SCITECH
RESEARCH ORGANISATION

Volume 5, Issue 1
August 4, 2017

Journal of Progressive Research in Chemistry
www.scitecresearch.com

Zeolite H-ZSM-5: an efficient and reusable catalyst for one-pot synthesis of amidoalkyl naphthols under solvent-free conditions

Sami Ullah Bhat*, Rawoof Ahmad Naikoo, Rayees Ahmad Bhat, Manzoor Ahmad Malla& Radha Tomar
School of Studies in Chemistry, Jiwaji University, Gwalior (M.P.)-474011 India.
Email: profsamibhat92@gmail.com

Abstract

Zeolites have been used as an excellent and highly efficient catalyst for one-pot synthesis of amidoalkyl naphthols. This route involves multicomponent reaction of 2-napthol, various aromatic aldhydes and amide in presence of catalyst Zeolite H-ZSM-5 under solvent free condition. The synthesized Zeolite was characterized by XRD, FTIR and SEM. The products were characterized by FTIR and ^{1}H-NMR. The method involves shorter reaction time, simple procedure, easy workup and the products are obtained in excellent yield.

Keywords: Amidoalkyl Naphthols; Zeolite H-Zsm-5; 2-Napthol.

1. Introduction

Zeolites are aluminosilicates mostly used in the synthesis of fine chemicals. In different areas of organic chemistry use of acidic zeolites has reached significant levels, not only for the possibility to perform environmentally benign synthesis, but also for high yield. The main features of zeolite include their low cost and efficient thermal stability which provide them economically feasible [1]. As a catalyst zeolites are widely used in the development of clean technology, since it avoids the drawback of the conventional technologies mainly environmental pollution. Multicomponent reactions (MCRs), in which three or more reactants are combined in a one-pot process, have become an efficient and excellent tool for the formation of complex molecules .The discovery of known multicomponent reactions (MCRs) has consequently became a popular area of research in organic chemistry. .

2. Review of Literature

Amidoalkyl napthol derive actives having great importance in organic reactions because they can be easily converted to the biological active compounds such as amide hydrolysis reaction. These classes of compounds have property such as hypotensive and braycadic [2].Further amidoalkyl napthols can also be easily converted to 1, 3 oxazine derivatives [3]. These oxazine derivatives have great importance in biological activities including antibiotic [4], antitumor [5], analgesic [6], anticonvulsant [7], antipsychotic [8], antimalarial [9] and antirheumatic properties [10]. Several synthetic methods have been reported in the literature for the synthesis of amidoalkyl napthol in presence of catalysis include $RuCl2(PPh_3)_3$ [11], sulfamic acid [12], $Ce(SO_4)_2$ [13], [FemSILP]-L-prolinate [14], $Bi(NO_3)_3{\cdot}5H_2O$ [15], $K_5CoW_{12}O_{40}{\cdot}3H_2O$ [16],MCM-41-N-propylsulfamic acid [17], $Sr(OTf)_2$,[18] ,$H_3PW_{12}O_{40}$ [19], $Yb(OTf)_3$ [20], $Fe(HSO4)_3$ [21], montmorillonite K10 clay [22], p-TSA [23], $H_4SiW_{12}O_{40}$ [24], 2,4,6-trichloro-1,3,5- trizine [25], iodine [26], PFPAT [27], MgSO4[28], Phosphonitrilic Chloride Acid[29] ,Zeolite H-BEA [30] Citric Acid[31], Tetrachlorosilane [32], Zwitterionic salt [33] $HClO_4$–SiO_2[34].However above these methods have some limitations such as long reaction time, the use of toxic, corrosive, expensive or non-reusable catalysts, low yields of products, the use of large amount of catalyst and strongly acidic conditions. In order to overcome these limitations here we present an excellent and highly efficient catalyst Zeolite H-ZSM-5 for the synthesis of amidoalkyl napthol derivatives.

