Synthesis of Benzoxazole via the Beckmann Rearrangement of Salicylaldoxime on Protonated Zeolites: A Green Continuous Process

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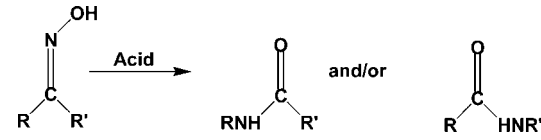
Benzoxazole was prepared through the Beckmann rearrangement of salicylaldoxime using a series of H-zeolites, K-10 montmorillonite clay, and some common oxide catalysts under well-optimized reaction conditions of temperature, weight hourly space velocity, and catalyst amount. Salicylaldoxime underwent a facile 1,2-*o*-hydroxyphenyl shift followed by an intramolecular cyclization to yield benzoxazole. Syn-anti isomerization of the oxime on acid catalysts is a key step in the reaction. *o*-Hydroxybenzonitrile, *o*-hydroxybenzamide, and salicylaldehyde were the main byproduct. We have observed definite correlations between acid sites distribution of the catalysts and different products formed during the reaction. 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, the deactivated catalysts can be regenerated without considerable loss of catalytic activity through an oxidative treatment.

Introduction

The acid-catalyzed rearrangement of ketoximes to amides is a well-studied reaction in organic chemistry, which is known as Beckmann rearrangement (BR) and a topic of great research interest.[1−4] Since the discovery of this reaction, many publications have appeared that deal with the mechanism, the determination of the stereochemical configurations of oximes employed, and its applications to synthesis of polyamides as well. Not only ketoximes, some aldoximes, and some of the esters and ethers of oximes also undergo BR. The reaction accomplishes in one stroke both the cleavage of a carbon−carbon bond and the formation of a carbon−nitrogen bond. As Beckmann rearrangement is stereospecific (the group anti to the leaving group migrates), the rearrangement is frequently used to determine the configuration of oximes by the identification of acid obtained by the hydrolysis of amide formed upon the rearrangement.[4] The general acid catalyzed Beckmann rearrangement of ketoximes is shown in Scheme 1.

The Beckmann rearrangement of cyclohexanone oxime is an important step in the production of ε-caprolactam, a valuable starting material for the manufacture of nylon-6. This is, perhaps the most studied one and generally requires high reaction temperatures and strongly acidic and dehydrating media.[4] The current commercial process demands the use of stoichiometric amounts of oleum to upshot BR. It carries many serious drawbacks, including high ammonium sulfate formation as a byproduct during the neutralization step to liberate the lactam produced. On these bases milder conditions were tried and several interesting variants developed. Recently, the Beckmann rearrangement was reported to occur in ionic liquids at room temperature.[5] Luca and co-workers[6−8] reported a very mild and highly selective procedure for the quantitative conversion of ketoximes into the corresponding amides. The procedure is based on the reaction of a complex formed by 2,4,6-trichloro[1,3,5]triazine (cyanuric chloride; TCT), an economical

Scheme 1. General Beckmann Rearrangement of Ketoximes to Amide by Acids



reagent, with a DMF solution of 1 mol equivalent of the ketoxime. On the other hand, Ishihara and co-workers[9] reported the successful BR of ketoximes to lactams by cyanuric chloride (CNC), without formation of any sulfate. This method provides a convenient route to lactams from oximes, but the rearrangement of cyclohexanone oxime to ε-caprolactam, which is the most important BR in industrial chemistry, was difficult to carryout in good yields (<30% in refluxing acetonitrile using 10 mol % of the catalyst) by CNC catalyst. Beckmann rearrangement of cyclohexanone oxime and cyclododecanone oxime to ε-caprolactam and laurolactam (raw material for nylon-12), respectively, using triphosphazene catalyst (1,3,5-triazo-2,4,6-triphosphorine-2,2,4,4,6,6-chloride; TADC) has also been recently reported.[10] However, these procedures too have environmental problems as the method uses toxic reagents. Nevertheless, until now the occurrence of mild conditions was related to the use of rather toxic solvents and expensive reagents or solvents. As a promising solution, replacing this environmentally harmful process with heterogeneous catalysis over solid-acid materials has been investigated over the past decade.[11−17]

Despite this, the Beckmann rearrangement of other oximes to the corresponding amides or dehydration to nitriles has not extensively been studied. Meshram[18] reported the dehydration of a series of aldoximes on K-10 montmorillonite clay. Cs-X zeolite has been employed for the synthesis of benzonitrile and 3,4-dimethoxybenzonitrile in high yield.[19] Candeias and Afonso[20] reviewed the use of zeolites and mesoporous materials in the preparation of nonfused heterocyclic compounds through epoxidations, aziridinations, and Beckmann rearrangement. The liquid-phase BR of cyclohexanone, acetophenone, and cyclododecanone oximes over β zeolites has also been reported.[21] Fernandez et al.[22] have recently studied the mechanistic aspects of the BR of acetophenone oxime over microporous molecular

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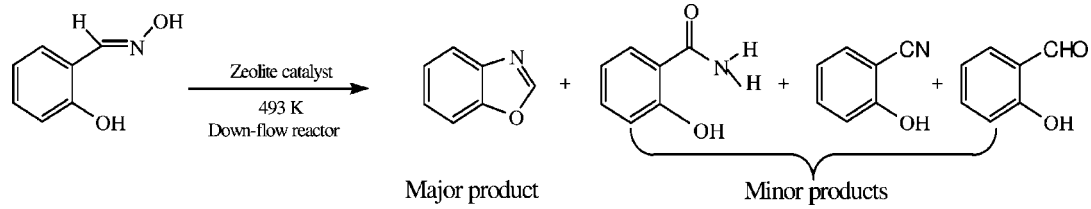
10.1021/ie800913q CCC: $40.75
Published on Web 12/01/2008

Scheme 2. Beckmann Rearrangement of Salicylaldoxime Producing Benzoxazole and Other Minor Products



sieves. We have reported a facile method for the synthesis of isoquinoline by the BR of *E,E*-cinnamaldoxime on zeolites.[23,24] Benzaldoxime and 4-methoxybenzaldoxime produce more nitriles (dehydration product) than amide (BR product) under the reaction conditions[25]

Over the past years much attention has been given to the preparation of benzoxazole and its myriad derivatives as these were found to have extensive application in different fields. Benzoxazole derivatives have been used as laser dyes,[26] whitening agents,[27] and as photoluminescents.[27] Benzoxazole derivatives show antiepileptic, antispasmodic, and antifungal properties.[28−30] Furthermore, benzoxazole units are found to be intermediates in many organic reactions.[31−33] Aromatic polybenzoxazoles (an example of specialty polymer) have excellent mechanical and thermal properties and can be spun into extra high strength fibers and molecular composites.[34,35]

Traditional methods of preparation of benzoxazole derivatives include condensation of 2-aminophenols with benzaldehyde or benzoic acid derivatives followed by intramolecular cyclization under corrosive acidic conditions.[36,37] Tandem Claisen rearrangement (TCR) is widely used for the preparation of bis[benzoxazole] derivatives.[38] Recently, Sardarin et al.[39] reported a proficient method for the synthesis of 2-substituted benzoxazoles through the BR of 2-hydroxyaryl ketoximes using diethyl chlorophosphate. Nevertheless, there are not many reports on a robust method for the synthesis of benzoxazole derivatives via green routes. Solid-acid catalysts have rarely been used for the synthesis of benzoxazole or its wide range of useful derivatives. In the present paper, we discuss the relevance of BR of salicylaldoxime for the synthesis of benzoxazole (Scheme 2) on a series of acid zeolites, K-10 clay, SiO_2, and γ-Al_2O_3.

