is prepared using homogeneous bases (i.e. KOH, NaOH) in more than stoichiometry. Recently, the heterogeneous solid bases take the center stage due to several problems faced by homogeneous catalysis systems such as severe environmental concerns in waste disposal, toxic, difficulty in handling and storing corrosive homogeneous catalysts, difficulty in separation and recycling problem (Alireza et al, 2010). Many solid base catalysts used to synthesize jasminaldehyde with high selectivity have been reported (Hamza, et al, 2010).

Hamza et al. (2015) observed that an aldol condensation reaction involving benzaldehyde and heptanal recorded low selectivity to jasminaldehyde when using microporous zeolite as a catalyst (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 (Koohsaryan et al, 2016 and Martins et al., 2010). Therefore, the formation of 2-pentyl-2-nonenal and diphenyl allyl cations take center 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 (Weitkamp et al. 2001). AlPO-n zeotype catalyst also displayed an excellent performant as the catalyst and appeared as the best catalyst among the catalyst tested (Li et al. 2006). The whole idea is attributed to the acid-base bifunctional character of the aluminophosphate. Hence, the benzaldehyde molecule was activated by weak acid sites *via* protonation of the carbonyl functional group (Li, et al, 2006, Fan et al, 2019 and Shang et al, 2011). This will in turn facilitate the attack of heptanal intermediate (enolate) produce from the weak basic site of the amorphous aluminophosphate catalyst (Shang et al, 2011).

The discovery of this amazing class of the mesoporous molecular sieves (M41S) by the researchers at Mobil R&D Corporation has brought rapid growth in the field of mesoporous materials (Kim et al, 1997, Wang et al. 2006 Narayan et al, 2018 and Martins et al., 2010). Particularly, MCM-41 is the best-studied member among the mesoporous materials (2-5 nm). It possesses uniform and tunable pore sizes and high specific surface area (up to 1000 m^2/g) which have made this material potential for the progressive applications such as catalyst, adsorbent and host-guest support (Prabhu et al, 2013, and On et al, 2003). The MCM-41 materials made up of only siliceous silica are of limited use due of the lack of acid sites and ion-exchange capacity (On et al, 2003 and Martins et al., 2010). Hence, isomorphous incorporation of metal cations into the siliceous MCM-41 framework, such as Al, B, Fe, Ti, etc. has been reported to modify its surface properties (polarity, ion exchangeability, acidity, basicity etc. (On et al, 2003, Abbaraju et al, 2014 and Martins et al., 2010).

In this research, MCM-41 was synthesized using Ludox AS-40 as a silica source, aluminum isopropoxide as alumina source. Cesium hydroxide to counterbalance the negative charge. The basicity of the MCM-41 was ascertained via an aldol condensation reaction to produce jasminaldehyde. The heating method to produce jasminaldehyde was taken in to consideration. These involved the use of microwave, non-microwave instant heating, refluxing method and the use of the oven.

Characterization Techniques

Currently, many useful characterization techniques that can be used to reveal the properties of a solid. The basic idea behind this is to come up with vital information about the morphological features and different properties of the materials, their chemical composition and their catalytic behaviors (Kresge et al. 1992). However, not all the techniques are suitable for all porous materials (On et al, 2003). Many instrumental and chemical techniques are important in characterizing the properties of these materials. Therefore, the brief scientific fundamentals of powder X-ray powder diffraction (XRD), Nitrogen adoption desorption isotherms, X-ray fluorescence (XRF) spectroscopy, and in-situ pyridine adsorption-IR spectroscopy.

Different Heating Method

Reflux encompasses heating the chemical reaction for a specific period (Aditha et al. 2016). For reflux heating, the reactants used must be in liquid form. The temperature used in the reaction is depending on the boiling point of solvents where a condenser is connected with water flow to allow condensation of solvent to occur (On et al, 2003 and Aditha et al. 2016). Many chemical reactions take a very long time for completing the reaction. Hence, a high temperature is applied to accelerate the reactions.

