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Cu/SBA-15 is an Efficient Solvent-Free and Acid-Free Catalyst for the Rearrangement of Benzaldoxime into Benzamide

Ganji Saidulu · Narani Anand · Kamaraju Seetha Rama Rao · Abhishek Burri · Sang-Eon Park · David Raju Burri

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Abstract Cu/SBA-15 catalysts with various Cu loadings in the range of 5–20 wt% were prepared by an impregnation method and characterized by N_2 adsorption, X-ray diffraction, temperature programmed reduction and X-Ray photoelectron spectroscopic techniques. Cu/SBA-15 catalysts are found to be highly active and selective for the Beckmann rearrangement of benzaldoxime into benzamide under solvent-free and acid-free conditions.

Keywords Cu/SBA-15 · Beckmann rearrangement · Benzaldoxime · Benzamide

1 Introduction

Typically, amides are potential precursors for the synthesis of various natural products and drug intermediates [1]. The isomerization of oximes to amides (Beckmann rearrangement) is one of the most straightforward synthetic routes for the production of amides [2]. However, in the Beckmann rearrangement, migration of alkyl or aryl group is facile rather than hydrogen. Hence it is not a general process for the transformation of aldoximes into primary amides [3]. Furthermore, Beckmann rearrangement (BR) generally requires high reaction temperature and strong acidic and dehydrating media [3]. Despite of these impediments in the Beckman rearrangement of aldoximes into primary amides, the recent efforts in getting considerable conversions and selectivities are worth noting. For instance, metal catalyzed approach for the rearrangement of aldoximes into primary amides involving the sequential dehydration and hydration via nitrile intermediate formation exhibited substantial improvements [4]. Williams and his co-workers revealed the successful conversion of aldoximes into primary amides using Ru and Ir metal complexes [4, 5]. It is proved that Rh complexes are good candidates for the rearrangement of aldoximes to primary amides [6–8]. However, Rh, Ir, and Rh containing catalytic materials are highly expensive and in addition, usage of these catalysts requires laborious workup procedure to separate the product. Furthermore, use of environmentally and biologically harmful solvents is one of the main difficulties in these chemical transformations.

In a recent report, solvent-free and acid-free Au/Ag co-catalysts are disclosed for the effective conversion of aldoximes to primary amides [9]. However, these Au/Ag co-catalysts are homogeneous in nature. In one of the reports, alumina supported rhodium hydroxide catalysts are used successfully as heterogeneous catalyst in water solvent [10], but rhodium is an expensive metal.

Recently, Williams and coworkers [11] reported a Cu based catalyst for the rearrangement of aldoximes to primary amides, in which most of the examples are covered by different homogeneous Cu^{2+} and Cu^{1+} salts. However, the study reveals that Cu based catalysts are highly effective. Off late, design and synthesis of transition metal active centers on molecular sieves has attracted increasing attention. SBA-15 is a mesoporous silica material with uniform hexagonal channels ranging from 50 to 300 Å, thick walls (31–64 Å), and with higher hydrothermal stability than those of MCM-41 [12, 13]. Because of its

G. Saidulu · N. Anand · K. S. R. Rao · D. R. Burri (✉)
Catalysis Laboratory, Indian Institute of Chemical Technology, Hyderabad 500 607, India
e-mail: david@iict.res.in

A. Burri · S.-E. Park (✉)
Department of Chemistry, Laboratory of Nano-green Catalysis, Inha University, Incheon 402-751, Korea
e-mail: separk@inha.ac.kr

unique features, SBA-15 has been under intensive investigation as a support for a variety of active components [14–22].

So far, no heterogeneous catalyst for the complete conversion of benzaldoxime into benzamide with 100% selectivity has been reported without using acids or solvents. Hence, herein for the first time, we report a new and efficient Cu/SBA-15 heterogeneous catalyst.

