

Dehydration of aldoximes over H-zeolites: A convenient and highly atom economic method for the preparation of nitriles

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Abstract

In this paper, an application of solid-acid catalysts in the dehydration/Beckmann rearrangement of aldoximes producing nitriles and amides is described. Vapor-phase dehydration/Beckmann rearrangement of benzaldoxime and 4-methoxybenzaloxime were carried out over different protonated zeolites, K-10 montmorillonite clay and γ -alumina at 473 K. Benzonitrile was obtained in (near) quantitative yields by the dehydration of benzaldoxime over H-Beta, H-MOR, H-ZSM-5 and H-Y zeolites. 4-Methoxybenzaloxime produced both Beckmann rearrangement (4-methoxyphenylformamide) and dehydration products (4-methoxybenzonitrile) in high overall yields. The difference in behavior of the aldoximes is explained in terms of electronic effects. The optimal protocol allows nitriles to be synthesized in excellent yields through the dehydration of aldoximes.

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Keywords: Beckmann rearrangement; Benzonitrile; Dehydration reaction; 4-Methoxybenzonitrile; 4-Methoxyphenylformamide; Zeolites

1. Introduction

Nitriles have been used in organic synthesis for a long time as precursors of biologically active compounds such as anti-peptidase tetrazole analogues [1], 1,2-diarylimidazoles as potent anti-inflammatory agents [2] and trizolo[1,5-*c*]primidines with potent anti-asthma activity [3]. Another application of nitriles is their reaction with β -aminoalcohol in the presence of a catalyst to give 2-oxazolines, which are used as chiral auxiliaries in asymmetric synthesis [4]. They are important intermediates in synthetic organic chemistry [5,6]. Many important multi-synthetic reactions pass through a nitrile intermediate. Examples include the synthesis of widely used pharmaceutical agents such as ibuprofen and ketoprofen [5,6]. Aromatic hydrocarbons such as benzene, phenolic compounds or phenyl ethers

have been cyanated using Cl_3CCN , BrCN or mercury fulminate [$\text{Hg}(\text{ONC})_2$] [7–9]. Aliphatic nitriles are accessed through nucleophilic substitution reactions of alkyl halides and tosylates with highly toxic cyanide ions as nucleophiles [5–9]. These are special reagents and their high cost, limited availability and very low bio-degradability are major concerns.

Dehydration of aldoximes and primary amides provides a convenient method for the preparation of both aliphatic and aromatic nitriles. Strong dehydrating reagents such as acetic anhydride, POCl_3 , P_2O_5 , PCl_5 , HMPA, trimethylsilyl polyphosphate, SOCl_2 and Burgess reagent (methyl *N*-(triethylammoniumsulphonyl)carbamate) are commonly employed for this reaction [10–21]. These methods employ either highly toxic or hygroscopic reagents and hence are unsatisfactory for routine applications. More recently, bacterial enzymes [22] and an alternate system using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}/\text{KI}/\text{H}_2\text{O}/\text{CH}_3\text{CN}$ [23] have been successfully employed for effecting the dehydration of aldoximes and primary amides. The normal work-up procedure with these reagents involves neutralization followed by water quench, which prevents them from being used again and leads to substantial quantities of aqueous waste. In all the methods discussed so far, the reagents are irreversibly lost leading to low overall atom efficiency.

Abbreviations: BAS, Brønsted acid sites; LAS, Lewis acid sites; TPD, temperature programmed desorption; TOS, time on stream; MOR, mordenite zeolite; HMPA, hexamethylphosphoramide; GC, gas chromatograph; GC–MS, gas chromatograph–mass spectrometer; HPLC, high performance liquid chromatography; NMR, nuclear magnetic resonance

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The ammoxidation of alkyl aromatics has been employed for long time as a commercial process to produce the corresponding nitrile. Recently, Lucke et al. [24] presented a comparative study of the vapor-phase oxidation and ammoxidation of different alkyl aromatics to their corresponding aldehydes and nitriles using various heterogeneous catalysts. Cavani and co-workers studied the ammoxidation of toluene to benzonitrile over V_2O_5 supported on TiO_2 (yield: 52%) [25,26]. Lately, Chary and co-workers [27–29] 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. Sanati et al. [30] reported that the selectivity of benzonitrile during the ammoxidation of toluene increases rapidly with increase in vanadia loading on zirconia and attains a value of about 80%. However, investigations of the ammoxidation reactions, emphasis was mostly given to the examination of reaction mechanism and catalyst development. Ammoxidation reactions usually require high temperatures [25,26,31,32].

However, there are barely few reports on nitrile synthesis through the dehydration of oximes over solid-acid catalysts. Rao et al. [33] has reported the synthesis of benzonitrile and 3,4-dimethoxybenzonitrile using Cs-X zeolite in high yield. Meshram [34] reported the dehydration of series of aldoximes over clay catalysts. In this present paper, we describe an efficient method for the synthesis of benzonitrile and 4-methoxybenzonitrile using environmentally benign solid-acid catalysts. Benzaldoxime underwent only dehydration while 4-methoxybenzaldoxime both dehydration as well as Beckmann rearrangement reactions. Thus, dehydration of aldoximes over zeolite catalysts is much more an efficient method for the production of nitriles compared to ammoxidation reaction. The activity–selectivity results of protonated zeolite catalysts are better to those in the existing reports [25,26,28–31,33,35,36].

