

Solid acid-catalyzed dehydration/Beckmann rearrangement of aldoximes: towards high atom efficiency green processes

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Abstract

Rare earth metal ion exchanged (La^{3+} , Ce^{3+} , RE^{3+}) KFAU-Y zeolites were prepared by simple ion-exchange methods and have been characterized using different physico-chemical techniques. In this paper a novel application of solid acid catalysts in the dehydration/Beckmann rearrangement of aldoximes; benzaldoxime and 4-methoxybenzaloxime is reported. Dehydration/Beckmann rearrangement reactions of benzaldoxime and 4-methoxybenzaloxime is carried out in a continuous down flow reactor at 473 K. 4-Methoxybenzaloxime gave both Beckmann rearrangement product (4-methoxyphenylformamide) and dehydration product (4-methoxybenzoxime) in high overall yields. The difference in behavior of the aldoximes is explained in terms of electronic effects. The production of benzoxime was near quantitative under heterogeneous reaction conditions. The optimal protocol allows nitriles to be synthesized in good yields through the dehydration of aldoximes. Time on stream studies show a fast decline in the activity of the catalyst due to neutralization of acid sites by the basic reactant and product molecules.

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1. Introduction

Responsible care and sustainable development have been the paradigms of industrial production. Therefore, the process has to be optimized in terms of energy efficiency, chemical utilization, and waste minimization [1,2]. Solid acid catalysis is a growing field of research as the demand for clean and eco-friendly chemical processes is increasing. Many organic reactions are known to be catalyzed by clays, ion-exchange resins and zeolites both in natural and modified form [1].

The acid amount and thermal stability of synthetic K-Y zeolite can be dramatically improved by ion exchanging with rare earth metal cations, and the

amount of improvement is controlled by the extent of cation exchange [3,4]. These zeolites have been extensively used for industrial applications. Lanthanum exchanged Na-Y zeolite plays an important role in the preparation of catalysts for fluid catalytic cracking, one of the most widely applied petroleum refining processes that make use of zeolite catalyst components [4,5].

Nitriles are very important intermediates in synthetic organic chemistry [6,7]. Many important multi-synthetic reactions pass through a nitrile intermediate. Examples include the synthesis of ibuprofen and ketoprofen; two widely used pharmaceutical agents that have variety of uses [6,7]. Benzoxime derivatives have been widely used as herbicides in agriculture [8]. Despite their wide applicability, preparation is a major concern. Aromatic hydrocarbons such as benzene, phenolic compounds or phenyl ethers are cyanated using Cl_3CCN , BrCN or mercury fulminate [$\text{Hg}(\text{ONC})_2$] [9,10]. These are special

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reagents. Their high cost, limited availability, sensitivity towards water and very low bio-degradability are major concerns. Aliphatic nitriles are accessed through nucleophilic substitution reactions of alkyl halides and tosylates with highly toxic cyanide ions as nucleophiles [7].

Two useful measures of the environmental impact of chemical processes are the *E-factor*, defined by the mass ratio of waste to desired product, and the *atom utilization*, which is the ratio of the molecular weight of the desired product and molecular weights of all substances produced in the stoichiometric equation. Processes employing acids and bases requiring neutralization, or stoichiometric redox reagents, and toxic metal reagents represent the major sources of waste production in the form of salts and heavy metals and have high *E-factors* and low *atom utilization* as the catalysts are irreversibly lost. Low bio-degradability is a serious problem in these environmentally conscious days. The work-up of products from nitrations, sulphonations, cyanation, and many other acid-catalyzed reactions involves neutralization and the concomitant generation of inorganic wastes such as NaCl, Na₂SO₄ and (NH₄)₂SO₄ [1,2,11,12]. *Green chemistry* demands the replacement of these highly corrosive, hazardous and polluting acid catalysts with eco-friendly solid acid catalysts. Hence, the idea of achieving chemical reaction that are economical, energy saving, safe and most importantly environmentally benign demands some alternative for conventional catalysts. Heterogeneous catalysis, long established in bulk-chemicals processing, is beginning to make inroads into the fine-chemicals industry also. This tendency is helped by the availability of novel catalytic materials and modern techniques of creating and investigating specific active sites on catalyst surfaces.

