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Towards a green synthesis of isoquinoline: Beckmann rearrangement of *E,E*-cinnamaldoxime over H-zeolites

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Abstract

Isoquinoline was prepared through the Beckmann rearrangement of cinnamaldoxime over different H-zeolites, K-10 montmorillonite clay, amorphous SiO_2–Al_2O_3 and γ-alumina under well-optimized conditions of temperature, weight hourly space velocity and catalyst loading. Cinnamaldoxime under ambient reaction conditions over the catalysts underwent migration of the anti-styryl moiety to electron deficient nitrogen (Beckmann rearrangement) followed by an intramolecular cyclization to yield isoquinoline. Cinnamo-nitrile (dehydration product) and cinnamaldehyde were formed as by-products. Isoquinoline formation was high on zeolite catalysts (ca. >86.5%) and mordenite (ca. 92.3%) was the most efficient in the series. Catalysts were susceptible for deactivation and the decrease in the percentage conversion of oxime with time is associated with a corresponding increase in the acid hydrolysis producing salicylaldehyde at later stages of the reaction. However, these catalysts retain activity considerably and can be recycled without loss of activity and change of product distribution.

Keywords: Beckmann rearrangement; Cinnamaldehyde; Cinnamaldoxime; Cinnamo-nitrile; *E–Z*-isomerization; Isoquinoline; Zeolites

1. Introduction

Isoquinoline derivatives such as 5-substituted isoquinoline-1-ones are potential inhibitors [1] of PARP (poly (ADP-ribose) polyamide). Pathophysiological effects of this are mediated through over activity of isoform PARP-1, which depletes stores of nicotinamide di-nucliotide (NAD^+), the PARP substrate leading to cell death. These derivatives have potential therapeutic application in several diseases including cancer [2], mayocardial infraction [3], diabetes [4], stroke [5], rheumatoid arthritis [6] and hemorrhagic shock [3]. It is the main heterocyclic ring for a class of alkaloids, which have medicinal and toxic properties [7]. A neurotoxin called MPTP (1-*N*-methyl-4-phenyl-1,2,3,6-tetrahydropyridine), the precursor to MPP^+ was found and linked to Parkinson's disease. The active neurotoxins destroy dopaminergic neurons leading to Parkinsonism and Parkinson's disease. Several tetrahydroisoquinoline derivatives have been found to have the same neurochemical properties as MPTP. These derivatives may act as neurotoxin precursors to active neurotoxins [8,9]. Dihydroquinolinium salts are widely used as potential catalyst for the synthesis of optically active epoxides in asymmetric synthesis [10]. Isoquinolines are used in the manufacture of dyes, paints, insecticides, anti-fungal agents, as a solvent for the extraction of resins and terpenes and as a corrosion inhibitor [9,11–13].

There are a number of methods for isoquinoline ring construction. Bischler–Napieralski cyclization [14] is one of the best routes for the synthesis of isoquinoline. In this reaction, the amide derived from a substituted phenethylamine (β-phenylethylamine) is cyclized under dehydrative

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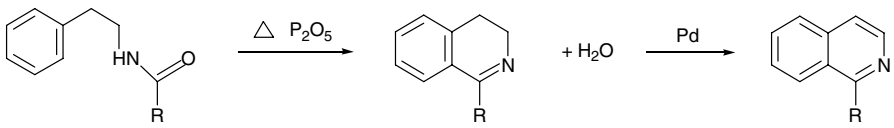
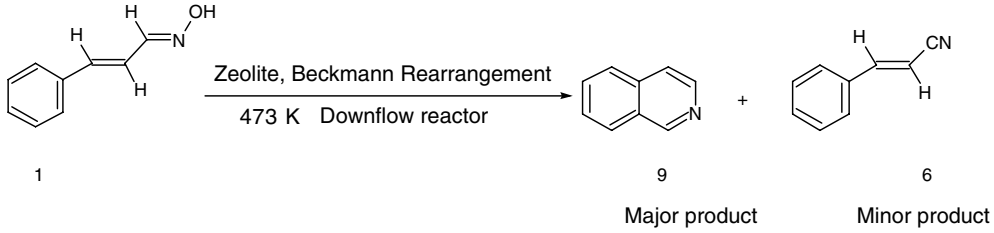


Scheme 1.

acidic conditions (intramolecular Vilsmeier reaction). The resulting 1-substituted-3,4-dihydroisoquinoline can then be dehydrogenated using palladium (Scheme 1). HCl, P_2O_5, PCl_5 and $POCl_3$ in boiling xylene or decaline are commercially used [15–18]. Herz and co-workers applied the Bischler–Napieralski and Pictet–Gams reactions for the synthesis of sulfur analogs of isoquinolines [19]. Arylidene amino acetals, when warmed with concentrated sulfuric acid or with sulfuric and arsenic acids, give isoquinoline or substituted isoquinolines [20]. This method is of limited application, although it has been utilized to prepare a number of bromoisoquinolines, which have been converted successively to the cyanides and to the carboxylic acids. Buck [21] reported the synthesis of a number of tetrahydroisoquinoline by starting from phenylethylamines and formaldehyde. β-phenylethylamine or β-phenylethylmethylamine was condensed with formaldehyde to give the *N*-methylene or *N*-hydroxymethyl derivative, respectively. By the action of hydrochloric acid this was cyclized to the corresponding tetrahydroisoquinoline hydrochloride. The hydroxy compounds were prepared by *O*-demethylating the methoxy compounds by appropriate methods [21]. Kido and Watanabe synthesized isoquinoline derivatives by the cyclization of 3,4-dimethoxybenzylideneaminoacetal with chlorosulfonic acid as a cyclizing agent [22]. Isoquinoline derivatives were synthesized from cyclobutenylmethylamine derivatives having an alkyne moiety in a tether using a second-generation ruthenium carbene complex under ethylene gas in good yields utilizing the ring-opening metathesis (ROM)-ring-closing metathesis (RCM) is a very attractive reaction [23]. Tsutsui and Narasaka recently reported the synthesis of isoquinoline derivatives by the palladium-catalyzed cyclization of olefinic ketone *O*-pentafluorobenzoyloximes [24].