2 Experimental

2.1 Catalyst Preparation

All the reagents and chemicals were obtained commercially and used without further purification. The parent mesoporous SBA-15 silica support was synthesized hydrothermally under acidic medium using triblockco-polymer (P123) as a template and Tetraethyl orthosilicate (TEOS) as a silica source according original report of Zhao et al. [12] and our previous publications [23–27]. To prepare Cu/SBA-15 catalysts, the parent SBA-15 (calcined at 500 °C for 10 h) was dried at 120 °C for 6 h prior to impregnation. The requisite amounts of aqueous $Cu(NO_3)_2 \cdot 3H_2O$ solution likely to be around 5, 10, 15, 20 wt% as Cu metal were impregnated. These catalyst samples were dried at 100 °C for 12 h and calcined at 450 °C for 6 h. A portion of each catalyst was reduced at 280 °C for 3 h in the flow of H_2 gas using a fixed bed reactor and denoted as CS-X, where X denotes the percentage loading of Cu by weight.

2.2 Catalyst Characterization

The X-ray diffraction (XRD) patterns were recorded at room temperature using a Rigaku, Multiflex, diffractometer with a nickel filtered CuKα radiation of wave length 1.5418 Å at a power of 40 kW and a current of 100 mA in the 2θ range of 0.5–5° and 5–80° for the verification of SBA-15 structural ordering and Cu phase behavior respectively. Low and wide angle XRD data were obtained for unreduced and reduced CS-X catalysts respectively.

N_2 adsorption–desorption isotherms were recorded for calcined catalysts using a Tristar 3000 V 6.08A instrument (M/S Micromeritics Instruments Corporation, USA) at −196 °C. The samples were outgassed at 300 °C for 4 h before the measurement. BET method was used to calculate the surface areas using the amount of N_2 adsorbed at −196 °C. BJH method was used to calculate the pore-size distribution considering the desorption branch of the isotherm. The pore volume was taken at a relative pressure $P/P_0 = 0.989$ (single point).

Temperature programmed reduction (TPR) studies of all the calcined catalysts were performed on a home-made TPR system which consists of a quartz reactor placed in a metal furnace equipped with a temperature programmer come controller with a k-type thermocouple and a GC with a thermal conductivity detector connected to the outlet of the reactor. The data station with standard GC software permits recording the profiles. About 50 mg of the catalyst sample was placed at the center of the quartz reactor and packed in between the two layers of quartz wool. It is heated linearly at a rate of 5 °C/min from ambient temperature to 700 °C and isothermal conditions were maintained for 30 min at 700 °C, while passing the reducing gas mixture (11% H_2 in argon). In between the out let of the reactor and GC, a molecular sieve trap was placed to remove the moisture. GC-17A with TCD (M/s. Shimadzu, Japan) was used for analyzing and recording the profiles.

The surface analysis of the calcined catalysts was made using a KRATOS Axis 165 photoelectron spectrometer (XPS) equipped with Mg Kα radiation (1253.6 eV). The binding energy correction was performed by using the C 1 s peak at 284.6 eV as a reference for all the elements recorded. The relative intensities of the surface composition of different elements were corrected with their corresponding atomic sensitivity factors using the vision 2 software in UNIX system.

2.3 Catalyst Evaluation Test

In a typical catalytic activity test, 1 mmol of benzaldehyde oxime and 25 mg of catalyst were taken in a 10 ml RB flask and stirred at 100 °C for 3 h. After completion of reaction, ethyl acetate was used to separate the products from the catalyst. The products were identified by GC–MS (QP-5050 model, M/s. Shimadzu Instruments, Japan) equipped with DB-5 capillary column (0.32 mm dia. and 25 m long, supplied by M/s. J & W Scientific, USA). The product analysis was made by a Shimadzu gas chromatograph (GC-17A, M/s. Shimadzu Instruments, Japan) using a OV-1 capillary column (0.53 mm × 30 m). The separated catalyst was washed with ethanol and dried under vacuum prior to reuse.

