Red Brick Waste-Derived Cu/RBW Catalyst: A Sustainable Catalyst for Beckmann Rearrangement of Benzaldoxime to Benzamide

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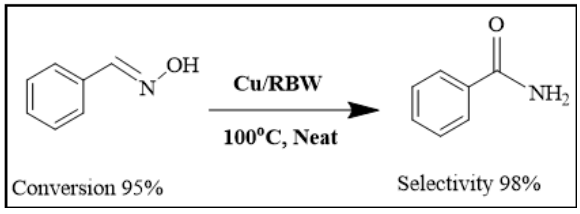
***Abstract*—A novel, green, and cost-effective Cu-based catalyst has been synthesized using red brick waste (RBW) as a support for the first time. The Cu/RBW catalysts were prepared via a facile wet impregnation method with varying Cu loadings (5-20 wt%). The catalysts were characterized using X-ray diffractometry, SEM-EDAX, and BET surface area analysis. The Cu/RBW catalysts demonstrated exceptional activity for the Beckmann rearrangement of benzaldoxime to benzamide under solvent-free conditions. Optimal results showed 95% oxime conversion and 98% amide selectivity, highlighting the potential of this sustainable catalyst for industrial applications.**



Graphical Abstract

***Index Terms*—Red Brick Waste, Copper, Benzaldoxime, Benzamide, Beckmannrearrangement.**

I. INTRODUCTION

Over the past three decades, unprecedented urbanization has swept through developing countries, including India, Russia, and Brazil. This rapid urbanization has resulted in the massive generation of brick waste, driven by the demolition of existing structures and the construction of new ones. The sheer scale of demolition waste, accounting for 30-40% of total municipal waste, has become a pressing environmental concern [1]. The unsustainable consumption of natural resources and the accumulation of waste have created immense pressure on authorities to adopt sustainable waste management practices [2]. Red brick dust, a highly siliceous waste material, is abundantly available near brick kilns and at construction demolition sites [3]. However, improper handling and inhalation of this dust can lead to serious health issues, including silicosis. Therefore, it is essential to explore safe and sustainable disposal methods for red brick dust, minimizing its environmental and health impacts [4]. Numerous studies have reported that incorporating red brick waste as an additive in concrete enhances its strength and durability. Additionally, red brick waste has also been explored as a potential catalyst in various chemical reactions, demonstrating its versatility and value as a recycled material [5, 6].

Waste from natural bricks is abundant and has excellent catalytic properties. Researchers can look into its catalytic potential for useful organic conversions. Brick debris contains silica (SiO_2), hematite (Fe_2O_3), and a trace amount of alumina (Al_2O_3). The chemical composition of brick debris varies depending on its color, origin, raw materials, and other attributes. The red brick waste powder was used to make red ornamental plaster for walls that was based on cement [7].

For a variety of uses, it is imperative to create highly selective, effective, affordable, and environmentally safe brick waste materials. This low-cost, environmentally friendly powder made from brick debris is perfect for supporting catalysts. For numerous chemical reaction changes, the red brick powder demonstrated exceptional catalytic activity. With good yields, RBW was utilized to selectively dehydrate 1,4-butanediol and cyclohexanol [8, 9]. Iron and Zinc supported brick grain nanocomposites have been reported as catalysts for photocatalytic oxidative

degradation of malachite green and Congo red dyes [10, 11]. The removal of heavy metals from industrial, agricultural, and other wastes has received a lot of interest. Numerous writers have made use of natural adsorbents such as activated carbon prepared from activated clay [12], agricultural solid waste [13], peanut hull [14] and fly ash [15].

The Beckmann Rearrangent is employed in both industrial and clinical settings and has a significant impact on the synthesis of organic compounds. A wide variety of pharmacological intermediates and natural compounds can be synthesized from amides as potential precursor [16]. The metal-catalyzed approach for the rearrangement of aldoxime into primary amides is a valuable transformation in organic synthesis. By involving the sequential dehydration and hydration via nitrile intermediate formation, this method offers substantial improvement over traditional methods [17, 18]. Copper based catalysts are proved to be best catalysts for the conversion of oximes to amides. Saidulu Ganji et.al reported the efficient conversion of benzaldoxime into benzamide over Cu/SBA-15 catalysts [19]. Herein, we report the synthesis, characterization of green and cost-effective Cu/BW catalysts for the conversion of benzaldoxime into benzamide.

II. EXPERIMENTAL

Preparation of Catalyst

All the reagents and chemicals were obtained commercially and used without further purification. Red brick waste was collected from demolished field. Brick puddles crushed into fine powder in mortar and dried. The brick powder was used as support to prepare the series of Cu/RBW catalysts. Aqueous solutions of Cu $(NO_3)_2 \cdot 3H_2O$ with copper metal contents of approximately 5, 10, 15, and 20 wt% were used for impregnation. The resulting catalyst samples were then dried at 100°C for 12 hours, followed by calcination at 450°C for 6 hours. Before conducting activity tests and characterization, the catalysts were pretreated by reduction at 280°C for 3 hours in a hydrogen gas flow using a fixed-bed reactor. After reduction, the catalysts were cooled to ambient temperature under a nitrogen flow. The catalysts were designated as CBW-X (%), where X represents the copper loading percentage.

