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Design of zeolite catalysts for nitroaldol reaction under mild condition

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ABSTRACT

NaY and KL zeolites were modified by impregnating with potassium fluoride for investigating their basicity and catalytic activity towards Henry nitroaldol reaction under different reaction conditions. Effects of solvents, temperature, catalysts and ratio of substrate versus reagents were studied to optimize the reaction conditions. The catalysts were characterized by FTIR, XRD and SEM techniques and the products were characterized by ^{1}H NMR, ^{13}C NMR and FTIR techniques. It was observed that NaY/KF zeolite with H_2O–MeOH pair as solvent showed good conversion and selectivity at room temperature. Both XRD and FTIR study showed no change of spectral patterns for both modified and parent zeolites. We have again showed a plot of Hammett free energy linear relationship in terms of percentage yield and Hammett substituent constant.

1. Introduction

Nitroaldol reaction is a classic C—C coupling reaction between a nitroalkane and an aldehyde or a ketone (Scheme 1) [1–3]. The importance of the reaction is due to the synthetic utility of nitroaldol product which can be easily converted into ketones, β-amino alcohols, carboxylic acids, nitro alkenes, etc. and also can act as suitable intermediate for synthesis of various biological compounds [4–9]. Again, possible competitive reactions like Cannizzaro reaction, base catalyzed elimination of water from nitroaldol and polymerization of nitroalkenes may occur simultaneously during progress of the reaction [10–15]. Thus to minimize side products an investigation of environmentally acceptable reaction conditions and effective catalysts is under the scope of study during these days.

Asymmetric Henry reaction has been carried out through two strategies from very early days, i.e. by pre-activation of nitroalkane species with a fluoride ion source and direct reaction of different aldehydes with unmodified nitroalkanes. Shibasaki's rare earth catalyzed metal complexes involving La with BINOL system and Li [16,17], metal catalyzed reactions like Zn and Cu based complexes, Co-SALEN complexes, organocatalysts like chiral guanidinium salts and bifunctional amine–thiourea complexes have been found successful for Henry reaction [18–22]. Again various heterogeneous catalysts like Amberlyst A-21, functionalized SBA-15, amine supported on silica gel, hydrotalcite catalysts in ionic liquid, supported BINOL complexes, etc. also have been reported [23–34]. Homogeneous catalysts like NaOH with surfactant catalyst hexadecyltrimethylammonium chloride, benzyltrimethylammonium hydroxide, tris-(2,4,6-trimethoxyphenyl) phosphine (TTMP), etc. are reported previously as efficient catalysts for Henry reaction [35,36]. However they have their limitations in recovery, as well as long reaction time, formation of multiple products, low yield, etc. In this report we have tried to optimize Henry reaction conditions using zeolite as base catalyst.

In recent years, zeolites and modified zeolites have been used as acid and base catalysts for a number of organic reactions [37–39]. However, their uses as base catalysts are limited as compared to acid catalyzed reactions. Due to their peculiar shape selectivity, thermal stability and ordered pore structures, reactions can occur inside the pores and give selective products [40,41]. Although many reactions have been carried out through exchanging extra framework cations of zeolites by alkali and alkaline earth metal cations, their uses in Henry nitroaldol reaction is not very common. In our work, we have modified NaY and KL zeolites by a wet impregnation method from aqueous solution of KF and used them for Henry reaction [42].