Solid acid catalysts pose a good substitute for such reactions. The ammoxidation of alkyl aromatics has been employed for long time as a commercial process to produce the corresponding nitrile. Cavani and co-workers studied the ammoxidation of toluene to benzonitrile over transition metal modified V₂O₅ (yield 52%) [13,14]. Recently, Chary and co-workers reported the ammoxidation of toluene to benzonitrile over a series of supported vanadium oxide catalysts under low and high conversions. The selectivity for benzonitrile remains almost the same under both conditions. The activities/selectivities in percentage under high conversion conditions over different supported V₂O₅ catalysts are 81/93 over V₂O₅/Nb₂O₅, 73/87 with V₂O₅/ZrO₂, 67/91 on V₂O₅/TiO₂ (anatase), 30/84 V₂O₅/Al₂O₃, 16/80 with V₂O₅/SiO₂, and 90/85 over 5% V₂O₅/TiO₂-Nb₂O₅ [15,16]. Stobbelaar reported the ammoxidation of toluene over supported metal oxide catalysts and concluded that V/NaY and Mn/NaY catalysts show relatively high benzonitrile yield under optimum conditions [17]. Sanati et al. reported that the selectivity for benzonitrile formation increases rapidly with increase in vanadia loading

on zirconia and attains a value of about 80% during the ammoxidation of toluene [18]. Also, in many investigations of the ammoxidation reactions studied, emphasis was mostly placed on the examination of reaction mechanism and catalyst development [19,20]. In the present paper we describe a convenient method for the preparation of nitriles through the dehydration of aldoximes (benzaldoxime and 4-methoxybenzaldoxime) over rare earth exchanged K-Y zeolites. Benzaldoxime underwent only dehydration while 4-methoxybenzaldoxime both dehydration as well as Beckmann rearrangement reactions. The activity-selectivity results of rare earth exchanged zeolite catalysts are also comparable to those in the existing reports [13–18,21,22].

2. Experimental

Potassium exchanged zeolite was prepared by ion exchange of H-Y (*Sud-Chemie*-India, Si/Al = 1.5) at room temperature with 0.1 M KCl solution (0.05 mol of KCl/g of zeolite) for three times [23,24]. Rare earth exchanged zeolites were obtained by contacting K-Y with a 0.5 M respective nitrate solution (0.025 mol of nitrate/g of zeolite, obtained from *Indian Rare Earths* Ltd. Udyogamandal, Kerala) at 353 K for 24 h [24,25]. All the samples were calcined after each exchange at temperatures from 423 to 773 K, and at 773 K for 5 h with a heating rate of 12 K/min with a constant flow of air (60 mL/min). H-Mordenite (Si/Al = 19) was a product of *Zeolyst International*, USA. K-10 montmorillonite clay was purchased from *Sigma-Aldrich* USA. SiO₂ was prepared in the laboratory by well-known procedures reported in literature [26]. Aldoximes were prepared by coupling the corresponding aldehydes (99% benzaldehyde was a product of *SD-Fine Chemicals*, India and 98% 4-methoxybenzaldehyde also was from the same company) with hydroxylamine hydrochloride (99%, *SD-Fine chemicals*, India) in presence of mild base such as NaHCO₃ at refluxing temperatures.

The percentage of metal ion-exchanged and framework Si/Al ratio were determined by EDX using a *JEOL JSM-840 A* (Oxford make model l6211 with a resolution of 1.3 eV). Samples were prepared by dusting the zeolite powder onto double sided carbon tape mounted on a metal stub. Sensitivity of the instrument was approximately 2-wt.%. Structural information was obtained from XRD performed using a *Rigaku D-max C* X-ray diffractometer with Ni-filtered CuK α radiation in the range 5–40° and IR performed using a *Nicolet Impact 400FT IR* spectrometer in the transmission mode (400–4000 cm⁻¹). The surface area and pore volume measurements were carried out with the help of a *Micromeritics Gemini* surface area analyzer using nitrogen adsorption at liquid nitrogen temperature. Acid struc-

tural properties were determined by temperature programmed desorption (TPD) of ammonia using a conventional equipment.

