Catal Lett (2014) 144:1751–1758
DOI 10.1007/s10562-014-1327-0

Investigation of Structural Change and Basicity of NaY Zeolite upon Loading KF and Their Application in Henry Nitroaldol Reaction Under Microwave Irradiation Condition

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Received: 24 April 2014 / Accepted: 24 July 2014 / Published online: 13 August 2014

Abstract Potassium salt modified NaY zeolite along with methanol–water mixture as solvent under microwave irradiation offers an environmentally benign way to synthesize β-nitroalcohols rapidly with excellent yield and selectivities. Here, NaY zeolite was modified with 0.5–20 % KF (w/w) by a wet impregnation method and characterized by X-ray diffraction, FT-IR and Hammett base strength measurement methods. It was observed that framework structure preserved even after 20 % loading of KF while crystallinity decreased from lower to higher loading. The obtained materials showed quite different base strengths with varying percentage of the salt over the support and with change of their activation temperatures. The effects of different reaction parameters such as amount of solvents, nature of solvents, microwave power and microwave irradiation time were studied to minimize the reaction time without compromising the yields. Among the loaded catalysts, 10 wt% KF loaded catalyst was found to be the best catalyst and gave 97 % yield within 2 min under optimized reaction conditions. Recovery of the catalysts was tested for three times and it showed similar conversions in each cycle.

Keywords NaY zeolite · Microwave · Nitroaldol reaction · β-Nitroalcohols · Hammett indicator

1 Introduction

Henry nitroaldol reaction has got interests from very early days due to diverse applications of the product β-nitro alcohol and its easy conversion possibility into other synthetically important compounds [1–4]. In the recent years, strategies have been made to improve the reaction conditions as well as to minimize side products with various catalyst systems and suitable reaction media [5–8]. Particularly, solid base catalysts like alkali and alkaline earth metal exchanged zeolite X and zeolite Y, supported zeolites and metal oxides, hydrotalcites etc. are used for this reaction to take advantage of their tunable basicity, easy product isolation and catalyst recycling [9–12]. In the flow of current research, a group of basic materials have been prepared by exchanging extra framework cations of zeolites with alkali and alkaline earth metal cations [13] and loading alkali metal salts over a variety of solid supports where potassium salt is the most common among other alkali salts [14–17]. Various supports such as porous oxides Al_2O_3, ZnO, ZrO_2 and SiO_2, zeolite NaX, NaY, ZSM-5, KL zeolite etc. [18–20] are used to prepare solid bases by using potassium salts as guest material. Although Al_2O_3 and ZrO_2 have been found as excellent basic materials in presence of potassium salts, their use is limited due to low surface area and disordered pore arrangements. Zeolites having aluminosilicate compositions are preferred as host material due to their high surface area, well organized pore channels, stability towards heating and its environmentally benign nature. Potassium fluoride has been supported onto a variety of solid host materials due to its different advantages such as it is easy to handle, inexpensive, thermally stable and can be easily dried. Zhu and his co-workers reported only mild basicity of NaY zeolite ($H_- = 9.3$) after loading 16 wt% KF and activated at 400 °C while 16 wt% KF loading over Al_2O_3 coated NaY zeolite and activated at 400 °C generates strong basic sites

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Electronic supplementary material The online version of this article (doi:10.1007/s10562-014-1327-0) contains supplementary material, which is available to authorized users.

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($H_- = 17.2$) without significant change in zeolite pore architecture [21]. Again, Sun et al. have reported quite low basicity of NaY/KF ($H_- = 7.2$) after activation at 600 °C and the structure collapsed upon activation [22]. Thus, loading of NaY zeolite with different amount of KF and activation at different temperatures would be interesting to observe their effect upon the structure, base strengths and catalytic activities.

Synthetic protocol using microwave irradiation are gaining value now a days due to its core heating mechanism and shorter reaction time than classical conditions [23–25]. The green approach lies in getting higher yields within short reaction time, energy efficiency, higher selectivities and possibility to carry out reactions under solventless conditions [26, 27]. However, solventless synthesis has got limitations in that they generally require liquid bases to ease mixing between the reactants and catalysts when all reactants are solid. Besides, larger amount of liquid reactants are used as reaction medium when both catalysts and other reactants are solid. Therefore, a large number of organic reactions have been carried out during these days under microwave irradiation using solid catalysts [28–30] with different reaction media. Although Henry nitroaldol reaction has been carried out with a variety of reaction media including water [31], ionic liquids [32], fluorous biphasic system [33] etc., investigation of suitable reaction media with heterogeneous catalytic system is an ongoing research. Moreover, the dehydrated nitroalkene predominates over the desired nitroaldol product in many cases [34, 35]. In this regard the use of microwave to speed up the reaction and aqueous alcoholic water as solvent is helpful due to its higher dielectric constant than most of the commonly used organic solvents and thus can couple with microwave easily. Although Henry nitroaldol reaction under microwave irradiation condition is not a new approach [36], the combined use of solid base along with microwave irradiation condition is not very common [37, 38].

