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RESEARCH ARTICLE

ZEOLITE-ZSM-5: AN EFFICIENT AND REUSABLE CATALYST FOR ONE-POT SYNTHESIS OF 2, 4, 5-TRI SUBSTITUTED IMIDAZOLE DERIVATIVES UNDER SOLVENT-FREE CONDITIONS

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ABSTRACT

Zeolites have been used as an excellent and highly efficient catalyst for one-pot synthesis of 2, 4, 5-tri substituted imidazoles under solvent-free conditions. This route involves multicomponent reaction of benzil, aldehydes and ammonium acetate under mild conditions. The synthesized zeolites were characterized by various techniques such as Fourier Transform-Infrared Spectroscopy (FTIR), X-Ray diffraction (XRD), Scanning electronic Microscopy (SEM). The synthesized products were characterized by FT-IR and proton ^{1}H NMR. This process was simple and environmentally benign with high to excellent yields. Furthermore, the catalyst could be recovered conveniently and reused for at least three times.

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INTRODUCTION

Imidazole derivatives are an important class of heterocycles because of their applications in chemical processes and pharmaceuticals (Wang, 2006). They have a wide range of biological activities and are well known analgesics, anti-inflammatory, antipar-asitic, anthelmintic, platelet aggregation inhibitors and antiepileptic agents (Shen, 2008). Several methods such as the hetero-Cope rearrangement (Kidwai, 2007) and four-component condensation (Khosropour, 2008) for the synthesis of trisubstituted imidazoles are reported. In recent years, the synthesis of 2,4,5-trisubstituted imidazoles has been catalyzed by I_2 (Sharma, 2008), $ZrCl_4$, ionic liquid, L-proline, microwave irradiation, $Yb(OPf)_3$, $InCl_3.3H_2O$, $NiCl_2.6H_2O$/ Al_2O_3, DABCO, magnetic Fe_3O_4 nanoparticles, nano $MgAl_2O_4$, Although some of the methods are actually efficient from the synthetic chemist's points, many of the synthetic protocols for imidazoles reported above suffer from one or more disadvantages, such as harsh reaction conditions, poor yields, and prolonged reaction time, use of hazardous and often expensive acid catalysts. Therefore, the development of efficient, simple, environmentally friendly and high- yielding methods using new catalysts for the preparation of these compounds is still necessary. In this paper, we describe an efficient and practical route for the synthesis of 2, 4, 5-tri substituted imidazoles derivatives under solvent free conditions using ZSM-5 as catalyst.

Experimental work

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.

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

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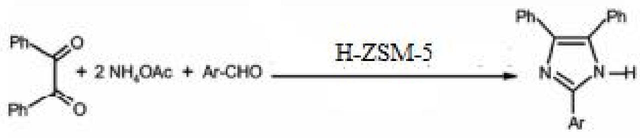
for 24 h. The ammonium form of zeolite was converted into H-form by calcination over 2 hrs at 500°C.

General procedure for synthesis of 2, 4, 5- trisubstituted imidazoles: A mixture of benzil (1 mmol), ammonium acetate (2 mmol), aldehyde (1 mmol) and 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 100°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 2, 4, 5- trisubstituted imidazoles derivatives.



Scheme1: Synthesis of 2, 4, 5- trisubstituted imidazoles catalyzed by Zeolite-ZSM-5

Characterization of Zeolites and reaction products

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°

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.

Fourier transform-infrared spectroscopy (FT-IR): For FT-IR 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}

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.

RESULT 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.

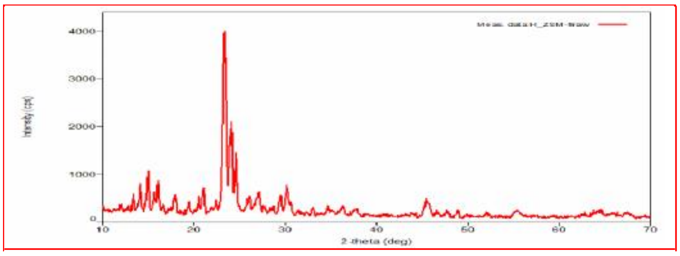


Fig. 1. XRD Spectrum of H-Zeolite 5

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

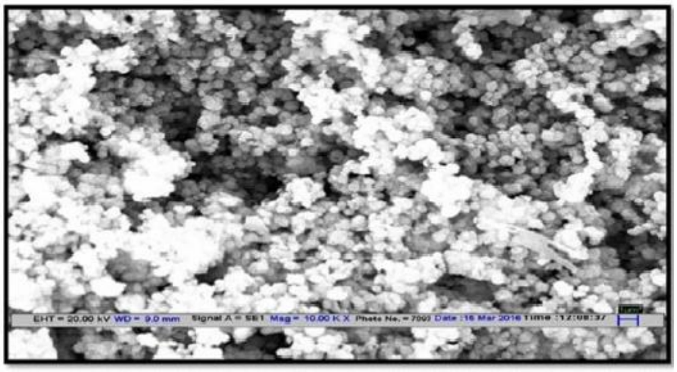


Fig. 2. SEM image of H-ZSM-5 Zeolite

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}.

