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Research Article

Waste Glass Tablets Cu(0)NP-Doped: An Easily Recyclable Catalyst for the Synthesis of Propargylamines and Nitrophenol Reduction

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ABSTRACT: The development of a greener, more efficient, and economically attractive synthetic methodology is one of the challenging tasks for the sustainable progress of organic synthesis. In recent years, considerable effort has been carried out in search of more sustainable catalysts that aims to minimize the generation of waste through the use of easily recyclable material. Glass waste is an accessible and abundant resource but suffers with challenges in the recycling and disposal process; therefore, its reuse as a support for the growth of metallic nanoparticles is extremely attractive from an environmental as well as economic point of view. Considering this, herein we report the synthesis and characterization of glass waste tablets used for the self-support of metallic copper nanoparticles. The synthetic utility of this new material was explored as a catalyst for the A^3 coupling reaction and access to biologically useful propargylamines as well as for the reduction of nitrophenol. Furthermore, due to the catalyst format, it was easily recovered using simple tweezers and reused without a significant loss of catalytic efficiency. In fact, the solvent-free approach, atom economy, ease of recycling, robustness, and efficiency make these tablets useful and environmentally suitable catalysts for A^3 coupling and the reduction of nitrophenols.

KEYWORDS: *glass catalyst, recyclable catalyst, heterogeneous catalysis, copper nanoparticles, multicomponent reactions, propargylamines, nitrophenol reduction*

■ INTRODUCTION

Propargylamines make up an important class of nitrogenous compounds with broad biological and synthetic applications. In organic synthesis, they are considered versatile building blocks and provide intermediates for access to important nitrogenous heterocycles,[1] such as pyrroles,[2] pyridines,[2] oxazoles,[3] isoxazoles,[4] thiazoles,[5] and imidazoles.[6] Furthermore, they are commonly found in pharmaceuticals that are of great relevance for the treatment of neurodegenerative diseases such as Parkinson's and Alzheimer's as they are considered selective and irreversible inhibitors of the enzyme monoamine oxidase-B.[7−10]

From a synthetic point of view, the three-component condensation reaction between aldehydes, amines, and alkynes, called A^3 coupling, represents an important alternative for accessing propargylamines as it allows the formation of multiple bonds via more economically accessible synthetic routes, with high efficiency and atomic economy.[11−13] For this, several transition metals such as Cu, Zn, Ni, Pd, Au, and Ag have been investigated as catalysts. Among them, copper catalysts stand out to be attractive ones due to their high catalytic efficiency and low cost.[14−22]

Though there are several interesting methodologies to access propargylamines, some of them suffer from complicated and environmentally harmful synthesis procedures, long reaction times, and dependence on toxic and carcinogenic solvents. Besides, the low recyclability of the catalyst is also a recurring limitation due to complex separation processes, leaching, and loss of mass and catalytic activity.[1,11] The aforementioned problems are recurrently found in catalysts proposed to be used in powder form or in unsupported nanoscale materials. Notwithstanding most of these catalysts are recovered by filtration, centrifugation, or magnetic processes,[1,23−28] reports on difficult manipulation are common, leading to partial loss of the catalyst or even to contamination of synthetic products. Not only can the support of the nanocatalysts be an alternative to the aforementioned drawbacks, but it can also maintain to

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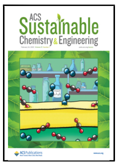

some extent the surface area for the reaction of nanoscale materials.

The limitations arising from these protocols become inconvenient for the reuse of the material, making it necessary to design heterogeneous catalysts that aim to minimize the drawbacks, i.e., make it easier to support and recover the catalyst. Taking this into consideration, an interesting alternative, still little explored in catalysis, is the development of catalysts supported by the sintering of the catalytic phase with glass, which incorporates the catalytic nanoparticles on the surface or in pores of the material, so that they are accessible for catalysis and at the same time show recovery without the need for centrifugation/filtration. A similar approach for catalyst support is the use of synthetic phosphate-based glasses, which allow the growth of nanoparticles when doped with metal oxides of interest that are self-supported by the growth process itself.[29−31] Silicate glasses, even those from waste, like phosphate-based glasses, can become catalysts when subjected to modification.[32] Glass waste that is widely found in city landfills can be a source of material for catalyst development. Waste silicate glass, despite its relative chemical stability, acts as an anchoring support and medium for the growth of catalyst nanoparticles.

Catalyst immobilization serves as an alternative to the disadvantages encountered in the recovery of unsupported nanoparticle catalysts. In this context, recently, Li and Xu (2021)[33] described the immobilization of metallic nanoparticles of Cu, Pd, Pt, and Rh by encapsulating powder catalysts in porous polyethylene tablets. These catalysts have been used in various hydrogenation reactions of alkenes, alkynes, nitro compounds, organo-azides, aldehydes, and ketones. The catalyst recovery showed that the polymer tablets can be easily recycled due to their format and reused without significant loss of catalytic activity in up to eight reaction cycles.[33] Additionally, Brandi et al.[34] developed an Ni catalyst supported on nitrogen-doped carbon in pellet format for application in aqueous phase hydrogenation reactions of glucose, xylose, and vanillin in a continuous flow system. Due to the format of the catalyst, it can be used in the proposed reactions for a period of 40 h of reaction in continuous flow, which can correspond to approximately 120 reaction cycles of reuse.