Reaction was carried out in a continuous, fixed-bed, down-flow reactor made of glass with 0.6 cm internal diameter and 30 cm height. Catalysts (700 mg) were activated for 12 h in presence of oxygen at 773 K, allowed to cool to room temperature in dry nitrogen and then heated to reaction temperature (473 K) and kept for an hour before the start of reaction. The reaction mixture [5% (w/v) solution of oxime in a 1:1 mixture of benzene acetonitrile (precaution was taken to use highly moisture free reagents)] was fed into the reactor in presence of dry N₂. Constant flow of nitrogen helps the smooth down flow of reagents to the catalyst bed. Products were collected after 2 h of reaction (TOS; 2 h) and analyzed with *Chemito GC1000* gas chromatograph using an *SE-30* capillary column of 30 m length (oven temperature 353–503 K (heating rate; 5 K/min), injector temp. 373 K, detector temperature 373 K). The products were further analyzed with a gas chromatograph–mass spectrometer (GC–MS) using a *Shimadzu-5050* spectrometer provided with a 30 m HP-30 capillary column of cross linked 5% phenylmethylsilicone. The mass spectrometer detector voltage was 1 kV. The *m/z* values and relative intensity (%) are indicated for the significant peaks. (Column temperature was adjusted between 323 and 533 K with a heating rate of 10 K/min, injector: 513 K and detector: 563 K). Further, the products were analyzed by FT-IR spectroscopy performed using a *Nicolet Impact 400FT IR* spectrometer.

3. Results and discussion

Energy dispersive X-ray analysis (EDX) measurements show an overall Si/Al ratio of 1.5 for all the as-exchanged zeolite systems. In all the cases more than 80%

exchange of potassium with rare earth metal cations was observed. Consistent with the earlier reports, X-ray diffraction patterns confirms crystallization of the parent and modified forms into cubic unit cell with space group F3dm. Vibrational spectra show bands both in the framework and hydroxyl regions. In the framework region (400–1300 cm⁻¹), a band in the range 900–1100 cm⁻¹ is observed, which corresponds to Si–O–Si vibration around 1090 cm⁻¹, Si–O–Ce around 970 cm⁻¹ (in the case of cerium exchanged samples) and Si–O stretching vibrations of the Si–O–R⁺ (R⁺ = H⁺) groups in the calcined state. In the hydroxyl region (3000–4000 cm⁻¹), a broad band is observed around 3450 cm⁻¹ in all the samples, which is assigned to ν_{OH} of Si–O–H. Generally SiOH groups cause a band at/or around 3740 cm⁻¹. This pretty large shift of this Si–O–H band to lower wave numbers is due to the possibility of hydrogen bonding of internal SiOH groups. Due to the in plane bending {δ_{OH} (H₂O)} of hydroxyl groups, a band around 1630 cm⁻¹ is observed.

As seen in Table 1, the total amount of ammonia desorbed by each sample varies with the nature of cation present. Catanach et al. in their paper identified three desorption peaks for Y type zeolites located at 463, 513 and 673 K which corresponds to the loss of about 45 (49.45%), 28 (30.77%) and 18 (19.78%) molecules of ammonia per unit cell [27]. Dehydroxylation occur only above 963 K. Lok et al. proposed for high silica to alumina ratio zeolites, the first NH₃-TPD (below 473 K) peak is associated largely with weakly chemisorbed NH₃ molecules rather than physically adsorbed NH₃ molecules. The second peak (between 473 and 673 K) is associated with NH₃ molecules adsorbed on zeolite hydroxyl groups (the Brönsted acid sites) and the third NH₃-TPD peak (between 673 and 873) is desorption from very strong Brönsted acid sites (BAS) or Lewis acid sites (LAS) [28]. In the present case too there are three desorption peaks in the specified temperature

Table 1

Acid amount and surface area and pore volume measurements of parent H-Y, different as-exchanged KFAU-Y, H-MOR zeolites, K-10 montmorillonite clay and silica