Salicylaldoxime under ambient reaction conditions on acidic zeolites, K-10 montmorillonite clay, and oxide catalysts undergo a facile BR leading to the formation of benzoxazole as the major product. Dehydration of salicylaldoxime to *o*-hydroxybenzonitrile and acid hydrolysis to salicylaldehyde are minor pathways. Also, BR of the syn isomer produces *o*-hydroxybenzamide in small amounts.

Experimental Section

Materials. H-Y zeolite (Si/Al = 1.506) was supplied by Sud-Chemie (India) Ltd. H ZSM-5 and H-β zeolites were purchased from National Chemical Laboratory, Pune, India. H-Mordenite (CBV-90) was procured from Zeolyst International, New York. K-10 montmorillonite clay was purchased from Aldrich Chemical Co., Milwaukee. SiO_2 and γ-Al_2O_3 were prepared in the laboratory applying well-known methods reported earlier.[40,41] Salicylaldehyde (+99%) was obtained from Aldrich Chemical Co. The syn content was about 99% and water content less than 0.001%. Benzene (+99%) used in the study was obtained from SD Fine Chemicals, India, and contained 99.4% benzene by analysis. The water content was approximately 0.02%. It was washed with concentrated H_2SO_4 and subsequently with 20% $NaHCO_3$. Acetonitrile (+99%), hydroxylamine hydrochloride (+99.3%), and sodium bicarbonate (+99.9%) were procured from SD Fine Chemicals, India. Ammonia (+99.99) and dry nitrogen (+99.99%) were purchased from Southern Gas Ltd., India. All chemicals except benzene were used without further purification.

Experiments. Crystallinity and phase purity were evaluated by X-ray diffraction studies on a Rigaku D-max C X-ray diffractometer with monochromatized Ni-filtered Cu Kα radiation in the radial range of 5−50°. Simultaneous determination of BET surface area and pore volume measurements was performed using a Micromeritics Gemini surface area analyzer using dinitrogen as an adsorbate at 77.3 K. The area per molecule of dinitrogen was taken as 16.2 Å^2. The calcined samples were preheated in a flow of nitrogen for 3 h at 473 K to remove all the volatiles and chemically adsorbed species from the surface. Nitrogen adsorption data were evaluated as monolayer surface coverage. This protocol gave specific surface area and also the total pore volume of the materials. Results were reproducible within an error limit of 5%.

Temperature programmed desorption of ammonia (NH_3-TPD) of the catalysts was carried out in a stainless steel reactor (i.d. = 4 mm × 5 mm) packed with about 100 mg of catalyst. The catalyst was activated in situ at 773 K for ca. 1 h in nitrogen flow (dry N_2, 99.99%) and allowed to cool to room temperature. It was then poisoned with NH_3 (>99%) and kept for 1 h to saturate. The ammonia adsorbed sample was purged with N_2 for ca. 2 h at 373 K in order to reduce the extent of physical adsorption on the catalyst surface. The adsorbate desorbed while heating from 373 to 873 K was measured quantitatively with a conventional ammonia detector. The amounts of ammonia desorbed were formally divided into three temperature ranges to denote three types of acid sites: (1) weak, 373−473 K; (2) moderate, 473−673 K; and (3) high, 673−873 K.

Catalytic Reaction Procedure. Catalytic reactions were carried out in a fixed-bed, down-flow quartz reactor with 0.6 cm internal diameter and 30 cm height with a high sensitivity temperature controller (accuracy ca. ±5 K) and a set up to carry out the reaction under gaseous atmosphere. The reactor was fitted with a water condenser downstream to condense the products of the reaction and was operated in isothermal mode by adjusting the external heater to give an isothermal temperature profile in the catalyst bed. Catalyst particles (700 mg and 30−40 μm mesh size) sandwiched between glass wool was filled between ceramic beads. Prior to the reaction, catalysts were heated in situ at a heating rate of 20 K/min to a final temperature of 773 K for 12 h in the presence of oxygen, allowed to cool to the reaction temperature (498 K) under dry nitrogen, and kept for ca. 1 h before commencement of the reaction. The reactant (5% (w/v) solution of oximes in a 1:1 mixture of benzene and acetonitrile) was fed to the reactor through an ISCO-model 500 D syringe pump in the 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}). The product was

Table 1. General Features of the Zeolites, K-10 Clay, SiO_2, and γ-Al_2O_3 Used in the Beckmann Rearrangement Reaction of Salicylaldoxime

catalyst	Si/Al[a]	S_{BET} ($m^2\ g^{-1}$)	pore volume[b] ($cm^3\ g^{-1}$)	amount of ammonia (mmol/g) desorbed within certain temperature range[c] (K)				crystallite size (μm)[f]
				W[d,e]	M[d]	S[d]	cumulative	
H-Y	1.51	398	0.266	0.69	0.41	0.33	1.43	0.90
H-ZSM-5	40	413	0.163	0.65	0.34	0.29	1.28	0.40
H-β	26	745	0.232	0.52	0.70	0.51	1.73	0.51
H-MOR	19	552	0.188	0.63	0.56	0.73	1.92	0.92
K-10 mont.	2.7	183	0.204	0.55	0.24	0.13	0.92	≈1.0
SiO_2		155	0.172	0.59	0.11	0.07	0.77	≈1.11
γ-Al_2O_3		162	0.181	0.56	0.19	0.13	0.88	≈1.04

[a] As determined by inductively coupled plasma−atomic emission spectroscopy (ICP-AES; Perkin-Elmer) analysis. [b] Total pore volume measured at 0.9976 P/P_0. [c] As determined by temperature programmed desorption of ammonia in the temperature range 373−873 K. [d] W, M, and S stand for weak (373−473 K), medium (474−673 K), and strong (674−873 K) acid sites. [e] Ammonia desorbed in the 373−473 K temperature range might contain some physisorbed ammonia too. [f] As determined by powder X-ray diffraction studies.

collected down stream at ambient conditions in a closed glass vessel for analysis. Mass balance was between 98 and 100%.

Analysis. Feed and product analysis was done by gas chromatography (Chemito GC1000). For quantification, a gas chromatograph with a flame ionization detector and for products identification, a gas chromatograph attached with a mass selective detector (Shimadzu-5050 spectrometer) was used. Both gas chromatographs were equipped with HP-30 methyl siloxane 30 cm × 200 μm × 0.5 μm columns for separation. The temperature program started at 323 K with a hold time of 5 min, followed by a temperature ramp to 403 at 4 K min^{-1} and then to 573 at 10 K min^{-1}. A response factor of unity was used for GC-FID data of BR products. Mass balances confirmed that the response factor used was appropriate.