2. Experimental

2.1. Materials used for dehydration/Beckmann rearrangement of aldoximes

H-Y zeolite (Si/Al ratio 1.508) was purchased from Sud-Chemie (India) Ltd. H-ZSM-5 and H-Beta zeolites (Si/Al ratios 40 and 26, respectively) were procured from National Chemical Laboratory, Pune, India. H-MOR (Si/Al ratio 19) CBV-90 was purchased from Zeolyst International, New York, USA. K-10 montmorillonite clay was supplied by Aldrich Chemical Company, USA. Aluminium oxide was prepared using well-known chemical routes in the laboratory [37,38] by the addition of ammonia to a boiling solution of aluminium nitrate. The hydrated oxide was washed free of electrolytes using de-ionized water and dried at 383 K in an air oven for 12 h. It was then calcined to 773 K at a heating rate of 20 K/min under a constant flow of air over the sample (60 mL/min). Benzaldehyde (>99% syn), 4-methoxybenzaldehyde (>99% syn), hydroxylamine hydrochloride and sodium bicarbonate were purchased from SD Fine Chemicals, India, and used without further purification. Benzene (SD Fine Chemicals, India) was

used after washing with concentrated H_2SO_4 and 20% sodium bicarbonate. Benzaldoxime (**1a**, mp 308 K, *syn*-isomer) and 4-methoxybenzaldoxime (**1b**, mp 339–340 K, *syn*-isomer) were prepared using standard procedures [39].

2.2. General remarks

The crystalline nature of the materials was established by X-ray diffraction studies performed using a Rigaku D-max C X-ray diffractometer with Ni-filtered $Cu K\alpha$ radiation. Simultaneous determination of surface area and pore volume was performed over a Gemini Micrometric surface area analyzer using the nitrogen adsorption method at liquid nitrogen temperature. Acid structural properties were determined using temperature programmed desorption of ammonia conducted using a conventional TPD apparatus. Reaction mixtures were analyzed using GC (Chemito GC1000 gas chromatograph with an SE-30 capillary column), GC–MS (Shimadzu-5050 spectrometer provided with a 30 m HP-30 capillary column of cross linked 5% phenyl-methylsilicone), HPLC (Shimadzu CLASS-VP V5.032) and FT-IR (Nicolet Impact 400FT IR spectrometer in the transmission mode in the range $400\text{--}4000\text{ cm}^{-1}$) spectral data. The presence of aluminium in the reaction mixture was determined by EDX using a JEOL JSM-840 A (Oxford make model I6211 with a resolution of 1.3 eV).

2.3. Apparatus and reaction procedure

Schematic representation of the catalytic reactor set-up is shown in Fig. 1. The reactor system employed for the present study was a bench top reaction system, which is a fixed-bed down-flow quartz reactor of 0.6 cm internal diameter and 30 cm

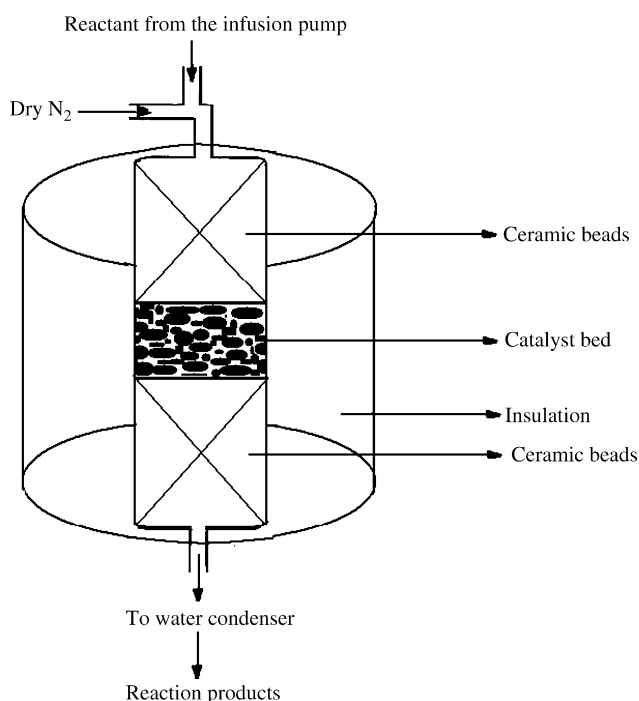


Fig. 1. Schematic representation of the fixed-bed down-flow reactor used for dehydration/Beckmann rearrangement of oximes.

height with a high sensitivity temperature controller (accuracy ± 5 K) operating under steady-state conditions. The reactor was fitted with a cold-water condenser down stream to allow condensation of reaction products. The catalysts particles (700 mg and 30–40 μm mesh size) were filled between porcelain ceramic beads. Prior to dehydration/Beckmann rearrangement reaction, catalysts were heated *in situ* at 773 K for 12 h under steady flow of air. The air flow varied with the help of mass flow controller. The catalyst was then allowed to cool to reaction temperature (473 K) under dry nitrogen flow (10 mL/min) and kept for 1 h before the commencement of reaction. The reaction mixture [5% (w/v) solution of oximes in a 1:1 mixture of benzene and acetonitrile] was fed through ISCO-MODEL 500 D syringe pump in presence of dry N_2 (mass flow controller: Brooks, Model 5896, flow rate: 10 mL/min) at a flow rate of 4 mL/h (weight hourly space velocity: 0.29 h^{-1}). Products were collected down stream after 2 h of reaction (TOS: 2 h). In a series of blank experiments, passage of the feed in a stream of N_2 in the absence of catalyst did not result in any detectable conversion. Mass diffusion contributions under the conditions of the reaction studied were found to be of negligible influence. The conversion of oxime and selectivity for the nitrile or amide were calculated as follows:

$$\text{Conversion (mol\%)} = \frac{N_{A0} - N_A}{N_A} \times 100 \quad (1)$$

where N_{A0} is the initial number of moles of the corresponding nitrile or amide and N_A is the number of moles of oxime at time t .

$$\text{Selectivity (mol\%)} = \frac{N_n}{N_{A0} - N_A} \times 100 \quad (2)$$

where N_n is the number of moles of product n .