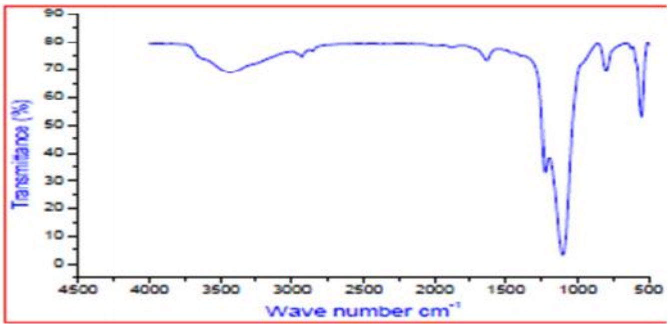


Fig. 3. FT-IR Spectrum of H-ZSM-5

In this study, to choose the appropriate catalyst some of the Lewis acids such as AlCl3, WCl6, ZrCl4, VCl3 were selected. Then, a comparative study was made by using benzaldehyde, benzil and ammonium acetate in the presence of these materials as catalyst (Figure 2). The samples were heated under conventional conditions at 100°C in the presence of each catalysts, separately. The corresponding results are summarized in table 1. The results indicated that H-ZSM-5 was the best catalyst and consequently it was selected for subsequent experiments. In the absence of catalyst, the yield of the product was found to be very low. In the course of this study we found that H-ZSM-5 was the most effective catalyst in obtaining the yield of triphenylimidazole (80%). The catalytic activity of H-ZSM-5 is remarkable for both quantitative and qualitative advantages such as cheap availability and non-toxicity.

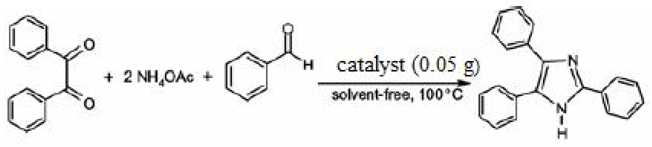


Fig.2 synthesis of 2,4,5-triphenyl-1Himidazole using H-ZSM-5 as catalyst

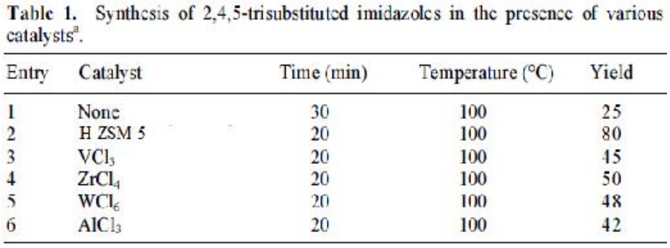


Table 1. Synthesis of 2,4,5-trisubstituted imidazoles in the presence of various catalysts[a].

Entry	Catalyst	Time (min)	Temperature (°C)	Yield
1	None	30	100	25
2	H ZSM 5	20	100	80
3	VCl_3	20	100	45
4	$ZrCl_4$	20	100	50
5	WCl_6	20	100	48
6	$AlCl_3$	20	100	42

To optimize the reaction conditions, the reaction of benzaldehyde, benzil and ammonium acetate was used as a model reaction (table 2). In the following study, we examined the reaction at different temperature to find out the effect on the reaction. It was found that at lower temperature, even if the reaction time was prolonged, it gave only low yield, and higher the temperature, higher the yield. The efficiency of the reaction is mainly affected by the amount of catalyst and temperature. As indicated in table 2, the best results have been obtained at 100°Cwith 0·1 mmol H-ZSM-5 Increasing the amount of H-ZSM-5 and temperature has not shown in the increase of yield.

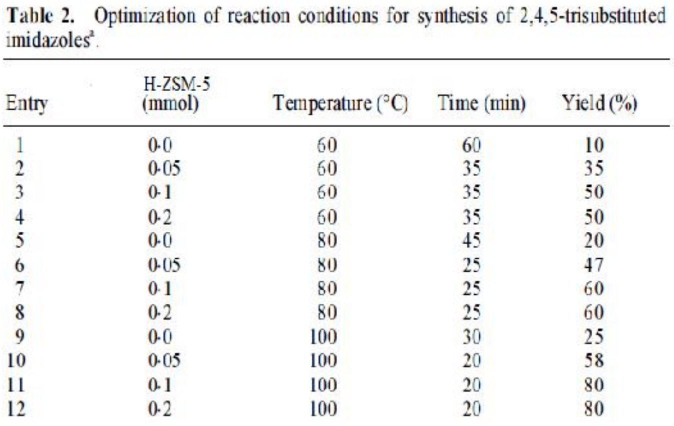


Table 2. Optimization of reaction conditions for synthesis of 2,4,5-trisubstituted imidazoles[a].