3 Results and Discussion

3.1 Catalyst Characterization

To assess the structural integrity of the catalysts, small-angle XRD patterns of CS-X catalysts including parent SBA-15 were recorded (patterns not shown). The parent SBA-15 exhibited well-resolved diffraction peaks with a sharp peak at about 0.89° and two weak peaks at about 1.56° and 1.80° on the 2θ scale. Similar to that of parent silica SBA-15 the calcined CS-X catalysts also exhibited

Table 1 Physico-chemical characteristics of CS-X catalysts and SBA-15 support

Characteristics	SBA-15	CS-5	CS-10	CS-15	CS-20
BET surface area (m^2/g)	500	391	378	301	244
Micropore area (m^2/g)	62	41	39	37	31
Total pore volume (cm^3/g)	0.75	0.69	0.65	0.53	0.58
Micropore volume (cm^3/g)	0.03	0.02	0.02	0.02	0.01
BJH adsorption volume (cm^3/g)	0.77	0.70	0.66	0.53	0.58
BJH desorption pore dia. (nm)	4.10	4.84	4.72	4.88	6.39
XRD $d_{(100)}$	9.90	9.44	9.62	9.71	9.53
Unit cell length (nm)	11.43	10.9	11.1	11.2	11.01
Pore-wall thickness (nm)	7.34	6.06	6.38	6.43	4.62
Cu crystallite Size (nm)[a]	–	25.02	30.81	34.54	39.55
Composition (Cu/Si)[b]	–	0.045	0.103	0.159	0.175
Surface composition (Cu/Si)[c]	–	0.013	0.025	0.042	0.055

[a] Determined by XRD

[b] Determined by AAS

[c] Determined by XPS

three diffraction peaks positioned at 0.91–0.92°, 1.59–1.60°, and 1.83–1.85° on the 2θ scale, revealing the retention of mesoporous structural ordering. The position of diffraction peaks are well matched with the reported XRD patterns of SBA-15 [12]. However, the intensities of the peaks are found to decrease with increase in Cu loading. The estimated unit cell lengths for the calcined CS-X catalysts are shown in Table 1, which are close or a little lower compared to parent SBA-15 sample. The lower unit cell lengths ruled out the incorporation of Cu in the silica framework. In other words, Cu phase may be dispersed on the surface of SBA-15 support.

The N_2 adsorption–desorption isotherms of parent SBA-15 and Cu/SBA-15 catalysts were generated at -196 °C. The isotherms of Cu/SBA-15 exhibit type IV isotherms with H1 hysteresis loops corresponding to the filling of uniform mesopores with open cylindrical geometry [28]. However, the amount of N_2 adsorbed is less in the isotherms of CS-X catalysts compared to the isotherms of parent SBA-15. The phenomenon of low amount of N_2 adsorption is an indication of lowering in the surface area and pore volume. With increase in Cu loading, the average pore diameter increases, which is due to the blockage of smaller pores or the porous nature of Cu. Since the pore-wall thickness is calculated from the difference between unit cell length and average pore diameter, decrease in pore-wall thickness with increase in Cu loading is obvious as there is an increment in the average pore diameter. The pore-size distribution curves (not shown) indicate that most of pores are distributed in the range of 5–8 nm.

The CS-X catalysts were characterized by wide angle XRD to determine the crystalline behavior and the sizes of crystallites. The XRD patterns are displayed in Fig. 1 and the crystallite sizes are depicted in Table 1. Figure 1 displays a strong diffraction peak at 2θ of 43.4°, followed by two more intense diffraction peaks at 50.5 and 74.1° characteristic of Cu (JCPDS 04-0836), which indicates that the presence of metallic Cu in all the CS-X catalysts. It is also observed two low intensity peaks corresponding Cu^{2+}. Compared to diffraction peak intensity of Cu, the peak intensity of Cu^{2+} is very small. The gradual increase in the peak intensity of metallic Cu (Fig. 1) and its crystallite sizes (Table 1) with increase in Cu loading from 5 to 20 wt% Cu on SBA-15 is observed.