2.4. Deactivation, recovery and reuse of the catalysts

The catalytic reaction was carried out continuously for 10 h to check the on stream stability of the catalyst. Products were collected at every hour and analyzed by GC. For a consecutive run, benzene was passed through zeolite catalysts for 1 h after the reaction and were continuously extracted with dimethyl ether and dried in an air-oven (383 K and 12 h) to remove the remaining surface adsorbed reagents and products. It was then activated

from 423 to 773 K over a period of 6 h and at 773 K for 5 h (dry nitrogen, 60 mL/min). Similar amounts of fresh reagents were used, with the reaction performed under the same conditions. The dry solid was weighed and reused in a next run, with the proportional amounts of reactants and catalyst used to keep the substrate-to-catalyst and the solvent-to-catalyst ratios constant.

3. Results and discussion

3.1. Physicochemical characterization of the catalysts

General physicochemical properties of the zeolites used are summarized in Table 1. For each zeolite, the values of surface area and pore volume matched well with the reported values [40]. The adsorption–desorption nitrogen isotherm shapes of the sample exhibited a hysteresis loop attributable to the presence of mesopores. Comparatively large amounts of mesopores were found in H-Y and H-Beta zeolites. H-MOR contained far fewer mesopores compared to these zeolites.

NH_3 -TPD provides general information about the acid strength, and number and distribution of the active sites. The amount of ammonia desorbed is formally divided into three temperature domains, namely 373–473 K (weak sites), 473–673 K (medium acid strength) and 673–873 K (strong acid sites) as seen in Table 2. For H-ZSM-5 and H-Y zeolites, the ammonia desorption occur mainly in the low temperature range, in the intermediate temperature range from H-Beta and in the high temperature domain from H-MOR zeolite. The overall amount of ammonia desorbed enabled us to evaluate the concentration of accessible acid sites. For different zeolites, the total acidity follows the order H-MOR > H-Beta > H-Y > H-ZSM-5.

Data on the chemisorption of ammonia in zeolites at different temperatures as obtained from step-wise thermal desorption is presented in Fig. 2. For pure H-Y and H-ZSM-5 zeolites, the amount of ammonia desorbed decrease gradually as the temperature increase. These zeolites invariably show higher desorption at low temperatures. The low temperature region is due to the interaction of ammonia with non-acidic sites in zeolites. Hence the number of acid sites measured by the ammonia chemisorption at lower temperature can be taken only as an upper limit of the acid sites in the zeolites. However, at higher temperatures (>623 K), the non-acidic ammonia interactions are weak

Table 1
General properties of the zeolites and K-10 montmorillonite clay used in the dehydration/Beckmann rearrangement reaction

Zeolite	Si/Al ^a	S_{BET} (m^2/g)	Pore volume ^b (cm^3/g)	General features		
				Dimensionality	Pore size (nm)	Crystal size ^c (μm)
H-Y 1.5	1.508	398	0.266	3D	Super cage: 1.18; window: 0.74×0.74	0.90
HZSM-5 40	40	413	0.163	3D	0.53×0.56	0.40
H-Beta 26	26	745	0.232	3D	0.66×0.67	0.51
H-MOR 19	19	552	0.188	2D	0.26×0.57	0.92
K-10 Mont	2.701	183	0.204	2D	Average pore size >1.0 nm	≈ 1.0

^a As determined by inductively coupled plasma–atomic emission spectroscopy (ICP-AES: Perkin-Elmer ICP 5500B) analysis.

^b Total pore volume measured up to a relative pressure of $0.9976P/P_0$.

^c As determined by X-ray diffraction measurements.

Table 2

Temperature programmed desorption ammonia from different zeolites H-Y, ZSM-5, H-Beta, H-MOR and other materials used in the dehydration/Beckmann rearrangement of benzaldoxime and 4-methoxybenzaldoxime

Catalyst	Amount of ammonia (mmol/g) desorbed within certain temperature range (K)			Cumulative (373–873)
	W ^{a,b}	M ^a	S ^a	
H-Y 1.508	0.69	0.41	0.33	1.43
H-ZSM-5 40	0.65	0.34	0.29	1.28
H-Beta 26	0.52	0.70	0.51	1.73
H-MOR 19	0.63	0.56	0.73	1.92
K-10 Mont	0.55	0.24	0.13	0.92
Al ₂ O ₃	0.56	0.19	0.13	0.88

The number after zeolite name indicate silica alumina ratio.

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

^b Ammonia desorbed in the temperature range 373–473 contains small amounts of physisorbed ammonia.

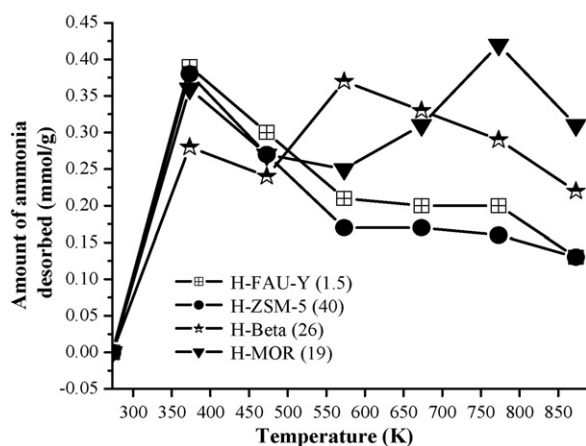
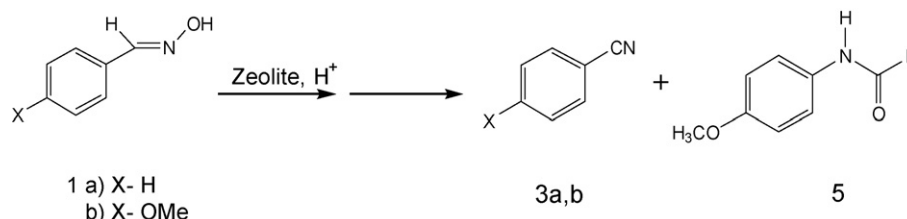


Fig. 2. Temperature dependence of chemisorption of ammonia on pure H-Y, H-ZSM-5, H-Beta and H-MOR zeolites. Values in parenthesis show the silica alumina ratio.

and hence the sites measured by chemisorption of ammonia are expected to be acidic ones. This part is considerably larger in the case of H-Beta and H-MOR zeolites compared to pure H-Y. This supports the enhanced acid structural properties of MOR and Beta zeolites.