Microwave is one of the electromagnetic radiations. Its wavelengths fall from 1 cm to 1 m and are operated from 0.3 to 30 GHz. Normally, the chemical reactions are performed using 2.45 GHz microwave radiation due to its right penetration depth in nearly all glass vessels. Microwave has a magnetic field and an electric field where its electric field can interact with dipolar or ionic molecules. Through an electric field, heating is generated where it happens *via* ionic conduction and dipolar polarization (Kappe, 2004).

Non-microwave instant heating is another new heating technique. The heating rate of this technique is reported to be comparable to microwave heating. Unlike microwave heating, this heating technique does not use any electromagnetic wave for heat energy conversion. Instead, it uses semiconducting SiC ceramic to heat the reaction solution. Due to the extremely high thermal conductivity and effusivity (the ability of exchanging thermal energy with the surrounding) of this SiC ceramic, the heat flow from the reactor to the reaction vessel is very fast and therefor fast heating occurs. At the same time, a fast stirring rate is also applied to transfer the heat homogeneously throughout the reaction solution (Surati et al., 2012). Several organic reactions used by non-microwave instant heating have been reported (Kappe, 2004; Chen et al. 2018; Surati et al., 2012; Kappe, 2018).

MATERIALS AND METHODS

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, 3.9627 g 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. Some amounts of aluminum isoproxide (0.6569 g) were added into the resulting solution to obtain gel mixtures with a molar composition of $4SiO_2$: xAl_2O_3: 1CTAB: $1Cs_2O$. The SiO_2/Al_2O_3 ratios from the compositions were twenty (20). The sample was denoted as CsM-20. The sample was placed in an oven at 100 ^oC for 24 h. Then, the pH of the mixture was adjusted to 10.0 with 5 wt% acetic acid. The sample was further heated for 24 h. 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 ^oC overnight. The sample was calcined in a furnace under air condition with a temperature ramp of 1 ^oC/min at 550 ^oC for 6 h to remove the organic template.

Catalytic Experiments

The catalytic Aldol condensation of heptanal and benzaldehyde was conducted using an Anton Paar's microwave reaction system (Multiwave 3000) under solvent-free conditions. Activated CsMCM-41 (0.500 g, 300 ^0C, h), heptanal (7.9 mmol, 97%, Merck) and benzaldehyde (39.6 mol, 99%, Merck) were loaded into a PTFE autoclave. The autoclave was capped and irradiated (600 W output power) at 180 ^0C for 50 min. For comparison study, the reaction was also carried out with non-microwave instant heating for 1 hour, and refluxing in an oil bath (180^0C) for 18h. The reaction was also carried out in an autoclave and oven for 24 h. The reaction mixture was withdrawn and analyzed using a gas chromatography (Agilent 7890A) equipped with a DB-5 capillary column.

RESULTS 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. 1). Two weak peaks were observed at $2\theta = 4.00°$ and 4.65°, which were corresponding to the (110) and (200) plane, respectively. The intense reflection line of (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).