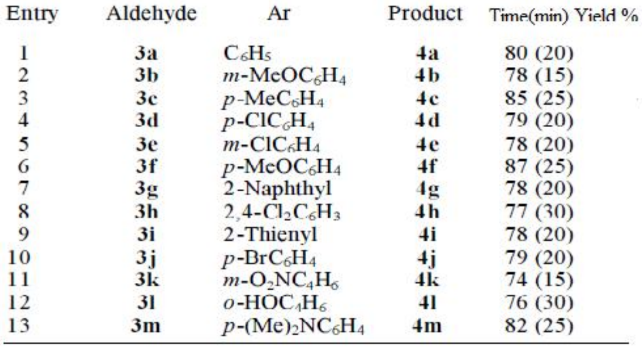
Entry	H-ZSM-5 (mmol)	Temperature (°C)	Time (min)	Yield (%)
1	0·0	60	60	10
2	0·05	60	35	35
3	0·1	60	35	50
4	0·2	60	35	50
5	0·0	80	45	20
6	0·05	80	25	47
7	0·1	80	25	60
8	0·2	80	25	60
9	0·0	100	30	25
10	0·05	100	20	58
11	0·1	100	20	80
12	0·2	100	20	80

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 3.In all cases, aromatic aldehyde 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.

Spectral Data

2-(3-methoxyphenyl)-4,5-diphenyl-1H-imidazole (4b): m.p.: 259–262°C; IR (cm–1, KBr): 3431·80, 3058·38, 2926·27, 1591·31, 1482·73, 1241·06, 768·39, 686·84; UV ($CDCl_3$): λmax = 314, 240 nm; ^{1}H NMR (400 MHz, DMSO-d6): δ = 12·70 (s, 1H, NH), 6·80–7·80 (m, 14H, Ar-H), 3·80 (s, 3H, OMe) ppm; ^{13}C NMR (100 MHz, DMSO-d6): δ = 160·00, 145·86, 137·63, 135·60, 132·15, 130·27, 129·20, 128·86, 127·70, 118·13, 114·70, 110·70, 55·70 ppm; Anal. Calcd. for $C_{22}H_{18}N_2O$: C, 80·96; H, 5·56; N, 8·58. Found: C, 80·94; H, 5·55; N, 8·57.

Table 3 H-ZSM-5 catalyzed synthesis of 2, 4, 5 trisubstituted imidazoles under solvent free condition



Entry	Aldehyde	Ar	Product	Time(min) Yield %
1	**3a**	C_6H_5	**4a**	80 (20)
2	**3b**	*m*-$MeOC_6H_4$	**4b**	78 (15)
3	**3c**	*p*-MeC_6H_4	**4c**	85 (25)
4	**3d**	*p*-ClC_6H_4	**4d**	79 (20)
5	**3e**	*m*-ClC_6H_4	**4e**	78 (20)
6	**3f**	*p*-$MeOC_6H_4$	**4f**	87 (25)
7	**3g**	2-Naphthyl	**4g**	78 (20)
8	**3h**	2,4-$Cl_2C_6H_3$	**4h**	77 (30)
9	**3i**	2-Thienyl	**4i**	78 (20)
10	**3j**	*p*-BrC_6H_4	**4j**	79 (20)
11	**3k**	*m*-$O_2NC_4H_6$	**4k**	74 (15)
12	**3l**	*o*-HOC_4H_6	**4l**	76 (30)
13	**3m**	*p*-$(Me)_2NC_6H_4$	**4m**	82 (25)

2-(2-naphthyl)-4,5-diphenyl-1H-imidazole (4g): m.p.: 273–276°C; IR (cm–1, KBr): 3429·00, 3054·16, 1600·50, 1500·35, 1447·26, 752·89, 697·10; UV($CDCl_3$): λmax = 330, 288, 244 nm; 1H NMR (400 MHz, DMSO-d6): δ = 12·80 (s, 1H, NH), 8·61 (s, 1H, Ar-H), 8·25 (d, 1H, 3J = 8·00 Hz, Ar-H), 7·92–8·02 (m, 3H, Ar-H), 7·53–7·61 (m, 6H, Ar-H), 7·46 (t, 2H, 3J = 7·90 Hz, Ar-H), 7·39 (t, 1H, = 7·60 Hz, Ar-H), 7·32 (t, 2H, 3J = 7·90 Hz, Ar- H), 7·24 (t, 1H, 3J = 7·60 Hz, Ar-H) ppm; 13C NMR (100 MHz, DMSO-d6): δ = 146·00, 137·90, 135·60, 133·50, 132·20, 131·50, 129·10, 129·00, 128·90, 128·70, 128·60, 128·30, 128·20, 127·60, 127·10, 127·00, 126·80, 124·10, 123·90 ppm; Anal. Calcd. for $C_{25}H_{18}N_2$: C, 86·68; H, 5·24; N, 8·09. Found: C, 86·66; H, 5·22; N, 8·08.

Conclusions: In summary, we presented an efficient, mild and rapid approach for the synthesis of 2, 4, 5- trisubstituted imidazoles via condensation of a representative 1,2-diketone (benzil) with various aromatic aldehydes and ammonium acetate, by using H-ZSM-5 as a new and highly effective catalyst under solvent-free and microwave conditions. Non-corrosiveness, safe, low waste, easy for separation, short time, high yields and environmentally benign are some of the advantages of this methodology.

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Conflicts of Interest: The corresponding author declared no conflict of interest.

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