



Synthesis, Spectroscopic Studies and Applications of CuNPs/SBA-15 Catalysts

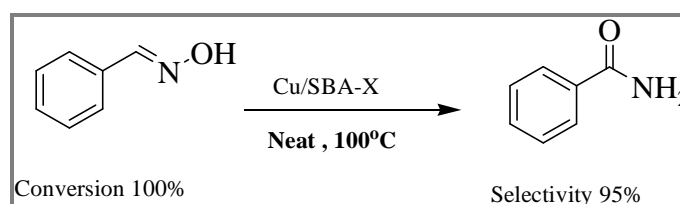
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ABSTRACT

CuNPs/SBA-15 catalysts have been synthesized using functionalized SBA-15 (SBA-NH₂, SBA-COOH) as support, copper acetate as a Cu precursor and characterized by XRD, N₂-adsorption-desorption isotherms and FT-IR techniques. These catalysts are found to be highly active and selective for the Beckmann rearrangement of benzaldoxime into benzamide under solvent-free and acid-free conditions.

Graphical Abstract



Highlights

- Compare to SBA-15 and SBA-NH₂ supported copper catalysts SBA-COOH supported copper catalysts shows superior catalytic activity in the rearrangement of benzaldoxime into benzamide.
- High surface area is the reason for its high catalytic activity

Keywords: CuNPs/SBA-15, Beckmann Rearrangement, Benzaldoxime, Benzamide.

INTRODUCTION

The isomerisation of oximes to amides (Beckmann rearrangement) is one of the most straightforward synthetic routes for the production of amides [1]. Generally, amides are ultimate precursors for the production of a variety of natural products and drug intermediates [2]. Important drug molecules containing amide group includes, Atorvastatin and Valsartan, are used as an angiotensin-receptor

blocker (ARB) that may be used to treat a variety of cardiac conditions including hypertension, diabetic nephropathy and heart failure. Beckmann rearrangement (BR) usually requires high reaction temperature and strong acidic and dehydrating media [3, 4]. So far used catalysts for the rearrangement of aldoximes to amides are Ruthenium, Iridium and Rhodium metal complexes [5-9]. Au/Ag co catalytic system has also been studied for the titled reaction [10]. But these are all very expensive catalysts. In view of green chemistry requirements, more environmental benign catalysts are required. Copper based catalysts are found to be effective for the rearrangement of aldoximes to amides [11]. Aiming in the investigation of eco-friendly and cheap catalysts, we have designed a Cu/SBA-15 catalytic system for the rearrangement of aldoximes into amides in acid and solvent free condition [12]. In continuation to our previous work, herein, we have designed and developed a new Cu based catalyst with organically functionalised SBA-15. These prepared catalysts shown superior catalytic activity in the conversion of benzaldoxime into benzamide in solvent and acid free conditions.

MATERIALS AND METHODS

The X-ray diffraction (XRD) patterns were recorded at room temperature using an X-ray diffractometer (Multiflex, M/s. Rigaku, Japan) with nickel filtered $\text{CuK}\alpha$ radiation. N_2 adsorption-desorption isotherms were recorded on a N_2 adsorption unit at -196°C (Quadrusorb-SI V 5.06, M/s. Quantachrome Instruments Corporation, USA). The samples were out-gassed at 200°C for 4 h before the measurement [13]. Rh contents of the sample were analysed with a simultaneous ICP-AES allied analytical system (Perkin Elmer 3100XL). The FT-IR spectra of the materials were recorded on a Perkin-Elmer FT-IR spectrometer under ambient conditions using KBr discs with a nominal resolution of 4 cm^{-1} and averaging 5 spectra.

RESULTS AND DISCUSSION

Catalyst Characterization

Low angle XRD patterns: To assess the structural integrity of the catalysts, small-angle XRD patterns of SBA-15 and modified SBA-15 catalysts were recorded and the resultant patterns are shown in figure 1. The parent SBA-15 and modified SBA-15 catalysts exhibited well-resolved peaks with a sharp peak at around 0.95° and two weak peaks at about 1.55° and 1.8° . The position of diffraction peaks are well matched with the reported XRD patterns of SBA-15.