Calculations. Conversion of salicylaldoxime includes BR to benzoxazole, dehydration to *o*-hydroxybenzonitrile, and other side reactions depicted in the reaction mechanism. Conversion and selectivity values are reported on percentage basis and are calculated as follows.

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

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

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

where N_n is the number of moles of product n.

Recovery, Regeneration, and Reuse of the Catalyst. For a consecutive run, benzene was passed through zeolite catalysts for 1 h after the reaction and was continuously extracted with dimethyl ether and dried in an air-oven (383 K for 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). The dry solid was weighed and reused in the next run, with the proportional amounts of reactants and catalyst used to keep the substrate-to-catalyst and the solvent-to-catalyst ratios constant.

Results and Discussion

Detailed studies and characterization of the present catalyst systems have already been reported elsewhere.[24,42] The main physicochemical characteristics of the materials used in the present work are depicted in Table 1. For each zeolite catalyst, the values of acid strength, surface area, and pore volume match well with reported values.[43]

Beckmann Rearrangement of Salicylaldoxime. Salicylaldoxime under well-optimized reaction conditions on acidic zeolites, K-10 montmorillonite clay, and oxide catalysts underwent BR to produce benzoxazole (**5**) as the major product. Syn-anti isomerization of salicylaldoxime on solid acid catalysts is a crucial step in the production of **5**. BR of syn isomer, under the reaction conditions, produced *o*-hydroxybenzamide in small quantities (**8**). The formation of *o*-hydroxybenzonitrile (**10**) by the dehydration of salicylaldoxime and *o*-hydroxybenzaldehyde (**11**) via the acid hydrolysis are minor reaction pathways. Reaction conditions such as, temperature, flow rate, and catalysts loading were optimized using H-Y zeolite to observe maximum formation of the desired product.

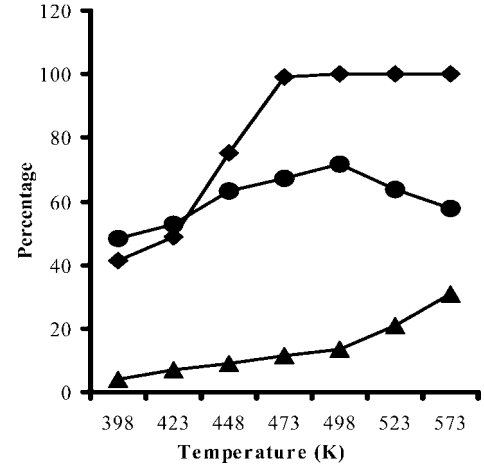


Figure 1. Temperature dependence on the salicylaldoxime conversion (♦) and selectivity to benzoxazole (●) and *o*-hydroxybenzonitrile (▲) over H-Y zeolite. Other reaction variables such as catalyst amount, flow rate, and molar ratio have been optimized and are given in Table 2.

Effect of Reaction Temperature. Total conversion of salicylaldoxime has been studied by varying the reaction temperature from 398 to 573 K using H-Y zeolite as the representative catalyst. Reaction products were collected after 3 h and results are depicted in Figure 1. Temperature has pronounced influence on the dehydration/BR reaction by solid-acid catalysts. Oxime conversion increased considerably from ca. 41.3 to 100% as the reaction temperature increased from 398 to 498 K. Benzoxazole formation were also improved from ca. 45 to 71.9% while increasing the temperature from 398 to 498 K. This could be ascribed to (i) the better catalyst activation at higher temperatures and (ii) easier products desorption from the catalyst surface. However, increasing the temperature further, thermodynamics of the byproduct formation is promoted and at 523 K there was a considerable decrease in the benzoxazole selectivity (decreased from 71.9% at 498 K to 63.8% at 523 K). Formation of heavy volatile products was observed at higher temperatures. There was continuous increase in the *o*-hydroxy-

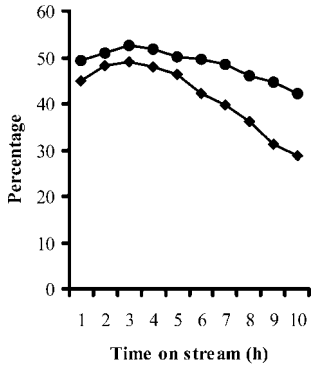


Figure 2. Typical time dependent percentage conversion (♦) and selectivity (●) plot showing the extent of deactivation during the Beckmann rearrangement of salicylaldoxime to benzoxazole at 423 K over H-Y zeolite. Other experimental conditions are as described in Table 2.

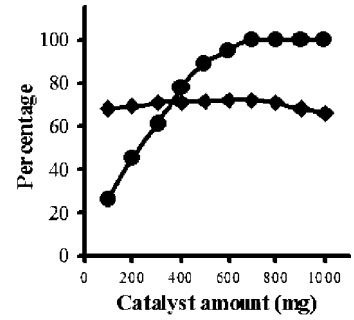


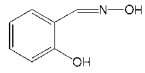
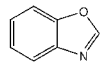
Figure 3. Dependence of catalyst amount (mg) on the conversion of salicylaldoxime (●) and the selectivity to benzoxazole (♦) over H-Y zeolite at 498 K. Other reaction variables such as temperature, flow rate, and molar ratio have been optimized and are presented in Table 2.

benzonitrile production with temperature (ca. 4.1% at 398 K to 30.9% at 573 K). The *o*-hydroxybenzonitrile formation can be attributed in two ways, that is, via abnormal BR or through the dehydration of the syn isomer. A relative low nitrile formation at lower temperatures and a steep increase with temperature infers that the formation of *o*-hydroxybenzonitrile is by the direct dehydration of the aldoximes. The increase in the yield of nitrile at high temperatures corroborates that there is an optimum temperature at which the syn−anti isomerization of oxime is productive. In addition, when the temperature was raised from 398 K there was relevant longer catalyst lifetime. Figure 2 shows the results of the on stream stability studies on H-Y zeolites at 423 K. The catalyst underwent 41.2% deactivation in 10 h and is much more than the deactivation at 498 K. This is attributed to the improvement in catalytic performances and more efficient products desorption at higher temperatures. Moreover, the acid-catalyzed hydrolysis of oxime to aldehyde was prominent at low temperatures. In general, product distribution at various temperatures shows that nitrile generation was considerable at higher temperatures, while benzoxazole formation was substantial at temperatures ca. 498 K. Hence, the optimum temperature with respect to oxime conversion, selectivity toward benzoxazole and catalyst deactivation under present reaction condition was found to be 498 K.