As seen in Table 2, the total amount of ammonia desorbed varies with the nature of zeolites. Catanach et al. [41] 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.



Scheme 1. The proposed reaction for the catalyst screening.

Dehydroxylation occurs only at 963 K. The acid strength distribution in H-Y zeolite is consistent with this observation. Lok et al. [42] proposed for high silica to alumina ratio zeolites, the first NH₃-TPD peak (below 473 K) 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 (typical BAS) and the third NH₃-TPD peak (between 673 and 873) is desorption from strong BAS or LAS. The first and second desorption peaks usually account for most of the ammonia adsorbed and the third peak is usually very small in absolute amount [43–45]. The high temperature fraction contains NH₃ desorbed from strong BAS and LAS.

3.2. Dehydration/Beckmann rearrangement of aldoximes

Three classes of solid-acid catalysts were employed for the dehydration/Beckmann rearrangement reaction of the two aldoximes: (1) H-zeolites, (2) K-10 montmorillonite clay and (3) Al₂O₃. A general scheme of dehydration/Beckmann rearrangement of aldoximes is depicted in Scheme 1. Benzaldoxime (1a) predominantly underwent dehydration producing benzonitrile (2a), while 4-methoxybenzaldoxime underwent both Beckmann rearrangement (4-methoxyphenylformamide; 3) and dehydration (4-methoxybenzonitrile; 2b) in high overall yields.

3.2.1. Effect of reaction temperature

Total conversion of 4-methoxybenzaldoxime has been studied by varying the reaction temperature from 398 to 523 K using H-Y zeolite as a standard catalyst. Reaction products were collected after 2 h. The results of the observations are depicted in Fig. 3A. Temperature has pronounced influence on the dehydration/Beckmann rearrangement potential of solid-acid catalysts. Oxime conversion increased considerably from 46.1 to 99.5% as the temperature of the reaction increased from 398 to 473 K. The nitrile formation increased from 40.3 to 63.8% whereas, amide selectivity decreased from 48.9 to 33.6%. This shows that the nitrile generation increases with the reaction temperature, while amide formation is considerable at lower temperatures. This is consistent with the general observation that dehydration of oximes is the most feasible reaction at high temperatures.

3.2.2. Effect of contact time

The effect of weight hourly space velocity (WHSV: h⁻¹) on the distribution of products was investigated at 473 K on H-Y zeolite for the dehydration/Beckmann rearrangement of 4-methoxybenzaldoxime. Results are presented in Fig. 3B. Influ-

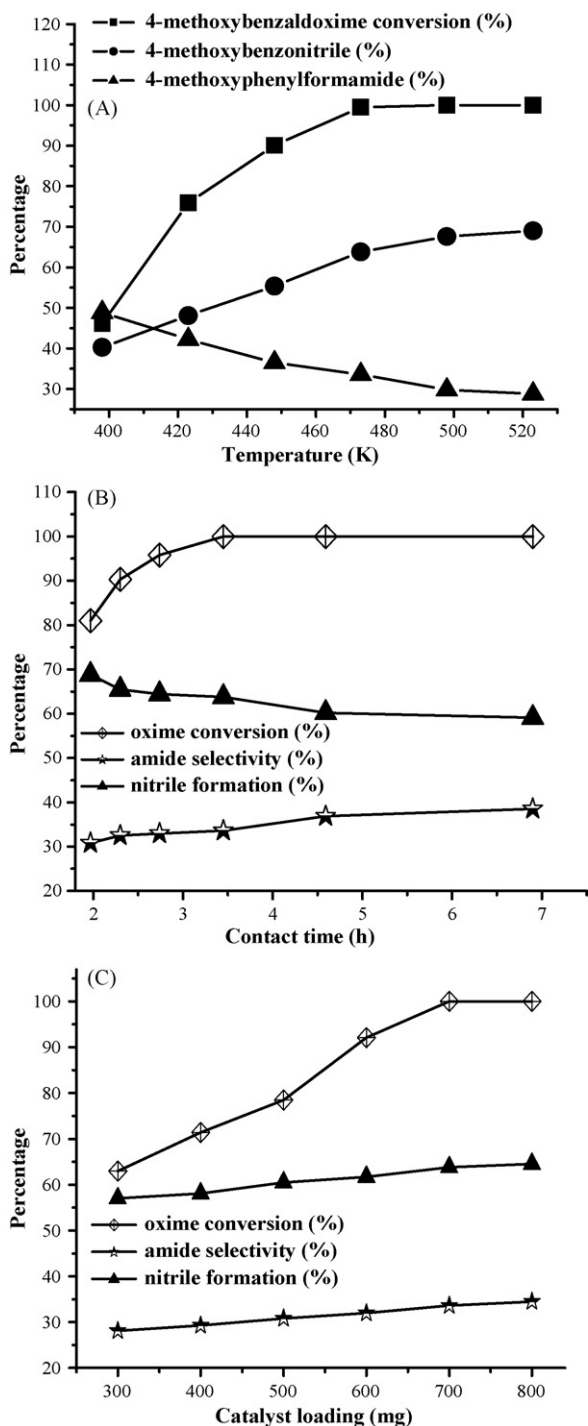


Fig. 3. The influence of: (A) reaction temperature, (B) contact time and (C) catalyst amount on the percentage conversion of 4-methoxybenzaloxime and formation of 4-methoxybenzoxonitrile and 4-methoxyphenylformamide on H-Y zeolite. Other reaction conditions are as described in Table 3.