Therefore, tablets can offer several advantages over powder catalysts as they minimize inhalation and dispersion of powders and are inherently easy to handle for operation in industrial catalytic reactors due to their convenient shape. Furthermore, if the immobilization of metallic nanoparticles is efficient and resistant support materials are employed, then, mechanically robust catalysts can be obtained. Given this, the use of supported catalysts could overcome some limitations of finely divided catalysts, such as additional recovery steps, pressure drop in fixed-bed reactors, easy handling, among others.[35]

Considering this, the design of robust, easily recyclable, ecological, and economically accessible catalytic systems for catalytic applications becomes highly desirable. The use of nanostructured catalysts supported on greener, highly resistant materials with a low leaching rate is the most sought-after to meet this type of demand.[19,36,37] For this purpose, reused glasses can be considered an alternative to the aforementioned needs since the vitreous matrix allows the growth of metallic nanoparticles on its surface and, recently, they have been used as a support for the production of heterogeneous catalysts applied in various organic transformations.[38−41] It is important to note that waste glass is abundant and nontoxic. Furthermore, it is abundantly found in our daily lives as a major source of nonbiodegradable waste in the environment. The development of additional alternatives for the environmental reuse of glass waste is desirable.[42]

Thus, in connection with our interest in greener synthesis and sustainable catalysis,[43−45] here, we describe a simple, efficient, and ecological method for accessing propargylamines under solvent-free conditions. For this, the heterogeneous catalysis of the A^3 coupling reaction and the reduction of nitrophenol (NP) by copper nanoparticles self-supported on waste glass tablets (Cu(0)NPs@waste glass tablet) were successfully achieved. Nitro-based compounds such as nitrophenols are organic pollutants usually, due to their uses in the pesticide/pharmaceutical industry, encountered in industrial wastewater, albeit nitrophenols were reported in remote areas.[46] Among these compounds, 4-nitrophenol (4-NP) is extensively applied in developing noble and non-noble nano-based catalysts.[47−49] The reduction of 4-nitrophenol by $NaBH_4$ is considered a model reaction that occurs only in the presence of a catalyst, thermodynamically feasible notwithstanding. Thus, the interest in the 4-NP reduction is not only due to the industrial uses but also due toenvironmental concerns, which include the study and development of catalysts for its remediation.[49,50]

The growth of nanoparticles using waste glasses, silica based, is a challenging task for the scientific community, and literature is still scarce, being basically restricted to specific glass matrices, mainly phosphate based and heavy metal glasses, such as Pb.[51] Ordinary glasses, like commercial silica-based glasses, aim for stability to avoid reactions with food/liquids. Turning these materials into catalysts opens new areas and applications, and it is attractive from a sustainable point of view, principally using waste materials.

Considering this, herein, we report the synthesis of waste glass tablets doped with Cu(0)NPsd as new catalysts using commercial reagents and a support material from solid waste. Additionally, obtaining the supported catalyst does not use any solvent, requiring only thermal treatment. Furthermore, the growth of nanoparticles through the bottom-up process allowed the self-support and efficient immobilization of nanostructures uniformly, allowing the catalyst to be easily recovered and reused with the use of simple tweezers. In the past, we explored the use of a powdered form of the catalyst.[29−31] Though powdered material has its advantages, in terms of sustainability and robustness, processed tablets are superior as they are easily recoverable. Furthermore, besides the reduction of nitro to amine, we have also successfully demonstrated its application in A^3 coupling reaction, which is a benign and novel approach.

■ MATERIALS AND METHODS

Synthesis of Glass Tablets and Characterization. The glass tablets were synthesized by doping soda-lime glass waste powders (mean size of 58.4 μm (Figure S1)) with copper(I) oxide (Cu_2O) at the mass base (% w/w): 1, 2, or 3%. The tablets were molded using a stainless steel mold of 0.8 cm diameter with approximately 160 mg of a copper oxide/glass waste solid-state mixture. The tablets were obtained by thermal treatment of the mixture in a resistive furnace at 680 °C for 1 h with a heating rate of 15 °C/min to obtain sintered glass waste-based tablets. The metallic copper nanoparticles were obtained on the glass waste surface by annealing the sintered copper-