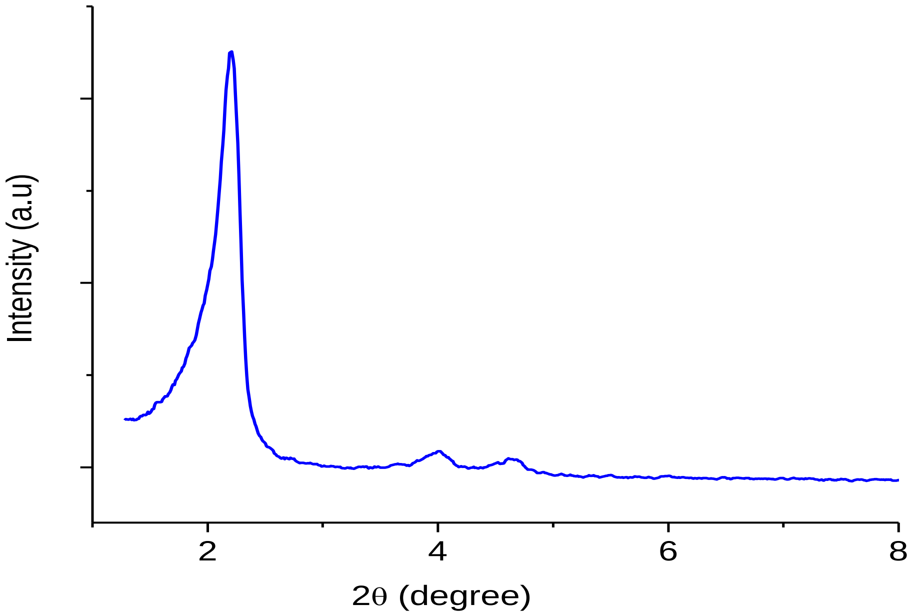

Figure 1: XRD patterns of calcined CsMCM-□□

The N_2 adsorption-desorption isotherms were recorded at 77 K. The profiles of the samples were of type IV isotherms according to the IUPAC classification, which was typical of the MCM-41 mesoporous molecular sieves (Wang et al. 2006 and Koohsaryan et al 2016). The CsMCM-41 showed the highest specific BET surface area of 685 m^2 g^{-1}. The isotherm at $p/p_o < 0.3$ represented the monolayer adsorption of N_2 on the wall of mesopore while that of $p/p_o > 0.4$ represented multilayer adsorption on the surface of the particle. The point at which the inflection started was corresponding to the capillary condensation within the mesopore and its diameter. However, there were inflection steps toward higher $p/p_o < 0.9$ in the MCM-41 framework. The pore size of CsMCM-41 is 20.7 Å and the pore volume is 0.991 cm^3g^{-1} (Wang et al. 2006).