Effect of Catalyst to Oxime Ratio. Figure 3 shows the effect of catalyst amount on the BR of salicylaldoxime. The catalyst amount was varied 10-fold, that is, from 100 to 1000 mg. The selectivity of benzoxazole improved initially with catalyst amount and decreased subsequently. Rate of reaction was low with 100 mg catalyst and only 31% conversion of salicylaldoxime attained. When the catalyst amount was increased from 700 to 1000 mg, the rate of reaction remained the same, while the selectivity of benzoxazole, which was ca. 71.9% at 700 mg decreased to ca. 66% at 1000 mg. The conversion saturation could be because beyond a certain amount, there exists an excess of catalytic active sites greater than actually required by the reactant molecules and a subsequent leveling-off of the reaction rate. As a result, the reaction system attains steady state and any further addition of catalyst to be of any consequence for the external mass transfer. The decrease in the benzoxazole yield is found to be associated with a slight increase in the nitrile generation.

Comparison of Catalytic Activities. Results of the BR of salicylaldoxime over different solid-acid catalysts are shown in Table 2. We have used three classes of solid-acid catalysts, namely H-zeolites (H-Y, H-ZSM-5, H-mordenite, and H-β),

Table 2. Products Distribution in the Vapor Phase Beckmann Rearrangement of Salicylaldoxime over Different Solid-Acid Catalysts[a]

Catalyst	Conversion (%)	Selectivity (%)					TOF of oxime consumption ($10^{-3}S^{-1}$)[c]
					others[b]		
H-Y	100	71.9	13.1	5.7	2.2	7.1	0.40
H-ZSM-5	100	70.1	11.4	8.2	2.8	7.5	0.45
H-β	100	79.6	14.4	2.5	1.5	2.0	0.34
H-MOR	100	77.3	16.9	2.2	2.0	1.6	0.30
K-10 Mont	77.4	50.4	8.3	17.1	3.2	21.0	0.31
SiO_2	58.4	48.7	4.8	12.7	4.6	29.2	0.49
γ-Al_2O_3	64.5	49.8	7.3	15.0	1.0	26.9	0.43

[a] Include mainly *o*-hydroxybenzamide (Beckmann rearrangement product of syn isomer), small amounts of salicylic acid, and benzene. [b] Millimoles of salicylaldoxime converted per millimole of the active sites of the catalysts per second. [c] Reaction temperature, 498 K; catalyst amount, 700 mg; reactant, 5% solution of oxime in 1:1 benzene:acetonitrile (v/v) mixture; flow rate, 4 mL/h (WHSV; 0.29 h); time on stream, 3 h.

K-10 montmorillonite clay, and oxide catalysts such as SiO_2 and γ-Al_2O_3. All materials show high activity and selectivity for the formation of benzoxazole (**5**). *o*-Hydroxybenzamide (**8**), phenol (**9**), *o*-hydroxybenzonitrile (**10**), and *o*-hydroxybenzaldehyde (**11**) were the main byproducts of the reaction. Dehydration of oxime occurred with all catalysts at different levels producing *o*-hydroxybenzonitrile. Iso-nitrile formation was not detected at any stages of the reaction. In the series, H-β zeolite showed highest selectivity to benzoxazole (ca. 79.6%), while SiO_2 the least (ca. 48.7%). Maximum nitrile formation occurred on H-MOR and H-β zeolites. Typical Lewis acid catalysts such as K-10 clay and γ-Al_2O_3 produced greater amounts of salicylaldehyde (17.1 and 15%, respectively) compared to zeolites. *o*-Hydroxybenzamide production was more facile on weakly acidic SiO_2, K-10 clay, and γ-Al_2O_3. *o*-Hydroxybenzamide can be resulted either from the BR of the syn isomer or via the hydration of *o*-hydroxybenzonitrile. But the analysis of selectivity to nitrile over various catalysts (Table 2) in the present study unveils a moderatively high selectivity on zeolite catalysts than on K-10 clay or other oxides, and the selectivity of *o*-hydroxybenzamide was found conversely. This confirms that the *o*-hydroxybenzamide was produced exclusively by the BR of the *syn*-isomer. In general, vapor phase dehydration/BR of oximes over zeolites is much more efficient than on common oxide catalysts or K-10 clay. The activity difference could be due to two important properties: acid structural properties and diffusional properties which are determined by the pore structure of the materials.

Since BR is an acid catalyzed reaction, there is rationality when the conversion of oxime to nitrile or to the BR product is correlated to the strength and distribution of acid sites obtained from NH_3-TPD and cumene cracking test reaction. As indicated in Table 1, zeolites are characterized by high total acidity and their acidic sites are much stronger than other common oxide catalysts and K-10 clay. Hence, it should be expected that zeolites would show activity higher than the conventional oxide catalysts. As the reaction is carried out in vapor-phase and all the 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 such as SiO_2 and γ-Al_2O_3 without regular pore structure are also found to be active toward the reaction. Hence, the acid structural properties of the catalysts should be the deciding factor for the difference in activity/selectivity. Zeolite catalysts show 100% conversion of oxime; however, they exhibit differences in the selectivity toward various products as shown in Table 2. In this series, highest selectivity for the desired product is exhibited by H-β zeolite (ca. 79.6%), whereas SiO_2 exhibits the least (ca. 48.7%). Hence, from the nature of product distribution as in Table 2, the formation of benzoxazole requires an optimum acid strength of the material. Zeolites with more strong acid sites result in greater dehydration compared to other catalysts. K-10 clay, SiO_2, and γ-Al_2O_3 produce more byproducts (mainly *o*-hydroxybenzamide) compared to zeolites. Their ineptitude for an effective syn−anti isomerization might be the reason for this and the syn isomer directly undergoes BR via 1,2-hydride shift to form *o*-hydroxybenzamide.

Product 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 BR is still a matter of several controversies. Subjects on the active sites responsible for the formation of benzoxazole and some side-products have been investigated. Acidic sites catalyze the main as well as the minor

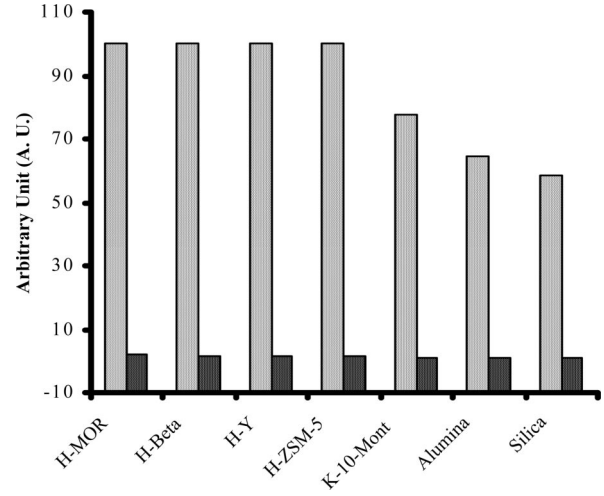


Figure 4. Dependence of the percentage conversion of oxime (gray) on the cumulative acid amount (mmol/g) (black) of zeolites, K-10 montmorillonite clay, SiO_2, and γ-Al_2O_3 during the Beckmann rearrangement of salicylaldoxime. Reaction conditions are as described in Table 2.