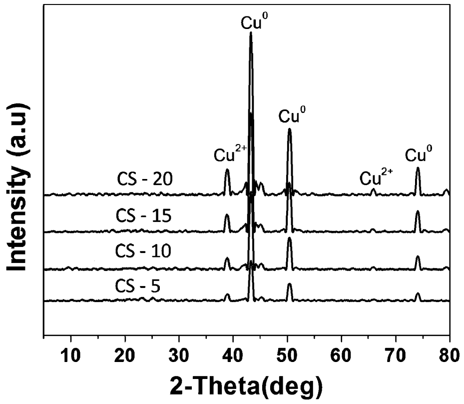


Fig. 1 XRD patterns of CS-X catalysts

The reducibility of CuO/SBA-15 catalysts has been measured by H_2-TPR and the TPR profiles are depicted in Fig. 2. The CS-5 gets reduced in two stages in the temperature range of 200–320 °C. It is reported that the reduction of dispersed CuO species to Cu^{1+} species takes place in low temperature region (below 300 °C) [29–31]. The high temperature signal in the temperature range of 320–480 °C can be attributed to the reduction of strongly interacted CuO species with the support to Cu^0 species or due to reduction of Cu^{1+}species to Cu^0 species. Similar kind of two-stage reduction of CuO is observed for CS-10 catalyst [32]. The low temperature peak maximum that observed for the low CuO loading catalysts was not seen in

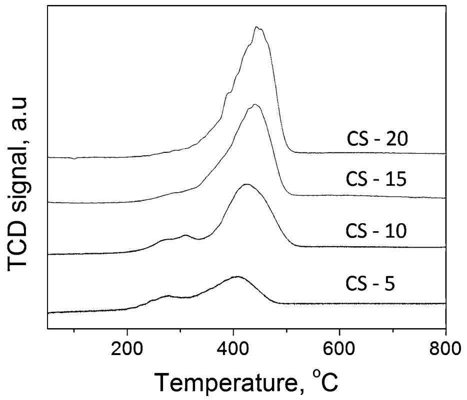


Fig. 2 TPR of CuO/SBA-15 catalysts

the profiles of higher loading catalysts. It was observed only one high temperature peak in the temperature range of 300–500 °C ($CuO + H_2 \rightarrow Cu + H_2O$). This peak may be corresponding to strongly interacted CuO species with the support [33]. However, there is a gradual shift in the high temperature peak maximum with increase in CuO loading. The high temperature peak maximum for CS-5 is at 400 °C, whereas for CS-20 the peak maximum is at 450 °C. Since the crystallite size (Table 1) of CS-20 (40 nm) is not too large compared to that of CS-5 (25 nm) one can expects an interaction between CuO and support which results in yielding a high temperature signal in the TPR pattern.

The surface and bulk composition of CS-X catalysts were determined by X-ray photoelectron spectroscope (XPS) and atomic absorption spectroscopy (AAS) respectively and the results were depicted in Table 1, wherein, the increase in Cu loading on SBA-15 similar to that of total composition of Cu from CS-5 to CS-20 (AAS) is observed. The lower Cu/Si ratio (surface composition) of CS-20 catalyst as obtained by XPS (Table 1) indicates presence of larger Cu-particles on the surface of SBA-15 support. Because of these Cu-sites whose size (35 nm) is larger than the average pore diameter ($\sim$5 nm) of SBA-15, one can expect the blockage of surface pores which results in lowering the BET surface area of the catalyst (244 m^2/g).

3.2 Catalytic Activity

The catalytic activity of CS-X catalysts for the transformation of benzaldoxime (oxime) into benzamide (amide) through BR without using any acids or solvents has been conducted in the liquid phase at atmospheric pressure. As it is reported by several authors [6–11], benzaldoxime transforms into benzonitrile (nitrile), benzaldehyde (aldehyde) and benzamide, of which benzamide is the main (desired) product. Indeed, the transformation of benzaldoxime into benzamide is a two-step process, wherein, the selective dehydration of benzaldoxime leads to benzonitrile, which on hydrolysis converts into benzamide. Benzaldoxime also converts into benzaldehyde through elimination of hydroxylamine followed by hydrolysis.