2. Experimental

2.1. Chemicals and reagents

NH_4Y zeolite was purchased from Sigma Aldrich, Germany; aldehydes from Merck and Sigma Aldrich, Germany; Nitromethane from G.S. Chemicals Testing Lab & Allied Industries, New Delhi; potassium fluoride (KF), sodium sulfate (Na_2SO_4), silica gel, iodine

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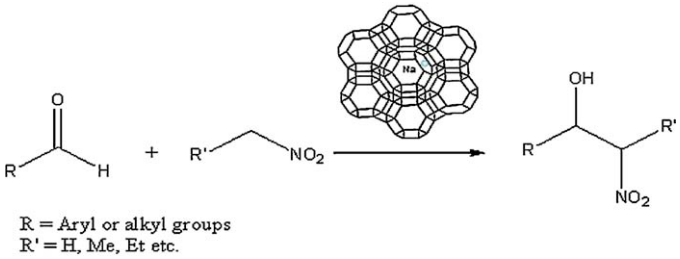

Scheme 1. Henry reaction catalyzed by zeolites.

and solvents were purchased from RANKEM and KL zeolite was obtained from National Chemical Laboratory, Pune.

2.2. Preparation of catalysts

At first NH_4^+ ion of parent NH_4Y zeolite were exchanged with Na^+ ion. In this procedure 5 g of NH_4Y zeolite was stirred with 100 mL of 1 M $NaNO_3$ solution for 6 h at 90 °C. The exchanged zeolites were then filtered and again stirred with fresh $NaNO_3$ solution. This was repeated for 4 times, filtered, washed and dried in oven for overnight at 110 °C. The modified NaY and KL basic zeolites were prepared by an impregnation method from aqueous solution of KF. Zeolite amount of 500 mg was taken to impregnate 0.40 mmol of KF. It was done for 24 h and slurries were dried in an oven at 100 °C for 14 h.

2.3. Catalysts characterization

All catalysts samples were characterized by X-ray diffraction method using a Rigaku (miniflex UK) X-ray diffractometer with Cu Kα radiation (1.5418 Å) at a scan speed of 2° min^{-1} and 2θ range of 10–40°. FTIR spectra of various catalysts and products were recorded on a Nicolet Impact Model-410 spectrometer with 1 cm^{-1} resolution and 32 scans in the mid IR (400–4000 cm^{-1}) region using the KBr pellet technique. The SEM measurements were carried out using a JEOL JSM-6390LV scanning electron microscope. The images were taken at an accelerator voltage of 15 kV and magnification of micrographs ranges from 10,000× to 5500×. The catalysts were secured onto brass stubs, sputter coated with Platinum and viewed in JEOL JSM-6390LV microscope. Flame photometry was carried out with FP-114 Flame Photometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS 400 taking Me_4Si as the internal standard in $CDCl_3$ and CD_3OD solvents. Preparative column chromatography was carried out with silica gel 60–120 mesh size and thin-layer chromatography (TLC) was carried out on glass plates with silica gel.

The strength of basic sites was measured qualitatively using Hammett indicator method [43]. In this technique, 25 mg of solid catalyst calcined at 450 °C was shaken with 1 mL solution (0.1% in methanol) of the indicator and left to equilibriate for 2 h. The color of the catalyst was then noted. The following Hammett indicators were used: neutral red (pK_{BH+} = 6.8–8.0) and phenolphthalein (pK_{BH+} = 8.0–9.6). The base strength is reported as stronger than the weakest indicator which exhibits a color change and weaker than the strongest indicator which exhibits no color change. The aqueous soluble amount of basic sites was determined by acid–base titration technique [42]. In this procedure 100 mg of calcined sample was shaken in 10 mL of water at room temperature for 24 h and the catalyst was separated by centrifuge. The filtrate was neutralized with 10 mL of 0.05 M aqueous HCL. Then the remaining acid was titrated with 0.01 M of standard aqueous NaOH. Oxalic acid dihydrate was taken for standardization of NaOH and a methanol solution of phenolphthalein (1 mL, 0.1 mg/mL) was taken as indicator.