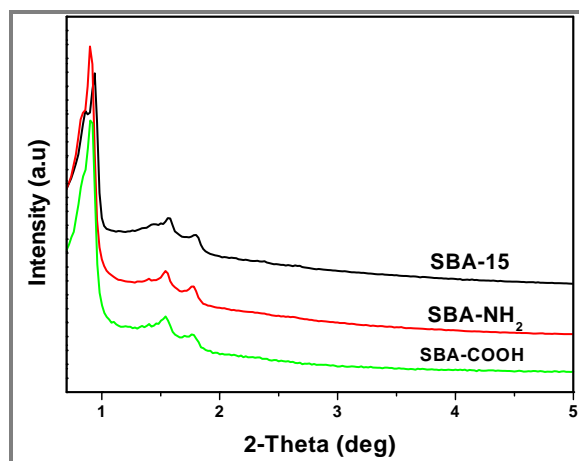


Figure 1. Low angle XRD patterns of SBA-15, SBA-NH₂ and SBA-COOH catalysts.

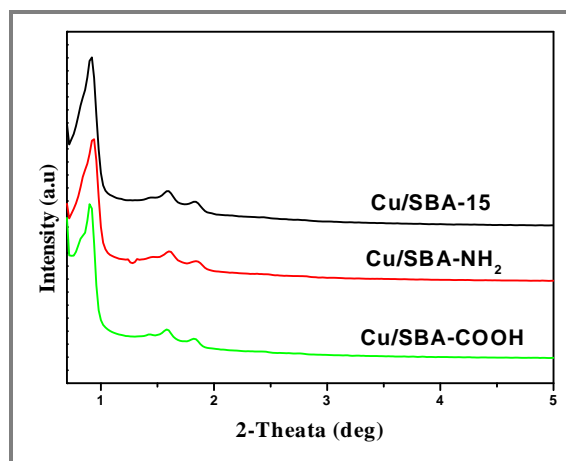


Figure 2. Low angle XRD patterns of Cu/SBA-15, Cu/SBA-NH₂ and Cu/SBA-COOH catalysts.

Low angle XRD patterns of Cu/SBA-X (X=15, NH₂, COOH) catalysts are shown in figure 2. Similar to that of parent silica SBA-15 the modified SBA-15 supported copper catalysts also exhibited

three diffraction peaks positioned at $0.91\text{--}0.96^\circ$, $1.52\text{--}1.65^\circ$, and $1.7\text{--}1.82^\circ$ on the 2Θ scale, revealing that the retention of mesoporous structural ordering.

Wide angle XRD patterns: The Cu/SBA-X catalysts were characterized by wide-angle XRD to determine the crystalline behaviour of the catalysts. The XRD patterns are displayed in figure 3. Pointed out in all cases the presence of the SBA-15 reflection peaks at $2\Theta = 21.5\text{--}21.9^\circ$.

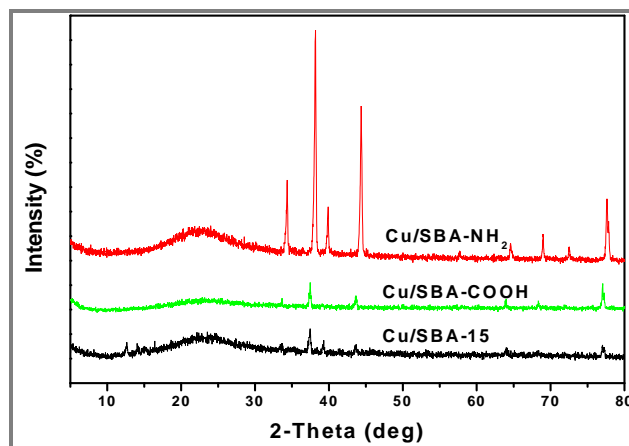


Figure 3. Wide angle XRD patterns of Cu/SBA-15, Cu/SBA-NH₂ And Cu/SBA-COOH catalysts.