Most of the above reagents are either corrosive or possess extreme affinity for water, which makes their handling very difficult. The normal work-up procedure for reactions employing the catalysts involves a water quench process, which prevents the acid being used again and subsequent neutralization leads to an aqueous waste stream. Hence under the reaction conditions, these reagents are converted to materials that are toxic and environmentally unfriendly. Since the reagents are irreversibly lost, the overall *atom-efficiency* of these reactions is low. In order to be cost-effective and eco-friendly, there is always a real need for better catalyst systems. These polluting technologies must be replaced by benign alternatives. Over the past several years, chemists have been mobilized to generate new chemistries that are less hazardous to human health and the environment. One current line in catalysis involves developing reusable and environmentally benign catalytic systems [25]. The solid-acid catalysts such as metal oxides, sulfated metal oxides, clays and zeolites are in fact a most favorable alternative for these problems. Introduction of solid-acids such as zeolites, removes the need for the quench step, facilitating the reusability of the catalyst (cost effective). Moreover, a solid-acids do not produce solid waste and hence are eco-friendly. We are currently working on the applicability of zeolites, clays, and common metal oxides on fine chemical synthesis [26]. The Beckmann rearrangement constitutes a common route employed in organic chemistry to transform ketoximes into amides. One of the main industrial applications is the transformation of cyclohexanone oxime into ε-caprolactam, a raw material in the production of nylon-6. Sulfuric acid as a catalyst plays an essential role in the conventional liquid-phase industrial production of ε-caprolactum. However, it poses significant environmental and operational problems such as generating undesirable salt and causing equipment corrosion [27]. To solve the problems derived from the use of concentrated sulfuric acid and the generation of this by-product, many solid-acid catalysts have been proposed. Among typical heterogeneous catalysts for this reaction include solid-acid catalysts such as boric acid, silica–alumina, zeolites like Y, ZSM-5, TS-1, B-ZSM-5 and tantalum oxide on silica [28–35]. Highly siliceous ZSM-5 and ZSM-5 modified with boron showed high activity and selectivity in the Beckmann rearrangement reaction [36]. Guo and co-workers recently reported a clean Beckmann rearrangement of cyclohexanone oxime in caprolactam-based Brønsted acidic ionic liquids [37].

However, this environmentally benign protocol is not very much extended to other oximes for the production of fine-chemicals. Candeias and Afonso recently reviewed the use of zeolites and mesoporous materials in the preparation of non-fused heterocycles compounds through epoxidations, aziridinations and the Beckmann's rearrangement [38a]. Corma and co-workers have reported the liquid-phase Beckmann rearrangement of cyclohexanone, acetophenone and cyclododecanone oximes over beta zeolites [38b]. Fernandez et al. recently studied the mechanistic aspects of the Beckmann rearrangement of acetophenone oxime over microporous molecular sieves [38c]. Recently, we have reported the vapor-phase Beckmann rearrangement of cinnamaldoxime to isoquinoline (Scheme 2) over different rare earth exchanged H–Y zeolites [26d]. As an extension of the protocol, we report the reaction over different H-zeolites, K-10 clay and some common metal oxides and our attempt to rationalize the results on the basis of physico-chemical properties. Side- reactions observed



Scheme 2.

include dehydration of cinnamaldoxime to give cinnamonitrile and hydrolysis to give cinnammaldehyde. Since there is comparatively less amount of waste formation (maximum for amorphous SiO_2–Al_2O_3; ca. 39.1%) in the reaction, the *E-factor* must be low and *atom efficiency* high.

2. Experimental section

2.1. Materials and methods

H–Y zeolite (Si/Al ratio; 1.509) was supplied by Sud-Chemie (India) Ltd. H ZSM-5 and H-beta zeolites were purchased from National Chemical Laboratory (NCL) India. H-mordenite was supplied by Zeolyst International, New York, USA. K-10 montmorillonite was procured from Aldrich Chemical Company, USA. Al_2O_3–SiO_2 and γ-Al_2O_3 were prepared in the laboratory applying well-known methods reported earlier [39]. *trans*-Cinnammaldehyde, hydroxylamine hydrochloride, sodium bicarbonate, sulfuric acid and acetonitrile were procured from SD-Fine Chemicals, India and used as received. Benzene (SD Fine Chemicals, India) was used after washing with concentrated H_2SO_4 and 20% sodium bicarbonate.

The crystalline nature of the materials was established by powder X-ray diffraction studies performed using a Rigaku D-max C X-ray diffractometer with Ni-filtered Cu Kα radiation. Temperature-programmed desorption (TPD) of ammonia (pre-chemisorbed at 373 K) over the zeolite catalysts was carried out in a stainless steel reactor (i.d. $= 4 \times 5$ mm) packed with about 100 mg catalyst from 373 to 873 K at a linear heating rate of 20 K min^{-1} in a flow of moisture-free nitrogen (40 mL min^{-1}). The adsorbate desorbed in the TPD was measured quantitatively with a conventional ammonia detector. Before carrying out the TPD, catalyst was pretreated in situ at 773 K for 1 h in a flow of nitrogen. Simultaneous determination of BET and Langmuir surface area and pore volume measurements were performed on a Micromeritics Gemini surface area analyzer using di-nitrogen as an adsorbate at 77 K. The area per molecule of di-nitrogen was taken as 16.2 Å^2. Results were reproducible within an error limit of 5%.

2.2. Typical procedure for Beckmann rearrangement

Catalytic reactions were carried out in an ordinary fixed-bed, down-flow reactor made of cylindrical quartz tube with 0.6 cm internal diameter and 30 cm height with a high sensitivity temperature controller (accuracy $\pm$ 5 K) and a set up to carryout reaction under gaseous atmosphere. The catalyst particles (700 mg and 30–40 μm mesh size) sandwiched between quartz–wool were filled between ceramic beads. During the operation, the reactants flow through the reactor tube and over the catalysts bed, and reaction takes place. Nitrogen was used as carrier gas in the reaction. Prior to the reaction, catalysts were heated in situ at a heating rate of 20 K/min to a final temperature of 773 K in presence of constant purging of air and was maintained at the final temperature for 12 h. 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% solution of salicylaldoxime in 1:1 benzene acetonitrile mixture) was fed into the reactor at a flow rate of 4 mL/h (weight hourly space velocity; 0.29 h^{-1} or contact time; 3.45 h) in presence of dry N_2 using an infusion pump. The product mixture was collected downstream after 3 h and identified using GC (GC1000, Chemito with an SE-30 capillary column), HPLC (Shimadzu CLASS-VP $V_{5.032}$), GC-MS (Shimadzu-5050 spectrometer having a 30 m HP-30 capillary column) and IR (Nicolet Impact 4000) spectroscopic techniques. Finally the product was characterized by ^{1}H NMR experiment (Bruker AMX-400 NMR spectrometer).

2.3. Recovery and reuse of the catalyst

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 experimental 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

Detailed studies of characterization of present catalyst systems have been already reported elsewhere [26a]. The

Table 1
General features of the zeolites used in the Beckmann rearrangement of *E*,*E*-cinnamaldoxime

Zeolite	Si/Al[a]	S_{BET} ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)[b]	General features		
				Dimensonality	Pore size (nm)	Crystal size (μm)[c]
H–Y	1.5	398	0.266	3D	Super cage: 1.18 Window:0.74 × 0.74	0.90
H-ZSM-5	40	413	0.163	3D	0.53 × 0.56	0.40
H-beta	26	745	0.232	3D	0.66 × 0.67	0.51
H-MOR	19	552	0.188	2D	0.26 × 0.57	0.92
K-10 Mont.	2.7	183	0.204	2D	Average pore size > 1.0 nm	1.0

[a] As determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis.
[b] Total pore volume measured up to 0.9976 P/P_0.
[c] As determined by powder X-ray diffraction studies.