To attest the benzaldoxime rearrangement is a catalytic process, an experiment was conducted without adding the catalyst to the reaction mixture, no appreciable conversion is observed (Table 2, run 1), which proves the particular process is catalytic. In the next experiment SBA-15 support was used as a catalyst and found that SBA-15 is capable of converting benzaldoxime into benzonitrile and benzaldehyde but not into the desired benzamide product (Table 2, run 2). To distinguish the catalytic activity of CuO and Cu metal, two different experiments were conducted with and without catalyst reduction (Table 2, run 3 and 4). The Cu metal obtained through H_2 reduction from the same bulk CuO exhibited superior activity (Table 2, run 4), compared to bulk unreduced CuO catalyst (Table 2, run 3). The catalytic activity of Cu metal is higher not only in the conversion of benzaldoxime but also in the selectivity of benzamide. Similar trend is observed even in the case of supported catalysts (Table 2, run 5 and 6).

To find out the influence of water on the catalytic activity of CS-20 catalyst in the rearrangement of benzaldoxime into benzamide, two experiments were conducted. In the first

Table 2 Transformation of benzaldoxime on different catalysts

Catalyst	Run no.	%Conv. of benzaldoxime	%Sel. of benzonitrile	%Sel. of benzaldehyde	%Sel. of benzamide
No catalyst	1	3.9	0.0	100.0	0.0
SBA-15	2	24.1	19.9	80.1	0.0
CuO (unreduced)	3	64.7	13.3	20.9	74.8
Cu (reduced)	4	84.6	4.0	8.6	87.4
CS-20 (unreduced)	5	80.1	11.7	18.0	70.3
CS-20 (reduced)	6	100.0	0.0	0.0	100.0
CS-20 (with H_2O)	7	91.7	8.9	17.0	74.1
CS-20 (anhydrous)	8	89.4	0.0	4.0	96.0
CSG-20 (reduced)[a]	9	72.8	3.2	4.8	92.0

Reaction conditions: Oxime = 1 mmol, catalyst weight = 25 mg, temperature = 100 °C, pressure = 1 atm, time = 3 h

[a] 20 wt% Cu/Silicagel

experiment 1 mmol of water was added to the reaction mixture, i.e., benzaldoxime: water = 1:1, wherein, both the conversion and the selectivity have been decreased, but not so significantly. However, the activity of the catalyst is lower compared to run 6, Table 2. In the second experiment the molecular sieves were added to scavenge the water that produced due to dehydration of oxime into nitrile. In the conversion point of view, the influence of water is not so significant, whereas, the selectivity of amide decreased considerably in the presence of water, in its absence the selectivity is 96% (Table 2, run 8), which is close to 100% as in run 6, Table 2. While conducting the experiment using the reduced CS-20 catalyst, N_2 gas was used to prevent the oxidation of Cu metal, where both the conversion and the selectivity were almost 100% (Table 2 run 6), which reveals that the transformation of benzaldehyde into benzamide is expected to takes place via benzaldoxime rather than benzoic acid. The conversion of alcohols and aldehydes into amides via oximes has recently been reported [5, 34] using iridium and palladium catalysts.

To attest role of mesopores in the conversion of benzaldoxime to benzamide calcined silicagel (184 m^2/g BET surface area) supported copper (20 wt%) catalyst was prepared by impregnation similar to that of CS-20 catalyst. The surface area of CSG-20 is 155 m^2/g. By using this catalyst the activity was determined and the data was depicted in Table 2, which implies that the porosity of the support plays a prominent role in the conversion of benzaldoxime and benzamide selectivity.

In general water present in the reaction mixture, inhibit the process of dehydration of aldoximes to benzonitrile to a greater extent. Unavailability of water in the reaction mixture ceases at the stage of benzonitrile, its further transformation into benzamide does not occur. The present study elucidate that the influence of water on the activity is negligible.