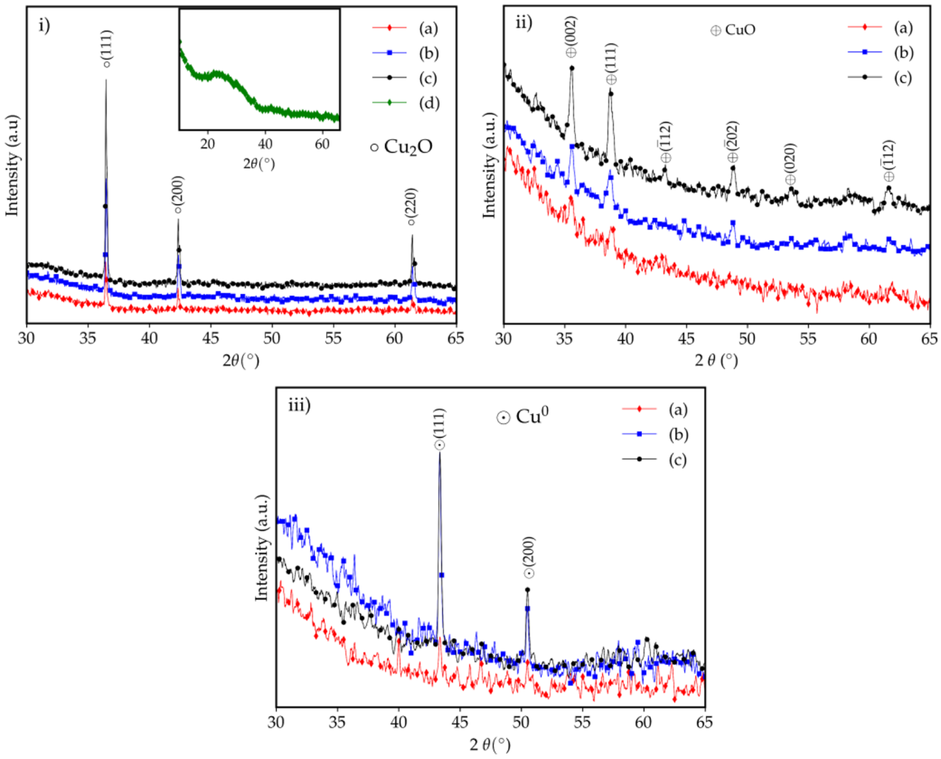

Figure 1. Powder X-ray analysis of the copper-doped waste glass-based catalyst: (i) mixture of waste glass powder and Cu_2O (without thermal treatment); (ii) after thermal treatment under an air atmosphere; (iii) after the heat treatment in reducing flow of H_2. The labels (a), (b), and (c) for each graph denote the addition of 1%, 2%, or 3% (w/w) of Cu_2O, respectively. The *y*-axis was shifted for better visualization.

doped tablets in a hydrogen gas (H_2) flow (150 mL/min) in a preheated tubular quartz furnace at 430 °C for 1 h. A schematic representation of the synthesis of catalysts is demonstrated in Figure S2.

The copper-based crystalline phases were assessed by X-ray diffraction (XRD) using CuKα radiation (λ = 1.5418 Å) between 30° and 65° (θ-2θ). The measurements were performed in reflection mode (Bragg−Brentano geometry) with the X-ray tube operating at 40 kV and 30 mA. The signal was collected using a 1D D/tex Ultra 250 detector mounted in a Rigaku Diffractometer model SmartLab SE. The LIBS measurements were performed using a J200 laser-induced breakdown spectrometer (Applied Spectra) with a laser operating at 30% of the maximum laser power (25 mJ) in collimated mode with a pulse duration of 6 ns. The detector consisted of six CCD spectrometers with a spectral window of 190−900 nm, and the delay time was set at 1.0 μs. The glass particle size distribution (PSD) of the waste was determined with an LA-960 Static Laser Scattering (SLS) particle analyzer from Horiba. The measurements were performed with a refractive index of 1.450 in dry mode with a red laser line and a vacuum in automatic mode.

The X-ray photoemission spectroscopy (XPS) measurements were performed using a Thermo K-Alpha XPS (Thermo Scientific) operating with a monochromatic X-ray source with an Al anode (Kα = 1486 eV). For survey spectra, 20 scans were obtained with a spot size of 300 μm, pass energy of 100.0 eV, energy step of 1.000 eV, and dwell time of 10 ms. For detailed spectra, 10 scans were accumulated using a spot size of 300 μm, pass energy of 50.0 eV, energy step of 0.10 eV, and dwell time of 50 ms.

General Procedure for the Preparation of Propargylamines. A tablet of copper nanoparticles self-supported on waste glass (3% Cu_2O (w/w) and mass = 0.16 g), aldehyde (0.50 mmol), amine (0.50 mmol), and acetylene (0.67 mmol) were placed in a test tube and stirred at 100 °C for the time indicated in Figure 4. The A^3 coupling reaction was monitored by thin layer chromatography (TLC) using an appropriate mixture of hexane and ethyl acetate as the eluent. After completion of the reaction, the organic compounds were extracted with ethyl acetate (3 × 5 mL) and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using gradients of hexane and ethyl acetate for elution. The identity and purity of the products were confirmed by ^{1}H NMR, ^{13}C NMR, and FT-IR, and all spectral data are in agreement with those reported in the literature (see the spectral data and all spectra in the Supporting Information).

Recyclability of the Catalyst. For the recyclability of the glass tablets containing self-supported nanoparticulate copper, after the completion of the reaction, the glass tablet was removed with metallic anatomical forceps, washed with ethyl acetate (3 × 5 mL), and then dried at room temperature for 24 h. The recovered tablet was reused in five subsequent A^3 coupling reactions under solvent-free conditions at 100 °C for 2.5 h.

Experimental 4-NP Catalytic Reduction. The evaluation of the catalyst in the reduction of 4-nitrophenol by sodium borohydride was carried out in a 100 mL jacketed reactor with constant stirring (200 rpm) using a C-MAG HS7 magnetic stirrer at 30 °C, controlled by a thermostatic bath TE-2005. A Femto 600plus spectrophotometer was used to measure the transmittance at 400 nm to monitor the reaction progress. The reaction was performed in a 0.2 cm path-length quartz cuvette with constant flow controlled by a Sci-Q300 series peristaltic pump from Watson-Marlow, operating at 8 rpm.