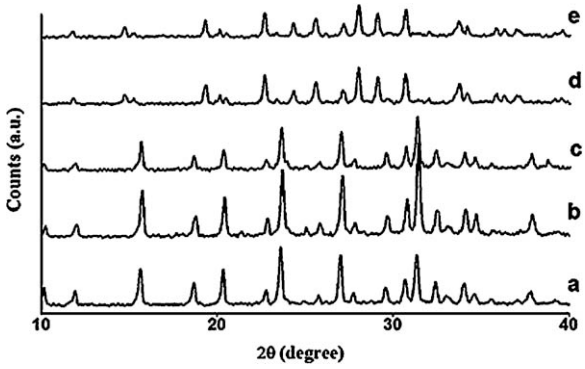

Fig. 1. XRD pattern of (a) NH_4Y, (b) NaY, (c) NaY/KF, (d) KL zeolite and (e) KL/KF.

2.4. Catalyst testing

The reactions were performed under two conditions, i.e. with solvents at room temperature and with solvents on increasing temperature. Solvent study was carried out by taking 1 mmol of the aldehyde, 1 mmol of the nitroalkane and 20 mg of the catalysts with various solvents at room temperature. All reactions were carried out for 48 h for comparison and reaction conditions were optimized by varying temperature, amount of Nitromethane and catalysts. The reactions were monitored via thin layer chromatography and yields were obtained from ^1H NMR analyses of the crude reaction mixture.

3. Results and discussion

The powder X-ray diffraction analyses were performed for both parent and KF modified zeolite samples. Results obtained from XRD analysis are shown in Fig. 1. XRD pattern of parent NaY zeolite corroborate well with the literature reports [44]. The peak positions of parent and KF modified zeolites are not altered which proves that modification does not affect the size and shape of the unit cell. Again no other additional peaks for KF are observed which indicates its well dispersion in zeolites. However, it is obvious from the decreased peak intensities of the modified samples that crystallinity of KF modified samples is decreased somewhat. Fig. 2 shows crystallinity differences of modified samples with that of references obtained by comparing intensities of some highest intensity peaks. Peak intensities of the modified samples decrease meagerly. It may be due to decrease in surface area and pore volume after modification.

Fig. 3 shows FTIR spectra of NH_4Y, NaY, NaY/KF, KL and KL/KF zeolites. All spectra were recorded after drying overnight in an oven at 100 °C. Infrared bands shown here in the region from 500 to 1200 cm^{-1} provide information of the structural features of zeolite framework. Strong vibrations at ~950 to 1050 cm^{-1} and at ~650 to 700 cm^{-1} are due to asymmetric and symmetric T—O (Si or Al) stretching mode, respectively, in tetrahedral co-ordination and these both arise due to internal tetrahedral vibrations. These stretching modes are responsible for Si/Al composition of the framework and may shift to higher or lower frequency depending on increase or decrease of Si to Al ratio. Again band at ~500 to 600 cm^{-1} is due to double ring and bands at ~1100 to 1200 cm^{-1} and 750–800 cm^{-1} are, respectively, due to asymmetrical and symmetrical stretching vibrations of T—O in external linkages. As reported earlier there is a possibility of dealumination in case of NaY/KF and KL/KF due to reaction of KF with aluminum in zeolites [44]. However no distinct shifting of these bands has been observed in our case, i.e. no dealumination occurs (Fig. 3). This may be due to small amount of KF loading in this study. Thus, FTIR spectra also agree well with our observation that KF is well