3. Methodology

3.1. Synthesis of zeolite-ZSM-5:

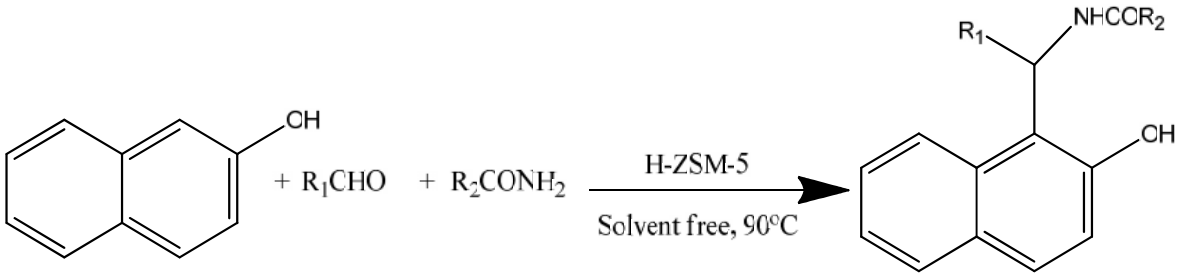
Batch preparation for zeolite-ZSM-5 was carried out by dissolving 0.0552 g of sodium hydroxide and 4.68 g of Tetra Propyl ammonium hydroxide (TAPOH) in 30 mL distilled water. 6.356 g of silicic acid was added in portions, under stirring and the solution shaking for one hour at ambident temperature. Now the mixture was kept for ageing at 100 ^{O}c for 16 h without stirring (Step-1). In next step 0.352 g of sodium hydroxide and 0.412 g of sodium aluminate were dissolved in 30 mL distilled water. 4.524 g of silicic acid was added in portions, under stirring and the solution was shaked vigorously for one hour at ambident temperature (Step-2). The above mixture (step-1) was dissolved into this solution (step-2) and shaked for one hour resulting in the formation of thick gel. The thick gel was kept in a PTFE- lined stainless steel Autoclave and heated in an oven at 180 ^{O}c for 40 h. After synthesis, the product was filtered, washed with distilled water and dried in an oven at 105 ^{O}c for 24 h.

3.2 Conversion of Zeolite –ZSM-5 into H-form

Na-form of zeolite-ZSM-5 was converted into H-form by mixing 9.0 g of synthesized zeolite, 7.230 g of NH_4Cl and 13.80 mL of deionized water with 0.1 M hydrochloric acid solution, in order to reach pH 4.0. The mixture was stirred at 80°C for 6 hrs. Then the material was filtered under suction and washed with deionized water. After the removal of chlorides, the resulting material, NH_4-zeolite, was placed in an oven at 60°C for 24 h. The ammonium form of zeolite was converted into H-form by calcination over 2 hrs at 500°C.

3.3 General procedure for the synthesis of Amidoalkyl naphthols

A mixture of 2-napthol (1mmol), amides (1mmol), an aldhydes (1mmol) and catalyst Zeolite H-ZSM-5 (0.05 g) was taken (as shown in scheme 1). The mixture was magnetically stirring on a preheated oil bath (paraffin oil) at 90^{0}C. After completion of the reaction (monitored by TLC, n-hexane-ethyl acetate, 3:2) .The mixture was cooled to room temperature and hot ethyl acetate was added. The catalyst was removed by simple filtration and the product obtained. The solid product was further re-crystallized from hot ethanol to afford the pure amidoalkyl napthol derivatives



Scheme1. One-pot three-component synthesis of amidoalkyl naphthols

3.4 Characterization of Zeolites and reaction products

3.4.1 X-ray diffraction

The catalyst was analyzed by powder X-ray diffraction (XRD) using a model Shimadzu XRD 6000 equipment. The operational details of the technique were set as follows: Copper Kα radiation at 40 KV/30 mA, with a goniometer speed of 2°/min and a step of 0.02° in the 2θ range scanning from 10° to 70°

3.4 .2 Scanning electron microscopy (SEM)

Surface micrographs of H-Form of zeolite ZSM-5were obtained by SEM instrument. Scanning electron micrograms of these materials were taken at 15,000× magnifications for understanding their surface morphology and to get the clear view of crystals**.**

3.4.3 Fourier transform-infrared spectroscopy (FTIR)

For FTIR analysis, the H-Form Zeolite ZSM-5 sample and reaction products was subjected to physical treatment in accordance with the KBr method, which consists of mixing 0.007 g of the sample and 0.1g KBr, grinding and pressing the solid mixture to 5 tons for 30 s in order to form a pellet that allows the passage of light. The H- Form of Zeolite ZSM-5 and its reaction products was performed using an infrared spectrophotometer Shimadzu FT-IR in the wavelength ranging from 4500 to 500 cm^{-1}.

3.4.4 Nuclear Magnetic Resonance (NMR) Spectroscopy:

^{1}H NMR Spectra were obtained on Bruker 400MHz spectrophotometer with $CDCl_3$ as solvent using tetramethylsilane (TMS) as an internal standard, the chemical shift values are in δ.

4. Data Analysis

N-((2-Hydroxynaphthalen-1-yl) (phenyl) methyl) acetamide: FT-IR (KBr, cm^{-1}): 3656, 3121, 1670, 1400. ^{1}H-NMR ($CDCl_3$): 2.03 (s, 1H, CH_3), 5.69 (s, 1H, OH), 7.11 (d, 1H, CH), 8.02 (s, 1H, NH), 7.13-7.26(9H, m, Ar-H), 7.22-7.29(3H, m, Ar-H), (Table 2, Entry 1, Fig 8, 9)