At this time we have impregnated 0.5–20 wt% KF in NaY zeolite by a wet impregnation method from aqueous solution of KF and calcined at a temperature range of 450–800 °C, measured basicities and checked catalytic activities towards Henry nitroaldol reaction under microwave irradiation conditions. The effect of KF loading upon zeolite framework structure, change in basic properties, their catalytic behaviour and selectivities towards Henry nitroaldol reaction with a variety of solvents under microwave irradiation conditions was studied systematically.

2 Experimental

2.1 Materials

NaY zeolite was purchased from HiMedia Laboratories Pvt. Ltd.; aldehydes from Sigma Aldrich and Merck, Germany; Phenolphthalein and Neutral red from Merck, Germany; Nitromethane from G. S. Chemicals Testing Lab & Allied Industries, New Delhi; potassium fluoride (KF), sodium sulphate (Na_2SO_4), silica gel, iodine and the solvents were purchased from RANKEM.

2.2 Preparation of the Catalysts

In the typical synthesis of potassium loaded NaY zeolites, sodium form of zeolite Y was used to impregnate KF in different proportions. In this procedure, KF amounts of 0.5, 1, 2, 3, 5, 10, 15 and 20 % KF (w/w) were impregnated over NaY zeolite by a wet impregnation method. To impregnate 10 % KF over NaY, 50 mg of KF was first dissolved in 10 mL distilled water and then added to 500 mg NaY zeolite. NaY zeolite was dried in an oven at 80 °C overnight before impregnation. The solution was stirred at room temperature for 24 h, slurries were dried at 100 °C for overnight and stored in a desiccator. Following the same procedure other catalyst samples were prepared by taking appropriate amount of KF and NaY zeolite. The catalysts were then calcined in a muffle furnace at temperature range of 450–800 °C for the required time.

2.3 Characterization

X-ray diffraction patterns of the prepared samples were recorded using a Rigaku (miniflex UK) X-ray diffractometer with Cu K_α radiation ($\lambda = 1.548$ Å) operated at 30 kV and 15 mA at a scan speed of $2°\mathrm{min}^{-1}$ and 2θ range of 2–50°. The % crystallinity of the samples were calculated from XRD peaks by using the formula, % Crystallinity = $(A_S \times 100)/A_R$, where, A_R = Integrated area of the reference material under the peaks between a set of 2θ limits and A_S = Integrated area of the sample under the peaks between the same set of 2θ limits as that of the reference. The crystallite sizes were calculated by X-ray line broadening method considering reflection planes at 2θ values 7.25, 24.05 and 30 using the Debye–Scherrer equation [$t = K\lambda/\beta\cos\theta$, where t is the crystallite size, K is shape factor (taken as 1), λ is the X-ray wavelength (1.542 Å for Cu target), β is the full width at half maximum (FWHM) in radians and θ is the Bragg's angle of diffraction] [39].The specific surface areas were determined from N_2 adsorption–desorption isotherms by Brunaur-Emmett-Teller method using a Quantachrome NOVA 1000e Surface area and Pore Size Analyzer at 77 K. FT–IR spectra were recorded on a Nicolet Impact Model-410 spectrometer at 32 scans and 1 cm^{-1} resolution in the mid IR (400–4,000 cm^{-1}) region using the KBr pellet technique. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS 400 by taking Me_4Si as internal standard in $CDCl_3$ and CD_3OD solvents. Thin-layer chromatography was carried out on glass plates with silica gel and preparative column chromatography was carried out with silica gel having 60–120 mesh size.