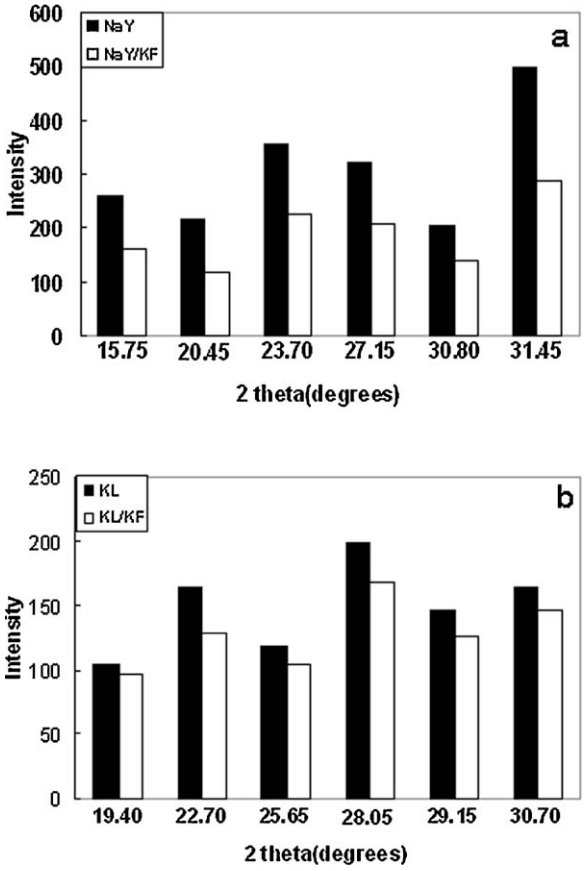

Fig. 2. The intensity ratio of the modified zeolites with parent zeolites at some points for (a) NaY zeolites and (b) KL zeolites.

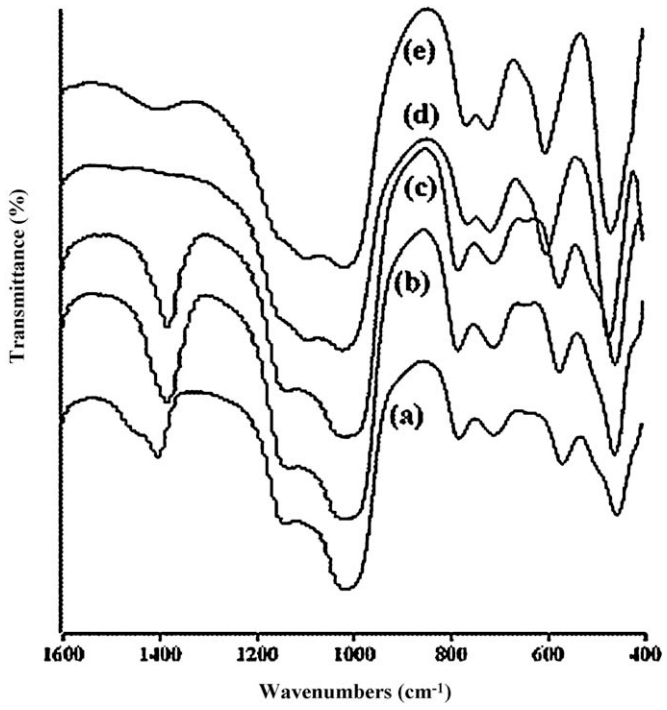

Fig. 3. FTIR spectra of (a) NH_4Y, (b) NaY, (c) NaY/KF, (d) KL and (e) KL/KF.

Table 1
Effect of solvents in Henry reaction of 4-nitrobenzaldehyde and Nitromethane catalyzed by NaY/KF.

Entry	Solvents	Time (h)	Conversion (%)[a]	Selectivity (%)[b]
1	No	10 min[c]	0	0
2	No	10 min[d]	0	0
3	MeOH	48	92	73
4	EtOH	48	90	85
5	$(Me)_2CHCH_2OH$	48	90	86
6	CH_2Cl_2	48	71	66
7	$CHCl_3$	48	78	78
8	THF	48	64	80
9	DMF	48	78	67
10	CH_3CN	48	71	57
11	H_2O–MeOH	12	98	88
12	H_2O–$CHCl_3$	48	98	76
13	H_2O–EtOH	48	88	60
14	H_2O–$(Me)_2CHCH_2OH$	48	82	80
15	H_2O	48	15	–

[a] Reaction were carried out with 1 mmol scale with molar ratio 1:1 of 4-nitrobenzaldehyde/Nitromethane, 2 mL solvent and 0.02 g NaY/KF at room temperature.
[b] Yields and selectivities were obtained from ^1H NMR data of crude reaction mixture (byproducts formed are dehydrated product and polymerized product 1,3-dinitro-2-(4-nitrophenyl)-propane).
[c] Reaction with *p*-nitrobenzaldehyde.
[d] Reaction with 1-naphthaldehyde.

dispersed in zeolite and their framework structures are not affected after modification.