Catalyst	Ammonia desorbed in the stipulated temperature ranges (K) in mmol/g				Textural properties		
	W ^{a,b}	M ^b	S ^b	Total acidity	BET surface area, m ² /g	Langmuir surface area, m ² /g	Pore volume ^c , cc/g
H-Y	0.41	0.63	0.30	1.34	398	593	0.266
K-Y	0.40	0.20	0.09	0.71	181	321	0.214
CeK-Y	0.62	0.38	0.23	1.23	473	684	0.303
LaK-Y	0.47	0.35	0.12	0.94	435	648	0.277
REK-Y ^d	0.52	0.37	0.21	1.10	461	667	0.295
H-MOR	0.63	0.56	0.73	1.92	552	748	0.188
K-10 Mont.	0.55	0.24	0.13	0.92	183	304	0.204
SiO ₂	0.59	0.11	0.07	0.77	155	280	0.172

^a Ammonia desorbed in the 373–473 K temperature range might contain some physisorbed ammonia too.

^b W, M, and S stand for weak (373–473 K), medium (474–673 K), and strong (674–873 K) acid sites.

^c Total pore volume at 0.9976 P/P₀.

^d REK-Y is mixed rare earth modified form containing mainly La, Ce, Nd, and Pr and very small amounts of Sm, Eu, etc.

ranges. Irrespective of the cation present, all samples show high values of acidity in the weak and medium regions. KCe-Y shows maximum acidity among the rare earth exchanged zeolites. However, there is a comparative decrease in the total acid amount values of as-exchanged zeolites when compared with pure H-Y. This might be due to the poisonous effect of K^+ ions on the BAS. It has been proposed that Na^+ ion has neutralizing effect over a large number of the existing protons [29,30]. Along similar lines, K^+ ions exhibit a neutralizing effect on BAS just like Na^+ . Low value in the acidity of LaK-Y is due to the formation of inaccessible Brönsted acid sites due to the migration of La^{3+} from super cages to small cages in the electrostatic repulsive field of residual cations upon heat treatment [31–33]. This is consistent with our observations from the ^{29}Si magic angle spinning (MAS) NMR studies on these samples. The results are discussed elsewhere [34].

Surface area and pore volume increase invariably on exchange with rare earth cations (Table 1). The increase of surface area might be due to the decrease in the crystallite size and improvement in the microporous nature when moving from the binder free K-Y to the rare earth modified forms. As expected, the as-exchanged lanthanum zeolite has lower surface area than the cerium or mixed rare earth form. This observation can easily be correlated to the results from ^{29}Si MAS NMR spectra [34].

Acid amount and surface area and pore volume of silica and K-10 montmorillonite clay are also shown in Table 1. Montmorillonite clay is a layered aluminosilicate with a dioctahedral layer, which is sandwiched

between two tetrahedral layers. This, unlike any other zeolites used does not have a regular pore structure. The pore size given in Table 1 is an average value. The structure of the clay constitutes micropores and mesopores. The amount of mesopores is very less when compared to the amount of micropores. This explains the reduced surface area and pore volume when compared to zeolites [35] (see Table 1).

3.1. Dehydration/Beckmann rearrangement of aldoximes

Four classes of solid acids have been used in this work for the dehydration/Beckmann rearrangement reaction of aldoximes; benzaldoxime and 4-methoxybenzaloxime. They include; (1) pure H-Y, (2) rare earth exchanged (La^{3+} , Ce^{3+} , RE^{3+}) KFAU-Y zeolite, (3) K-10 montmorillonite, and (4) silica. Under the well-optimized reaction conditions, benzaldoxime or 4-methoxybenzaloxime undergo dehydration/Beckmann rearrangement producing respective nitriles and amides.

The catalytic activities of the parent, various as-exchanged rare earth zeolites, K-10 montmorillonite clay, and silica are shown in Table 2. Benzaldoxime undergoes dehydration exclusively producing benzonitrile as the only major product. Benzaldehyde and benzoic acids were formed in very small amounts as by products (see Table 2). All zeolites exhibit >90% nitrile selectivity. Amide formation was not detected in the case of benzaldoxime. However, 4-methoxybenzaloxime undergoes dehydration as well as Beckmann rearrangement (producing 4-methoxyphenylformamide) almost to the same extent over rare earth zeolites whereas; dehydra-

Table 2
Activity of different catalysts towards dehydration/Beckmann rearrangement reaction of benzaldoxime and 4-methoxybenzaloxime