SBA-15 supported Cu metal catalysts with various Cu loadings were studied to verify the influence of support and the effect of Cu loading on the SBA-15 support for the rearrangement of benzaldoxime, and the results obtained are depicted in Fig. 3, which implies that Cu is capable of catalyzing benzaldoxime into benzamide in a single step even at a low loadings of Cu, i.e., CS-1. When the loading of Cu increased from 1 to 2.5%, there is a significant increment both in conversion and selectivity (Fig. 3). At and above 5% Cu loading catalysts, the conversion attained almost 100%. When CS-20 is used as a catalyst complete transformation of benzaldoxime into benzamide occurred.

To understand the nature of reaction, different experiments were conducted using CS-20 as a catalyst by varying the period of reaction time keeping the other reaction conditions constant and the data obtained were presented as Fig. 4. When the reaction was conducted for a period of 10 min, three different products (benzamide, benzonitrile and benzaldehyde) were formed. It seems that the isomerization of benzaldoxime proceeds through benzonitrile and benzaldehyde intermediates. To confirm this observation, different experiments were conducted for a period of 20, 60 and 120 min. With increase in reaction time, both the conversion of benzaldoxime and the selectivity of benzamide were enhanced. When the reaction was conducted for 180 min, both the conversion of benzaldoxime and the selectivity of benzamide attained 100% (Fig. 4). The results reveal that at low loading catalysts and at low reaction timings the benzonitrile and benzaldehyde intermediates are more, which gradually converts into amide.

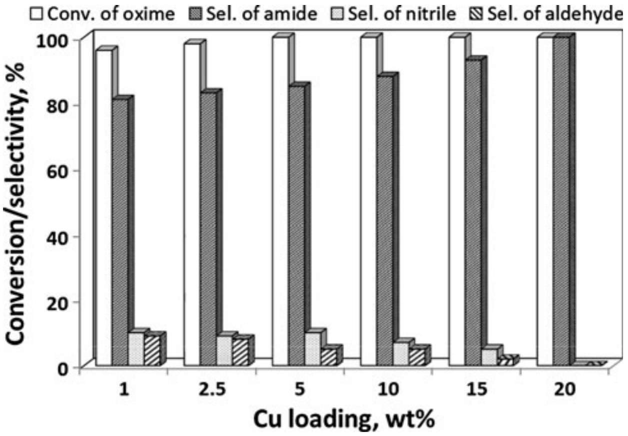


Fig. 3 Influence of Cu loading amount on SBA-15 for the transformation of benzaldoxime

The activity of CS-20 catalyst towards the rearrangement of benzaldoxime into benzamide has been investigated using 12.5, 25, 35 and 50 mg catalyst. When 12.5 mg catalyst is used the conversion of benzaldoxime is 96% with the benzamide selectivity of 79%. At and above 25 mg catalyst the conversion of benzaldoxime is nearly 100% with high selectivity of benzamide, which reveals that there are no considerable mass transport limitations.

Catalyst reusability is studied using CS-20 catalyst in 4 repeated cycles. The conversion of aldoximes over all the 4 cycles is nearly 100%, whereas the selectivity of benzamide decreased from cycle-1 to cycle-4. The reason for decrease in the selectivity of benzamide in repeated cycles is due to the presence of unconverted intermediate products like nitriles and aldehyde. In other words the catalyst lost some of its activity towards the conversion of intermediate products (nitrile and aldehyde) into desired benzamide product due to partial oxidation of Cu metal into CuO_x from cycle-1 to cycle-2 etc. Omission of reduction step in the subsequent cycles leads to deactivation of the catalyst. No deactivation of the catalyst is observed when the catalyst is subjected to reduction in each repeated cycle.