Catalyst characterization

The X-ray powder diffraction (M/S. Rigaku Corporation, Japan) patterns were recorded at room temperature with a scanning step of 0.02° using Ni filtered Cu Kα radiation of wavelength λ=1.5406 Å at power of 40kW and current of 100 mA and with scan speed of 6° min^{-1} in the 2θ range of 5-80°. Textural features of reduced catalysts were recorded by N_2 adsorption-desorption at liquid nitrogen temperature on a Quadrasorb SI system (M/s. Quantachrome Instruments, USA). BJH method was applied to calculate pore-size distribution considering the desorption branch of the isotherms. The pore volume was taken at a relative pressure P/Po = 0.989 (single point). Scanning Electron microscopy analysis of reduced catalysts were recorded by using (M/s. JEOL, Switzerland). FT-IR patterns were recorded on a spectrum GX spectrometer (M/s. Perkin Elmer, Germany) in the scan range of 4000-400 cm^{-1}.

Catalytic Evaluation Tests

In a typical experiment, 25 mg of Cu/RBW catalyst and 1 mmol of benzaldoxime are taken in a round bottom flask and stirred under solvent and acid free conditions at 100 °C. The product analysis was made using a gas chromatograph (GC-17A, M/s. Shimadzu Instruments, Japan) with an OV-1 capillary column (0.53 mm 30 m). The products were identified using a GC-MS (QP-5050 model, M/s. Shimadzu Instruments, Japan) equipped with a DB-5 capillary column (0.32 mm dia. and 25 m long, M/s. J & W Scientific, USA).

III. RESULTS AND DISCUSSION

X-ray diffraction (XRD) is a powerful technique used to analyse the crystalline structure of CBW catalysts. The XRD patterns are shown in Fig. 1. The stronger diffraction peak at 2θ values 43.44° and two more intense diffraction peaks at 50.32° and 74.17° corresponds to the (111), (200) and (220) planes of metallic copper (JCPDS-04-0836) in all CBW catalysts. The XRD data indicates that the major diffraction peak of SiO_2 (Quartz mineral) is present in brick waste powder. It is also observed low intense peaks of hematite 2θ at 27.50° and alumina at 68.11°.

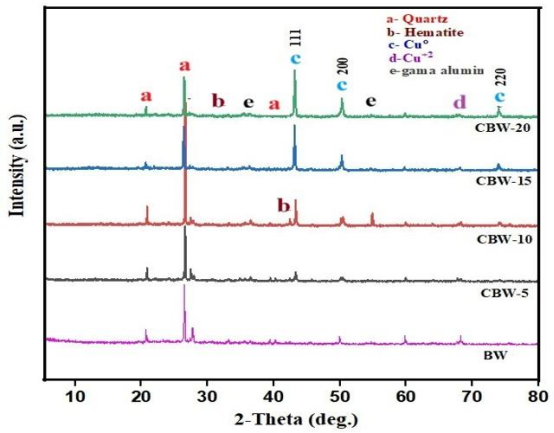


Fig. 1. Wide angle XRD patterns of CBW-X catalysts.

The FT-IR spectrum of CBW catalysts displayed various stretching and bending vibrations bands. The infrared spectra patterns are shown in Fig. 2 were recorded in the region of 4000-400 cm^{-2}. The Cu catalysts prominent broad bands at 3472 cm^{-1}, 3142 cm^{-1} and 1636 cm^{-1} which are due to the stretching and bending absorbance of -OH group of the absorbed water molecule. The peaks at 1066 cm^{-1} and 777 cm^{-1} associated with the stretching vibrations of bands of Si-O, whereas 450 cm^{-1} allied to the bending vibrations of Si-O-Si linkage [20]. These absorption peak indicates that the presence of silicon oxides in the brick waste.

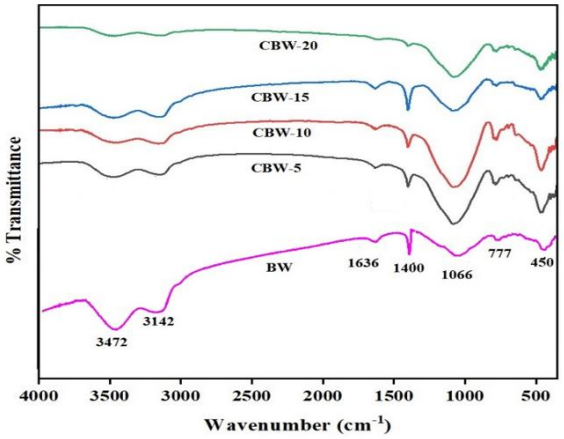


Fig. 2. FT-IR spectra of CBW-X catalysts.

The adsorption-desorption isotherms of series of catalysts shown in Fig. 3. The Brunauer-Emmette-Teller (BET) surface area of CBW catalysts was analysed by nitrogen adsorption-desorption isotherms showed hysteresis and Type-IV isotherms. The BET surface area of the brick waste powder was 5.923 m^2g^{-1}. The surface area of 5CBW, 10CBW,15CBW and 20CBW catalysts were 3.348m^2g^{-1}, 4.585, 4.293 and 3.623 respectively.