The strength of basic sites was measured by using Hammett indicators [40]. The following Hammett indicators were used: Neutral red ($H\_ = 6.8$–8.0), Phenolphthalein ($H\_ = 8.0$–9.6) and Tropaeolin-O ($H\_ = 11.1$–12.7). In this method 25 mg of solid calcined at 450, 600 and 800 °C was shaken with 1 mL solution of indicator (0.1 % in methanol) and left to equilibriate for 2 h. The colour of the catalyst was then noted. The aqueous soluble amount of basic sites was determined by acid–base titration technique reported previously [22]. In this procedure 100 mg of calcined sample was shaken in 10 mL water at room temperature for 24 h and the catalyst was separated by centrifugation. The filtrate was neutralized with 10 mL of aqueous HCL (0.05 M) and then the remained acid was titrated with 0.01 M standard aqueous NaOH. Oxalic acid dihydrate was used for standardization of NaOH and a methanol solution of phenolphthalein (1 mL, 0.1 mg/mL) was taken as indicator.

2.4 Catalytic Test

All catalytic reactions were performed in “Catalyst system Scientific Microwave systems” scientific microwave reactor having power output 700 Watt (2,450 MHz), power levels from 140 to 700 Watt and automatic temperature sensors with flexible proble up to 600 °C (Fig. 1). In a typical procedure of synthesis of β-nitroalcohols, 15 mg of calcined catalyst was added to a mixture of 1 equivalent aldehyde, 4 equivalent Nitromethane and 3 mL solvent in a long necked microwave flask fitted with a reflux condenser in at 280 Watt (40 % of 700 Watt) microwave power and 50 °C. The reaction was monitored by thin layer chromatography, stopped after completion of the reaction and cooled to room temperature. Organic portion was then extracted, dried over sodium sulphate (Na_2SO_4) and concentrated under vacuum to obtain the crude product. The product was then purified by thin layer chromatographic technique and analyzed by ^1H and ^{13}C NMR techniques. The conversions and selectivities were calculated on the basis of integration of ^1H NMR signals of the reactants and products from crude reaction mixture. Catalysts were recovered by centrifuge, dried at 100 °C for overnight calcined and reused. Catalytic activities of the recovered catalysts were then checked under similar reaction conditions.

3 Results and Discussion

The X-ray diffraction patterns of parent NaY zeolite and KF modified zeolites calcined at 450 °C (Fig. 2) suggests that zeolite framework structure remains preserved even after 20 % loading of KF. However, peak intensities (Fig. 2) and crystallinity (Fig. 3) decrease gradually from

Fig. 1 Catalyst system scientific microwave

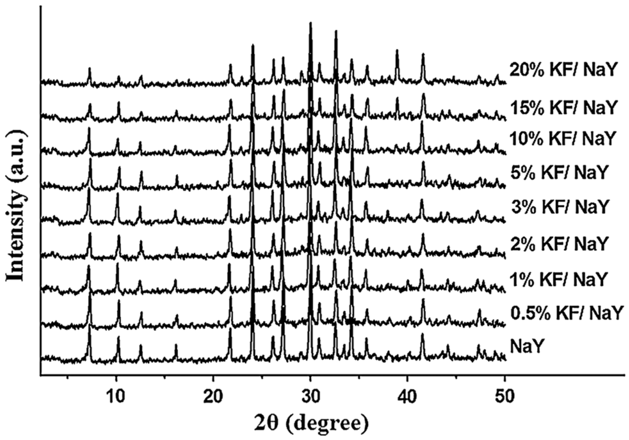


Fig. 2 XRD patterns of NaY and KF/NaY zeolites calcined at 450 °C

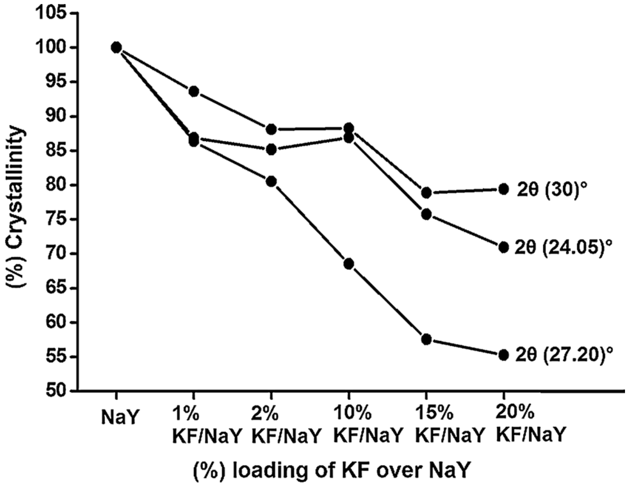


Fig. 3 Differences of (%) crystallinity of NaY and different KF/NaY zeolites calcined at 450 °C