N₂ adsorption-desorption-desorption isotherms: The nitrogen adsorption-desorption isotherms of pure SBA-15 and its modified catalysts were found to be Type IV isotherms in nature and exhibited a H1 hysteresis loop, which implies the mesoporous nature of the solid samples. This is a characteristic of capillary condensation within uniform pores.

The N₂ adsorption-desorption isotherms of parent SBA-15 and Cu/SBA-15 catalysts generated at -196°C are displayed in figure 4. The isotherms of catalysts are clear type IV isotherms with H1 hysteresis loops corresponding to the filling of uniform mesopores with open cylindrical geometry.

Catalyst	$S_{\text{BET}}^{\text{a}}$ (m ² /g)	V_{t}^{b} (cm ³ /g)	$D_{\text{BJH}}^{\text{c}}$ (nm)	d_{100}^{d} (nm)	a_0^{e} (nm)	t^{f} (nm)
SBA-15	881.213	1.445	6.43	9.35	10.87	4.44
Cu/SBA-15	651.19	1.11	6.51	9.09	11.22	4.71

a BET surface area, b total pore volume, c BJH pore diameter, d periodicity of SBA-15 derived from low angle XRD, e unit cell length ($a_0 = 2d_{100}/\sqrt{3}$), f pore wall thickness ($t = a_0 - D$).

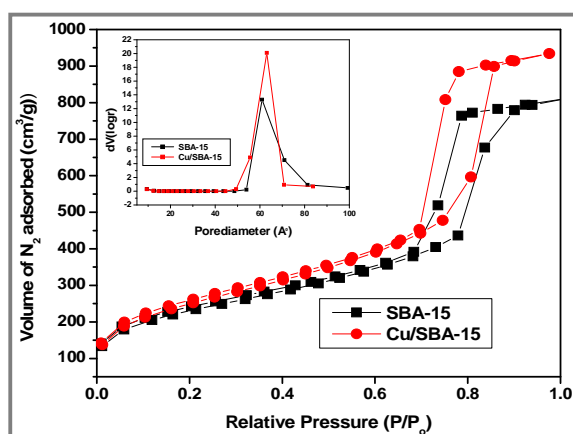


Figure 4. N₂ adsorption-desorption isotherms of SBA-15 and Cu/SBA-15 catalysts.

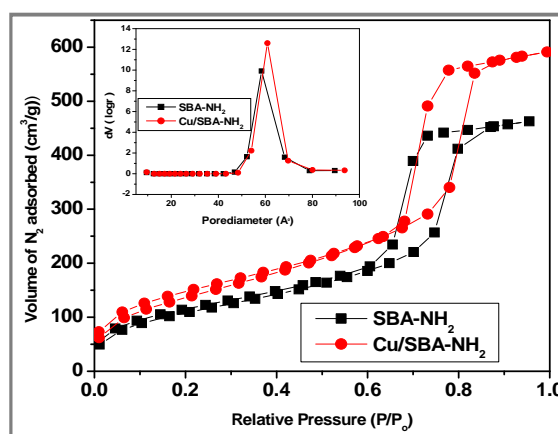


Figure 5. N₂ adsorption-desorption isotherms of SBA-NH₂ and Cu/SBA-NH₂ catalysts.

The N₂ adsorption-desorption isotherms of SBA-NH₂ and Cu/SBA-NH₂ catalysts generated at -196°C are displayed in figure. 5. The isotherms of catalysts are clear type IV isotherms with H1 hysteresis loops corresponding to the filling of uniform mesopores with open cylindrical geometry.

Catalyst	S _{BET} ^a (m ² /g)	V _t ^b (cm ³ /g)	D _{BJH} ^c (nm)	d ₁₀₀ ^d (nm)	a ₀ ^e (nm)	t ^f (nm)
SBA-NH ₂	504.806	0.914	5.62	9.86	11.38	5.76
Cu/SBA-NH ₂	324.5	0.589	3.25	9.28	10.99	7.74