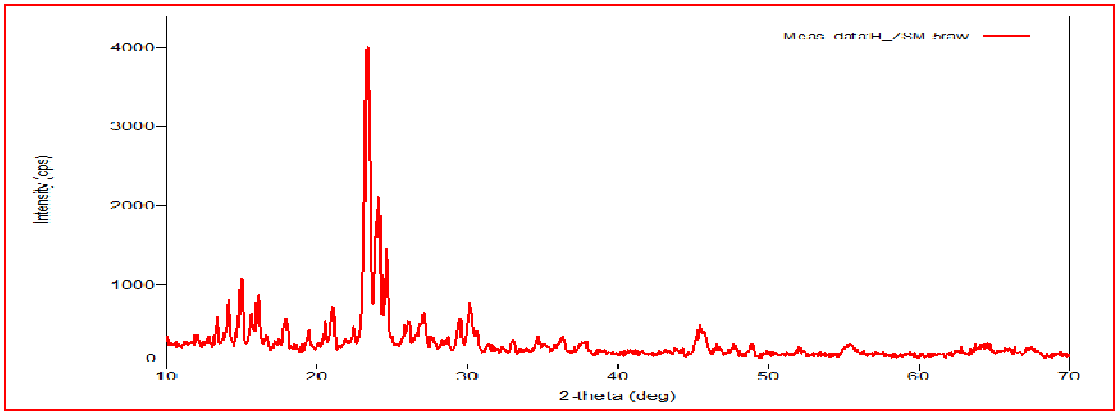
N-((2-hydroxynaphthalen-1-yl) (phenyl) methyl) benzamide: FT-IR (KBr, cm^{-1}): 3612,3525, 3308, 2925, 1660, 1273, 713. ^{1}H-NMR ($CDCl_3$): 6.89 (s, 1H), 7.10-7.11(d, 2H), 7.13 (s, 1H), 7.26-7.40 (m, 4H), 7.42-7.44(m, 6H), 7.46(d, 1H), 7.51 (d, 1H), 7.53-7.55(m, 3H) (Table 2, Entry 2, Fig 10, 11)

N-((4-chlorophenyl) (2-hydroxynaphthalen-1-yl) methyl) acetamide: FT-IR (KBr, cm^{-1}): 3656, 2837, 1668, 1457, 1216. ^{1}H-NMR ($CDCl_3$): 5.57 (s, OH), 2.15-2.02 (t, 3H), 7.46 (s, NH), 7.39-7.11 (m, 11H, Ar-H) (Table 2, Entry 3, Fig 12, 13)

N-((4-hydroxyphenyl) (2-hydroxynaphthalen-1-yl) methyl) benzamide: FT-IR (KBr, cm^{-1}): 3671, 3292, 2848, 1666, 1216, 812, 749. ^{1}H-NMR ($CDCl_3$):7.11 (Ar, 2H), 7.14 (Ar, 2H), 7.29 (Ar, 4H), 7.33(Ar, 2H), 7.46(Ar, 6H), 2.18 (s, 1H), 7.56 (s, NH) (Table 2, Entry 4, Fig 14, 15)

5. Results and Discussion

The X-ray diffraction pattern of H-Form Zeolite ZSM-5 is shown in fig 1. In the X-ray diffraction pattern represents that degree of crystallinity is very high and all the material are crystalline in nature without any amorphous phase. The sharp peak 2θ value for H-Form Zeolite ZSM-5 is 26.13 which is clearly observed.



6. Fig .1 XRD Spectrum of H-ZSM-5 Zeolite

The SEM Morphology of H-form Zeolite ZSM-5 is shown in fig 2. The Scanning Electron Microscopy (SEM) shows spherical morphology of

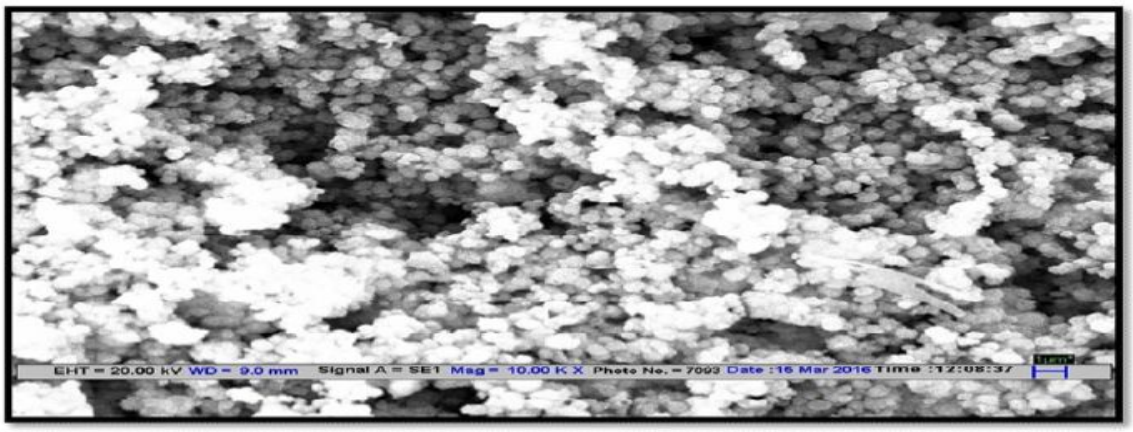


Fig 2. SEM image of H-ZSM-5 Zeolite

The FTIR spectrum of H-Form Zeolite ZSM-5 is shown in fig 3. FTIR spectrum shows absorption bands at 500 cm^{-1} which is attributed to Si, Al-O band, and those at 1050 cm^{-1} and 650 cm^{-1} are respectively attributed to asymmetric and symmetric stretches of the zeolite framework.A band for the OH group is clearly observed at 3400 cm^{-1}.