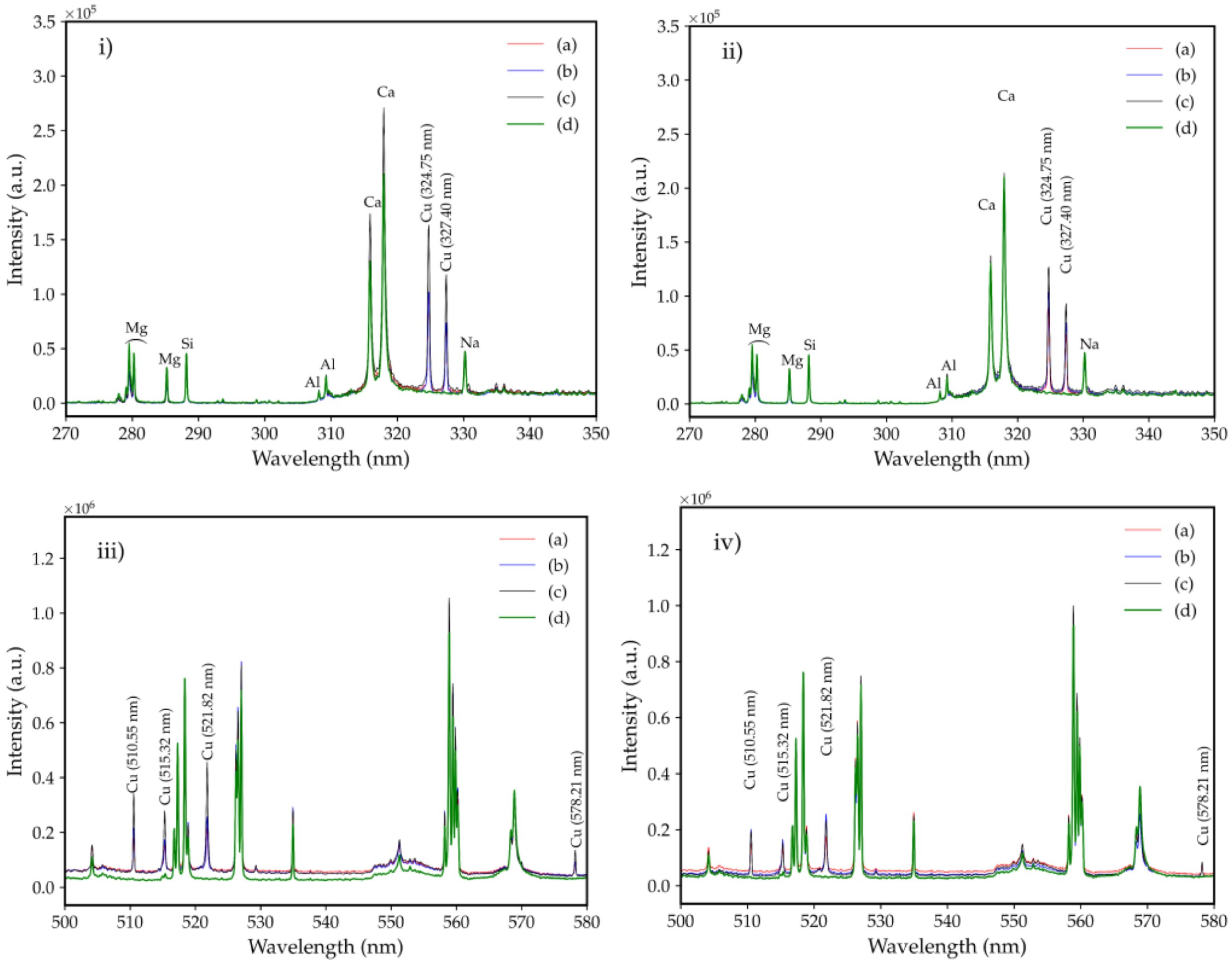

Figure 2. Laser-induced breakdown spectroscopy analysis for copper-doped soda-lime waste glass for selected regions 200−350 nm ((i) and (ii) before and after thermal treatment, respectively) and 500−570 nm ((iii) and (iv) before and after thermal treatment, respectively). The labels (a), (b), and (c) for each graph denote the addition of 1%, 2%, or 3% (w/w) of Cu_2O, respectively. The LIBS spectrum for soda-lime waste glass without the addition of copper (green line (d) at graphs (i), (ii), (iii), and (iv)) was added for comparison.

For the reactions, 5 mL of a 50 mM aqueous solution of 4-nitrophenol was mixed with 10 mL of a fresh solution of $NaBH_4$ (250 mM) and 35 mL of pH 10 water. The solution was pumped until a constant absorbance was achieved. After that, 317 mg of the copper-based glass waste catalyst was added. The catalyst reuse was performed three times with a simple tablet pinch, and the catalyst was washed with 30 mL of distilled water. The experiment with undoped glass was performed with glass waste tablets without copper, following the same procedure previously described.

RESULTS AND DISCUSSION

Characterization of Cu(0)NPs@Waste Glass Tablets. Figure 1 shows the diffractograms of the mixture (precursors) of the tablets and glass waste without Cu_2O. Figure 1i (a−c) shows the powder mixture of Cu_2O and soda-lime waste glass powders. The peaks noticed at 2θ (degree) 36, 42, and 61 are attributed to the face-centered cubic phase of Cu_2O added.[45] Figure 1i (d) shows the XRD analysis of the soda-lime waste glass, which, as expected, shows only the halo associated with the amorphous materials.