The scanning electron micrographs of NaY, NaY/KF, KL and KL/KF zeolites are shown in Fig. 4. Magnification of micrographs at 10,000× and 5500× clearly shows homogeneity in shapes and highly crystalline nature of all samples. From the micrographs no aggregation of salt particles on support is observed, i.e. KF is highly dispersed on support.

The strength of basic sites and their amounts were measured using acid–base titration and the Hammett indicator methods. As expected from our catalytic experiment, the base strength of KF modified NaY and KL zeolites are found to be higher ($8.0 < pK_{BH+} < 10.0$) than the parent zeolites ($6.8 < pK_{BH+} < 8.0$). In neutral red solution NaY remains as red, KL slight yellow, KL/KF comparatively brighter than the previous two and NaY/KF shows the brightest yellow color. This indicates that NaY/KF possesses the highest base strength among the four catalysts with pK_{BH+} value greater than 8.0 but less than 10.0. Moreover, no change in color of the four catalysts in phenolphthalein solution indicates that the base strengths (pK_{BH+}) of the catalysts are less than 10.0. The amount of soluble basicity in all the catalysts is almost same.

In our attempt to investigate environmentally benign reaction conditions, we have first used NaY/KF catalyst to study whether the reaction proceeds without solvent or not. We have ground 1 equiv. of *p*-nitrobenzaldehyde and 1 equiv. of Nitromethane with 20 mg catalyst using mortar and pestle for 10 min. Thin layer chromatography observation showed no conversion for both solid and liquid substrates (Table 1, entries 1 and 2). It may be due to inadequate contact between catalysts and reactants to precede the reaction further. Therefore we have initially studied the effect of solvents to optimize conditions for Henry reaction. For this purpose we have chosen *p*-nitrobenzaldehyde and Nitromethane as model reactants and performed the reaction at room temperature with different organic solvents and 50% aqueous solution of organic solvents. Both polar aprotic and protic solvents, less polar organic solvents and organic solvents with water were screened to understand the effects. As observed from Table 1, dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$) having similar polarity gives comparable conversion of 71% for CH_2Cl_2 and 78% for $CHCl_3$. Aprotic polar solvents DMF, acetonitrile, THF have similar effects on reaction rate and we