lower to higher loading. Again, occurrence of no additional peaks up to 10 % KF loading suggests high dispersion of KF over zeolites while emergence of an additional peak at 2θ position 39.95° for both 15 and 20 % loaded zeoiltes can be attributed to the formation of $KAlF_4$ phase (JCPDS card number 84-1009). This observation indicates some interaction of zeolite structure with KF and thus loading of KF beyond 10 % is strictly prohibited. Crystallinity differences between modified samples and the original NaY zeolite are compared by taking three high intensity peaks at 2θ positions of 24°, 27° and 30°. Figure 3 shows a gradual decrease of % crystallinity upon increased loading of KF. However, calculation of crystallite sizes from XRD peaks of both NaY zeolite and 10 %KF/NaY zeolites shows that crystallite sizes of 10 %KF/NaY are almost similar to the original zeolites (Table 1). This further confirms that KF loading up to 10 % is not harmful for zeolite structure..

Table 1 Surface properties and particle size of zeolites

Sample	BET area (m^2g^{-1})	Crystallite size (nm)		
		7.25 (2θ)	24.05 (2θ)	30 (2θ)
NaY	450	63	52	45
10 %KF/NaY	447	73	48	46

FTIR spectra of parent as well as modified samples were recorded after calcinations at 450, 600 and 800 °C. Figure 4 shows vibrations in the region 400–1200 cm^{-1} which is a clear evidence of the presence of zeolite framework structure in the parent as well as modified samples. Band at around 1,650–1,700 cm^{-1} can be ascribed to bending vibration of water molecules [41, 42] attached to zeolite structure which remain intact in all samples activated at 450 °C while it disappeared after calcinations at 600 °C (b1) and 800 °C (b2, b3). This clearly shows that high activation temperature is not recommended for zeolite structure in presence of guest species. Distinct bands for internal tetrahedral vibrations i.e. in the ranges 1,050–1,000 cm^{-1} and 700–650 cm^{-1} are due to asymmetric and symmetric T-O (Si or Al) stretching mode respectively in tetrahedral co-ordination while band in the range 650-500 cm^{-1} is for tetrahedral T-O-T bending mode and 500–410 cm^{-1} is for external linkages between tetrahedra which is assigned for double ring [43]. Figure 4 shows that no alteration of all these bands takes place up to 15 % loading of KF while 20 % loaded samples have very weak vibrations for these bands (a9). This is in good agreement with XRD observation that KF loading beyond 10 % is restricted for NaY zeolite structure. We have also observed from the XRD pattern of the calcined samples that both internal and external zeolite structure exists for 5 % loaded sample activated at 600 °C (b1) while the band for double ring is absent in samples activated at 800 °C (b2, b3). It shows that both high activation temperature and higher loading of KF have harmful effect over the support. Therefore, 10 % KF loaded catalyst calcined at 450 °C can be considered as optimum in this study.

The basic property investigation of different samples shows quite different basicities of parent and modified zeolites (Table 2). The base strengths of parent NaY and 0.5–3 % KF loaded NaY zeolites are the same and lies in the range of $8.0 < H\_ < 10$ while it lies in the range $10 < H\_ < 11.1$ for 5–20 % loaded samples. This shows that basicity increases on increasing KF loading. It is interesting to note that the framework structure remains preserved even after activation of 20 % loaded zeolite at 450 °C and simultaneously basicities increases. This indicates that KF does not have negative effect on zeolite structure at 450 °C. However, appearance of an additional phase (XRD) upon 15 % loading prohibits the possibility to