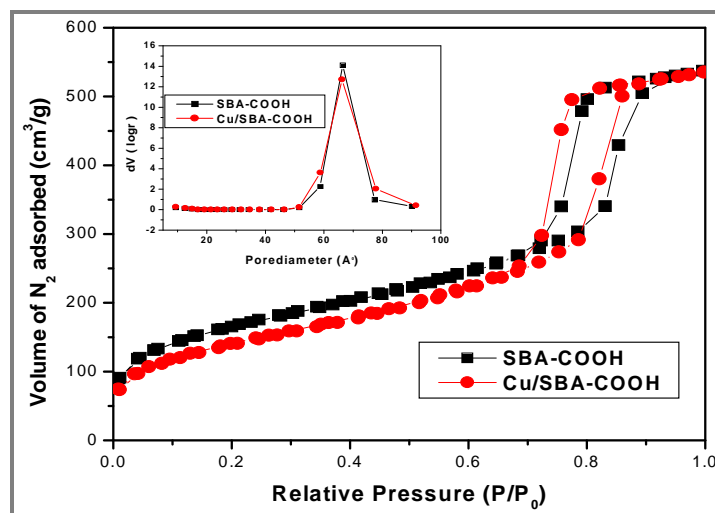


Figure 6. N₂ adsorption-desorption isotherms of SBA-COOH and Cu/SBA-COOH catalysts.

The N₂ adsorption-desorption isotherms of SBA-COOH and Cu/SBA-COOH catalysts generated at -196°C are displayed in figure 6. The isotherms of catalysts are clear type IV isotherms with H1 hysteresis loops corresponding to the filling of uniform mesopores with open cylindrical geometry

Catalyst	S _{BET} ^a (m ² /g)	V _t ^b (cm ³ /g)	D _{BJH} ^c (nm)	d ₁₀₀ ^d (nm)	a ₀ ^e (nm)	t ^f (nm)
SBA-COOH	577.25	0.831	6.45	9.17	10.59	2.51
Cu/SBA-COOH	490.83	0.828	6.391	9.00	11.33	4.939

In all the cases we observed there is a gradual decrease in surface area and total pore volume after modification of SBA-15 with different functional groups and also in copper modified catalysts. As shown in above tables, no substantial variation in the structural parameters like d spacing, unit cell length and pore wall thickness, implies the retention of parent SBA-15 mesophase structure in all the catalysts.

FT-IR Spectra: FT-IR spectrums of SBA-15, amine and acid modified SBA-15 were displayed in figure 7. A broad band observed in between 3437-3369 cm⁻¹ in all the samples, which indicates typically -OH stretching vibration, the band at 1634.6 cm⁻¹ in SBA-15 and modified SBA-15 samples due to -OH deformation band, the sharp band around 967 cm⁻¹ is associated with Si-OH and the band at 3129 cm⁻¹ in SBA-NH₂ is due to -NH₂ stretching vibration, which is in hydrogen bonding with -OH groups. The band at 1417 cm⁻¹ is corresponds to NH stretching vibration in propyl amine. The peak at 1730.6 cm⁻¹ is due to C=O stretching frequency of carboxylic group.

Catalytic activity: The catalytic activity of Cu/SBA-X (X= 15, NH₂ and COOH) catalysts for the transformation of benzaldoxime into benzamide through Beckmann rearrangement (BR) under solvent free conditions has been conducted in the liquid phase at atmospheric pressure. The transformation of benzaldoxime into benzamide is shown schematically represented in scheme 1.

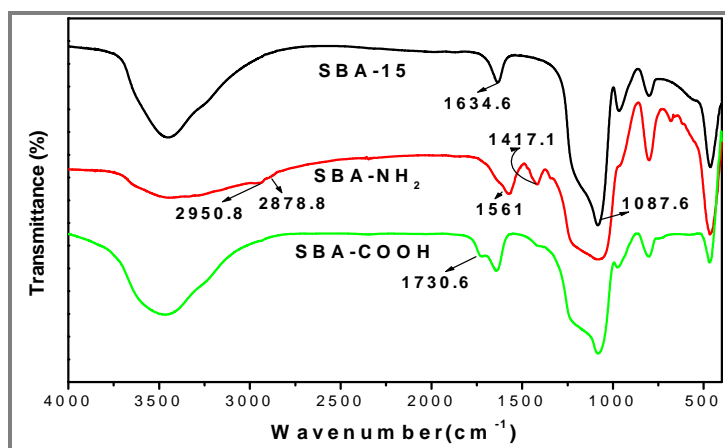
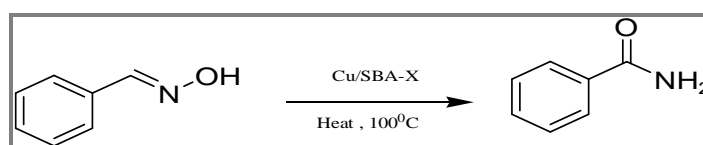