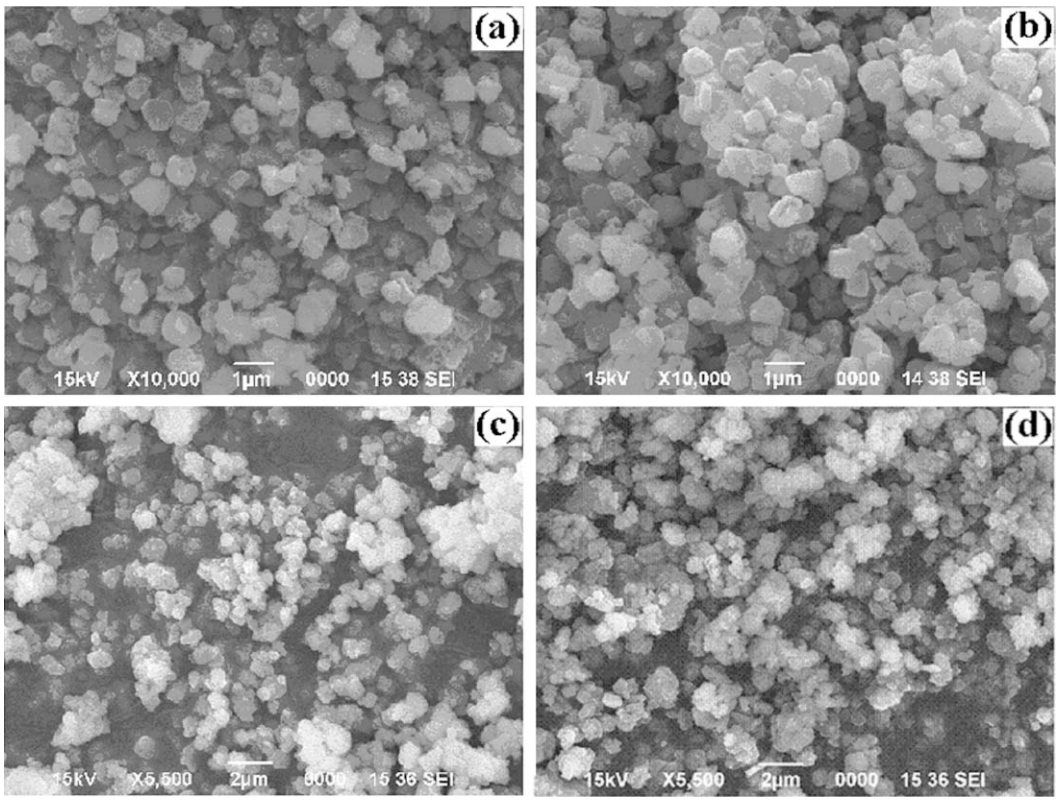

Fig. 4. SEM images of (a) NaY, (b) NaY/KF, (c) KL and (d) KL/KF.

found enhanced rate and selectivity with 50% aqueous alcoholic solution. From Table 1, it is observed that conversion increases in the order MeOH–H_2O > EtOH–H_2O > isobutanol–H_2O. It may be due to steric effect of alkyl groups from MeOH to isobutanol which affects the activation of catalysts through solvation process. The reaction in H_2O was very slow. This is due to the fact that the differences in hydrophobic nature of the reactant molecules place them in heterogeneous phases. Among different solvents, MeOH–H_2O (1:1 ratio) gives the highest percentage of conversion and selectivity. Therefore MeOH–H_2O pair is the best solvent in our study and hence we performed other subsequent reactions presented in Tables 2–6 in this solvent.

As shown in Table 2, temperature effect was studied by taking Nitromethane, *p*-nitrobenzaldehyde and MeOH–H_2O (1:1) as solvent. It can be seen from Table 2 that temperature has a great effect on reaction time. Reaction time decreases from 12 h at RT to 1 h at 60 °C (entries 1 and 4) and selectivity decreases slightly on increasing temperature. Formation of side products of similar nature was observed both at room temperature and at higher temperatures. However, formation of side products decreases significantly with higher amount of Nitromethane at room temperature. At higher temperatures both speed of reaction and formation of side products become faster. So, the further studies were performed at room temperature.

We next investigated the effect of amount of catalyst on reaction time and percentage conversion. The results are summarized in Table 3. As the catalysts amount increases, the conversion and selectivity also increases. We have selected 20 mg catalyst as our optimum amount for further studies.

We have also performed stoichiometry study with 20 mg of the catalyst at room temperature to observe the effect of molar equivalent of Nitromethane on yield of Henry reaction. From Table 4 it is seen that with increasing the amount of Nitromethane the reaction time gradually decreases. It can be seen that the best result was obtained from 1:5 and 1:10 ratio (entries 4 and 5) of aldehyde and nitroalkane. However, in order to have maximum atom economy we chose 2 mmol Nitromethane as our optimum amount for Henry reaction.

In order to study the effect of pore architecture we performed Henry reactions in two large pore zeolites namely faujasite and zeolite-L having supercage and straightly channel, respectively. The basicity of both the zeolites was enhanced by impregnating KF.