Table 2
Temperature programmed desorption of ammonia from different zeolites; H–Y, H-ZSM-5, H-beta and H-mordenite and other solid-acid catalysts used in the Beckmann rearrangement of *E*,*E*-cinnamaldoxime

Catalysts	Amount of ammonia (mmol/g) desorbed within certain temperature range K				
	Weak[a] (373–473)	Medium (473–673)	Strong (673–873)	373–873 (cumulative)	s/w + m[b]
H–Y1.5	0.69	0.41	0.33	1.43	0.30
H-ZSM-5 40	0.65	0.34	0.29	1.28	0.29
H-beta26	0.52	0. 70	0.51	1.73	0.42
H-MOR19	0.63	0.56	0.73	1.92	0.61
K-10 Mont.2.7	0.55	0.24	0.13	0.92	0.16
SiO_2–Al_2O_3	0.55	0.18	0.10	0.83	0.14
γ-Al_2O_3	0.56	0.19	0.13	0.88	0.17

[a] Ammonia desorbed in the temperature range 373–473 K contains small amounts of physisorbed ammonia.
[b] Ratio of the strong to weak plus medium strength acid sites from ammonia TPD studies. Number after the zeolite and K-10 clay name indicates the silica–alumina ratio.

main physico-chemical characteristics of these materials are presented in Tables 1 and 2. Phase purity of the catalysts was monitored by a combination of powder X-ray diffractograms. Powder X-ray diffraction patterns are given in the supporting information. For each zeolites system, the values of acid sites strength and surface area and pore volume match well with reported values [40].

3.1. Synthesis of isoquinoline

We have used four classes of solid-acid catalysts; zeolites (H–Y, H-ZSM-5, H-beta and H-mordenite), K-10 montmorillonite clay, amorphous silica–alumina and γ-alumina.

3.1.1. Influence of reaction variables

Reaction variables such as temperature, catalyst loading, flow rate or the weight hourly space velocity and time on stream have prominent effect on the percentage conversion and selectivity of the products. Following section explains the possible influence of these parameters on the Beckmann rearrangement of cinnamaldoxime to isoquinoline and other by-products.

3.1.2. Effect of contact time

Weight hourly space velocity (WHSV) or the contact time has prominent influence on the vapor phase Beckmann rearrangement of cinnamaldoxime to isoquinoline. Results of the study are presented in Fig. 1a. Influence of contact time on the performance of model H–Y zeolite catalyst was checked by conducting the reaction at different space velocities. Total conversion of cinnamaldoxime increased from 72% to 97.8% as the contact time increased from 1.97 h (flow rate: 7 mL h^{-1}) to 3.45 h (flow rate: 4 mL h^{-1}), whereas the corresponding isoquinoline selectivities were 72.3% and 89.8% respectively. Lower space velocities imply higher contact time of the reactants on the active sites of the catalyst and a subsequent increase in the percentage conversion. There was qualitative increase in isoquinoline formation with increasing contact time.

3.1.3. Effect of catalyst loading

Fig. 1b illustrates the effect of catalyst loading on the oxime conversion and selectivity to desired product. Catalyst amount of 400 mg produced an oxime conversion of 59.1% which increased to 100% with 900 mg catalyst. However, isoquinoline formation increased up to 700 mg and a further increase of catalyst loading decreased its production. A catalyst loading of 700 mg produced 89.8% isoquinoline and 900 mg decreased the formation to 80.8%. Cinnamo-nitrile formation was 4.3% at 700 mg of catalyst and 10.1% at 900 mg. Thus, under the reaction conditions of 473 K, time on stream: 2 h, and weight hourly space velocity: 0.29 h^{-1}, dehydration/Beckmann rearrangement of cinnamaldoxime gave 97.9% conversion with 89.8% isoquinoline, 4.3% nitrile and 5.9% by-products at 700 mg

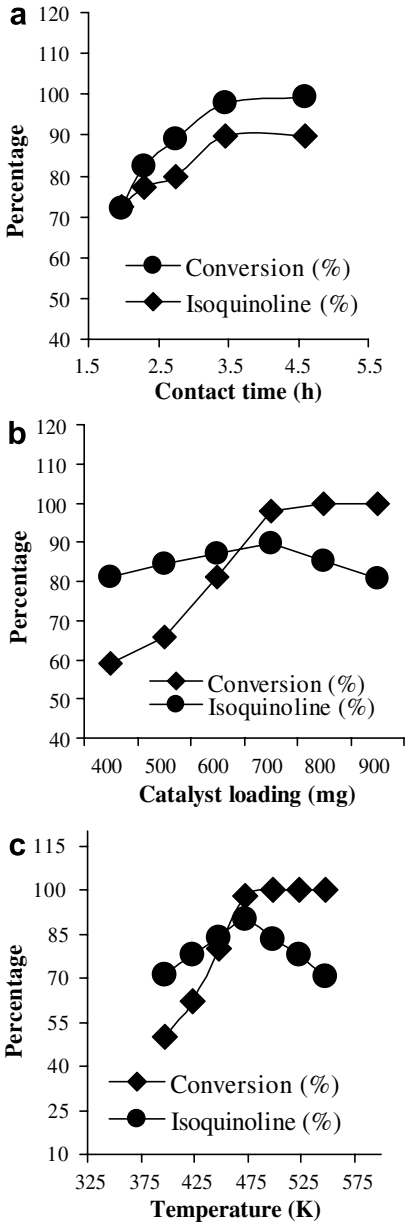


Fig. 1. The influence of (a) contact time, (b) catalyst amount and (c) reaction temperature on the percentage conversion of cinnamaldoxime and formation of isoquinoline on representative H–Y zeolite. Other reaction conditions are as described in Table 3.

catalyst loading. Increase in the oxime conversion with catalyst amount is due to an effective increase in the number of catalyst active sites available for the reaction.