reaction pathways. In addition to the Brönsted and Lewis acidity in the material, the formation of a large number of weakly acidic hydroxyl groups and the existence of transient hydroxylated aluminum[44] and various species of extra-framework aluminum (EFAL) (e.g., cationic aluminum ions) and silica−alumina amorphous phase[45,46] have been proposed as active centers for BR. Some EFAL species confer Lewis acidity of different strength[47] and some other EFALs have a synergistic effect with Brönsted acid sites (BAS) resulting in an increased acid strength and catalytic activity.[48]

Dependence of oxime conversion with cumulative acid site strength of different solid-acid catalysts is shown in Figure 4. The zeolites, having higher cumulative acidity than K-10 clay or other oxide catalysts show superior activity toward the conversion of oxime (ca. 100%). K-10 clay, SiO_2, and Al_2O_3 converted ca. 77.4, 58.4, and 64.5% oxime, respectively. These results suggest that the oxime conversion is directly related to the amount of acid sites present; the more acid sites present in the catalyst, the higher the oxime conversion attained. Studies of the BR of cyclohexanone oxime over MCM-41 (characterized by the presence of large number of weakly acidic silanol groups) catalyst support this observation. Because of insufficient acidic strengths of these silanol groups, the rearrangement of oxime to lactam was not effectively catalyzed, resulting in low oxime conversion and lactam selectivity.[49]

The catalyst that gave high conversion also exhibited high selectivity to the desired product. Oxime conversion was 100 percent over zeolites. For K-10 clay, SiO_2, and Al_2O_3, total conversion, selectivity for benzoxazole, and total acid amounts correlate directly. Figure 5a depicts a simple correlation of the benzoxazole formation and weak plus medium acid sites strength of zeolites and K-10 clay. There is a one to one relationship between the two parameters. These results suggest that the acid sites responsible for benzoxazole formation are weak plus medium acid sites (including both BAS and Lewis acid sites (LAS)) of the catalyst. Under vapor phase conditions, weakly acidic groups and medium strength acid sites have been suggested to be responsible for the formation of ε-caprolactam in the vapor-phase BR of cyclohexanone oxime.[7,11,50] Figure 5b reflects the correlation observed between benzene formed in the hydocracking of cumene and benzoxazole selectivity. Benzene is supposed to be produced on BAS of the acid catalyst.[51,52] There is a linear relation between the two

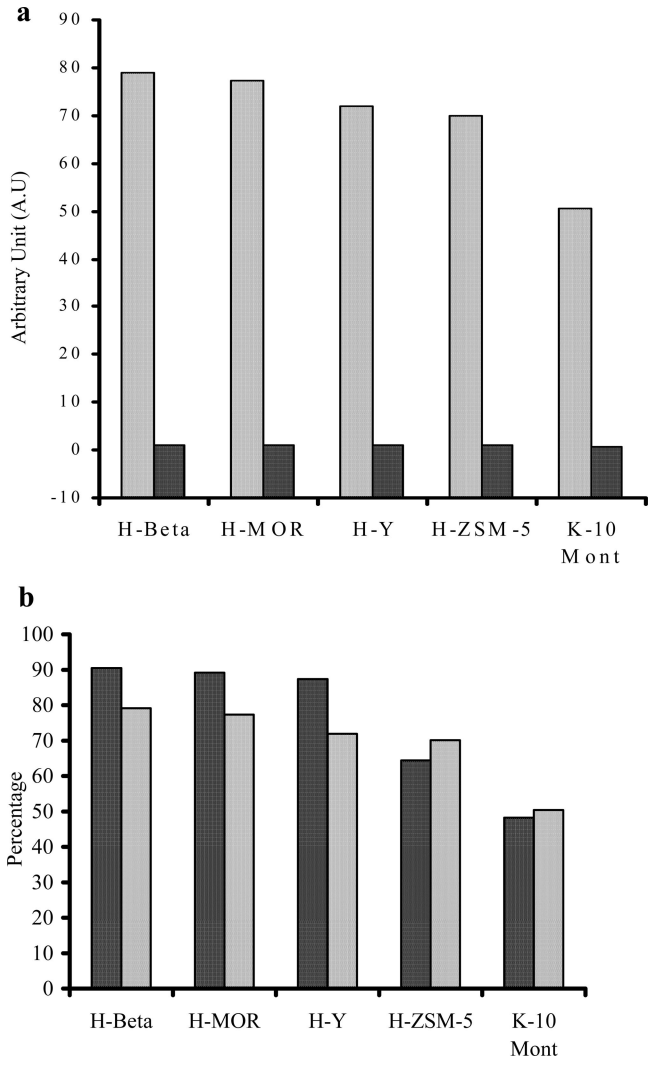


Figure 5. Dependence of (a) number of weak plus medium strength acid sites (black) (mmol/g) and (b) benzene selectivity (black) (%) during the cumene cracking reaction, and benzoxazole formation (gray) (%) on acidic zeolites and K-10 clay during the vapor phase Beckmann rearrangement of salicylaldoxime. Reaction conditions are as in Table 2.

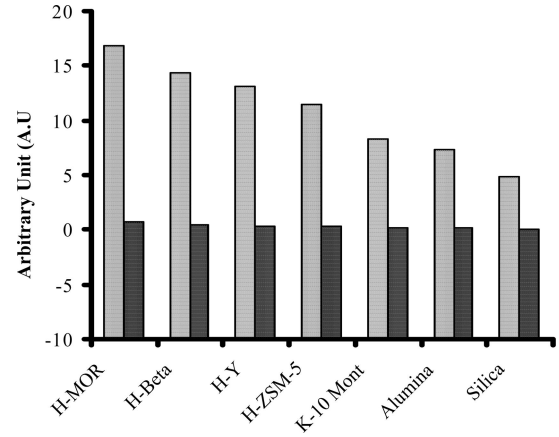


Figure 6. Correlation showing the dependence of amount of strong acid sites (mmol/g) (black) on the percentage formation of *o*-hydroxybenzonitrile (gray) during the vapor phase Beckmann rearrangement of salicylaldoxime over acidic zeolites, K-10 clay, γ-Al_2O_3, and SiO_2. Reaction conditions are as in Table 2.

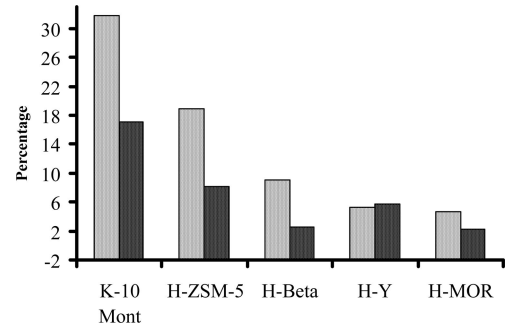


Figure 7. Correlation showing the dependence of the percentage of α-methylstyrene (gray) formed during the hydrocracking of cumene and the percentage of salicylaldehyde (black) produced during the vapor phase Beckmann rearrangement of salicylaldoxime over zeolites, and K-10 clay catalysts. Reaction conditions are as in Table 2.

parameters which supports our argument that benzoxazole is produced over BAS. This reflects the superior performance of BAS to weakly acidic hydroxyl groups in vapor phase BR.