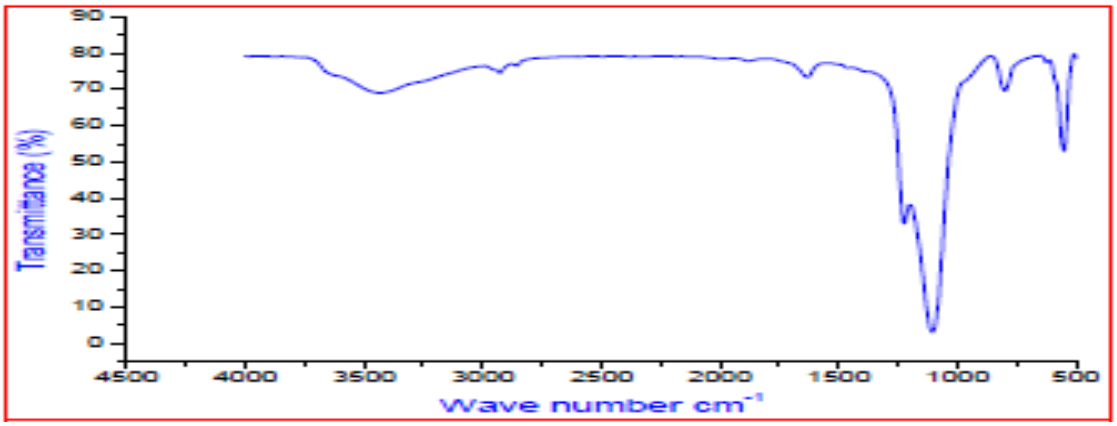
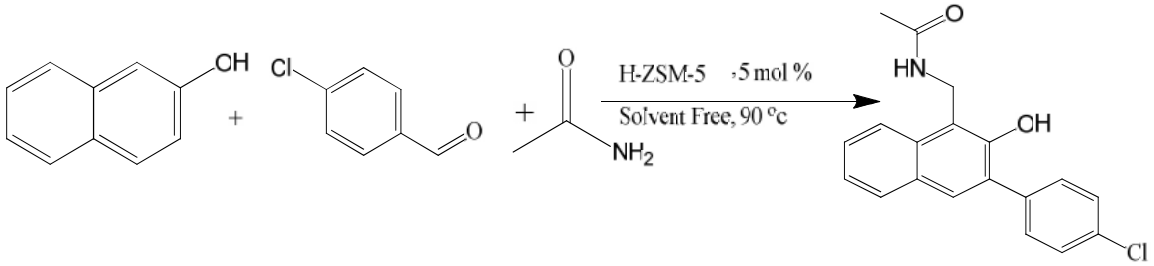


Fig 3. FTIR pattern of H-ZSM 5 Zeolite

We have developed an excellent and highly efficient method for the synthesis of Amidoalkyl napthol derivatives from the reaction of 2-napthol, various derivatives of aldhydes, amide or benziamide and catalyst H-Zeolite ZSM-5 (0.05 g or 50 mol %) under solvent free condition at temperature 90°C .So the model reaction was carried out between 4-chlorobenzaldhyde, Acetamide, and 2-napthol as shown in scheme 2.



Scheme 2: The concerned reaction for the synthesis of amidoalkyl napthols

To select optimized reaction conditions, first effect of various solvents on the rate of reaction for the synthesis of N-((4-chloro-phenyl)-(2-hydroxynaphthalen-1-yl) methyl) acetamide by three component reaction of 2- napthol, 4-chlorobenzaldhyde, and acetamide in presence of catalyst H-ZSM-5 (0.05 g) under different solvents as shown in fig 4.