3.1.4. Effect of temperature

Total conversion of *E–Z*-cinnamaldoxime has been studied by varying the reaction temperature from 398 to 548 K using H–Y zeolite as a representative catalyst. Reaction products were collected after 2 h and the results are depicted in Fig. 1c. Temperature has pronounced influence on the dehydration/Beckmann rearrangement ability of solid acid catalysts. Cinnamaldoxime conversion increased with increasing temperature of reaction and at 523 K it was cent percentage, however isoquinoline selectivity increased from ca. 71% to 89.8% when temperature is raised from 398 to 473 K, then it decreased to 70.5% (548 K). This phenomenon can be ascribed to (i) a better catalyst activation and (ii) an easier tar desorption from the catalyst surface, nevertheless by increasing the temperature, the thermodynamics of by-product formation is promoted so, at 548 K, we observe a decrease of isoquinoline yield and verify the formation of higher quantities of heavy volatile products. In addition, when temperature was raised from 398 K we observed a relevant longer catalyst lifetime. Fig. 2 shows the results of the on stream stability studies on H–Y zeolites at 423 K. The catalyst underwent 39.5% deactivation in 10 h and is much more than the deactivation at 473 K. This is attributed to the improvement of catalytic performances and more efficient heavy products desorption at high temperatures. There was an increased probability of dehydration of oxime at elevated temperatures (21.7% at 548 K). Acid catalyzed hydrolysis of oxime to aldehyde was prominent at lower temperatures.

3.1.5. Effect of solvent

The effect of solvent in the vapor-phase Beckmann rearrangement of cinnamaldoxime was studied in order to improve the performance of the catalysts. Various solvents having different dipole moment were chosen to dissolve the oxime. As shown in Table 3, although there is scatter in the data, a general trend is seen toward increasing isoquinoline yield with polarity of the solvent. The highest isoquinoline

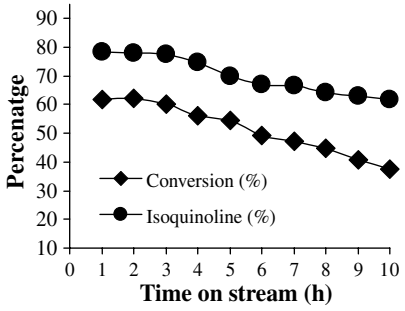


Fig. 2. Time on stream studies of H–Y zeolite during the Beckmann rearrangement of *E,E*-cinnamaldoxime to isoquinoline at 423 K. Other experimental conditions are as described in Table 3.

Table 3
Polarities of the solvents used as solvent and selectivities for isoquinoline

Solvent	Dipole moment (*D*)	Isoquinoline (%)
Benzene	0	80.8
Toluene	0.36	80.2
Trichloromethane	1.01	80.8
THF	1.63	82.5
Acetone	2.88	83.5
Acetonitrile	3.92	84.3
Benzene:Acetonitrile (1:1)	–	89.9

Experimental conditions; catalyst; H–Y zeolite, catalyst amount; 700 mg, reaction temperature; 473 K, reactant; 5% oxime solution in 1:1 benzene acetonitrile mixture, time on stream; 3 h, nitrogen flow; 10 mL/min.

yield (84.3%) was reached when acetonitrile with highest polarity was used as solvent. There are several contradicting reports on the beneficial and harmful effects of highly polar, medium polar and non polar solvents [41]. However, Yashima and co-workers [41c] proposed that, after investigating the influence of various solvents, no clear influence of polarity could be established on MFI type zeolites. Different ratios of a polar (acetonitrile) and a non-polar solvent (benzene) were tried as solvent for the oxime and a 50:50 mixture produced maximum selectivity of isoquinoline. Currently we are working on the effect of solvents for an improved the selectivity of isoquinoline.

3.2. Performance of different solid-acid catalysts

A comparison of the catalytic activity of different systems is given in Table 4. All catalytic systems invariably exhibit good activity towards Beckmann rearrangement of cinnamaldoxime to isoquinoline. Zeolite systems consistently exhibit high selectivity towards Beckmann rearrangement of *E*,*E*-cinnamaldoxime to isoquinoline (**9**). K-10 montmorillonite, amorphous silica–alumina and γ-Al_2O_3 produce more than 60% of isoquinoline. Cinnamo-nitrile (**6**) and cinnamaldehyde (**8**) were the main by-products of the reaction. Iso-nitrile formation was not detected by careful examination of the product mixture. Analysis of the product mixture using GC and GC-MS confirms the formation of small amounts of cinnamic acid and styrene. Dehydration of oxime occurred with all catalysts at different levels producing cinnamo-nitrile. In general, H-zeolites show better results compared to K-10 clay, SiO_2–Al_2O_3 or γ-Al_2O_3. Under similar experimental conditions H-beta and H-MOR show cent percentage activity, where as H–Y and H-ZSM-5 have activity greater than 95%. Optimum number and strength of acid sites on the zeolite catalysts seems to work well in effecting the intramolecular cyclization of the intermediate (**7**) (see Scheme 4), which eventually producing isoquinoline.

H-MOR (0.65×0.70 nm) has a 2D zeolitic channel structure. All other zeolites are 3D structured and hinder diffusion of the products. H-BEA has a 3-dimensional interconnecting pore system with pores of 0.55×0.55 and 0.76×0.64 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 and has a 3-dimensional pore system (0.51×0.55 and 0.53×0.56 nm) [42–45]. K-10 montmorillonite is a layered alumino-silicate with a dioctahedral layer sandwiched between two tetrahedral layers. Unlike zeolites K-10 clay does not have a regular pore structure [46]. The pore size given in Table 1 is an average value. The amount of mesopores is less when compared to the amount of micropores. This explains the reduced surface area and pore volume when compared to zeolites (Table 1). SiO_2–Al_2O_3 and alumina do not have regular pore structure. SiO_2–Al_2O_3, alumina and K-10-clay produce more side products, though the main product is isoquinoline. This is due to the weak acid structural properties, which intern reduces their ability to effect the *E*–*Z* isomerization; the vital step to produce the desired product. The isoquinoline formation seems to be a function of the total acid sites strength of the catalytic materials.

Beckmann rearrangement of cinnamaldoxime is an acid catalyzed reaction and the conversion of oxime to isoquinoline or to by-products could be correlated to the strength and distribution of acid sites obtained from NH_3-TPD studies. Zeolites are characterized by their total acidity and their acidic sites are much stronger than γ-alumina, amorphous silica–alumina and K-10 clay. Hence, it should be expected that zeolites would show higher activity than K-10 clay and other oxide catalysts. As the reaction is carried out in the vapor phase and all zeolites show comparable activity, diffusion properties are supposed to have a limited role. This argument is supported by the fact that other solid-acid catalysts are also found to be active towards the reaction. Consequently, acid structural properties of the catalysts are the deciding factor for any difference in activity/selectivity.