Figure 7. FT-IR spectra of SBA-15, SBA-NH₂ and SBA-COOH.



Scheme 1. Transformation of benzaldoxime into benzamide over Cu/SBA-X catalysts.

The use of supports like SBA-15, SBA-NH₂ and SBA-COOH gave essentially no benzamide formation in the reaction system, confirming as expected the need of a metal to perform the rearrangement reaction.

Table 1. Transformation of benzaldoxime on different catalysts

S. No.	Catalyst	%Conv. of benzaldoxime	%Sel. of benzonitrile	%Sel. Of benzaldehyde	%Sel. of benzamide
1	No catalyst	3.9	0.0	100.0	0.0
2	SBA-15	24.1	19.9	80.1	0.0
3	SBA-NH ₂	25.5	73.84	7.68	18.31
4	SBA-COOH	23.2	96.51	3.49	0

Reaction conditions: Oxime = 1 mmol, catalyst = 25 mg, temperature = 100°C, pressure = 1atm, time = 6 h

The effect of modified SBA-15 supported copper catalysts on the rearrangement of benzaldoxime to benzamide was studied and the results were depicted in figure 8.

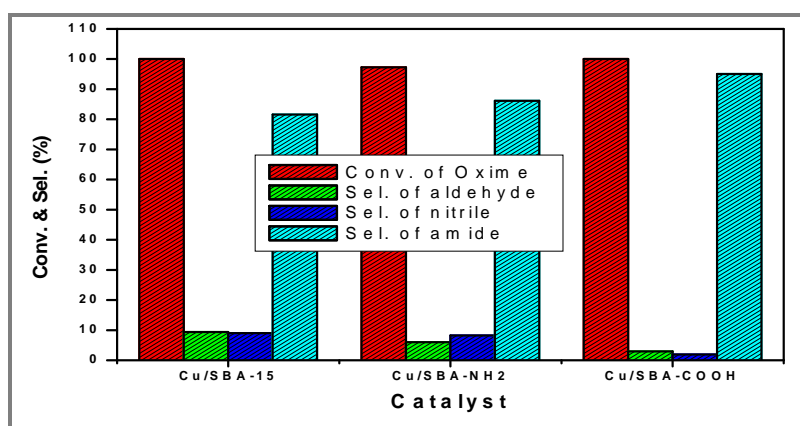


Figure 8. Transformation of benzaldoxime into benzamide with different catalysts.

The effect of acid-base functional groups attached to SBA-15 supported copper catalysts in the rearrangement of benzaldoxime to benzamide under solvent free conditions has been studied. In all the catalysts the conversion of benzaldoxime is almost 100% but selectivity to benzamide is varied with functional group. The conversion of benzaldoxime with Cu/SBA-15 is 100% and the selectivity to benzamide is 81.6%, the selectivities of aldehyde and nitrile is around 9%. With Cu/SBA-NH₂ catalyst, 97.29% conversion of oxime and 86.16% selectivity to benzamide is observed. In case of Cu/SBA-COOH catalyst it is observed a remarkable catalytic activity, in which 100% conversion of oxime and 95.1% selectivity to amide are obtained.

APPLICATION

A variety of amides can be synthesized by using this method with Cu catalysts under solvent and acid free conditions.

CONCLUSION

Compare to SBA-15 and SBA-NH₂ supported copper catalysts SBA-COOH supported copper catalysts shows superior catalytic activity in the rearrangement of benzaldoxime into benzamide. The high catalytic activity of Cu/SBA-COOH catalyst compare with other copper catalysts is may be because of its high surface area.

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