Catalyst	Benzaldoxime			4-Methoxybenzaloxime				
	Conversion (%)	Selectivity (%)			Conversion (%)	Selectivity (%)		
		Nitrile ^a	Amide ^b	Others ^c		Nitrile ^d	Amide ^e	Others ^f
H-FAU-Y	100	98.8	–	1.2	100	63.8	33.6	2.6
K-Y	77.9	95.7	–	4.3	77.9	59.5	30.5	10.0
CeK-Y	100	91.1	–	7.9	99.3	49.1	36.6	14.3
LaK-Y	98.4	99.1	–	0.9	98.4	60.0	36.8	3.2
REK-Y	100	94.7	–	5.3	98.9	57.1	37.7	11.2
H-MOR ^g	100	99.5	–	0.5	99.3	71.3	19.8	8.9
K-10 Mont. ^h	80.5	91.5	–	8.3	91.1	51.7	38.6	11.7
SiO ₂ ⁱ	78.3	86.9	–	13.1	77.8	85.3	12.3	2.4

Reaction temperature: 473 K, catalyst loading: 700 mg, reactant: 5% (w/v) solution of oxime in 1:1 mixture of benzene–acetonitrile, nitrogen flow: 10 mL/h, time on stream: 2 h.

^a Benzonitrile.

^b Phenylformamide.

^c Benzaldehyde, benzoic acid, etc.

^d 4-Methoxybenzonitrile.

^e 4-Methoxyphenylformamide.

^f 4-Methoxybenzaldehyde, 4-methoxybenzoic acid and anisole.

^g H-MOR was a product from *Zeolyst International USA*, with a Si/Al ratio of 19.

^h K-10 Mont (Si/Al ratio 2.7) was purchased from *Sigma–Aldrich Chemical Company, USA*.

ⁱ Silica was prepared using available literature.

tion (4-methoxybenzoxime formation) was the main reaction with other common catalyst systems such as mordenite, K-10 montmorillonite and SiO₂. CeK-Y and REK-Y produce relatively more side products compared with other rare earth exchanged zeolites.

Both Beckmann and dehydration reactions are acid catalyzed and it is a simple logic to correlate the catalytic activity of different catalyst systems with their acid structural properties. In general, zeolites, as seen from Table 1 have greater acid amount in the medium acid strength region. Ammonia desorbed in the medium temperature region is due to BAS [27,28]. Hence zeolites have relatively more number of protonic acid sites than other catalyst systems and consequently show better conversion of aldoximes. Silica and K-10 montmorillonite with a comparative low BAS shows inferior activity towards the reaction. A similar explanation can be given to the increased amide formation (4-methoxyphenylformamide) over the rare earth exchanged zeolites in the case of 4-methoxybenzaloxime. With both the aldoximes CeK-Y and REK-Y zeolite produce more side products. These side products as seen from Table 2 include benzaldehyde, benzoic acid (in the case of benzaloxime) and 4-methoxybenzaldehyde, 4-methoxybenzoic acid and anisole, etc. (in the case of 4-methoxybenzaloxime). These are all oxidation products. A comparative greater formation of side products on CeK-Y and REK-Y (REK-Y too contains small amount of cerium) might be due to their slight oxidation potential. Among different zeolites, mordenite produce the least amide (with 4-methoxybenzaloxime). The decreased level of Beckmann rearrangement and a corresponding enhancement in dehydration reaction might be due to its strong acid centers. From the above discussion, we conclude that dehydration needs strong acid sites whereas; Beckmann rearrangement is accomplished over low acid strength.

The synthesis of nitrile or amide was conducted under the reaction conditions in the continuous mode for 10h by maintaining a flow rate of 4mL/h of oxime (4-methoxybenzaloxime) in a 1:1 mixture of benzene and acetonitrile through the reactor (HFAU-Y, CeK-Y or H-MOR zeolites, catalyst loading; 700mg, reaction time; 10h). For carefully dehydrated reagents, the conversion decreases quickly with reaction time. Periodic checks by gas chromatography and gas chromatography-mass spectrometer showed this decrease in the total conversion. Fig. 1 presents the effect of time on stream (TOS) on the percentage conversion of 4-methoxybenzaloxime and the selectivity for the formation of amide over selected solid acid catalysts. The catalysts undergo quick deactivation with time. Cent percentage conversion after 2h of the reaction decreased to 49.2%, 58.1%, and 40.5% respectively for H-Y, CeK-Y, and H-MOR zeolites in 10h (extent of deactivations were 50.8%, 41.9%, and 59.5% respectively for three zeolites). A comparative fast