3.3. Products distribution and nature of acid sites

Though the performance over solid-acid catalysts with acidity of a different nature and strength has been tested, the nature of active sites in the catalysts for the Beckmann

Table 4
Beckmann rearrangement[a] of *E*,*E*-cinnamaldoxime for the synthesis of isoquinoline; variation of catalyst

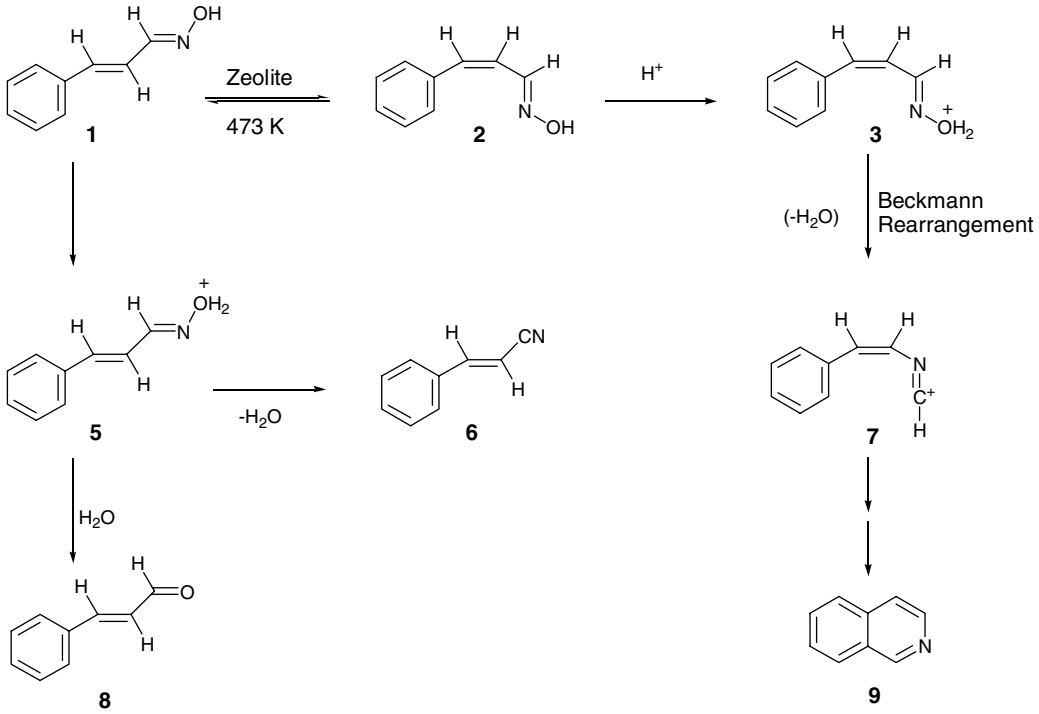
Catalyst	Oxime conversion (%)	Selectivity (%)			
		Isoquinoline	Cinnamo-nitrile[b]	Cinnamaldehyde[c]	Others[d]
H–Y	97.9	89.8	4.3	5.3	0.6
H-ZSM-5	96.1	90.1	3.8	5.1	1.0
H-beta	100	86.5	8.5	4.4	0.6
H-MOR	100	92.3	4.6	3.0	0.1
K-10 Mont.	73.2	78.2	3.5	9.1	9.1
SiO_2–Al_2O_3	65.0	60.9	2.7	19.0	17.4
γ-Al_2O_3	69.4	65.7	3.5	19.2	11.6

[a] Experimental conditions are as described in Table 3.
[b] Dehydration product of the cinnamaldoxime.
[c] Acid-catalyzed hydrolysis of **1** will lead to the formation of *trans*-cinnamaldehyde.
[d] Include cinnamic acid and small amounts of styrene.

rearrangement is still a matter of several controversies. In previous publications, strong Brønsted acid sites (BAS) in zeolites were reported to be active to catalyze the rearrangement [47]. Later, it was shown that these sites favor the formation of by-products; mainly dehydration (nitrile) products. Both activity and selectivity of the amide is improved in the presence of high-silica zeolites with intermedium or weak BAS [48]. Finally, it has been suggested that weakly acidic or neutral silanol nets are active catalysts for the rearrangement reaction [28b,28c,49,50]. Again, the superior performance of BAS compared to silanol groups during the liquid phase Beckmann rearrangement cyclohexanone, acetophenone and cyclododecanone oximes over β-zeolites shows that the results reported for the vapor phase reaction cannot be extrapolated when the reaction is performed in liquid phase [38b]. It was proposed that the rearrangement of cyclohexanone oxime is not necessarily catalyzed by acidic centers but by sites with rather low or no acidity, which are sufficient to achieve high selectivity at high conversion, while maintaining the long life of the catalyst [49]. Recent results indicate that BAS as well as strongly hydrogen bonded silanol groups and silanol nests, located in the pores of zeolites and MCM-41, are active in the reaction. When the external surface or the outer shell of ZSM-5 crystals is considered, the bridging hydroxyl groups appear to be active whereas silanol groups do not show any activity in the Beckmann rearrangement of cyclododecanone [51]. Sullivan and co-workers showed that a low ratio of strong/weak acid sites is important in achieving a high yield of caprolactam [52]. Most of these studies address the activity/selectivity-acid sites relation studies of Beckmann rearrangement of cyclohexanone oxime and there are not many correlation studies on other oximes. In the following section we try to correlate our results from acidity studies (ammonia-TPD) and products distribution during the Beckmann rearrangement of cinnamaldoxime to isoquinoline.

There was a rough correlation among total acid sites amount, rate of reaction and isoquinoline yield attained. The reaction mechanism shown in Scheme 3 shows that the main as well as side-reaction pathways are catalyzed by acid sites of different strengths and kinds. A simple relation between the total acid amount and total conversion of oxime is shown in Fig. 3a. With an increase in the number of acid sites, conversion of oxime over the catalysts also increased. This is consistent with the observation that the possible reactions of oxime over solid-acid catalysts at high temperature such as Beckmann rearrangement, dehydration and hydrolysis are catalyzed by acid sites [48]. Fig. 3b shows a one-to-one correlation that exists between the total acid amount and isoquinoline selectivity. H-mordenite with comparatively greater cumulative acidity produces more isoquinoline attributed to an efficient *E–Z* isomerization on optimum strength acid sites. K-10 clay, alumina and amorphous silica–alumina with comparative low total acidity show inferior performance probably due to a mediocre *E–Z* isomerization ability.

Fig. 4a showed the plot of the rate of reaction and isoquinoline yield with the corresponding number of Brønsted acid sites. According to Catanach and co-workers and many others [53], the amount of ammonia desorbed in the medium temperature range (473–673 K in NH_3-TPD)



Scheme 3.