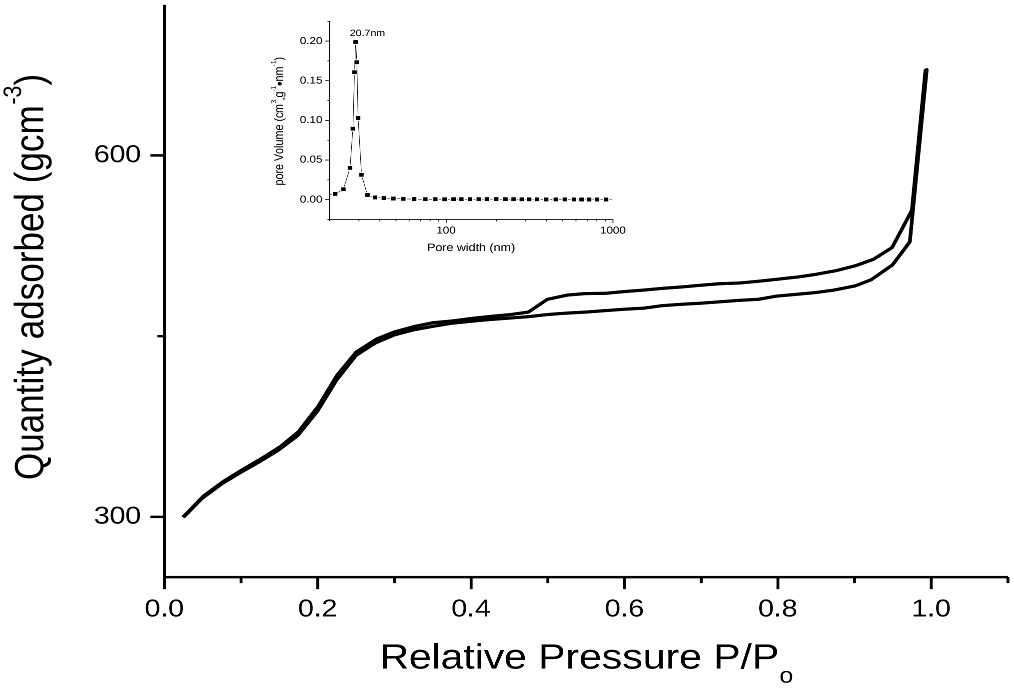

Figure 2: Nitrogen Adsorption-desorption isotherms, and the insert BJH isotherms

The chemical composition of the solids was determined using XRF spectroscopy. The elemental composition of the sample was shown in Table 1. It revealed that Al, Si, Cs and O were the main elements that made up 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 counterbalance the negative charge raised by Al ions to counter balance the negative charge and electrostatically hold the extra-framework Cs^+ cations $(Si–O^-)Cs^+$. This is the reason for the framework's basicity.

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

sample	Weight (%)				Si/Al ration	Basicity (μmol g^{-1})	Pore size	Pore volume	Surface area
	O	Al	Si	Cs			A°	(m^2g^{-1})	S_{BET} (m^2g^{-1})
CsMCM-41	50.87	2.43	34.86	11.84	13.3	101.57	20.7	0.991	685

Effect of heating method

The effect of the heating method on heptanal conversion was investigated at 180 °C using microwave, non-microwave instant heating, refluxing and heating and oven at different heating times, 45 min, 1 hour, 18 hours and 24 hours, respectively. The results were presented in Table 2. A common trend was observed with the increase in heptanal conversion (78.2%) with microwave heating method, which recorded high selectivity (70.2 %) because there was no heat lost. The use of the oven recoded low conversion (29.4 %) and low selectivity (53.1%), and experience a longer period (24 hour). The microwave heating method obtained a higher conversion and selectivity to desires production.

Table 2. Effect of Al content in CsMCM-41 mesoporous framework on the Aldol condensation reaction[a].

Heating method	Time (hours)		Selectivity (%)	
		Conversion (%)	Jasminaldehyde	2-*n*-Pentyl-non-2-enal
Microwave	0.75	78.2	70.2	29.8
Non-microwave instant heating	1	74.8	72.3	27.7
Refluxing method	18	62.8	65.4	34.6
Oven	24	29.4	53.1	46.9

[a]Benzaldehyde: heptanal ratio = 1:5; catalyst loading = 0.50 g; temperature = 180 °C;

Effect of temperature

The effect of temperature on aldol condensation reaction of heptanal and benzaldehyde over CsMCM-41 catalyst was studied at different temperatures (150, 160, 170 and 180 °C) and various reaction times (10 to 60 min) (Fig. 2) using Microwave irradiation. At 150 °C, 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 180 °C. At 180 °C for 60 min, a heptanal conversion of 76.8% with 72.3% selectivity to jasminaldehyde was recorded. In addition, higher temperature under microwave heating led to higher selectivity to jasminaldehyde (Martins et al. 2010). Based on the obtained results, the optimum catalytic performance (highest conversion, highest selectivity to jasminaldehyde) was achieved at 180 °C for 60 min.