ence of WHSV on the catalytic activity on H-Y zeolite was checked by conducting the reaction at different space velocities under standard reaction conditions. Total conversion of 4-methoxybenzaloxime increased from 81 to 100% as the space velocity decreased from 0.51 h^{-1} (flow rate: 7 mL/h) to 0.29 h^{-1} (flow rate: 4 mL/h). Lower space velocities imply higher contact time ($1/\text{weight hourly space velocity}$: h) of the reactants on the

active sites of the catalysts and results in increased conversion. There was slight increase in the selectivity of amide and a corresponding decrease in the nitrile formation at higher contact times. The chances of dehydration of aldoximes to the corresponding nitrile reduced at higher space velocities. This could be due to less time the reactants spend inside the zeolite pores, which promote the much viable Beckmann rearrangement generating amide in good yields. The optimum WHSV obtained was 0.29 h^{-1} to get the best yield of the products.

3.2.3. Influence of catalyst loading

The effect of catalyst concentration on oxime conversion (4-methoxybenzaloxime) shows that a catalyst concentration of 400 mg produced an oxime conversion of 63.4% which increased to 100% with 700 mg catalyst, while the nitrile formation increased to 63.8% from 57%. Observations of these studies are illustrated in Fig. 3C. Small increase in the amide formation (28.1–34.5%) was observed on increasing the catalyst amount from 300 to 800 mg. Consequently, under the reaction conditions of 473 K, TOS: 2 h and weight hourly space velocity: 0.29 h^{-1} , the reaction produced 100% conversion of oxime with 63.8% 4-methoxybenzoxonitrile, 33.6% 4-methoxyphenylformamide and 2.6% by-products with H-Y zeolite. The increase in oxime conversion with catalyst loading is due to an increase in the number of active sites which are accessible for the reaction.

3.2.4. Catalytic activity of different systems

The performance of various H-zeolites, K-10 clay and Al_2O_3 towards dehydration and/or Beckmann rearrangement of benzaloxime (**1a**) and 4-methoxybenzaloxime (**1b**) is summarized in Table 3. In most cases, few minor products (<13.2% combined yield) were produced. Benzaloxime yields benzoxonitrile (**2a**; dehydration product) exclusively and 4-methoxybenzaloxime produces both 4-methoxybenzoxonitrile (**2b**; dehydration product) and *N*-(4-methoxyphenyl)formamide (**3**; Beckmann rearrangement product). In the case of benzaloxime, protonated zeolites produced cent percentage conversion and >99% nitrile selectivity. Therefore, nitrile was quantitatively generated over zeolite catalysts. Best results were obtained with zeolites H-Beta and H-MOR, where cent percentage nitrile selectivity was observed. In the case of 4-methoxybenzaloxime cent percentage conversion was achieved over zeolite catalysts and dehydration was the predominant reaction (yield >60%). Beckmann rearrangement generating *N*-(4-methoxyphenyl)formamide was less probable over zeolites than other catalytic materials. Among various zeolites, H-Beta and H-MOR promote dehydration to a much higher extents compared to H-Y and H-ZSM-5. H-ZSM-5, H-Y and K-10 Mont clay are proficient in promoting Beckmann rearrangement producing amide. Dehydration was the predominant reaction observed with alumina and K-10 Mont clay.

Vapor-phase dehydration/Beckmann rearrangement of oximes over zeolites is much more efficient than K-10 clay or $\gamma\text{-Al}_2\text{O}_3$. The activity difference may be attributed to two important properties: acid structural properties and diffusional properties, which are determined by the active sites distribution and the pore structure of the materials. H-MOR has a bi-directional pore system with parallel circular 12-ring

Table 3
Activity of different catalysts with benzaldoxime and 4-methoxybenzaldoxime during the catalytic reaction

	Benzaldoxime			4-Methoxybenzaldoxime				
	Conversion (%)	Yield (%) nitrile ^a	Amide ^b	Others ^c	Conversion (%)	Yield (%) nitrile ^d	Amide ^e	Others ^f
H-Y	100	99.5	–	0.5	100	63.8	33.6	2.6
H-ZSM-5	100	99.1	–	0.9	100	60.3	34.2	5.5
H-Beta	100	100	–	–	100	70.4	20.1	9.5
H-MOR	100	100	–	–	100	73.3	17.8	8.9
K-10 Mont	80.5	91.7	–	8.3	91.1	51.7	38.6	11.7
γ -Al ₂ O ₃	76.2	87.9	–	12.1	80.6	48.4	24.5	27.1

Reaction conditions: temperature, 473 K; catalyst loading, 700 mg; reactant, 5% (w/v) solution of oxime in a 1:1 mixture of benzene–acetonitrile; nitrogen flow, 10 mL/min; weight hourly space velocity = 0.29 h⁻¹; 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, anisole, etc.

channels (0.65 nm × 0.70 nm) and elliptical 8-ring channels (0.26 nm × 0.57 nm). However, it practically function as unidirectional pore system as the 8-ring channels are in effect is inaccessible for most organic compounds. H-Beta also has a three-dimensional interconnecting pore system with pores of 0.55 nm × 0.55 nm and 0.76 nm × 0.64 nm and H-Y has a 3D interconnecting pore systems with super cages of 1.18 nm connected by circular 12-ring 0.74 nm windows. H-ZSM-5 is a medium pore (10-membered ring) zeolite having a three-dimensional 0.51 nm × 0.55 nm and 0.53 nm × 0.56 nm pore system (straight channels) [46–50]. γ -Al₂O₃ does not have a regular pore structure. K-10 montmorillonite clay is a layered alumino-silicate with an octahedral layer sandwiched between two tetrahedral layers. This, unlike zeolites does not have a regular pore structure. However, the average pore size is greater than zeolites (>1.0 nm) [51].