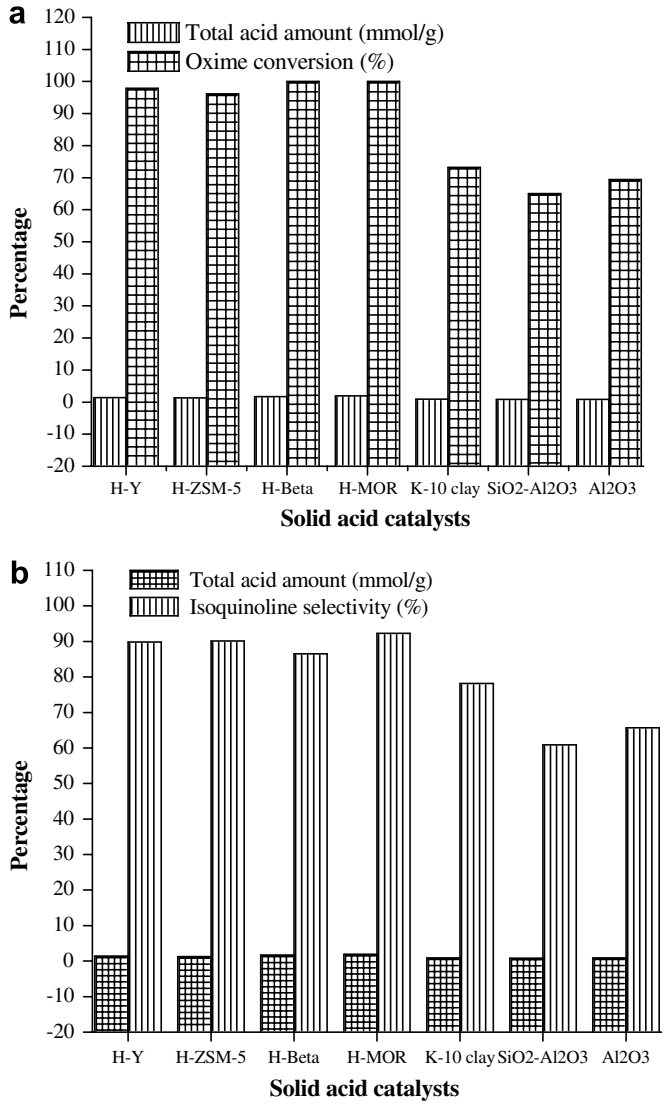


Fig. 3. Dependence of the cumulative acid amount (from NH_3-TPD) and (a) total conversion of cinnamaldoxime and (b) isoquinoline formation over different solid-acid catalysts. Reaction conditions are as described in Table 3.

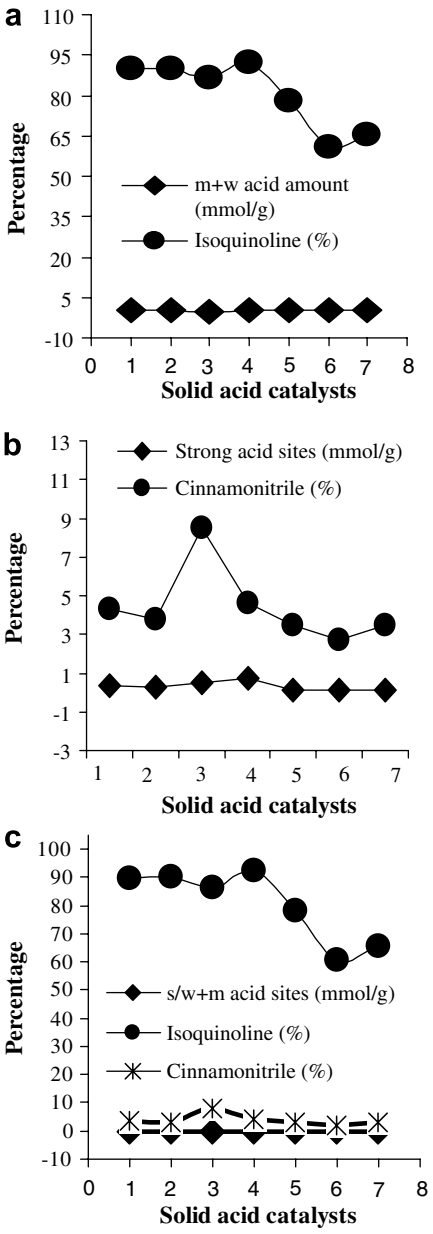


Fig. 4. Dependence of (a) medium strength acid sites on the isoquinoline selectivity (b) strong acid sites on nitrile formation and (c) ratio of strong to weak plus medium strength acid sites on the production of isoquinoline and nitrile over different solid-acid catalysts; (1) H–Y, (2) H-ZSM-5, (3) H-beta, (4) H-mordenite, (5) K-10 clay, (6) SiO_2–Al_2O_3 and (7) alumina. Reaction conditions are as described in Table 3.

is due to typical BAS in NH_3-TPD studies in the case of zeolites. A linear relationship could be established in both cases, indicating that BAS are active and selective for the Beckmann rearrangement of cinnamaldoxime. Camblor and co-workers [54] showed this in the case of Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. The improvement in the Beckmann rearrangement reaction is consistent with reports that activity/selectivity is improved in presence of zeolites with intermedium or weak BAS [28a,30,38a,48]. This has been further supported by the performance of less Brønsted acidic catalysts such as K-10 clay and alumina in the present case. These catalysts have comparatively less number of BAS and consequently show decreased formation of isoquinoline. Due to insufficient acid strength, the rearrangement of cinnamaldoxime to isoquinoline was not effectively been catalyzed.

Fig. 4b depicts a possible correlation between the amount of cinnamo-nitrile (dehydration product) formed and total number of strong acid sites (both Brønsted and Lewis) as determined by ammonia desorbed in the temperature range 673–873 K during thermodesorption studies. In the case of zeolites, the high temperature portion is mainly composed of strong BAS. It was reported by Sato that the strong acid sites (mainly BAS) favor the formation of by-products and that the activity and selectivity of amide improved in presence of weak or medium BAS. More the amount of strong acid centers, higher the nitrile formation.

This observation is consistent with the well-documented observation that dehydration takes place over strong acid sites in the case of Beckmann rearrangement of cyclohexanone oxime and cinnamaldoxime [26b,48]. In earlier publications, strong acid sites (mainly BAS) in zeolites were reported to catalyze the rearrangement. Aucejo et al. [47b] investigated the relationship between the activity and the acid properties of HNaY zeolite catalysts by changing the level of H^+, and concluded that BAS of strength $pK_a \leqslant 1.5$ were important for the selective formation of caprolactam. However, later, it was shown that these sites favor the production of side products [28a,30,48]. A high isoquinoline yield on H-mordenite zeolite could be correlated to an optimum strength of its acid strengths as evidenced by the s/w + m acid strength value (ca. 0.61 mmol/g). Results of this observation are shown in Fig. 4c. K-10 clay, amorphous silica–alumina and alumina also show direct correlation between this ratio and isoquinoline and nitrile yields. However, H–Y, H-ZSM-5 and H-beta zeolites greatly deviated from this observation. H-ZSM-5 zeolite with a ratio of 0.29 produces much more isoquinoline (ca. 90.1%) than H-beta zeolite (ca. 86.5). This is reflected in the cinnamon-nitrile yield also.