Figure 1(ii shows the XRD analysis of the copper-doped waste glass after the thermal treatment step (1 h) under air. During the thermal treatment at 680 °C, Cu_2O was oxidized to CuO. The peaks noticed correspond to the monoclinic phase of CuO.[52,53]

Finally, Figure 1(iii) presents the diffraction results obtained after thermal treatment at 430 °C for 45 min under a reducing flow of hydrogen gas (150 mL/min), intending to obtain metallic copper nanoparticles. The peaks at 2θ (degree) 43 and 50 with narrow shapes are associated, respectively, with the (111) and (200) Miller planes of the face-centered cubic structure of metallic copper (JCPDS 04−0836), thus evidencing the formation and presence of metallic copper on the surface of the glass waste particles.[54]

Platzman et al.[55] showed the oxidation of metallic copper at room temperature immediately, just 1 h, after exposure to the ambient atmosphere. Torres-Ochoa et al.[56] performed a detailed study for the discrimination of copper species when a deposited copper metallic film was oxidized under a controlled oxygen atmosphere. For copper, the Cu 2p peaks for Cu^0 and Cu^+ overlap. The detection of Cu^{2+} can be monitored by the presence of satellites in the $2p_{3/2}$ and $2p_{1/2}$ regions. The XPS analysis was performed to show the formation of the expected oxide layer on the copper nanoparticles due to ambient air exposure. Figure S3 shows the survey spectra with special attention to copper present in the catalyst. As expected, the tablet with only glass waste

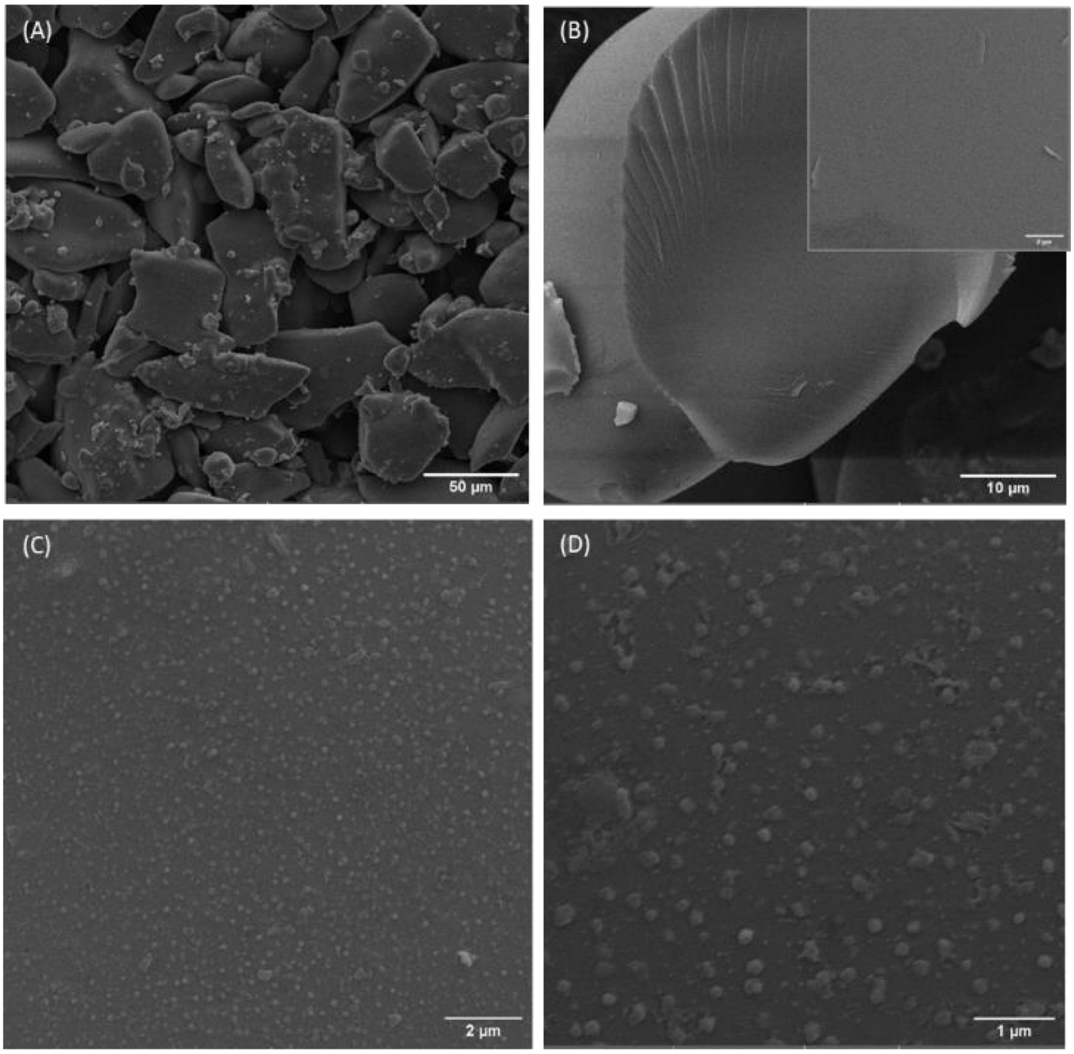

Figure 3. Micrographs obtained for the tablet: (A, C, and D) after doping with copper and (B) before doping.