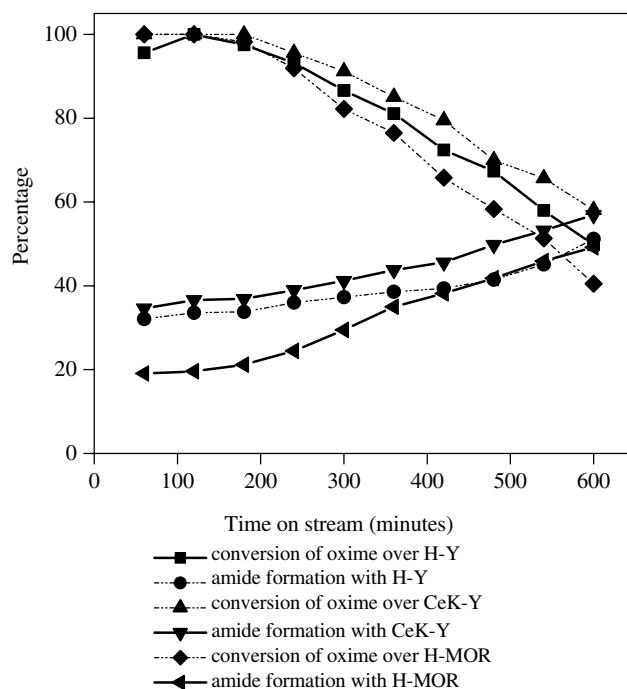


Fig. 1. Probe of deactivation of the solid acid catalysts during the dehydration/Beckmann rearrangement reaction of 4-methoxybenzaloxime; H-Y, CeK-Y, and H-MOR zeolites. Solid acid catalysts: HFAU-Y, CeK-Y, and H-MOR zeolites, reaction temperature: 473K, catalyst loading: 700mg, nitrogen flow: 10mL/h, flow rate: 4mL/h, reactant; 5% (w/v) solution of oxime in 1:1 mixture of benzene-acetonitrile.

deactivation of H-MOR might be due to rather fast neutralization of its strong acid sites. H-MOR has maximum amount of ammonia desorbed in the high temperature domain. However, the selectivity for amide formation (4-methoxyphenylformamide) increases slowly from 32.1% to 51.2% in an equal time on stream on H-Y zeolite (34.6% to 56.9% on CeK-Y and 19.1% to 49.2% with H-MOR zeolite). The deactivation of catalysts is generally due to the formation and trapping in the zeolite pores of secondary products of the reaction [36,37] (called coke for sake simplification). In the present case the deactivation of the catalyst is due to the neutralization of acid sites (very strong interaction between the active centers and the basic reactant and the product molecules (oxime and amide)). However, the formation of amide (Beckmann rearrangement) increases upon deactivation. This could be explained by considering the fact that the dehydration reaction needs strong acid centers whereas; even mild acid strength sites can effect Beckmann rearrangement of oximes. This is supported by the performance of mordenite zeolite. It is the most acidic among all the zeolites and produce maximum dehydration (see Table 2). As most of the acid sites getting deactivated during the course of reaction by reactants and products, the dehydration become

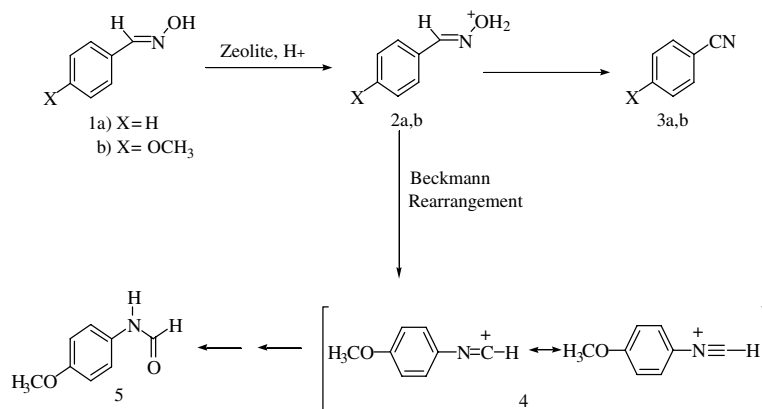


Fig. 2. Scheme showing the possible mechanism of the reaction.

nominal and at the same time the probability of Beckmann rearrangement increases slightly (see Fig. 1).