A plot of cinnamaldehyde yield against the number of weak acid sites (ammonia desorbed in 373–473 K range in TPD) is shown in Fig. 5. The low temperature portion from these materials contains greater percentage of Lewis acid sites (LAS) bound ammonia. Ngamcharussrivichai et al. [55] reported that the LAS of these catalysts catalyze mainly the hydrolysis of oxime. With an increasing number of weak acid sites, acid hydrolysis of the oxime to aldehyde over zeolite catalysts increased. In contrast, the data of H-mordenite zeolite greatly deviated from this relationship. These results indicate that weak acid sites present in mordenite zeolite are less harmful to rearrangement, and should have a different structure and acidity than those sites responsible for the hydrolysis reaction. A drop in the aldehyde yield over H–Y zeolite with comparatively greater number of weak acid sites implied that some acid sites were not involved in the aldehyde formation. More typical Lewis acid catalysts such as K-10 clay and γ-alumina produce more aldehyde though it shows lower amount of NH_3 desorption at low temperature region. The low temperature portion from these materials contains greater percentage of LAS bound ammonia and hence an increased formation of aldehyde. Time on stream studies shows a continuous decrease in the conversion of oxime with time. This is associated with a decrease in the isoquinoline formation and a slight increase in aldehyde production. These results suggested that the active sites responsible for isoquinoline formation were gradually deactivated and mostly lost with time. As a consequence, the surviving relatively weak acid sites catalyzed the reaction instead at the subsequent stages. A previous study over MCM-41 catalyst found inferior performance of abundantly present silanol groups in the Beckmann rearrangement of cyclohexanone oxime [56]. Due to insufficient acidic strength, the rearrangement of cinnamaldoxime to isoquinoline was not effectively catalyzed producing low oxime conversion and selectivity. As the MCM-41 structure was known to be of significant disorder, comparative experiments have been performed with amorphous Al_2O_3–SiO_2 which has similar acid sites distribution. Substantial cinnamaldehyde formation occurs over SiO_2–Al_2O_3 catalyst.

Strong acid sites were likely to be associated with dehydration of oxime, dimerization or formation 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 also creates sample deactivation.

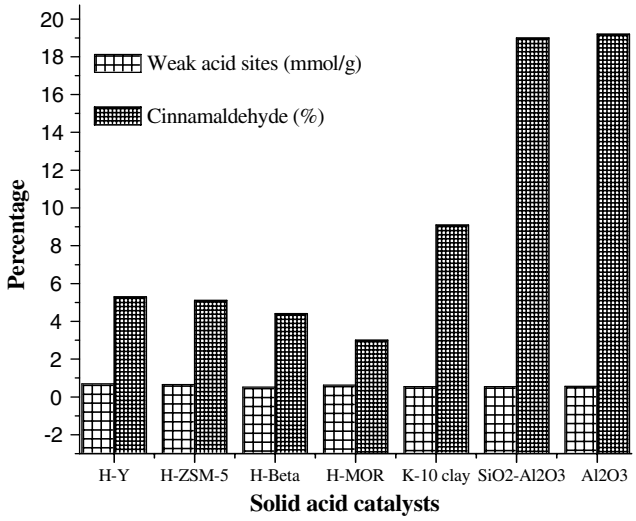


Fig. 5. Dependence of weak acid sites (373–473 K) on cinnamaldehyde selectivity over different solid-acid catalysts. Reaction conditions are as described in Table 3.

3.4. Deactivation, regeneration and reuse

Dehydration/Beckmann rearrangement reaction of *E*,*E*-cinnamaldoxime was performed over H–Y and H-MOR zeolites for 10 h. For carefully dehydrated reagents, the conversion decreases quickly with reaction time. Periodic checks by GC and GC-MS showed this decrease in conversion. Fig. 6a and b presents the effect of time on stream (TOS) on the percentage conversion of oxime and the selectivity for the formation of isoquinoline over zeolites H–Y and H-MOR respectively. Generally, deactivation of the zeolites is due to coke formation [29,57,58]. Takahashi et al. [29] elucidated the effects of silica/alumina ratio and boron modification on the catalyst deactivation rate on HZSM-5 zeolite and proposed that the deactivation of the MFI-type zeolite was mainly due to the adsorption of volatile material on the acid sites. In the present case the catalyst deactivation would be due to the adsorption of reaction by-products on the active sites. The decrease in the isoquinoline formation with time might be due to less

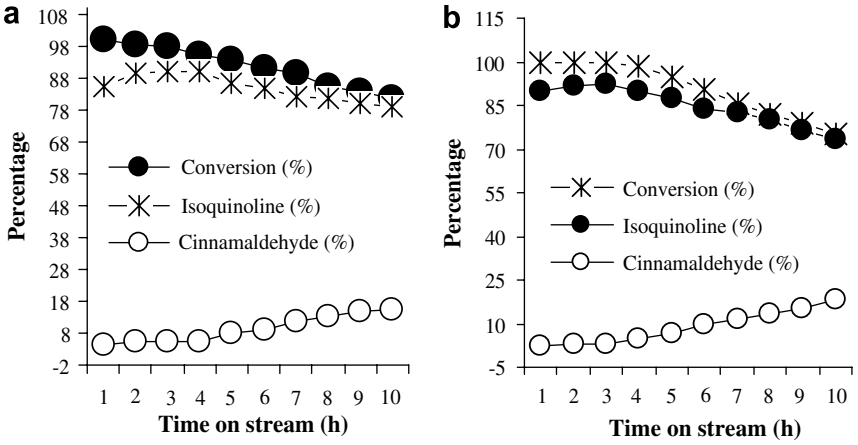


Fig. 6. Kinetic profiles during the conversion of *E*,*E*-cinnamaldoxime to isoquinoline and cinnamaldehyde as a function of time on stream on (a) H–Y and (b) H-mordenite zeolites. Experimental conditions are as described in Table 3.

efficient *E*–*Z* isomerization at later stages of reaction. As most of the acid sites getting deactivated by the adsorbed products, water formed during dehydration reaction and by the deposition of high molecular weight products, the dehydration and other side reactions become nominal and the probability of acid hydrolysis of oxime to aldehyde increases slightly. This is supported by the performance of mordenite zeolites, which is the most acidic among all the zeolites and effect maximum Beckmann rearrangement in the early hours of reaction. H–Y zeolite underwent 20.8% deactivation, while H-mordenite 26.4% in 10 h on stream.