(Figure S3A(i)) does not show any peak related to copper. The inset graphic (Figure S3A) shows the Cu 2p region, evincing the absence of copper ions in the glass waste. For the 2p region, detailed spectra were obtained for these samples (Figure S3B). As can be noticed and previously reported in the literature, the position of Cu^0 and Cu^+ does not change considerably.[56] Figure S3C, shows the deconvolution of the detailed spectra for the Cu 2p region for the copper-doped glass waste-based tablet without thermal treatment in hydrogen gas. The peaks at binding energies of about 932.6 and 952.4 eV are due to the spin−orbit doublet of the Cu 2p (Δ = 19.8 eV) core-level transition for Cu^+ species. The presence of the CuO phase at 933.4 eV (Cu $2p_{3/2}$ with a spin−orbit doublet of Δ = 20.8 eV) is in agreement with the PXRD analysis (Figure 1ii). Furthermore, for CuO, a satellite (named sat., Figure S3C) peak is expected to be centered around 942 eV, observed at 8.6 eV above the peak at 933.4 eV (Cu $2p_{3/2}$). For the sample without thermal treatment under hydrogen gas, we did not expect the presence of metallic copper. It is worth mentioning that the presence of copper species in the glass can contribute to the overall signal due to the presence of copper ions in the silica glass matrix. The presence of satellites in the detailed spectrum of Cu 2p for the sample treated under H_2 gas (Figure S3D) confirms the presence of Cu^{2+} ions[55] from ions in the glass matrix and/or superficial oxidation of copper nanoparticles obtained by thermal treatment in H_2 gas (Figure S3D). The Cu $2p_{3/2}$ and $2p_{1/2}$ peak intensity increases with thermal treatment in H_2 gas, indicating more metallic copper on the surface of copper-doped tablets (Figure S3Bii,iii). This observation supports the presence of metallic copper noticed in PXRD experiments (Figure 1iii). However, the presence of satellites in the XPS spectrum indicates probably a native oxide layer, considering that pure metal does not show satellites.[56]

In order to identify the elemental composition of the tablets, they were characterized by using the LIBS technique. In the total spectrum, 190−900 nm, of the glass matrix (Figure S2) it is possible to notice in the glass matrix the emission lines mainly associated with Na, Si, Ca, Al, and Mg (Figure 2). Despite the complexity of the spectra, upon thorough comparison of the waste glass without Cu_2O (Figure S4) and after copper doping before thermal treatment (Figure S5) and after thermal treatment (Figure S6), it is possible to confirm its absence in residual glass from the emission lines characteristic of copper. To interpret the spectra of the copper-doped tablets, two regions of interest for this metal were selected, 270−350 nm and 500−580 nm. Figure 2 shows emission lines for the selected regions. Figure 2i,ii refers to the 270−350 nm region before and after thermal treatment in H_2,

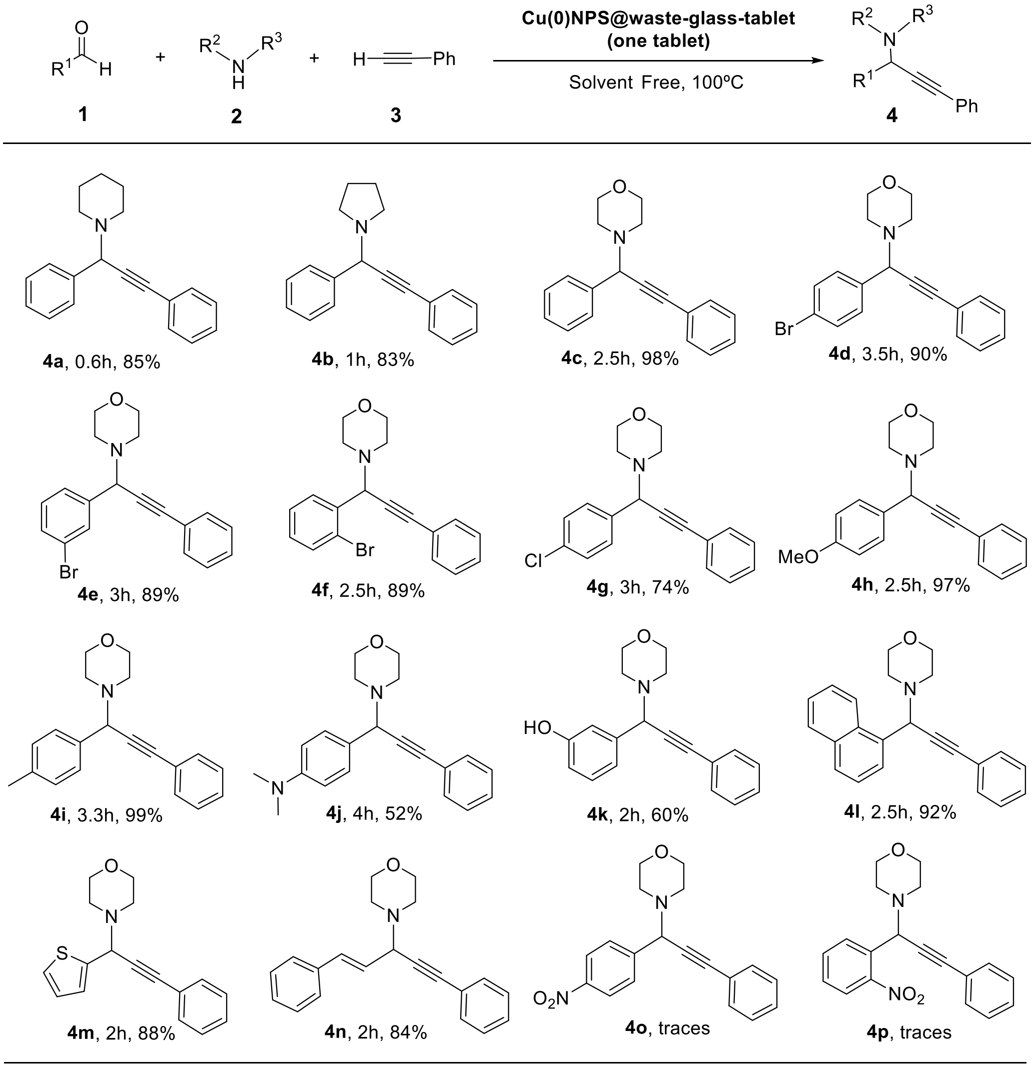

Figure 4. Synthesis of propargylamines catalyzed by Cu(0)NPs@waste-glass-tablet. Reaction condition: aldehyde (0.50 mmol), amine (0.50 mmol), phenylacetylene (0.67 mmol), and a Cu(0)NPs@waste-glass-tablet (0.16g). Isolation of products using column chromatography.