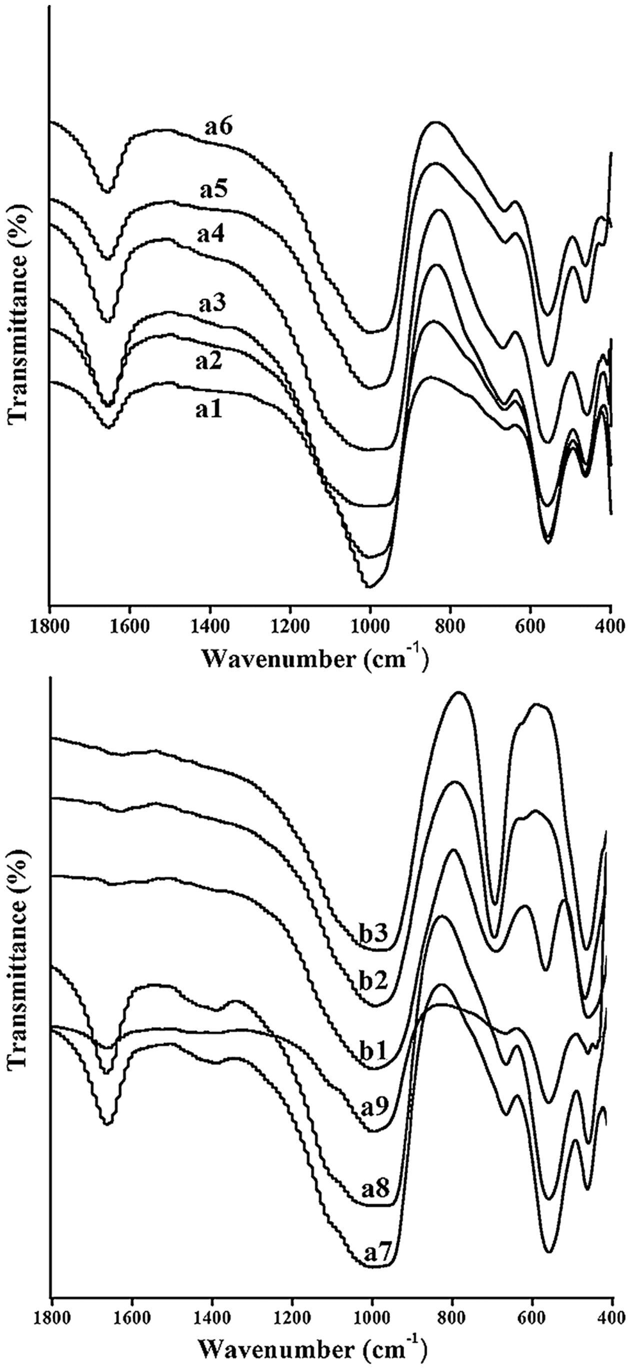


Fig. 4 FTIR spectra of parent as well as KF modified samples calcined at various temperatures. (*a1*) NaY, (*a2*) 0.5 % KF/NaY, (*a3*) 1 % KF/NaY, (*a4*) 2 % KF/NaY, (*a5*) 3 % KF/NaY, (*a6*) 5 % KF/NaY, (*a7*) 10 % KF/NaY, (*a8*) 15 % KF/NaY and (*a9*) 20 % KF/NaY (calcined at 450 °C); (*b1*) 5 % KF/NaY (calcined at 600 °C); (*b2*) 5 % KF/NaY (calcined at 800 °C); (*b3*) 10 % KF/NaY (calcined at 800 °C)

Table 2 Base strength of KF modified zeolites calcined at 450 °C

Sample	Base strength (H_)	Amount of soluble basic sites (mmol g^{-1})
NaY	8.0 < H_ < 10	0.292
0.5 %KF/NaY	8.0 < H_ < 10	
1 % KF/NaY	8.0 < H_ < 10	
2 %KF/NaY	8.0 < H_ < 10	0.419
3 %KF/NaY	8.0 < H_ < 10	
5 %KF/NaY	10 < H_ < 11.1	0.475
10 %KF/NaY	10 < H_ < 11.1	0.507
15 %KF/NaY	10 < H_ < 11.1	
20 %KF/NaY	10 < H_ < 11.1	0.797
0.5–5 % KF/NaY[a]	8.0 < H_ < 10	
10 %KF/NaY[a]	10 < H_ < 11.1	
15 %KF/NaY[a]	10 < H_ < 11.1	
3–10 %KF/NaY[b]	8.0 < H_ < 10	
15 %KF/NaY[b]	10 < H_ < 11.1	

[a] The activation temperature was 600 °C

[b] The activation temperature was 800 °C

load KF beyond 10 %. Thus 10 % loading has been conceded as the optimum amount in this study. This shows concomitant result with previous reports confirming that activation temperature and amount of loading both have their role on basic properties. Hence, 5 and 10 % loaded catalysts were further activated at 600 and 800 °C and basicities were checked (Table 2). The base strengths decrease upon increasing activation temperature. It may be attributed to the interaction of KF with zeolite structure thus reducing some basic sites at high temperature. The result of titrimetric analysis shows that the original NaY itself have some soluble basicities and it goes on increasing upon increasing KF loading.