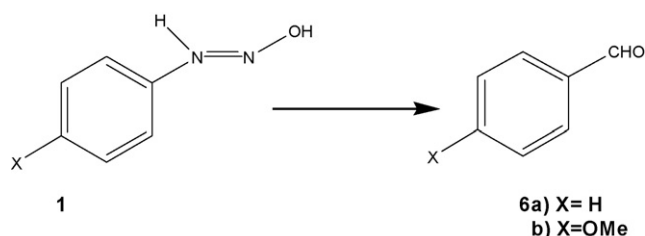
As the reactions were carried out in the vapor phase and all the zeolites show comparable activity, diffusional properties of the reactants through the pores of catalysts have only limited role on the course of the reaction. This argument is supported by the fact that other solid-acid catalysts lacking the regular pore structure (diffusion of reactants is not very critical for these materials) of zeolites are also found to be active towards the reaction. Based on these observations, we conclude that the acid structural properties of the catalysts would be the deciding factor for the difference in dehydration/Beckmann rearrangement activity.

Both Beckmann rearrangement and dehydration are acid catalyzed reactions. Hence, it is logical that the conversion of oximes to either the nitrile (dehydration) or to the amide (Beckmann rearrangement) should be correlated with the strength and distribution of acid sites of catalysts as obtained from NH₃-TPD profiles (Table 2). As indicated in Table 2, zeolites are characterized by high total acidity and their acidic sites are much stronger than that of K-10 Mont clay and alumina employed in this study. So it should be expected that the zeolites would show much higher activity than the conventional catalysts. A greater nitrile formation with H-MOR zeolite may be explained using the higher total acid amount. A relative large acid amount of H-

MOR zeolite effect greater dehydration reaction of aldoximes compared to other zeolite catalysts in the case of both aldoximes.

With more typical Lewis acid catalysts such as K-10 clay and alumina, there is consistently greater formation of by-products, mainly benzaldehyde (**6a**) and 4-methoxybenzaldehyde (**6b**), respectively, with two oximes (Scheme 2). Drop in the aldehyde formation over zeolites is an indication of their poor Lewis acidic nature. Hydrolysis occurred mostly in the later stages, suggesting generation of water in the reaction systems. Lewis sites with strong acidity were likely to be associated with the dimerization or formation of high-molecular-weight compounds, yielding water as a by-product, which is used for hydrolysis in the subsequent stages.

A simple plot of 4-methoxybenzonitrile yield with total amount of acid sites (obtained from NH₃-TPD studies) exhibited a perfect linear relationship (Fig. 4A). These results suggest that acid sites (weak, medium and strong) are active centers for the dehydration reaction of oximes. Further, a plot between the amount of ammonia desorbed in the high temperature domain, 673–873 K (both Brønsted and Lewis) and nitrile formed during the reaction yields a perfect one-to-one correlation (Fig. 4B). More the amount of strong acid centers, higher the nitrile formation. This observation is consistent with the observation that dehydration takes place over strong acid sites in the case of Beckmann rearrangement of cyclohexanone oxime and cinnamaldoxime. Strong acid sites were also likely to be associated with dehydration of oxime dimerization or for-



Scheme 2. Hydrolysis of oxime over the catalysts during the reaction.

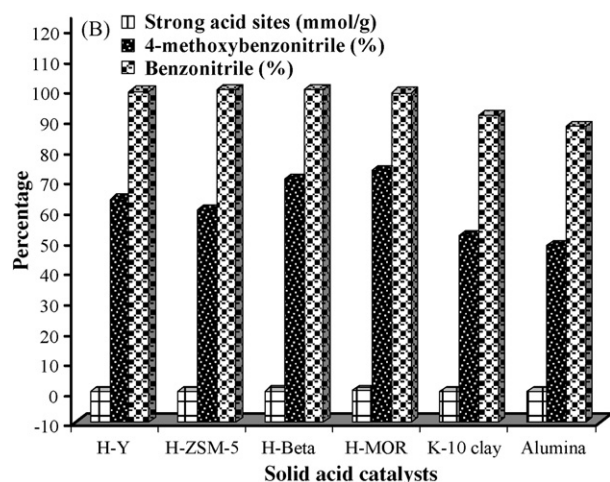
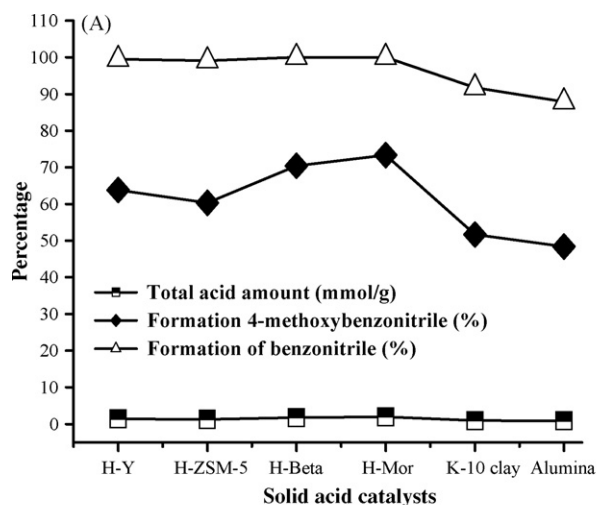


Fig. 4. Plot showing a simple correlation between: (A) total acid amount and (B) strong acid sites as determined by NH_3 -TPD studies and percentage of nitrile formed during the dehydration of benzaldoxime and 4-methoxybenzaldoxime on various solid-acid catalysts. Reaction conditions are as described in Table 3.

mation of high-molecular-weight compounds yielding water as a by-product. Hydrolysis occurs mostly in the later stages, suggesting generation of water during the reaction. An increase in the cinnamaldehyde formation with time over zeolites confirms this observation. Water generation in the reaction medium can also create sample deactivation.