Figure 6 shows the possible correlation between the amount of *o*-hydroxybenzonitrile produced in the reaction and amount of ammonia desorbed in the temperature range 674−873 K (i.e., amount of strong acid sites; include both BAS and LAS) during NH_3-TPD. The more the amount of strong acid sites there are, the higher the nitrile formation is. This is consistent with the well-documented observation that the presence of strong acid sites results in the dehydration of oximes.[13,15,23,53] According to Aucejo et al.,[15] *ε*-caprolactam obtained by the BR of cyclohexanone oxime is decomposed to nitriles on Na^+, Lewis acid sites, and on zeolites. Shouro and co-workers[53] attributes high selectivity of nitriles during the BR of cyclohexanone oxime on Al_2O_3/FSM-16 catalysts as a result of strong acid sites of $\Delta H(\text{Et-NH}_2) = 150$ kJ mol^{-1} (strong acid sites). These observations points to the likely involvement of strong acid sites in the dehydration of salyciladoxime producing *o*-hydroxybenzonitrile.

Typical Lewis acid catalysts such as K-10 clay and γ-Al_2O_3 produce more salicylaldehyde; namely 17.1 and 15%, respectively. Figure 7 shows a plot of α-methylstyrene formed during the hydrocracking of cumene (not discussed in detail) against the amount of salicylaldehyde produced. α-Methylstyrene formation during cumene cracking reaction is taken as a measure of the Lewis acidity of the acid catalysts.[51,52] There seems to be a straightforward relationship between α-methylstyrene formed and the amount of hydrolysis product. This suggests that LAS are active centers for the hydrolysis of salicylaldoxime to aldehyde. Thus, it is assumed that with an increasing Lewis acid strength, salicylaldehyde formation over the catalysts increased. In the zeolite series, H-ZSM-5 and H-Y generate maximum hydrolysis. Thus, LAS present in H-Y and H-ZSM-5, may belong to an EFAL-rich phase or hydroxylated Al that partially attaches to the framework by one or two Si−O−Al bonds. These species are present as octahedral Al coordinated with water molecule.[54] Therefore, weak Lewis acid sites responsible for the hydrolysis of oxime are probably located in an aluminum rich amorphous phase. In contrast, the data of H-β deviated from this relationship. This result indicates that LAS present in H-β zeolite thus should be of a different structure and acidity nature than those sites responsible for the hydrolysis of the oxime. This drop in the salicylaldehyde yield with a catalyst of high Lewis acid content implied that some Lewis sites were not involved in the acid hydrolysis of oxime.

Figure 8 shows the correlation between the crystallite size of the materials and corresponding catalytic activity. In general, the smaller the crystallite size is, the greater the percentage conversion and benzoxazole selectivity are. This is more

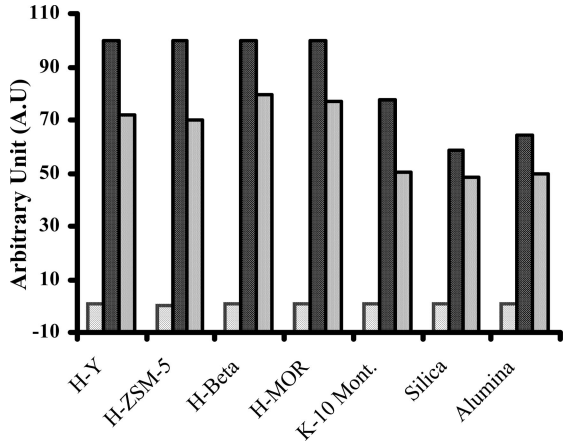


Figure 8. Dependence of crystallite size (μm) (light) on the conversion (black) and selectivity (gray) of benzoxazole over zeolites, K-10 clay, SiO_2, and γ-Al_2O_3 during the vapor phase Beckmann rearrangement of salicylaldoxime. Reaction conditions are as in Table 2.

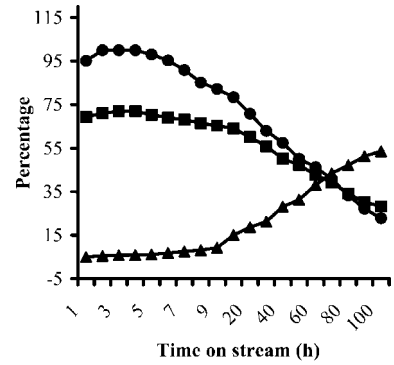


Figure 9. Typical time dependent conversion (●) and percentage selectivity to benzoxazole (■) and salicylaldehyde (▲) plot showing the stability of the catalyst during the Beckmann rearrangement of salicylaldoxime to benzoxazole at 498 K over H-Y zeolite. Reaction conditions are the same as in Table 2.

Table 3. Catalytic Performances of Fresh H-Y and H-β Zeolites after One to Three Regeneration Cycles[a]

	fresh	I cycle	II cycle	III cycle
salicylaldoxime conversion (%)	100 (100)	98.8 (99)	97.3 (97.9)	98.1 (98.3)
benzoxazole selectivity (%)	71.9 (79.6)	71.7 (79)	70.9 (78.1)	71.7 (77)

[a] Values in parenthesis are the conversion of oxime and selectivity for benzoxazole on H-β zeolite. Reaction conditions are as described in Table 2.

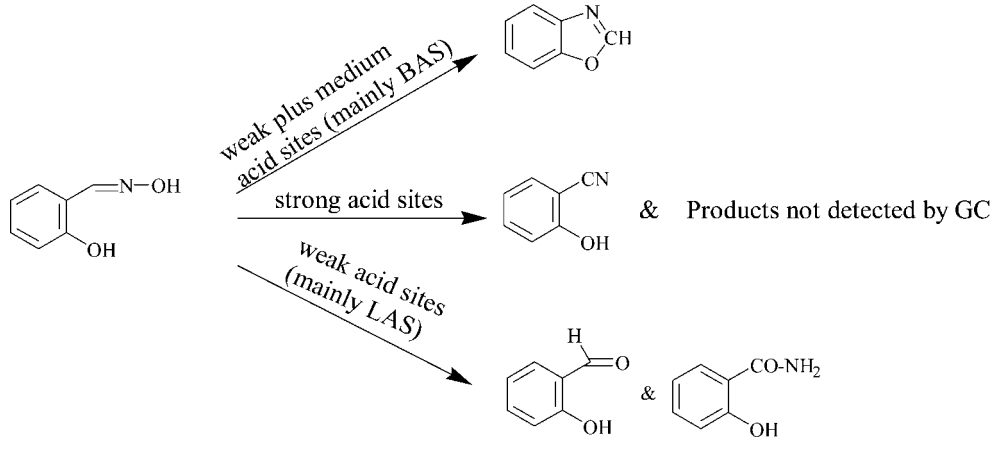
pronounced in the case of K-10 clay, SiO_2, and γ-Al_2O_3. Zeolites deviated greatly from the general trend, and with comparatively smaller crystallite size, they produced more oxime conversion and benzoxazole selectivity. There was no clear correlation involving catalytic activity, product distribution, and surface area and pore volume of various solid-acid catalysts. This confirms that the reaction is not strictly diffusion controlled.