Optimization of reaction conditions for Henry Niroaldol reaction was carried out first by performing the reaction under solvent free conditions and then in presence of variety of solvents. Thin layer chromatography monitoring showed no conversion at all (entries 1 & 2, Table 3) in case of solvent free conditions. This may be due to inability of the catalyst to abstract a proton in the absence of a reaction medium. In our previous report [44], we have found methanol as the optimized solvent among a variety of polar and non-polar solvents for this reaction at room temperature. Therefore, a variety of alcohols and H_2O–alcohol mixtures as solvents were screened at this time to understand the role of reaction medium (Table 3) under microwave irradiation. The reaction is faster for alcohols containing small alkyl groups than with alcohols containing bulky alkyl groups. Octanol shows only 12 % conversion in comparison to methanol which gives 95 % conversion within 2 min and this can be attributed to decrease of polarity of alcohols on increasing bulky nature of alkyl groups. This result goes hand in hand with our previous report and the conversions follow the order

Table 3 Henry nitroaldol reaction of 4-nitrobenzaldehyde and Nitromethane catalyzed by 10 %KF/NaY in different solvents

Entry	Solvents	% Conversion (time in min)	% Selectivity[c]		
			A	B	C
1	Solvent free[a]	No (5)	–	–	–
2	Solvent free[b]	No (5)	–	–	–
3	MeOH	95 (2)	92	8	
4	EtOH	97 (2)	98		2
5	*n*-Butanol	86 (2)	94	3	3
6	Octanol	12 (2)	88	2	
7	Isopropanol	51 (2)	93	5	2
8	Isobutanol	6 (2)	100		
9	H_2O	71 (1)	97		3
10	MeOH–H_2O	97 (1)	95		5
11	EtOH–H_2O	94 (1)	97		3
12	Butanol–H_2O	21 (1)	100		
13	Octanol–H_2O	21 (1)	100		
14	Isopropanol–H_2O	96 (1)	98		2
15	Isobutanol–H_2O	40 (1)	97		3
16	Ethylene glycol	50 (30)	77	1	16
17	Ethylene glycol–H_2O	58 (30)	76	6	18

All reactions were carried out with aldehyde (0.5 mmol), Nitromethane (2 mmol), 10 %KF/NaY (10 mg), solvent (3 ml), MW power (40 %), Temperature (50 °C)

[a] Solvent free condition between *p*-Nitrobenzaldehyde and Nitromethane

[b] Solvent free condition between Benzaldehyde and Nitromethane

[c] Conversions and selectivities of the products were obtained from 1H NMR data of crude reaction mixture [[*A: 1-(4-nitrophenyl)-2-nitroethanol, B: 1-(4-nitrophenyl)-2-nitroethene and C: 1,3- dinitro-2-(4-nitrophenyl)-propane*]]