3.2.5. Study of the deactivation, reusability and heterogeneity of the catalysts

Dehydration/Beckmann rearrangement reaction of aldoximes is performed over H-Y and H-MOR zeolites as described in Section 2 for 10 h. Periodic checks by GC and GC-MS showed decrease in conversion with reaction time. Fig. 5 presents the effect of time on stream (TOS) on the percentage conversion of 4-methoxybenzaldoxime and the selectivity for the formation of amide over the catalyst. Cent percentage conversion after 2 h of the reaction decreased to 49.2 and 40.5% in 10 h on H-Y and H-MOR zeolites, respectively. H-Y zeolite underwent 50.2% deactivation, while H-MOR 59.5% in 10 h on stream. However, the yield of amide

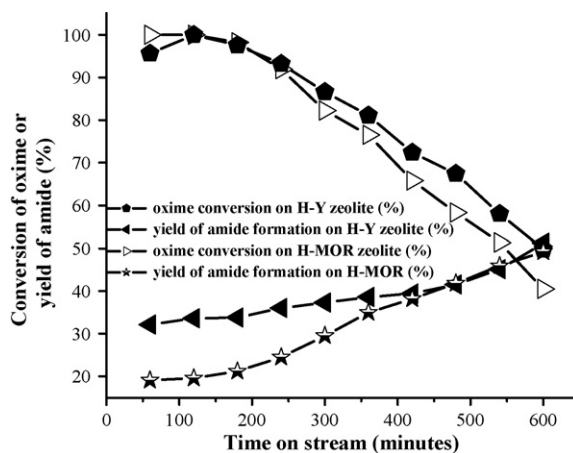


Fig. 5. A plot of deactivation of the catalysts during dehydration/Beckmann rearrangement reaction over solid-acid catalysts, H-Y and H-MOR zeolites. Reaction conditions are as demonstrated in Table 3.

formation (4-methoxyphenylformamide) increases slowly from 32.1 to 51.2% in equal time on stream (19.1–49.2% over H-MOR zeolites). The deactivation of catalyst is generally due to the formation and trapping in the zeolite pores of secondary products of the reaction (called coke for sake simplification) [52–54]. The coke is composed of reactants, various products of the reaction especially polymeric products which are trapped inside the zeolite pores.

The increase in the amide formation with time can be explained by considering the fact that the dehydration reaction needs strong acid centers, while mild or weak acid sites can achieve Beckmann rearrangement. This suggests that the active sites responsible for nitrile formation were gradually deactivated and mostly lost when the conversion reached 49.8% in 10 h. Consequently, the surviving relatively weak acid sites catalyzed the Beckmann reaction generating amide at subsequent stages. Due to insufficient acid strength, dehydration of oximes to nitrile was not effectively been catalyzed, resulting in low conversion and nitrile selectivity. Substantial amide formation occurs over these catalysts at later stages. This is supported by the performance of MOR zeolite, which is the most acidic among all zeolites and effects maximum dehydration at early stages of the reaction.

The deactivated zeolites can be partially regenerated by solvent extraction followed by oxidative treatment. The deactivated zeolite is extracted with benzene to remove the products from the catalyst surface. Further, washed with de-ionized water, dried at 383 K overnight and regenerated by activating to 773 K at a heating rate of 12 K per minute and at 773 K it has kept for 5 h. Regenerated H-Y zeolite converted 97.8% oxime, while H-MOR 97.1% under the similar reaction conditions. There was no substantial loss of catalytic activity for both H-Y and H-MOR zeolites even after three cycles. Results are depicted in Table 4. H-Y and H-MOR zeolites converted 96.1 and 96.5% oxime, respectively, after three cycles. This demonstrates that zeolites catalysts can be regenerated without loss of their catalytic activity.

To understand the stability and perfect heterogeneity of the catalysts, we conducted experiments under the standard

Table 4
Catalytic performances for H-Y and H-MOR zeolites after one to three regeneration cycles

	Fresh	I cycle	II cycle	III cycle
Benzaldoxime conversion (%)	100 (100)	97.8 (97.1)	96.3 (96.9)	96.1 (96.5)
Benzonitrile selectivity (%)	99.5 (100)	98.5 (98.9)	98.1 (98.4)	97.9 (98.1)

Catalytic tests are carried out at 473 K and values are referred to the second hour of reaction. Values in parenthesis are the conversion of benzaldoxime and selectivity for benzonitrile on H-MOR zeolite. Reaction conditions are as described in Table 3.

reaction conditions. The reaction mixture (4-methoxy benzaldoxime; **1b**) was passed through H-Y and H-MOR zeolites under standard reaction conditions for 10 h. Aluminium was not detected in the reaction mixture by the energy dispersive X-ray analysis. Furthermore, no aluminium was detected while qualitative analysis of the mixture also. These results strongly suggest against the possible aluminium leaching during the reaction.