The deactivated zeolites can be partially regenerated by solvent extraction followed by oxidative treatment. The deactivated zeolites (we studied H–Y and H-MOR) are extracted with dimethyl ether to remove the products from the catalyst surface. It is further washed with de-ionized water, dried at 383 K overnight and regenerated by activating at 773 K in air (oxidative treatment). There was no substantial loss of catalytic activity for both H–Y and H-mordenite zeolites even after three cycles. Results are depicted in Table 5. H–Y and H-mordenite zeolites converted 95.1% and 96.3% oxime respectively after three cycles. This demonstrates that zeolites catalysts can be regenerated without loss of their catalytic activity.

Table 5
Catalytic performances for H–Y and H-mordenite zeolites after one to three regeneration cycles

	Fresh	I cycle	II cycle	III cycle
Cinnamaldoxime conversion (%)	97.9 (100)	97.9 (100)	96.7 (98.1)	95.1 (94.3)
Isoquinoline selectivity (%)	89.8 (92.3)	89.9 (92.8)	90.1 (90.9)	89.6 (92.1)

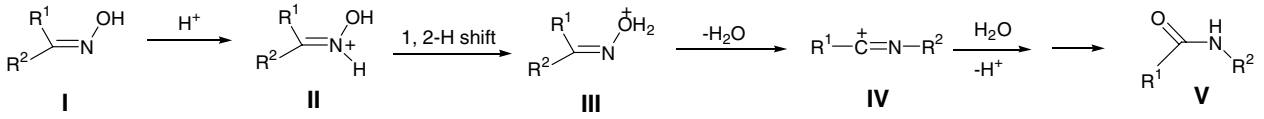
Values in parentheses are the conversion of oxime and selectivity for isoquinoline on H-mordenite zeolite. Reaction conditions are as described in Table 3.
Catalytic tests are carried out at 473 K and values are referred to the third hour of reaction.

We conducted experiments to obtain clear evidence for the true heterogeneity of the reaction on zeolite catalysts. The reaction mixture was passed through H–Y and H-MOR zeolites under standard reaction conditions for 10 h. No aluminium was detected in the reaction mixture by the energy dispersive X-ray analysis (JEOL JSM-840A; Oxford make model l6211). Furthermore no aluminium was detected during qualitative chemical analysis of the reaction mixture. These results strongly rule out aluminium leaching during the reaction.

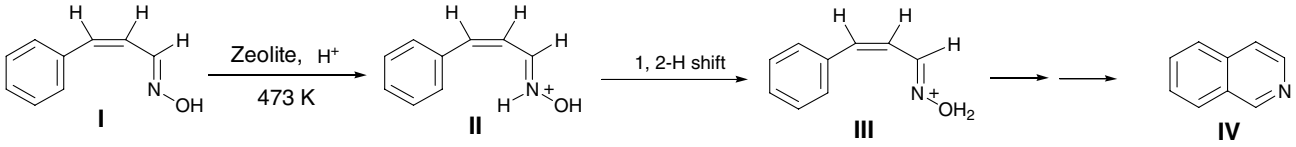
3.5. Mechanism of isoquinoline formation

E,*E*-cinnamaldoxime (**1**, mp 72–74 °C) [59] was prepared by a well-known procedure from cinnamaldehyde (99% *trans* available from Aldrich). The mechanism assumed for the Beckmann rearrangement reaction is described in Scheme 3. This is analogous to the commonly prescribed mechanism for the reaction [47a]. This pathway initially involves the protonation of the oxime at the oxygen atom to give an oxime cation (**3**), followed by the migration of the alkyl group *anti* to the hydroxyl group, the liberation of water, and the formation of nitrilium ion.

All these steps are activated by the acid sites with the different acid strength. Perhaps, the increased selectivity for isoquinoline formation might be due to the fact that cyclization of intermediate **7** is a facile step leading to stable heterocyclic compound. Since *E*,*E*-cinnamaldoxime lacks the geometrical requirements to undergo isoquinoline formation; we propose that *E*–*Z* isomerization of cinnamaldoxime is a major reaction pathway. Reports on similar *E*–*Z* isomerization of aldoximes are widely reported [60–63]. Thus, *E*,*E*-cinnamaldoxime (**1**) undergo facile isomerization to give the *Z*,*E*-isomer **2** in presence of acidic zeolites under the given reaction conditions. In a mechanism analogous to that suggested for Beckmann rearrangement of aldoximes, migration of the *anti* styryl moiety to electron deficient nitrogen in **3** leads to intermediate **7**. Intramolecular cyclization of **7** will eventually leads to



Scheme 4.



Scheme 5.

isoquinoline (**9**). Amide formation is not observed under the reaction conditions. Two reasons may be suggested for this observation; (1) intramolecular cyclization in **7** is a very facile pathway; (2) our reactions are carried out in the absence of water. It appears that protonation of **1** result in the loss of a molecule of water to give *trans*-cinnamonitrile (**6**). Acid-catalyzed hydrolysis of **1** will lead to the formation of *trans*-cinnamaldehyde (**8**). This is a minor pathway since the reactions are carried out under moisture-free conditions.

However, 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) [64]. More recently, quantum-chemical calculations suggested that the transfer of the alkyl group and simultaneous elimination of water to form the nitrilium ions (IV) is the rate determining step when gas-phase reaction occurs over solid oxide catalysts [65]. Based on these reports a modified possible mechanism for isoquinoline 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 [38c] reported experimental evidence on the intermediates formed in the initial stages of Beckmann rearrangement of acetophenone oxime over zeolites-β 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 on a similar strategy for the Beckmann rearrangement of cinnamaldoxime to isoquinoline.

4. Conclusions

Isoquinoline is synthesized in good yields over eco-friendly solid-acid catalysts under well-optimized conditions. Since *E*,*E*-cinnamaldoxime lacks the geometrical requirements to undergo isoquinoline formation via Beckmann rearrangement, it undergoes a *E*–*Z* isomerization over the catalysts. Zeolites exhibit comparable selectivity for isoquinoline. In conclusion, an example of practical continuous and highly atom economic version of the synthesis of isoquinoline is presented by using common laboratory down flow reactor and mild experimental conditions. Catalysts were susceptible for deactivation (H–Y: 20.8% deactivation and H-mordenite: 26.4% in 10 h) and the decrease in the conversion of oxime is associated with a corresponding increase in the acid hydrolysis producing salicylaldehyde at later stages of the reaction. However, they retain activity considerably and can be recycled without loss of activity and change of product distribution. These results, in principle, afford an attractive alternative for the synthesis of isoquinoline via Bischler–Napieralski cyclization of substituted phenylamines using corrosive acid catalysts such as P_2O_5 and studies addressed towards the extension of this protocol to substituted cinnamaldoximes and understanding the mechanistic aspects of the reaction using NMR studies are actually under investigation.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.micromeso.2006.12.006.

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