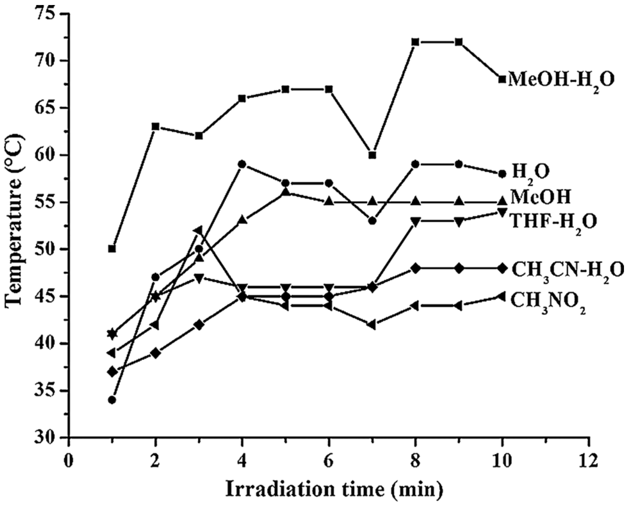


Fig. 5 Effect of microwave irradiation time on different polar solvents

MeOH $\sim$ EtOH > n-butanol > isopropanol > octanol > isobutanol for pure alcohols. This shows that straight chain alcohols with smaller alkyl groups are more favourable than the bulkier alkyl group containing alcohols. With 50 % aqueous alcoholic solution, the reaction becomes more rapid giving excellent conversions and selectivities within 1 min irradiation time. Water miscible alcohols offer a reaction medium suitable for both reactant and catalysts thus making the conditions favourable for the reaction. On the other hand bulky alcohols are less soluble in water and place the reactants and catalysts in different phases thus lowering the feasibility of the reaction. At this time, the trend follows H_2O–MeOH $\sim$ H_2O–EtOH $\sim$ H_2O–iso-propanol > H_2O–isbutanol > H_2O–butanol > H_2O–Octanol. This shows that water miscible alcohols speed up the reaction. The feasibility of the reaction in water miscible alcohols can be suggested that the tendency of H-bonding of alcohols with basic sites of zeolites makes the alkoxide ions to interact with acidic protons of nitromethane. This further increases the acidity of acidic protons of nitromethane and thus basic sites of zeolites can easily abstracts a proton from it. We have also observed that the catalytic activity of used zeolite decreases in the next run which may be due to blockage of some active sites of zeolite by these solvent molecules in the process of the polar interaction as described above. The feasibility of the reaction in aqueous alcoholic mixture has been further confirmed by observing the absorbed microwave energy by some polar solvents when irradiated with 40 % microwave power for 10 min and keeping the amount of solvents fixed (Fig. 5). The highest microwave energy (in terms of temperature) was absorbed by H_2O–MeOH (1:1 ratio) amongst a variety of screened solvents. In addition, a gradual increase of absorbed energy was observed on increasing microwave irradiation time for the same solvent and fixed amount of solvent. Thus, aqueous methanol has been considered as the best solvent in our study.

The investigation of effect of microwave energy on amount of solvent is important as well to minimize energy used in the process and is summarized in Fig. 6. This was studied at constant irradiation time where the microwave power was changed first by keeping amount of solvent fixed and then changed the amount of solvents by keeping microwave power fixed. In both cases absorbed energy increases on increasing amount of solvent and MW power. However, no significant effect was observed upon changing MW power for small amount of solvents. On increasing MW power from 140 to 560 Watt, temperature rise for 1 mL H_2O is from 36 to 47 °C respectively i.e. a rise of 11 °C while it shows 20 °C rise (71–91 °C) for 4 ml H_2O under same conditions. This shows that MW power does not have vast effect for small amount of solvents. Hence,

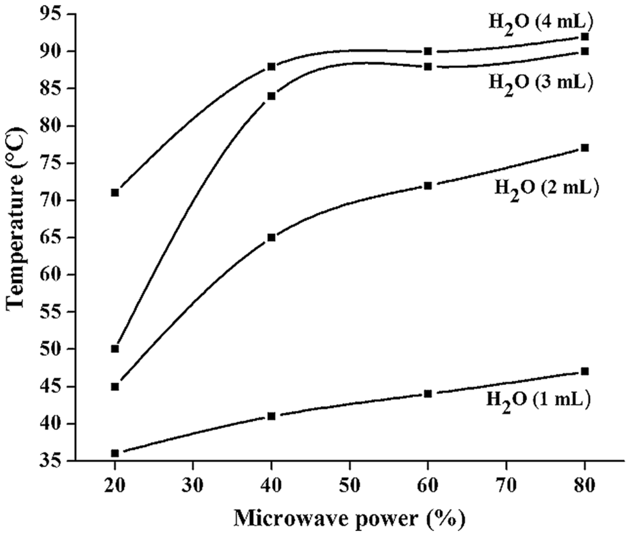
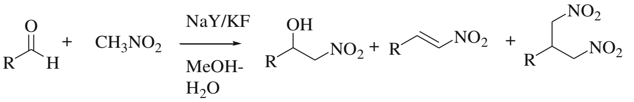


Fig. 6 Effect of microwave irradiation power on amount of solvent

40 % power with 3 mL solvent has been chosen as optimum amount in this study.

Following this step, Henry reaction with variety of aldehydes have been carried out by taking 3 mL H_2O–MeOH, 1 mmol aldehyde, 4 mmol Nitromethane and 280 Watt microwave power at 50 °C (Scheme 1) to understand the effect of specific heating of microwave on formation of the desired product. The results are summarized in Table 4. In comparison to room temperature methodology [43], the reaction time greatly reduces from hours to minute (Table 4) under microwave irradiation giving moderate to excellent yields (64–92 %) within 2–15 min. The improved conversions and selectivites is not only the effect of rise of temperature of MeOH–H_2O solvent under microwave can be suggested by heating the reaction mixture at 50 °C without any microwave source. Table 4 shows that the reaction takes 2.5 h [43] to complete with reduced selectivity while it takes only 1 min under microwave. The usefulness of MeOH–H_2O as reaction media under microwave can again be noted by comparing the previous reports where performing nitroaldol reaction at 50–60 °C ionic liquid medium [45], supercritical CO_2 medium [46] shows inferior results in comparison to the present system. The reaction goes well with aromatic, heterocyclic and polycyclic aromatic aldehydes to afford the desired nitroaldol product in good yields where aromatic aldehydes having electron withdrawing groups (entries 3–5, Table 4) are comparatively faster than aldehydes containing electron donating groups (entries 6–8, Table 4) and gives excellent yields within 1 min (entry 3, Table 4). Again, reaction with substituted nitrobenzaldehyde at para position (entry 3) is faster than that at ortho and meta positions (entries 4 and 5) while heterocyclic and ploycyclic aromatic aldehydes (entries 9 and 10) react slowly and gives good to moderate yields within 15 min. The conversion with recovered catalysts was lowered somewhat and gives 88 % conversion of the product within 3 min.