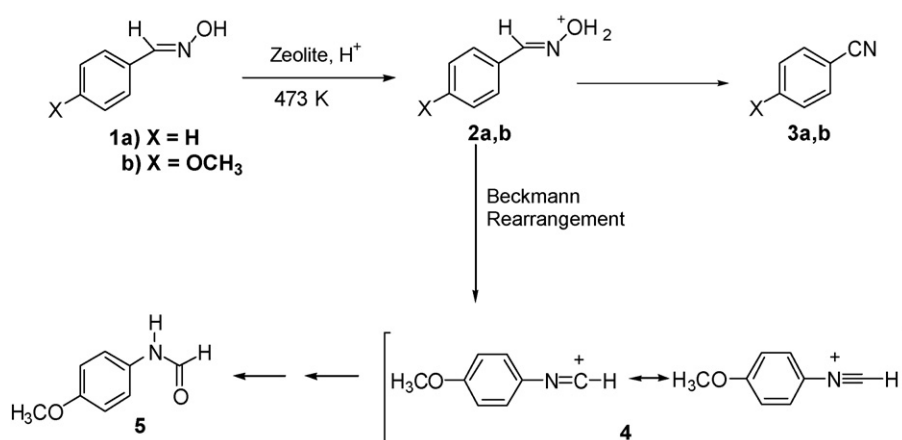
3.2.6. Mechanism of the reaction

A plausible mechanism for the formation of various products is presented in Scheme 3. The oxime molecules 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. have established that substituent effects (as illustrated by the linear relationship existing between the Hammett σ^+ values and observed rate constants) are important

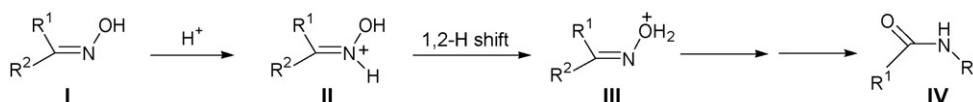
for Beckmann rearrangement involving aryl migration [55]. The rate of migration of 4-methoxyphenyl group is estimated at three to four times higher than that of phenyl group.

However, there is controversy regarding the molecular mechanism of the reaction. *Ab initio* molecular-orbital calculations on the isolated gas-phase system suggested that the first step is the *N*-protonation of the oxime (I) to give II, and the actual rate determining step is the 1,2-hydride shift to *O*-protonated oxime III (Scheme 4) [56–59]. More recently, quantum-chemical calculations suggested that the transfer of the alkyl group (BR) and simultaneous elimination of water to form the nitrilium ions is the rate determining step when gas-phase reaction occurs over solid oxide catalysts [60]. Based on these reports, a modified feasible mechanism for nitrile and amide formation is depicted in Scheme 5. However, at present, there is no experimental proof and the Beckmann rearrangement reaction pathway is not well established.

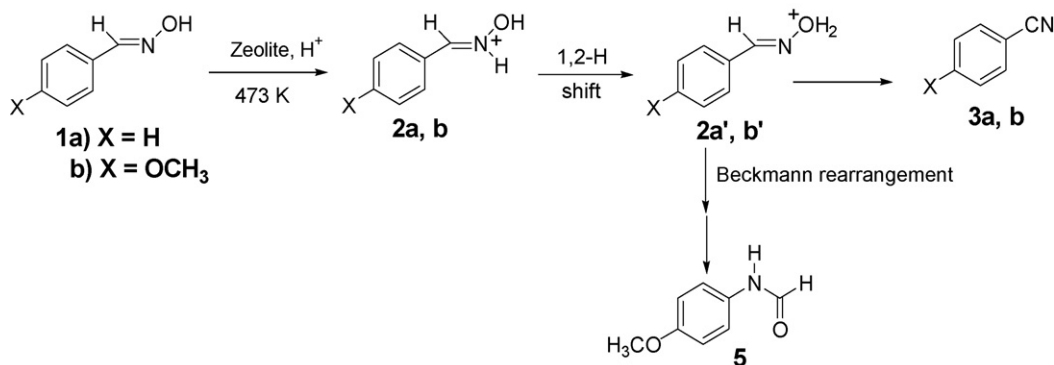
Recently, Corma and co-workers [61] reported experimental evidence on the intermediates formed in the initial stages of Beckmann rearrangement of acetophenone oxime over various modified β -zeolites through solid-state NMR spectroscopy and theoretical calculations. The group has demonstrated over zeolites β -D, H- β -D and Al-H- β -D that there are two possible reaction pathways (*N*-protonation or the *O*-protonation) for the Beckmann rearrangement of acetophenone oxime, depending on the acid strength of the active centre. We are currently working



Scheme 3. Proposed mechanism of the dehydration/Beckmann rearrangement of benzaldoxime and 4-methoxybenzaldoxime.



Scheme 4. Proposed reaction mechanism for general Beckmann rearrangement.



Scheme 5. Proposed alternative mechanism for the dehydration/Beckmann rearrangement of benzaldoxime and 4-methoxybenzaldoxime.

on a similar strategy for the determination reaction mechanism by solid-state nuclear magnetic resonance studies.

4. Conclusions

Dehydration/Beckmann rearrangement reaction was carried out in the vapor-phase over series protonated zeolites, K-10 clay and alumina. Thanks to their favorable acid structural properties, zeolites exhibited much higher activity than other catalysts. 4-Methoxybenzaldoxime underwent both dehydration and Beckmann rearrangement with dehydration as the predominant reaction. In contrast, benzaldoxime underwent exclusive dehydration yielding benzonitrile. Dehydration of aldoximes over zeolites offers a superior method for the preparation of nitriles. Time on stream studies show that 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. In conclusion, an example of practical continuous and atom economic version of nitrile synthesis is presented using common laboratory down flow reactor and mild experimental 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 actually under investigation.

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