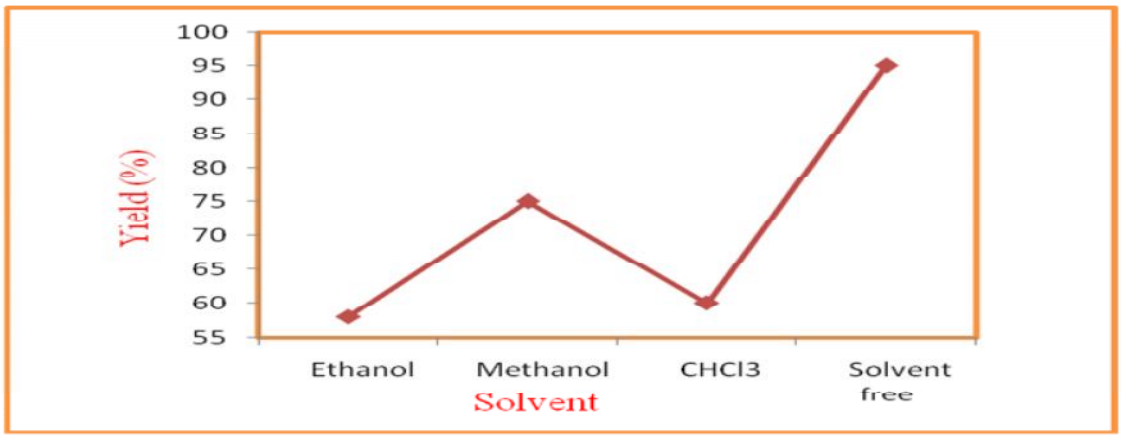


Fig 4: Effect of various solvents for the synthesis N-((4-chloro-phenyl)-(2-hydroxynaphthalen-1-yl) methyl) acetamide

Reactions conditions: 2-napthol, 4-chlorobenzaldhyde, Acetamide, acetamide, solvent free

It was found that best results were obtained when the reaction occurs under solvent free condition (table 1, entry 4). Next study carried out effect of reaction temperature. The effect of reaction temperature on the condensation of 2-napthol, 4-chlorobenzaldhyde, and acetamide to obtain amidoalkyl napthol derivatives at various temperatures ranging from 0^o to 90^o in presence of catalyst H-ZSM-5 (0.05 g) and the result are shown in fig 5.

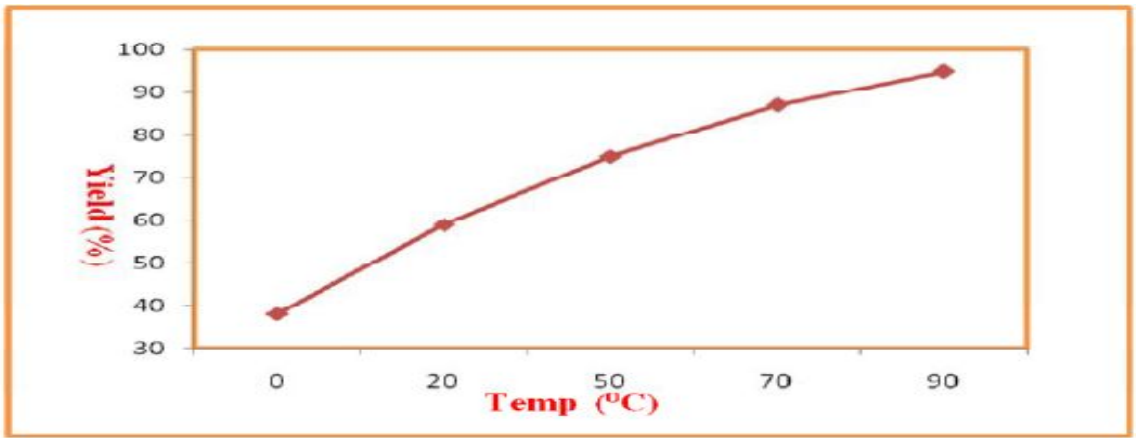


Fig 5: Effect of various reaction temperature for the synthesis N-((4-chloro-phenyl) - (2- hydroxynaphthalen-1-yl) methyl) acetamide*

*Reaction conditions: 2-napthol, 4-chlorobenzaldhyde, acetamide, Temp. 90 ^{0}C

It was found that at temperature 0^oC the yield obtained 25%, with increase the reaction temperature from 20 to 90 ^{o}C towards the product formation and at 90^oC maximum yield was obtained within 2 minutes. Due to this study reaction temperature of 90^oC is optimum for the synthesis of amidoalkyl napthols. The next study carried out to determine amount of catalyst H-ZSM-5 .The reaction was occurred by varying different amounts of catalyst. It was shown that best result was found with (0.05 g or 5 mol %) of the catalyst .Further increase the amount of catalyst in the above mentioned did not have any change in the reaction product as summarized in fig 6.