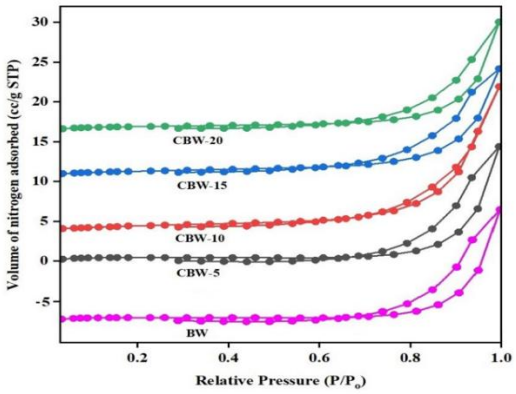


Fig. 3. N_2 adsorption-desorption isotherms.

Fig.4. presents a combination of Scanning Electron Microscope (SEM) micrographs and corresponding Energy Dispersive X-ray Spectroscopy (EDS or EDX) spectra. The SEM images reveal a rough, granular surface, likely composed of agglomerated particles. The EDS spectra show elemental peaks that suggest the presence of common elements such as carbon (C), oxygen (O), and possibly metals like silicon (Si), Aluminium (Al), and others.

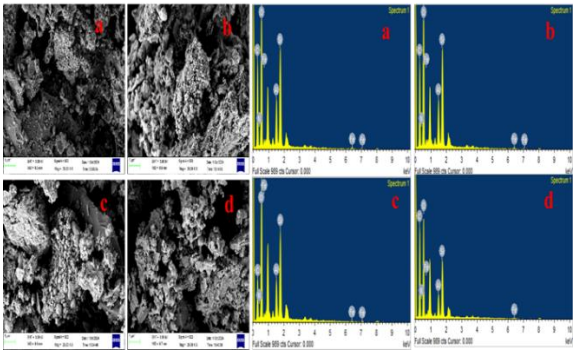


Fig. 4. SEM images of Cu/BW catalysts along with its EDS spectrum

Catalytic Activity

The catalytic behaviour of copper on red waste brick powder material is the inexpensive and environmentally benign process for the production of benzamides from benzaldoxime. The reaction did not occur without a catalyst, highlighting the importance of the metal in facilitating the conversion of benzaldoxime. RBW did not exhibit any catalytic

activity, indicating that the support material itself is not sufficient to promote the reaction. That the reaction progressed with CBW indicates the need for metal to perform the reaction. Four different catalysts are prepared with varying metal concentrations were tested for the conversion of benzaldoxime to benzamide under solvent and and acid free conditions. CBW-5 catalyst shows 63.75 benzaldoxime conversion and 89.1% selectivity to the targeted product benzamide. CBW-10 catalyst shows 94.59% conversion of the reactant and 98.09% selectivity to the product benzamide. With the increase in copper loading beyond 10 wt%, the conversion and selectivity are decreased. Among the series of catalysts, the CBW-10 catalyst has higher catalytic activity due to high surface area and its small crystalline size confirmed by XRD. The catalytic activity of the catalysts is shown in Fig.5.

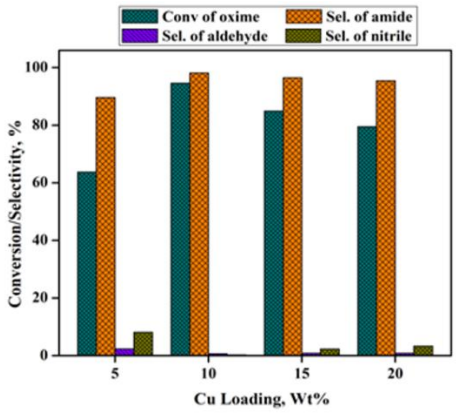


Fig. 5. Effect of Cu loading on BW for the transformation of benzaldoxime to benzamide Reaction Conditions: Benzaldoxime (1mmol), Catalyst (25 mg), 100°C, 3h.

IV. CONCLUSION

We have developed an efficient and environmentally benign Cu/RBW catalysts for the rearrangement reaction of benzaldoxime to benzamide. The green synthesis of amide using waste brick powder supported Cu catalysts was performed in liquid phase at atmospheric pressure under solvent free conditions. Among all the CBW catalysts, CBW-10 catalyst shows superior activity due to high surface area and smaller crystalline size. CBW is a first example for this inexpensive, cost-effective, highly efficient and eco-friendly heterogeneous catalysts.

ABBREVIATIONS AND NOTATIONS

RBW, Red Brick waste; CPW, copper on brick waste; 5CPW, 5 wt% copper on brick waste; 10CPW, 10 wt% copper on brick waste; 15CPW, 15 wt% copper on brick waste; 20CPW, 20 wt% copper on brick waste; XRD, X-Ray Difractometer; SEM-EDAX, Scanning Electron Microscopy-Electron Dispersive X-ray Analysis; BET surface area, Brunauer-Emmett-Teller surface area.

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