Easily recoverable and reusable solid acid catalysts are valuable candidates for the design of highly performing continuous down flow processes. The recycle of the reaction media could contribute to develop environmentally more benign processes [38]. The present catalytic system can address this issue and the variation of the reaction conversion on repeated usage in the reaction is checked. When the catalyst is used for the first time, cent percentage conversion of oxime is observed. But when the catalyst is used for the second time (after continuous extraction with DCM followed by oxidative treatment), the reaction conversion was only 95%, 97.5%, and 94.6% respectively for H-Y, CeK-Y, and H-MOR zeolites. When reused for the third time only 91.4%, 95%, and 90.8% conversion were obtained for the three zeolites. Deactivation/regeneration results show that the solid acid catalysts could be regenerated and reused effectively. Time on stream studies show that the catalysts when fresh, deactivated quickly. When some coke is deposited on the catalyst, rate of deactivation of the catalysts decrease. Since there is no waste formation in the reaction, the *E-factor* must be low and *atom efficiency* high. In conclusion, a simple, efficient, and highly environmentally friendly protocol is described for the production of nitriles and amides (in the case of 4-methoxy benzaldoxime).

3.2. Mechanism of the reaction

A plausible mechanism for the formation of various products is presented in Fig. 2. The oxime molecules (1a and 1b) adsorbed to the catalyst surface are efficiently protonated to give 2. Dehydration of 2 over the catalyst surface will lead to the formation of nitriles 3. Alternatively, migration of anti-aryl group to nitrogen concomitant with the removal of a molecule of water will lead to the resonance stabilized intermediate 4. Further transformation of 4 (addition of water followed by

tautomerization) will lead to amide 5. The difference in chemoselectivity exhibited by benzaldoxime (1a) and 4-methoxybenzaldoxime (1b) is explainable on the basis of electronic factors. We conclude that the electron-donating 4-methoxyphenyl group stabilizes intermediates such as 2b and 4 over 2a. Furthermore, based on detailed kinetic analysis, Gregory et al. [39] have established that substituent effects (as illustrated by the linear relationship existing between the Hammett σ^+ values and observed rate constants) are important for Beckmann rearrangement involving aryl migration. The rate of migration of 4-methoxyphenyl group is estimated at 3–4 times higher than that of phenyl groups.

4. Conclusions

In conclusion, acidic zeolites, K-10 clay and silica are highly active and selective catalysts for the dehydration/Beckmann rearrangement reactions of aldoximes (benzaldoxime and 4-methoxybenzaldoxime) for the synthesis of nitriles and amides. Thanks to their favorable acid structural properties. Dehydration/Beckmann rearrangement reaction of benzaldoxime and 4-methoxybenzaldoxime is carried out in a continuous down flow reactor at 473 K. 4-Methoxybenzaldoxime gave both Beckmann rearrangement product (4-methoxyphenylformamide) and dehydration product (4-methoxybenzoxime) in high overall yields. All the solid acid catalysts showed >95% selectivity towards benzonitrile formation. 4-Methoxyphenylformamide formation was almost similar over rare earth exchanged K-FAU-Y zeolites. However, in this case the main product also is nitrile. The catalysts undergo fast deactivation due to the neutralization of the acid sites by basic reactants and products. Also, these catalysts show considerable activity loss upon regeneration by oxidative treatment at 773 K. Examples of practical continuous and highly atom economic version is presented by using common laboratory down flow reactor and mild exper-

imental conditions. These preliminary results, in principle, afford an attractive alternative for the high temperature ammoxidation of alkyl aromatics for the synthesis of nitriles and studies addressed towards the extension of this protocol to other type of reactors and other aldoximes are currently under investigation.

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