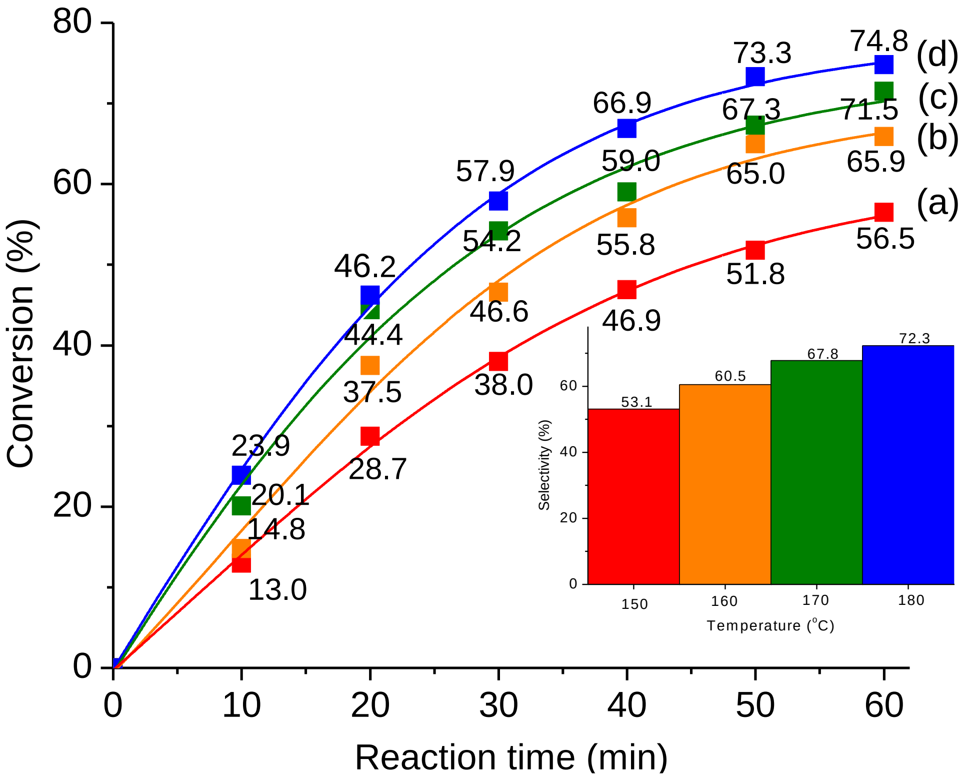

Figure 2: Effect of temperature and reaction time on heptanal conversion over CsMCM-41 nanocatalyst at (a) 150 °C, (b) 160 °C, (c) 170 °C and (d) 180 °C. Inset: The selectivity to jasminaldehyde at 180 °C after 80 min of reaction

Effect of catalyst loading

The catalytic performance can be influenced by the catalyst amount. In the present study, the CsMCM-41 0 amount was varied within the range of 0 – 1.00 g. The catalytic reaction results were shown in Fig. 3. 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 (Alireza et al, 2010 and Api et al 2015). Beyond 0.500 g of CsMCM-41 catalyst, a slight increase in the conversion of heptanal with the decline in selectivity to jasminaldehyde, however observed. This is due high viscosity of the reacting mixture which resulted to 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).