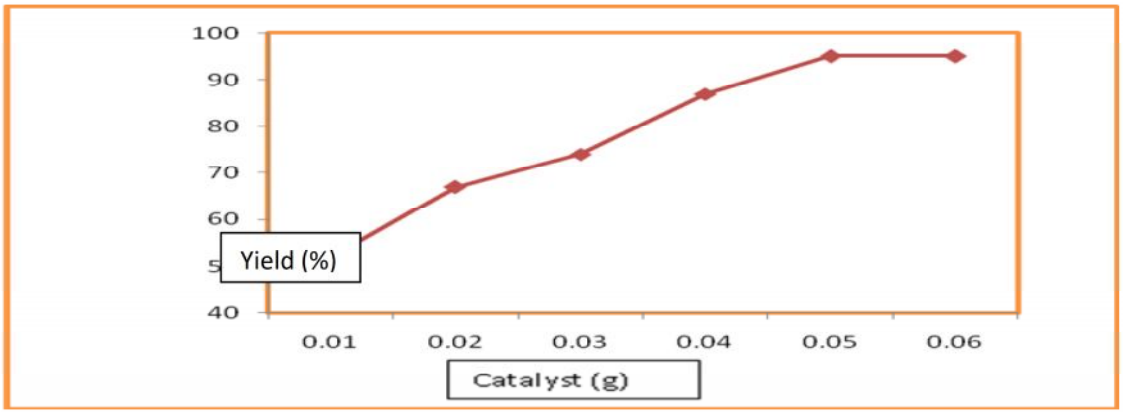


Fig 6: Effect of various amount of catalyst for the synthesis N-((4-chloro-phenyl)-(2-hydroxynaphthalen-1-yl) methyl) acetamide

Reaction conditions: 2-napthol, 4-chlorobenzaldhyde, catalyst (0.05 g), acetamide, Temp. 90 ^{o}C

The reason is that the additional acid sites cause no effect because the reactants may reduce sufficient sites to bind with. The reusability of the catalyst was clarified in the synthesis of N-((4-chloro-phenyl)-(2-hydroxynaphthalen-1-yl) methyl) acetamide. After each run ,the catalyst was recovered, washed with solvents viz chloroform and ethyl acetate, dried in an oven at 100 ^{o}C for 2 h before to use and tested for its activity in the consecutive runs with no fresh catalyst added. The catalyst was tested for four runs as shown in fig 7.

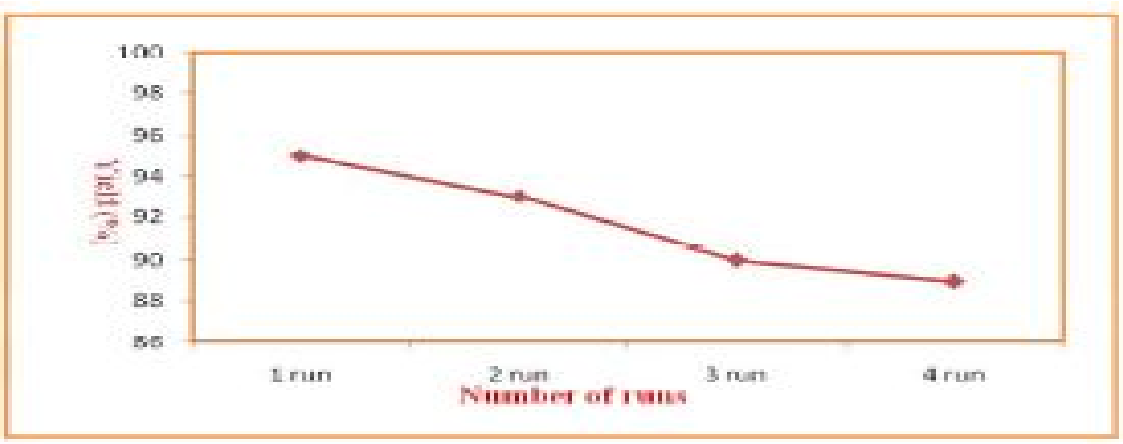


Fig 7 .Effect of recyclability of H- ZSM-5 for the synthesis of N-((4-chloro-phenyl)-(2- hydroxynaphthalen-1-yl) methyl) acetamide