respectively. Figure 2iii,iv belongs to the second region (500−580 nm), before and after thermal treatment, respectively. The characteristic copper emission lines can be identified in the 270−350 nm region at 324.7 and 327.4 nm and in the 500−580 nm region at 510.6, 515.3, 521.8, and 578.2 nm, both before and after treatment in hydrogen gas. As expected, the soda-lime glass waste (Figure 2d) does not show the presence of copper in the composition. The copper concentration increases in Cu(0)NP-doped tablets with the addition of Cu_2O, resulting in concentrations of 0.86, 1.41, and 2.34% (w/w) in the waste glass-based catalyst in a linear trend (Table S1 and Figure S7).

Figure 3 shows the scanning electron microscopy (SEM) analyses of the tablets. The thermal treatment of the glass waste provides sinterization of the powders (Figure 3A). Furthermore, it can be seen that the tablet is composed of small fragments of glass with irregular shapes from the glass crushing process. Figure 3B shows the magnified SEM image of the surface of the glass waste powder without the addition of Cu_2O. The absence of metallic copper nanostructures is evinced in the inset image (Figure 3B).

For copper-doped tablets, scanning electron microscopy (SEM) analysis was applied to verify the morphology and diameter of metallic copper nanoparticles. Figure 3C shows the images of Cu(0)NPs@waste-glass-tablet surface after thermal treatment in hydrogen gas, where the formation of sphere-like nanostructures homogeneously covers the glass surface.

The magnification SEM image (Figure 3B) evinces the formation of metallic nanoparticles after annealing in a reducing atmosphere, allowing the copper nanoparticles to grow uniformly over the entire surface of the glass.

Figure S8 shows a histogram with an estimate of the frequency of the size distribution of the obtained nanostructures. In the SEM images, it is possible to verify the presence of larger nanostructures dispersed among the smaller nanoparticles (Figure 3D). In the distribution graph, it is estimated that the size of the investigated nanoparticles varied approximately between 40 and 220 nm, with an average diameter of 120 ± 36 nm.

The EDS technique was used to analyze the chemical elements that make up the glass tablets. It provides an estimate of the elemental composition in a semiquantitative way in the specific mapping region. Figure S9 shows the EDS mapping of the surface of the Cu(0)NPs@waste-glass-tablet doped with 3% Cu_2O. As the images show, through EDS mapping, it is possible to evince that copper is present and distributed homogeneously on the surface of the tablet.

Synthesis of Propargylamines. To verify the applicability of Cu(0)NPs@waste-glass-tablets, their catalytic activity was tested in A^3 coupling reactions for the synthesis of propargylamines. To this end, initially, the best reaction conditions were determined based on the coupling between benzaldehyde **1a**, piperidine **2a**, and phenylacetylene **3a** as a reaction model under solvent-free conditions for the synthesis of propargylamine **4a**. Several reaction parameters were investigated, and the reaction time was determined by the consumption of starting materials through thin-layer chromatography analysis (Table S2).

The first tests were carried out to evaluate the ideal temperature for the reaction, using a tablet containing 3% Cu_2O, 325−250 mesh, and 2 h of sintering. Initially, the reaction was carried out at room temperature; however, after 9 h of reaction, the formation of product **4a** was not observed, and the starting materials were recovered (entry 1). When the reaction was carried out at 80 and 100 °C, the desired product **4a** was obtained in 55 and 85% yield, respectively, after 40 min of reaction (entries 2 and 3). Subsequently, the reaction time was increased to 50 min, but there was no significant increase in product yield (entry 4).

Having determined the temperature and reaction time, we investigated the catalyst load for the reaction. The amount of Cu_2O added to the tablet (0.16 g) was tested at 3%, 2%, and 1% (% w/w) (entries 3, 5, and 6). As a result, lower yields were obtained as the amount of copper decreased. Thus, the best yield (85%) was obtained for the 3% tablet (entry 3).

After the amount of catalyst was determined, the influence of some physical properties of the catalyst was analyzed. For example, when the grain of the glass was decreased to 150−100 mesh (entry 7), a lower yield was observed compared to the grain of 325−250 mesh, and interestingly, the tablet suffered a crumbling process due to the continuous mechanical agitation of the reaction. Furthermore, a significantly lower yield (58%) was observed when decreasing the tablet sintering time to 1 h (entry 8).

Finally, the influence of applying heat treatment on the growth of Cu(0) nanoparticles on the surface of the tablet was investigated. Failure to complete this step (entry 9) led to considerably lower yields (30%). It is also important to note that an insignificant yield was observed when using the pure glass matrix (entry 10). These results demonstrate the efficiency of Cu(0)NPs@waste-glass-tablets for A^3 coupling and highlight that the presence of copper nanoparticles on the surface of the tablet significantly affects the catalytic efficiency of the reaction.