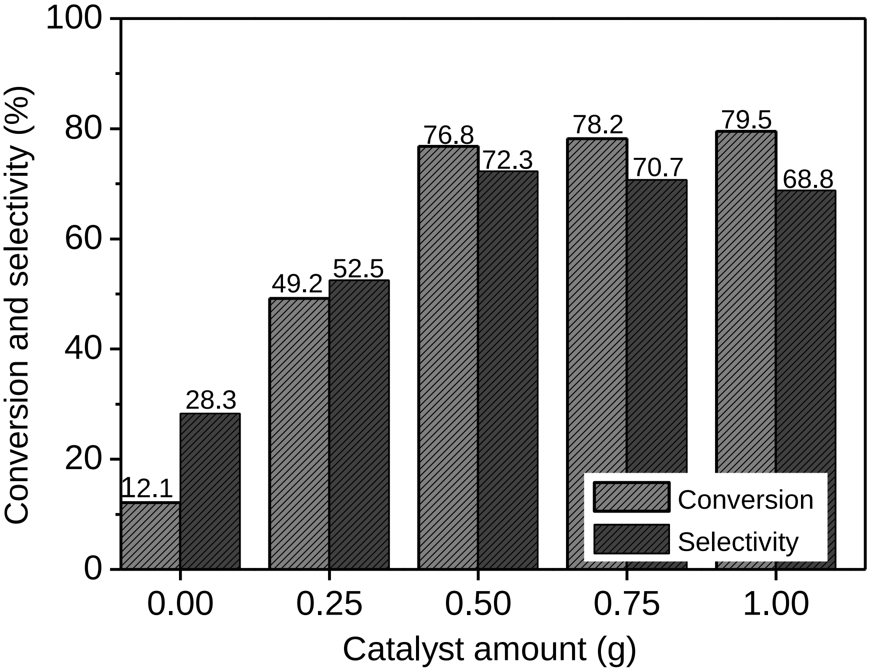

Figure 3: Conversion of heptanal and selectivity of jasminaldehyde catalyzed using different amounts of catalyst. Catalyst: CsM-20, heptanal: benzaldehyde feed ratio = 1:5, temperature = 180 °C, time = 60 min, microwave power = 800 W.

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. 4). The conversion increment thus indicated a positive reaction order with respect to benzaldehyde (Hamza, 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 (Fan 2019 and Hamza, et al, 2010). 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).

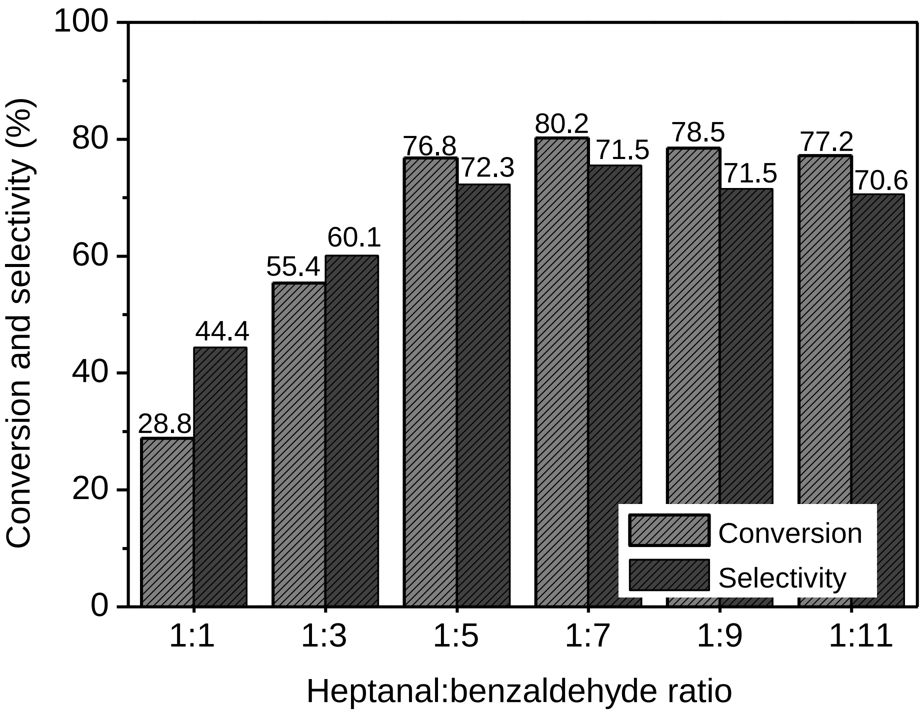

Figure 4: Conversion of heptanal and selectivity of jasminaldehyde using different heptanal: benzaldehyde molar ratios. Catalyst: CsM-20, catalyst loading = 0.5 g, temperature = 180 °C, time = 80 min, microwave power = 800 W.

Catalyst recycling test

The catalyst reusability was studied by successive running the reaction for five times over CsM-20 and the results were presented in Fig. 5. The conversion slightly decreased after multiple cycles of reaction due to the loss of catalyst during separation and washing (Fan, 2019). In addition, the selectivity to jasminaldehyde showed nearly the same in all the five cycles. Hence, the catalyst was stable and it can be recycled several times (Parida et al. 2009).