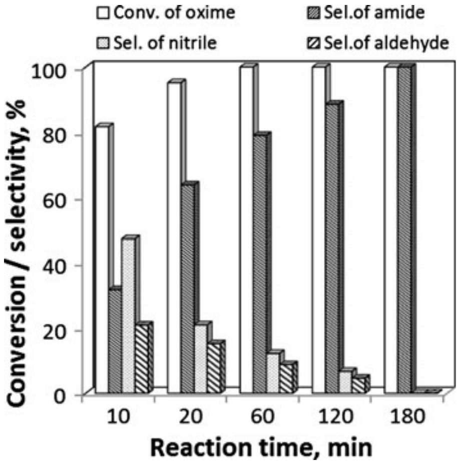
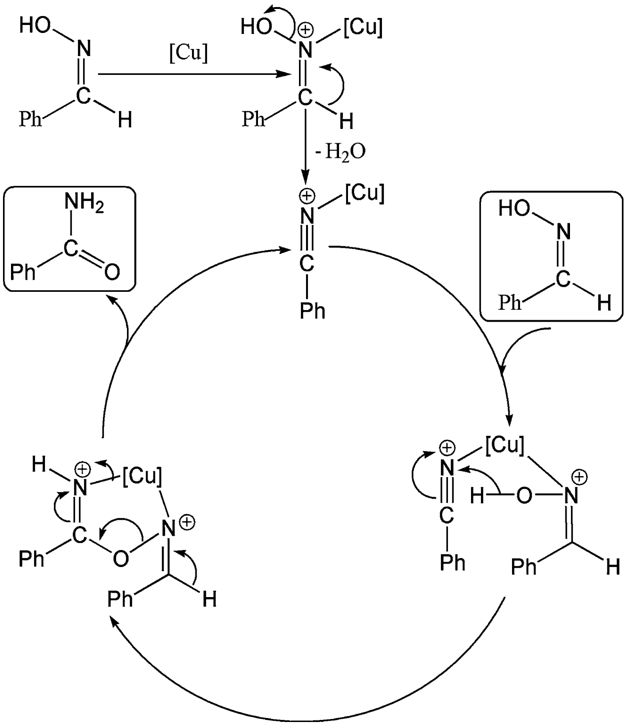


Fig. 4 Effect of reaction time on the catalytic activity of CS-X catalysts



Scheme 1 The proposed mechanism of benzaldoxime into benzamide over CS-X catalysts

If the rearrangement of benzaldoxime into benzamide proceeds through conventional Beckmann rearrangement, addition of acids is mandatory and furthermore selective formation of benzamide limits through the formation of nitrile intermediate. Recently, it is reported that Cu^{2+} salts are capable of catalyzing aldehydes into amides, wherein the presence of water is compulsory for driving the benzonitrile intermediate into benzamide. In another report, Cu^{2+} salts are used as catalysts for the rearrangement of oximes into amide, wherein certain amount of unconverted nitrile intermediate is present in the product mixture [11]. In the present study, conversion and selectivity are nearly 100% over CS-20 catalyst. The present study implies that the reaction is occurring through metal catalyzed approach similar that of late transition metal catalyzed process rather than the conventional Beckmann rearrangement. Based on our catalytic results and literary reports a mechanism is proposed (Scheme 1). In the proposed mechanism, benzonitrile transforms into benzamide by abstracting the required water molecule from the benzaldoxime leaving a new benzonitrile intermediate, there by maximizing the selectivity of benzamide.

4 Conclusions

CS-X is a highly efficient catalyst for the rearrangement of benzaldoxime into benzamide selectively in the liquid phase even in the absence of any acid or solvent. Isolated distribution of Cu species on the surface of SBA-15 support, minimized diffusion limitations and rearrangement through metal catalyzed transformation may be responsible for the superior activity of this catalyst. CS-X is a first example of inexpensive, highly efficient and eco-friendly heterogeneous catalyst.