Table 2
Effect of temperature on Henry reaction of 4-nitrobenzaldehyde and Nitromethane catalyzed by NaY/KF.

Entry	Temperature (°C)	Time (h)	Conversion (%)[a]	Selectivity (%)[b]
1	RT	12	98	88
2	40	5	98	80
3	50	2.5	99	77
4	60	1	97	63

[a] Reactions were carried out in 1 mmol scale with molar ratio 1:1 of 4-nitrobenzaldehyde/Nitromethane, 2 mL solvent (MeOH–H_2O) and 0.02 g NaY/KF.
[b] Yields and selectivities were obtained from ^{1}H NMR data of crude reaction mixture.

Table 3
Effect of the amount of catalyst used in the conversion (%) and selectivity (%) of Henry reaction.

Entry	Catalyst (mg)	Time (h)	Conversion (%)[a]	Selectivity (%)[b]
1	10	15	91	78
2	15	13	94	82
3	20	12	98	88
4	25	12	99	92

[a] Reactions were carried out in 1 mmol scale with molar ratio 1:1 of 4-nitrobenzaldehyde/Nitromethane and 2 mL solvent (MeOH–H_2O) and 0.02 g NaY/KF at room temperature.
[b] Yields and selectivities were obtained from ^{1}H NMR data of crude reaction mixture.

Table 4
Effect of amount of Nitromethane on conversion (%) and selectivity (%) for various Henry reactions.

Entry	4-Nitrobenzaldehyde (mmol)	Nitromethane (mmol)	Time (h)	Conversion (%)[a]	Selectivity (%)[b]
1	1	1	12	98	88
2	1	2	4	99	91
3	1	3	3	99	93
4	1	5	3	99	91
5	1	10	45 min	99	93

[a] Reactions were carried out in 1 mmol 4-nitrobenzaldehyde with different molar amount of Nitromethane, 2 mL solvent (MeOH–H_2O) and 0.02 g NaY/KF at room temperature.
[b] Yields and selectivities were obtained from ^{1}H NMR data of crude reaction mixture.

Table 5
Effect of catalysts on Henry reaction of 4-nitrobenzaldehyde and Nitromethane.

Entry	Zeolite	Time (h)	Conversion[a] (%)	Selectivity[b] (%)
1	KL	12	87	63
2	NaY	12	90	75
3	KL/KF	7	95	67
4	NaY/KF	4	99	91

[a] Reactions were carried out in 1 mmol scale with molar ratio 1:2 of 4-nitrobenzaldehyde/Nitromethane, 2 mL solvent (MeOH–H_2O) and with different catalysts at room temperature.
[b] Yields and selectivities were obtained from ^{1}H NMR data of crude reaction mixture.

NaY/KF is found to be the best catalyst among all. This may be due to the presence of the supercages in NaY which allow bulkier transition states to form during the reaction. Table 5 shows effect of different catalysts on Henry reaction. NaY/KF again was found to show superior conversion and selectivities among the four. In all cases, we have observed from Tables 1–5 that there are very less amount of formation of dehydrated and polymerized products. Further studies with different substrates were carried out with NaY/KF.

Table 6 shows Henry reaction with variety of aldehydes, e.g. simple aromatic aldehydes, heterocyclic aldehyde and polycyclic aromatic aldehydes. As expected reactions with substrates having electron withdrawing groups (entries 1, 2, 3) are faster giving up to 92% yield (entries 1) and reactions with substrates having electron donating groups (entries 6, 7, 8) are slower (entry 6, 53% yield). Reactions for 1-naphthaldehyde and 2-furaldehyde rates are somewhat faster giving 78% and 72% yield, respectively. From results of Table 6 for various meta- and para-substituted benzaldehydes it would be interesting to see whether there is a linear relationship between the percentage yield and the Hammett substituent constants. As observed from Fig. 5 Henry reaction with these modified zeolites shows a linear relationship between the percentage yield and the Hammett substituent constants (σ).