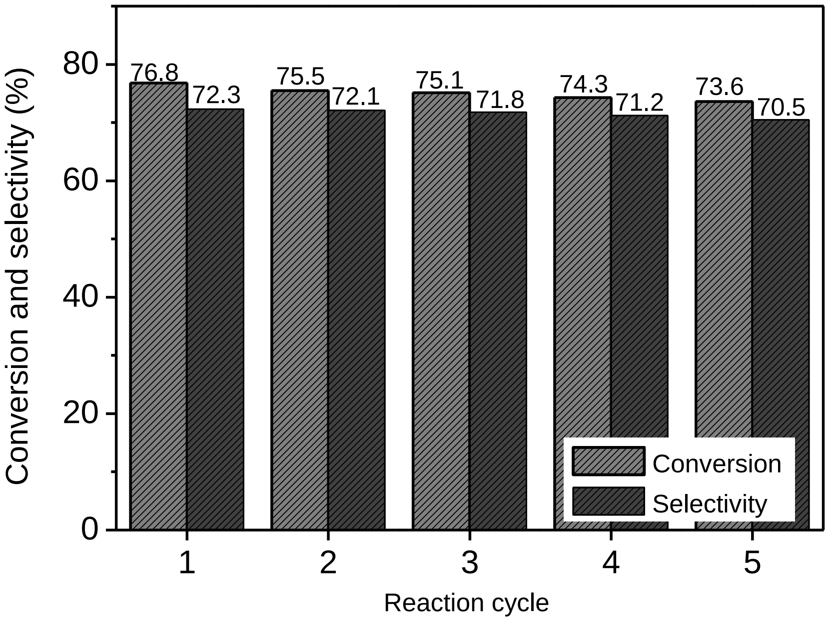

Figure 5: Recycling test of CsM-20 mesoporous nanocatalyst in Aldol condensation reaction.

CONCLUSION

In this study, the mesoporous (CsMCM-41) material was obtained with high specific BET surface area was found to be 678 m^2g^{-1}. The basicity was proven via aldol condensation reaction of heptanal and benzaldehyde using microwave irradiation with microwave power of 800 W, non-microwave heating, refluxing with heating mantle set at 180°C and oven. CsMCM-41 gave a higher conversion of heptanal (73.8%) with high selectivity (70.1%) to jasminaldehyde with microwave heating method. The Oven method of heating recorded lower conversion (29.4%) and lower selectivity (53.1%) to jasminaldehyde. microwave heating method emerge as the best heating method followed by non-microwave instant heating. 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.

REFERENCE

A. Alireza, J. Kalbasi, R. Zamani, F. Kalbasi, (2010). Highly Selective Aldol Condensation Using oxide under Solvent-free Condition. *Chin. J. Chem, 28,* 2074-2082

A. Fan, "Environmental Effects Acid – base bifunctional magnesium oxide catalyst prepared from a simple hydrogen peroxide treatment for highly selective synthesis of jasminaldehyde," Energy Sources, Part A Recover. Util. Environ. Eff. (2019) 1-15.

A. Hamza, N. Nagaraju, "Amorphous metal-aluminophosphate catalysts for aldol condensation of n-heptanal and benzaldehyde to jasminaldehyde", Chin. J. Catal. 36 (2015) 209-215.

A. Prabhu, M. Palanichamy, "Mesoporous cubic Ia3d materials for the preparation of fine chemicals: Synthesis of jasminaldehyde", Micropor. Mesopor. Mater. 168 (2013) 26-131.

A.M. Api, D. Belsito, S. Bhatia, M. Bruze, P. Calow, M.L. Dagli , W. Dekant "Short Review RIFM fragrance ingredient safety assessment , α-amylcinnamaldehyde", Food Chem. Toxicol. 82 (2015) 20-28.

C.O. Kappe "My twenty years in microwave chemistry: from kitchen oven to microwave that aren't microwave", Chem. Rec. 18 (2018) 1-26.

C.O. Kappe, "Controlled Microwave Heating in Modern Organic Synthesis Angewandte", Angew. Chem. Int. Ed. 43 (2004) 6250- 6284.

C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, "Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism", Nature 359 (1992) 710-712.