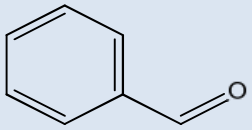
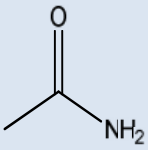
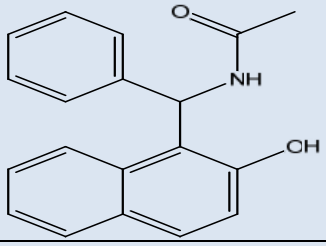
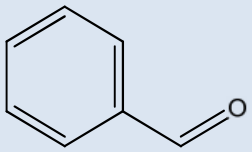
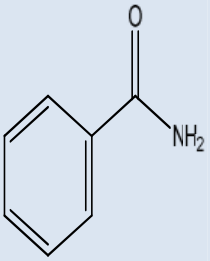
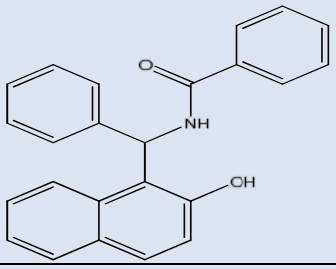
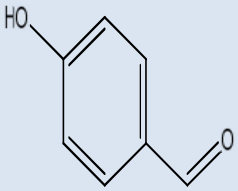
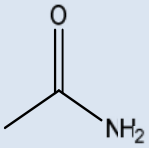
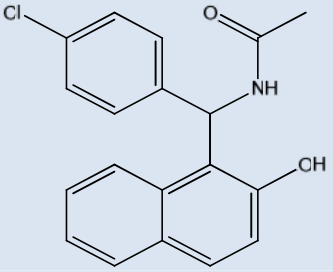
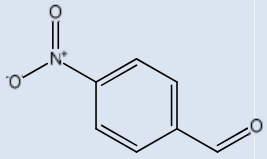
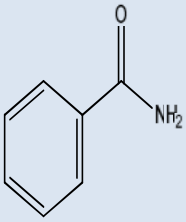
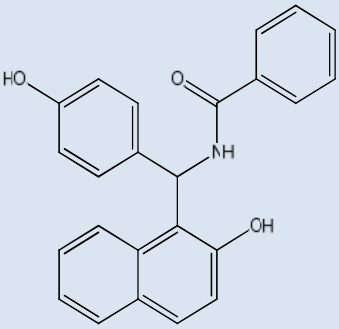
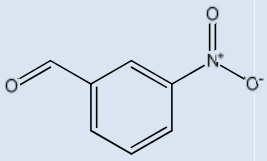
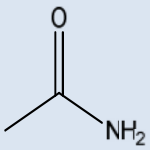
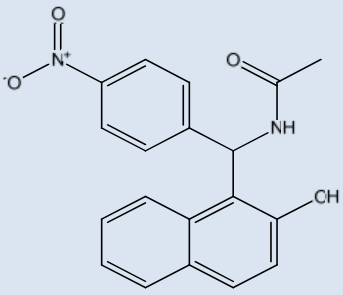
The small reduction in the catalytic activity is because mainly due to the loss of the catalyst structure during recovery process. To show the advantages of H-ZSM-5 in comparison with some other reported catalysts, we found that some results for the synthesis of N-((4-chloro-phenyl)-(2- hydroxynaphthalen-1-yl) methyl) acetamide shown in (table 1) indicates that H-ZSM-5 is an efficient and excellent catalyst with respect to reaction time and yield than previously reported literature

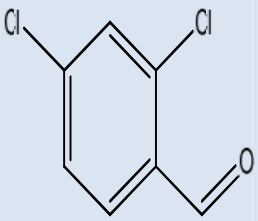
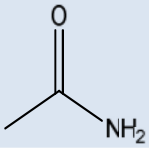
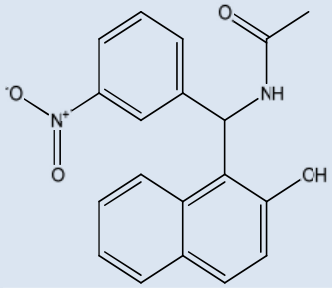
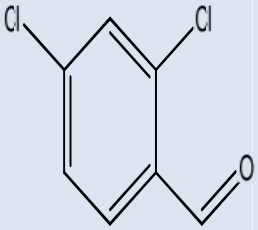
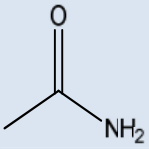
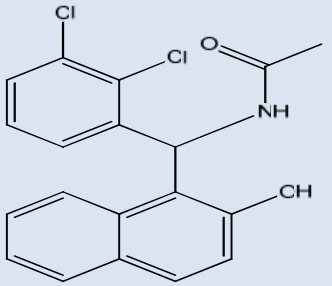
Table 1 .Comparison of H-ZSM-5 for the synthesis of amidoalkyl napthol derivatives

Entry	Catalyst	Condition	Time(min)	Yield (%)	Ref.
1	Zwitter ionic salt	80°C	73	60	33
2	Montmorillonite K10	125°C	30	96	22
3	P-TSA	125°C	240	90	23
4	Iodine	125°C	300	81	26
5	$K_5CoW_{12}O_{40}\cdot 3H_2O$	125°C	180	78	16
6	$HClO_4$-SiO_2	110°C	30	95	34
7	H-ZSM-5	90 °C	2	95	This work

To study the scope of the reaction we utilized various derivatives of aromatic aldehydes to evaluate this procedure. The reaction time and % yield of the products are shown in table 2

Table 2: One-pot synthesis of amidoalkyl napthol derivatives catalyzed by H-ZSM-5

Entry	Aldehyde	Amide	Product	Time (min)	Yield (%)
1				5	88
2				5	89
3				2	95
4				8	89
5				4	92

6				3	93
7				6	91

In all cases, aromatic aldehydes with substituent's carrying either electron-donating or electron-withdrawing groups reacted successfully and gave the products in high yields. No significant substituent effect was observed on the yields of the products

6. Conclusion

We have developed that H-ZSM-5 as an efficient and highly excellent catalyst for the synthesis of amidoalkyl napthols. Amidoalkyl napthol derivatives prepared via a 3- component reaction of an aromatic aldhydes, 2-napthol and acetamide or benzamide in presence of catalytic amount of H-ZSM-5. The main advantage of this reaction involves shorter reaction time, simple procedure, easy workup and the products are obtained in excellent yield.