Table 6
Henry reaction of Nitromethane with different aldehydes.

Entry	Aldehyde	Time (h)[a]	Yield (%)[b]
1	4-Nitobenzaldehyde	4	92
2	2-Nitrobenzaldehyde	7	90
3	3-Nitrobenzaldehyde	7	84
4	1-Naphthaldehyde	24	78
5	2-Furfuraldehyde	24	72
6	4-Hydroxybenzaldehyde	48	53
7	*p*-Tolualdehyde	48	63
8	4-Chlorobenzaldehyde	48	70

[a] Reactions were carried out in 1 mmol scale with molar ratio 1:2 of 4-nitrobenzaldehyde/Nitromethane, 2 mL solvent (MeOH–H_2O) and 0.02 g NaY/KF at room temperature.
[b] Isolated yields after TLC purification. All products were characterized by FT-IR, ^{1}H NMR and ^{13}C NMR. Byproducts formed were not isolated.

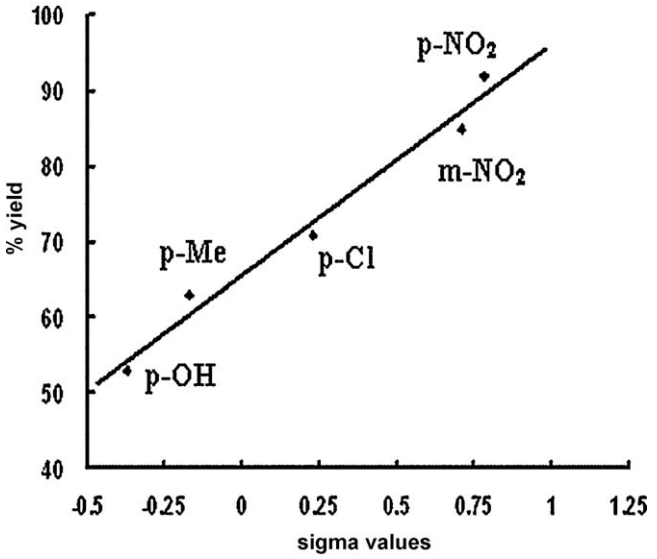

Fig. 5. Hammett plot for Henry reaction.

The recyclability of NaY/KF was investigated for three times and performed the reaction with 4-nitrobenzaldehyde and Nitromethane (1:5 ratio) using MeOH–H_2O solvent. Used Catalyst was dried for 24 h in an oven at 150 °C before performing the reaction. Reaction time gradually increases after each run. It may be due to slight leaching or deactivation of active sites of zeolite through adsorption of polar solvent molecules. To investigate the leaching phenomena we performed flame photometry for K^+ ion. Negligible amount of K^+ leaching (0.001 g/L) was detected and it has not hamper the reaction rate considerably.

4. Conclusions

In conclusion we have found NaY/KF as an efficient catalyst for nitroaldol reaction in MeOH–H_2O solvent at room temperature with good to moderate yields. The presence of H_2O with alcohol as reaction medium greatly effects the reaction rate and selectivities. Both temperature and molar ratio of Nitromethane with aldehydes play important role in the reaction.

Spectral data

2-Nitro-1-(4-nitrophenyl)ethan-1-ol (entry 1, Table 6)
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.52 (s, 1H), δ 4.58–4.60 (m, 2H), δ 5.59–5.61 (m, 1H), δ 7.62 (d, J_{HH} = 8 Hz, 2H), 8.22 (d, J_{HH} = 8 Hz, 2H); ^{13}C NMR (400 MHz $CDCl_3$): 69.7, 80.3, 123.8, 126.7, 144.9, 147.7 ppm; IR (KBr): 1338, 1536, 1604, 3444 cm^{-1}.

Acknowledgments

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