D.T. On, D. D. -Giscard, C. Danumah, S. Kaliaguine, "Perspectives in catalytic applications of mesostructured materials", Appl. Catal. A: Gen. 253 (2003) 545-602.

E. Koohsaryan, M. Anbia, "Nanosized and hierarchical zeolites: A short review", Chin. J. Catal. 37 (2016) 447-467.

F. Shang, H. Liu, J. Sun, B. Liu, C. Wang J. Guan, Q. Kan, "Synthesis, characterization and catalytic application of bifunctional", Catal. Commun. 12 (2011) 739-743.

H. Knozinger, S. Huber, "IR spectroscopy of small and weakly interacting molecular probes for acidic and basic zeolites", J. Chem. Soc. Far. Trans. 94 (1998) 2047-2059.

I. Slowing, B.G. Trewyn, V.S. Lin, "Effect of Surface Functionalization of MCM-41-Type Mesoporous Silica Nanoparticles on the Endocytosis by Human Cancer Cells", J. Am. Chem. Soc. 128 (2006) 14792-14793.

J. Weitkamp, M. Hunger, U. Rymsa, "Base catalysis on microporous and mesoporous materials: recent progress and perspectives", Micropor. Mesopor. Mater. 48 (2001) 255-270.

J.-H. Kim, M. Tanabe, M. Niwa, "Characterization and catalytic activity of AlMCM-41 prepared by a method of gel equilibrium adjustment", Micropor. Mater. 10 (1997) 85-93.

K. Wang, Y. Lin, A. Morris, J.D. Holmes, "Preparation of MCM-48 materials with enhanced Hydrothermal stability", J. Mater. Chem. 16 (2006) 4051-4057.

K.M. Parida, D. Rath, "Amine functionalized MCM-41: An active and reusable catalyst for Knoevenagel condensation reaction", J. Mol. Catal. A: Chem. 310 (2009) 93-100.

N. La-Salvia, J.J. Lovón-Quintana, A.S.P. Lovón, G.P. Valença, "Influence of Aluminum Addition in the Framework of MCM-41 Mesoporous Molecular Sieve Synthesized by Non-Hydrothermal Method in an Alkali-Free System", Mater. Res. 20 (2017) 1461-1469.

L. Martins, W. Hölderich, P. Hammer, D. Cardoso, "Preparation of different basic Si-MCM-41 catalysts and application in the Knoevenagel and Claisen-Schmidt condensation reactions", J. Catal. 271 (2010) 220-227.

M.A. Surati, S. Jauhari, K.R. Desai, "A Brief Review: Microwave Assisted Organic Reaction", Int. J. Chem. 4 (2012) 645-661.

N. Li, Y. Ma, S. Xiang, N. Guan, "Capturing an aluminophosphite intermediate in the new route of synthesizing zeolite-like aluminophosphates", Chem. Mater. 18 (2006) 975-980.

P.L. Abbaraju, A.K. Meka, S. Jambhrunkar, J. Zhang, C. Xu, A. Popat, C. Yu, "Floating tablet from mesoporous silica nanoparticle", J. Mater. Chem. B 2 (2014) 8298-8302.

R. Narayan, U.Y. Nayak, "Mesoporous Silica Nanoparticles : A Comprehensive Review on Synthesis and Recent Advances", Pharmaceut. 10 (2018**)** 1-49.

S.K. Aditha, A.D. Kurdekar, L.A.A. Chunduri, S. Patnaik, V. Kamisetti, "Aqueous based reflux method for green synthesis of nanostructures: Application in CZTS synthesis", MethodsX 3 (2016) 35-42.

Y. Chen, C. Li, X. Chen, Y. Liu, C. Liang, "Synthesis of ZSM-23 zeolite with dual structure directing agents for hydroisomerization of n-hexadecane", Micropor. Mesopor. Mater. 268 (2018) 216-224

Z.A. Alothman, "A Review: Fundamental Aspects of Silicate Mesoporous Materials", Materials 5 (2012) 2874-2902