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References

1. Humphrey JM, Chamberlin AR (1997) Chem Rev 97:2243
2. Beckmann E (1886) Ber Dtsch Chem Ges 19:988
3. Smith MB, March J (2001) Adv Org Chem, 5th edn. Wiley, New York, p 1415
4. Owston NA, Parker AJ, Williams JMJ (2007) Org Lett 9:3599
5. Owston NA, Parker AJ, Williams JMJ (2007) Org Lett 9:73
6. Park S, Choi Y-a, Han H, Yang SH, Chang S (2003) Chem Commun 1936
7. Kim M, Lee J, Lee H-Y, Chang S (2009) Adv Syn Catal 351:1807
8. Lee J, Kim M, Chang S, Lee H-Y (2009) Org Lett 11:5598
9. Ramon RS, Bosson J, Diez-Gonzalez S, Marion N, Nolan SP (2010) J Org Chem 75:1197
10. Fujiwara H, Ogasawara H, Yamaguchi K, Mizuno N (2007) Angew Chem Int Ed 46:5202
11. Sharma SK, Bishopp SD, Allen CL, Lawrence R Bamford MJ, Lapkin AA, Plucinski P, Watson RJ, Williams JMJ (2011) Tet Lett 52:4252
12. Zhao D, Feng J, Huo Q, Melossh N, Fredrickson GH, Chmelka BF, Stucky GD (1998) Science 279:548
13. Zhao D, Huo Q, Feng J, Chmelka BF, Stucky GD (1998) J Am Chem Soc 120:6024
14. Rioux RM, Song H, Hoefelmeyer JD, Yang P, Somorjai GA (2005) J Phys Chem 109:2192
15. Sun J, Ma D, Zhang H, Liu X, Han X, Bao X, Weinberg G, Pfander N, Su D (2006) J Am Chem Soc 128:15756

16. Lopes I, Hassan NE, Guerba H, Wallez G, Davidson A (2006) Chem Mater 18:5826
17. Segura Y, Cool P, Kustrowski P, Chmielarz L, Dziembaj R, Vansant EF (2005) J Phys Chem B 109:12071
18. Yang C-M, Liu P-H, Ho Y-F, Chiu C-Y, Chao K-J (2003) Chem Mater 15:275
19. Feng X, Yan M, Zhang T, Liu Y, Bao M (2010) Green Chem 12:1758
20. Zhao M, Church TL, Harris AT (2011) Appl Catal B 101:522
21. Wang H, Liu C-J (2011) Appl Catal B 106:672
22. Palcheva R, Spojakina A, Dimitrov L, Jiratovac K (2009) Microporous Mesoporous Mater 122:128
23. Burri DR, Choi K-M, Lee J-H, Han D-S, Park S-E (2007) Catal Commun 8:43
24. Burri DR, Shaikh IR, Choi K-M, Park S-E (2007) Catal Commun 8:731
25. Burri DR, Jun K-W, Kim Y-H, Kim JM, Park S-E, Yoo JS (2002) Chem Lett 212
26. Reddy SS, Burri DR, Kumar SV, Padmasri AH, Narayanan S, Rama Rao KS (2007) Catal Commun 8:261
27. Anand N, Reddy KHP, Swapna V, Rama Rao KS, Burri DR (2011) Microporous Mesoporous Mater 143:132
28. Sing KSW, Everett DH, Haul RAW, Moscou L, Pierotti RA, Rouquerol J, Siemieniewska T (1985) Pure Appl Chem 57:603
29. Khristova M, Ivanov B, Spassova I, Spassov T (2007) Catal Lett 119:79
30. Diaz G, Perez-Hernandez R, Gomez-Cortes A, Benaissa M, Mariscal R, Fierro JLG (1999) J Catal 187:1
31. Sarkany J, Itri JLD, Sachtler WMH (1992) Catal Lett 16:241
32. Wan Y, Ma J, Wang Z, Zhou W, Kaliaguine S (2004) J Catal 227:242
33. Patel A, Rufford TE, Rudolph V, Zhu Z (2011) Catal Today 166:188
34. Ali MA, Punniyamurthy T (2010) Adv Synth Catal 352:288