Table 4 Henry Nitroaldol reactions with various aldehydes



R = Aryl or Alkyl groups

Entry	R	Time (min)	% yield[a]
1	C_6H_5 (No catalyst)	5	0
2	C_6H_5	5	75
3	4-(NO_2)C_6H_4	1	92
		4 h	92[b]
		2.5 h	99[c]
		7 h	81[d]
4	3-(NO_2)C_6H_4	2	88
5	2-(NO_2)C_6H_4	2	84
6	4-ClC_6H_4	10	76
7	4-$CH_3C_6H_4$	15	73
8	2-OHC_6H_4	15	64
9	2-Furyl	10	70
10	1-Naphthyl	15	77
11	4-(NO_2)C_6H_4[e]	3	88

All reactions were carried out with aldehyde (1 mmol), Nitromathane (4 mmol), 10 %KF/NaY (15 mg, calcined at 450 °C), MeOH–H_2O (3 ml), MW power (40 %) at 50 °C

[a] Isolated yields

[b] Reactions with 1:2 of 4-nitrobenzaldehyde/Nitromethane, 2 mL solvent (MeOH–H2O) and 0.02 g NaY/KF at room temperature

[c] Reaction with 1:1 of 4-nitrobenzaldehyde/Nitromethane, 2 mL solvent (MeOH–H2O) and 0.02 g NaY/KF at 50 °C

[d] Reactions 0.5 mmol of aldehyde, 0.75 mmol of nitromethane, 19–30 mg Mg–Al HT in 1 mL of ionic liquid

[e] Reactions with recovered catalysts

To confirm effect of aqueous wash basicity upon conversion, we have stirred the catalyst with water–methanol mixture for 24 h and separated the catalyst by centrifugation and perfomed the reaction with the filtrate under same reaction conditions. No conversion was observed from thin layer chromatography observation and this proves that the basicity was imparted by the catalyst itself and the reaction was heterogeneously catalyzed.

4 Conclusions

In conclusion, we have described microwave assisted Henry nitroaldol reaction with KF modified NaY zeolite as a suitable method to obtain β-nitro alcohol in good yield within short time. The reaction rate greatly enhances due to the combined effect of microwave and water–alcohol mixture as reaction media.

4.1 Spectral Data

4.1.1 2-Nitro-1(4-nitrophenyl)ethan-1-ol:(entry 3, Table 4)

^{1}H NMR (400 MHz, CDCl3): δ 8.22 (d, 2H), δ 7.62 (d, 2H), δ 5.59–5.61 (m, 1H), δ 4.48–4.60 (m, 2H), δ 3.52 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): 147.7, 144.9, 126.7, 123.8, 80.3 and 69.7 ppm.

4.1.2 2-Nitro-1(4-chlorophenyl)ethan-1-ol:(entry 6, Table 4)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, 2H), δ 7.35 (d, 2H), δ 5.47–5.43 (m, 1H), δ 4.46–4.46 (m, 2H), δ 3.92 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): 140.1, 134.8, 129.8, 126.1, 80.7 and 70.3 ppm.

4.1.3 2-Nitro-1-naphthyl-ethan-1-ol:(entry 10, Table 4)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.0–7.98 (m, 1H), δ 7.90–7.88 (m, 1H), δ 7.86–7.85 (m, 1H), 7.74–7.70 (m, 1H), δ 7.60–7.51 (m, 3H), δ 6.28–6.27 (m,1H), δ 4.68–4.66 (m, 2H), δ 2.93 (bs, 1H); ^{13}C: 133.6, 133.5, 130.7, 130.2, 129.6, 129.5, 126.2, 124.6, 123.8, 121.9, 80.8 and 68.3 ppm.

Acknowledgments This work was supported by the Department of Science and Technology, New Delhi. The authors acknowledge Dr. Pankaj Bharali, Tezpur University for fruitful discussion and valuable suggestions.

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