Scheme 3 shows the proposed active sites for the reaction system of salicylaldoxime-acetonitrile-benzene in presence of different solid-acid catalysts. Benzoxazole is produced actively and selectively over weak plus medium acid sites (include mainly BAS), whereas LAS or weak acid sites are responsible for salicylaldehyde formation. Furthermore, water used in the hydrolysis reaction, may be generated through the dehydration of protonated intermediate over strong acid sites forming nitrile.

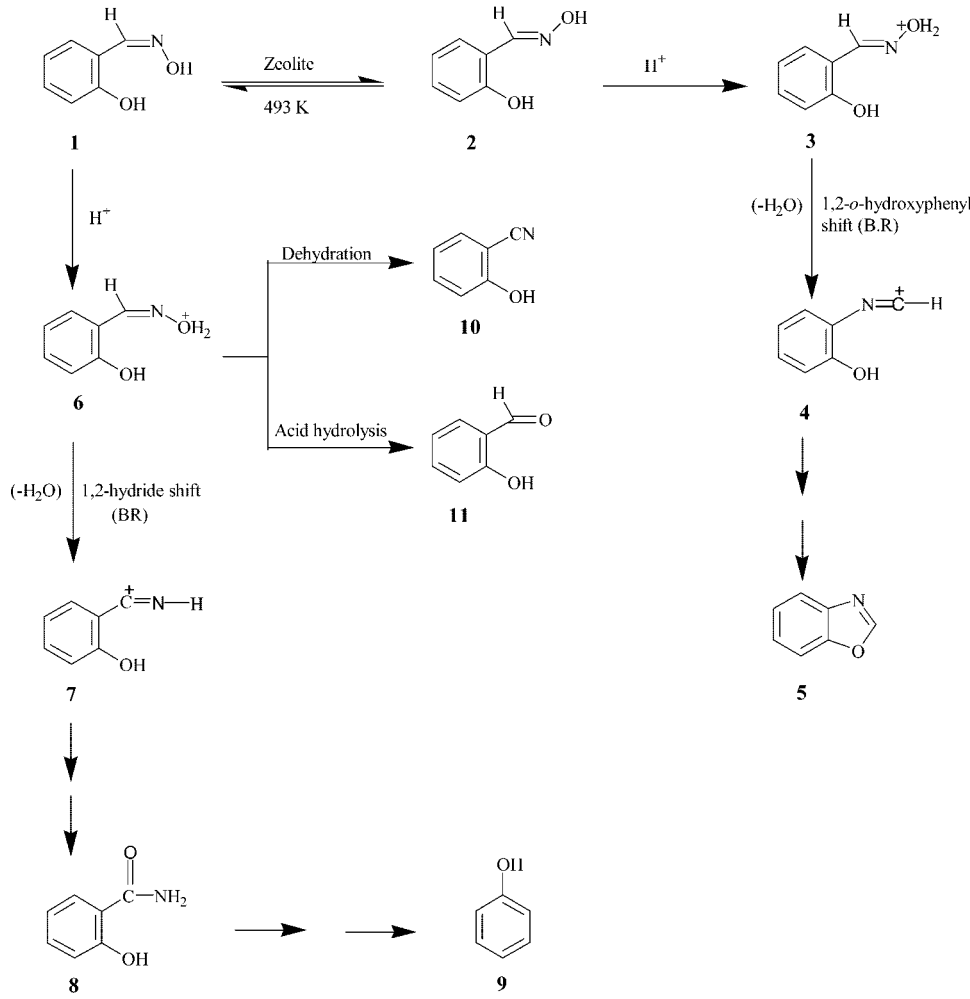
Deactivation, Reusability, And Heterogeneity Studies. The reaction was carried out continuously for 100 h over H-Y and H-β zeolites, and products were collected at intervals of every 1 h up to 10 h and later at every 10 h. Conversion decreases with reaction time and the nature of zeolite deactivation is similar to what we have reported previously.[25] H-Y (Figure 9) and H-β (not shown) zeolites underwent 77.2 and 80.9% deactivation, respectively, in 100 h. Decrease in the oxime conversion was associated with a corresponding decrease in the benzoxazole formation and a substantial increase in the extent of acid hydrolysis producing salicylaldehyde. In the present case, the catalyst deactivation would be due to the deposition of reactants and products on the active sites. Decrease in the formation of benzoxazole with time would perhaps be due to less efficient syn−anti isomerization at later stages of the reaction. As most of the acid sites get deactivated by the deposition of reactants and products and by water formed during dehydration of the oxime, BR, dehydration, and other side reactions become nominal and the probability of acid hydrolysis of oxime to aldehyde increases marginally. Acid hydrolysis occurs mostly at later stages of the reaction, suggesting generation of water in the reaction medium via a dehydration reaction (nitrile formation) or during the formation of higher molecular weight products.

However, these deactivated materials can be partially regenerated by solvent extraction to remove most of the trapped products. Thus, the deactivated zeolites (H-Y and H-β) were washed with methylene chloride resulting in the removal of products from the catalyst surface. This was followed by

Scheme 3. Active Sites Involved in the Beckmann Rearrangement Reaction System of Salicylaldoxime−Acetonitrile−Benzene in Presence of Different Solid-Acid Catalysts



Scheme 4. Suggested Reaction Network for the Beckmann Rearrangement of Salicylaldoxime over Solid-Acid Catalysts



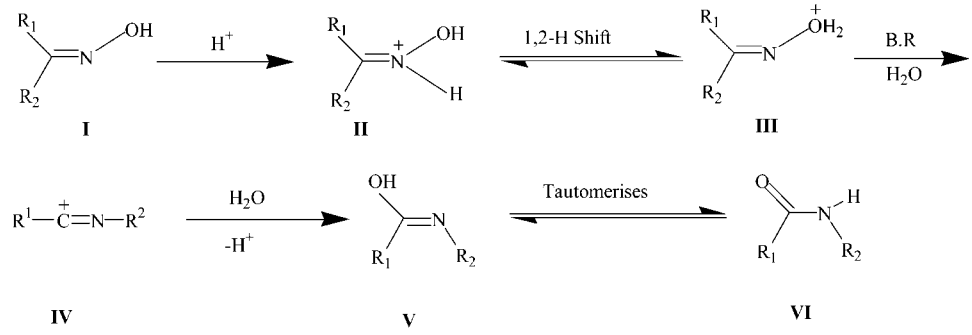
oxidative treatment at 773 K for 5 h, resulting in the H-Y zeolite converting 98.8% oxime on second and 97.3% on third regenerations. There was no substantial loss of catalytic activity or change in the product distribution for both H-Y and H-β zeolites even after three cycles (Table 3). Furthermore, ^{27}Al MAS NMR spectra of the regenerated H-Y and H-β zeolites (see Supporting Information Figure S1 and S2) show no considerable increase in the amount of extra-framework aluminum compared to the ones before catalytic reaction. This demonstrates that the zeolite catalysts can be regenerated without framework damage and loss of catalytic activity. As the waste formation is to a small extent, the reaction must proceed with low *E*-factor and high atom efficiency. In conclusion, a simple, efficient, and relatively environmentally benign protocol is described for the production of benzoxazole.