Acknowledgements

We are highly thankful to IIT Delhi, Jammia Milia University, IIT Patna, Aligarh Muslim University and Jammia Hamdard University for the characterization of the synthesized materials.

7. References

[1] Varma R S. Clay and clay-supported reagents in organic synthesis. (2002), Tetrahedron 58 1235–1255.

[2] Khodaei M.M, Khosropour A R and Moghanian H. Synlett (2006), 916-920.

[3] Darmodran M, Selvam NP and Perumal PT. Tetrahedron Lett. (2009), 5474-5478.

[4] Kusakabe Y, Hirose C and Shirato. S.J. Antibiotic (1972), 25, 44.

[5] Chylińska J B, Urbański T and Mordarski M. J. Med. Chem (**1**963) 6, 484.

[6] Lesher G Y and Surrey A.R. J. Am. Chem. Soc (1955) 77, 636.

[7] Mosher H S, Frankel M.B and Gregory M. J. Am. Chem. Soc (1973) 75, 5326.

[8] Peglion J L, Vian J, Gourment B and Millan M. Bioorg. Med. Chem. Lett (1997)881.

[9] Ren H , Grady S, Gamenara D , Heinzen H , Croft S , Kendrick H , Yardley V and Moyna G. Bioorg. Med. Chem. Lett (2011) 11, 1851.

[10] Matsuoka H , Ohi N , Mihara M , Suzuki H , Miyamoto K , Maruyama N, Tsuji K and Kuroki T. J. Med. Chem (1997) 40, 105.

[11] Xiaoyan Z, Yong R. L and Kim S. H.Bull. Korean Chem. Soc (2012) 2779-2802.

[12] Patil S B, Singh P. R, Surpur, M. P and Samant S D. Ultrason. Sonochem (2007) 14,515
(b) Nagawade R. R and Shinde D B. Chin. J. Chem (2007) 25, 1710.

[13] Selvam N P and Perumal P. T. Tetrahedron Lett. (2006) 47, 7481.

[14] Rashinkar G and Salunkhe R. J. Mol. Catal. A (2010), 316,146.

[15] Wang M, Liang Y, Zhang T T and GAO J J. Chin Chem Lett (2012) 23, 65-68.

[16] Nagarapu L, Baseeruddin M, Apuri S and S. Kantevari. Catal. Commun. (2007) 7, 1729.

[17] Hajjami M, Ghorbani F and Bakht F. Appl. Catal. A: Gen (2014) 470, 303– 310**.**

[18] Su W K, Tang W Y and Li J. J. J Chem Res (2008) 123-128.

[19] Gawand P, Deokar H, Langi B and A .Yadav. Synth. Commun (2009) 39, 4171– 4179.

[20] Kumar A, Rao M S, Ahmad I and B .Khungar. Can J Chem (2009) 87, 714.

[21] Hamid R S, Hossein Y and Majid G. Bioorg. Med. Chem. Lett (2008) 18, 788.

[22] Kantevari S and Nagarapu L. Catal. Commun. (2007) 8, 1857.

[23] Khodaei M M, Khosropour A and Moghanian R H. Synlett (2006) 916.

[24] Supale A R and Gokavi G S. J Chem Sci (2010) 122:189.

[25] P.Zhang, Z.H .Zhang, Monatsh Chem (2009) 140:199.

[26] (a) Nagawade R. R and D. B. Shinde, Mendeleev Commum (2007)17, 299;
(b) Das B, Laxminarayana K, Ravikanth B and Rao B. R. J. Mol. Catal. A: Chem. (2007) 261, 180.

[27] Samad K, Roshanak N, Mojtaba S. O and Mahgol T .World Appl. Sci. J (2012**)** 20,656.

[28] Ashalua K C and Raoa J. N. IJCPS (2013) 5(2), 44-47.

[29] Tigote R M, Haval K.P, Kazi S K and Sagar A D. IJCPS (2015) 39-44.

[30] Mistry S R , Joshi R. S. and Maheria K. C. J. Chem. Sci. (2011) 427–432.

[31] Shaikh K A and Ningdale V B. IOSR Journal of Applied Chemistry (2014) 90-93.

[32] Said S B, Mashaly M. M. A and A. M. Sheta. International Journal of Organic Chemistry 2015, 191-199.

[33] Kundu D .Majee A and Hajra A. Catal. Commun (2010) 11, 1157.

[34] Shaterian H R, Yarahmadi H and Ghashang M. Tetrahedron (2008) 64, 1263.

Authors' Biography

Mr. Sami Ullah Bhat
Research Scholar
Supervisor- Prof. Radha Tomar
School of Studies in Chemistry,
Jiwaji University Gwalior
M.Sc, M.Phil Chemistry
Presently Pursuing Ph.D
No. of Publications = 09