We have conducted further experiments to obtain clear evidence for the true heterogeneity of reaction. Catalytic reaction mixture was passed through H-Y and H-β zeolites under standard reaction conditions for 10 h. No aluminum was detected in the product mixture by energy dispersive X-ray (JEOL JSM-840A; Oxford model 16211) analysis or by qualitative chemical analysis of the product mixture. These results strongly suggest against the possible aluminum leaching during the reaction.

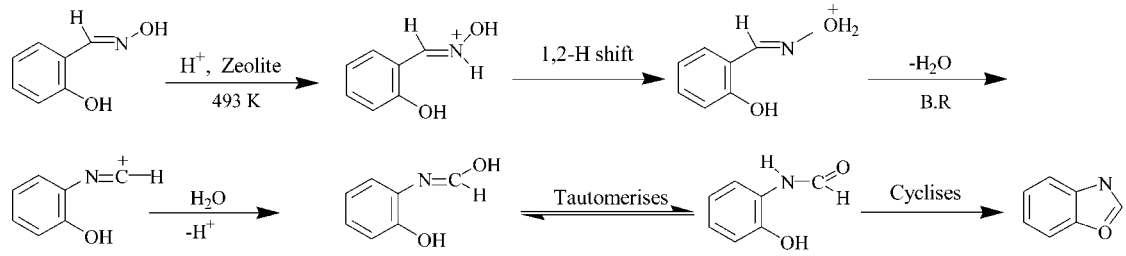
Mechanism of the Reaction. Salicylaldoxime was prepared by the well-known procedure from salicylaldehyde (99% syn available from Sigma Aldrich Chemical Co.).[55] Salicylaldoxime is an example of oxime, which exists as a pair of sterioisomers (syn and anti). The anti isomer rearranges by a 1,2-*o*-hydroxyphenyl shift, whereas the syn isomer undergoes a 1,2-hydride shift to form the corresponding BR product. The former reaction is much faster than the latter, presumably because it proceeds via a relatively stable phenonium ion intermediate. Also, the energy barrier in the case of hydrogen as the migrating group is much higher.[56] As benzoxazole is the major product and resulted from anti isomer, we propose a syn−anti isomerization of salicylaldoxime on acidic solid-acid catalysts as the major reaction pathway. Reports on similar isomerizations of aldoximes can be found in the literature.[57−62] Syn−anti isomerization of salicylaldoxime and the formation of various products may be understood in terms of the pathways described in Scheme 4. Thus, *syn*-salicylaldoxime (**1**) undergoes facile isomerization to give anti isomer (**2**) in the presence of acidic zeolites under the given reaction conditions.

In a mechanism analogous to that suggested for the BR of aldoximes, migration of 1,2-*o*-hydroxyphenyl group to the electron deficient nitrogen in **3** leads to the formation of intermediate **4**. Now the hydroxyl group is ideally located to bind to the electrophilic carbon of the intermediate **4**, and consequently product from the *anti*-isomer is a benzoxazole heterocyclic ring (**5**). Two reasons can be suggested for this observation: (1) intramolecular cyclization of **4** leading to the formation of benzoxazole is a highly facile pathway; (2) our reactions are carried out in the absence of water. Protonation of **1** followed by the loss of a molecule of water gives *o*-hydroxybenzonitrile (**10**). Acid-catalyzed hydrolysis of **1** leads to the formation of salicylaldehyde (**11**) and is a minor pathway

Scheme 5. General Beckmann Rearrangement Mechanism Involving an N-Protonation Followed by 1,2-Hydride Shift



Scheme 6. Suggested Alternative Reaction Network for the Formation of Benzoxazole Involving an N-Protonation and 1,2-Hydride Shift during the Beckmann Rearrangement of Salicylaldoxime



since reactions are carried out under strict moisture-free conditions. The syn isomer undergoes BR through a 1,2-hydride shift leading to the formation of *o*-hydroxybenzamide **8**, which ultimately produces phenol (**9**).

The generally accepted mechanism[63] of BR assumes an initial protonation at oxygen of an oxime giving an oxonium cation, followed by the anti migration together with the elimination of a molecule of water leading to a nitrilium cation. This in turn undergoes hydrolysis to yield an amide. However, ab initio molecular orbital calculations on the isolated gas phase system suggested the mechanism of BR as described in Scheme 5.[56] The first step is the N-protonation of oxime to give an N-protonated form (II), and the direct 1,2-H shift producing O-protonated isomer (III) is the rate-determining step for the gas phase process. Recent quantum mechanical investigations suggested the anti migration of the leaving group plus elimination of water to nitrilium ion (IV) as the rate-determining step when the gas-phase reaction occurs over solid oxide catalysts.[64] On the basis of these reports, we have suggested a possible modified mechanism for benzoxazole formation as depicted in Scheme 6.

However, at present there is no experimental proof and the BR reaction pathway is not well established. The investigations of Fernandez et al.[22] on the mechanism of BR of acetophenone oxime over zeolite-β using solid-state NMR spectroscopy and theoretical calculations recognized that the acid strength of the active catalyst is responsible for the formation of O-protonated or N-protonated oxime. We are currently working on a similar strategy for the BR of salicylaldoxime to benzoxazole.

Conclusions

To conclude, a mild and efficient method for the synthesis of benzoxazole through the BR of salicylaldoxime has been developed using a series of solid-acid catalysts. The combination of high activity analogous to the corrosive P_2O_5, PCl_5, and $POCl_3$, short reaction time, moderately high yield, stability and handling advantages of zeolites and other solid-acid catalysts is unique and makes a very attractive catalyst for the BR of salicylaldoxime. Moreover, the process is associated with features such as simple work-up procedures, high atom efficiency, and above all rather environmentally benign nature. In this series of catalysts, highest selectivity for the desired product is exhibited by H-β zeolite (79.6%), whereas SiO_2 exhibits the least (48.7%). Nevertheless, these catalysts are susceptible to deactivation (ca. 77.2 and 80.9% deactivation in 100 h over H-Y and H-β zeolites, respectively) but can be regenerated through the oxidative treatment without considerable loss of activity or selectivity and damage to the zeolite framework. Studies addressed toward the extension of this protocol to other types of substituted salicylaldoximes through a fully green methodology and efforts to understand the exact mechanism of BR are currently under investigation.

Acknowledgment

Authors are thankful to Dr. C. V. Asokan, School of Chemical Sciences, MG University, Kerala, India, for GC−MS results and Dr. S. Prathapan, Department of Applied Chemistry, CUSAT, Kochi, India, for inspiring discussions at various stages of this work. B.T. thanks Council of Scientific and Industrial Research, Govt. of India, New Delhi, for a Senior Research Fellowship.

Supporting Information Available: Sample preparation for ^{27}Al MAS NMR studies, experimental details, and ^{27}Al MAS NMR spectra of H-Y and H-β zeolites before catalytic reaction and after regeneration of the deactivated catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review June 10, 2008
Revised manuscript received October 25, 2008
Accepted October 27, 2008

IE800913Q