After the best reaction conditions were established (Table S2, entry 3), the versatility and scope of the reaction were evaluated. For this purpose, the developed methodology was extended to different aldehydes (**1a**−**n**) and amines (**2a**−**c**), leading to the synthesis of a variety of products **4a**−**n** (Figure 4).

In general, the cyclic secondary amines evaluated—piperidine **2a**, pyrrolidine **2b**, and morpholine **2c**—presented excellent results in the reaction with benzaldehyde **1a** and phenylacetylene **3a** since propargylamines **4a**−**c** were obtained in 85, 83, and 98% yield, respectively.

Optimal reaction conditions were also evaluated for aromatic and heteroaromatic aldehydes containing a wide range of functional groups. In most cases, the varied aldehydes, in the presence of morpholine **2c** and phenylacetylene **3a**, provided the corresponding propargylamines (**4d**−**n**) in good yields (52−99%). In general, substituted *para*-, *meta*-, and *ortho*- halogenated aldehydes acted as excellent substrates for the reaction, providing the desired products (**4d**−**g**) in good yields (74−90%). Electron-donating groups were also well tolerated, and the corresponding products (**4h**−**k**) were obtained in 52−99% yield.

The catalytic system was also active for sterically hindered substrates, such as 1-naphthaldehyde, which contains a fused aromatic system (**4l**). Likewise, it proved to be efficient for heteroaromatic substrates. For example, when 2-thiophene carboxaldehyde was used, product **4m** was obtained in 88% yield. Additionally, a yield of 84% was obtained for a propargylic amine in the presence of a conjugated aromatic system (**4n**) by the use of an α,β-unsaturated aldehyde, trans-cinnamaldehyde. However, the protocol was not applicable for the coupling of substituted nitro aldehydes (**4o** and **4p**) due to the formation of a complex mixture of byproducts.

The protocol developed was compared with some reports described in the literature, which involved the use of Cu(0) and recyclable supported catalysts for the A^3 coupling multicomponent reaction (Table S3). Compared with the previous literature, the present work demonstrated satisfactory results regarding synthesizing propargylamines with several interesting features, such as excellent yields, ease of catalyst recovery, a robust methodology, and solvent-free conditions. Finally, a proposed mechanism for a multicomponent A^3 coupling reaction using Cu(0)NPs@waste-glass-tablet as a catalyst is also presented in (Figure S13).

Catalyst Recycling. The simplicity of the recovery and reuse process is one of the main characteristics of Cu(0)NPs@waste-glass-tablet, attributed to its intrinsic shape. Due to its shape, the tablet could simply be "pinched" from the reaction medium, as shown in Figure 5.

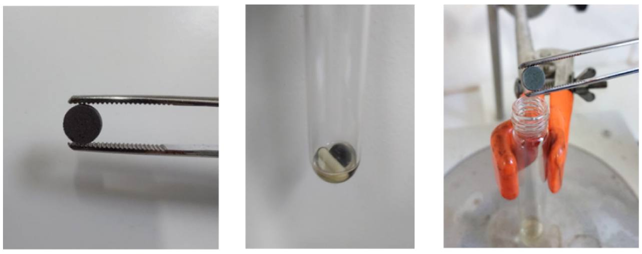

Figure 5. Images of the ease of recovering the catalyst, from left to right: catalyst before the reaction, catalyst inside the reaction, and catalyst after recovery.

Therefore, in order to evaluate the recyclability efficiency, after the first cycle, the tablet was separated using simple tweezers, washed with ethyl acetate, and dried at room temperature for 24 h. The recovered catalyst was reused for another 5 subsequent catalytic cycles between benzaldehyde (**1a**), morpholine (**2c**), and phenylacetylene (**3a**) under ideal reaction conditions (Figure 6). Fortunately, the catalyst maintained its catalytic activity throughout all cycles without significant decreases in the product yields of **4c**.

A gradual change in the color of the tablet surface can be observed (Figure S10), which was intensified after the third recycling cycle. Therefore, in order to investigate the stability of the catalyst, X-ray diffraction (XRD), scanning electron

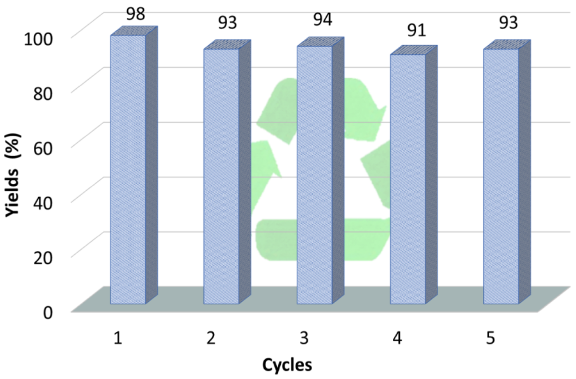

Figure 6. Recyclability of the catalyst. Reaction conditions: benzaldehyde **1a** (0.50 mmol), morpholine **2c** (0.50 mmol), phenylacetylene **3a** (0.67 mmol), and a Cu(0)NP@waste-glass-tablet (0.16g). Isolation of products using column chromatography.

microscopy (SEM), and energy-dispersive spectroscopy (EDS) analyses were carried out on the tablet after catalysis.

In order to identify the stability of the catalytic metallic copper species, an XRD analysis of Cu(0)NPs@waste-glass-tablet recovered after a reaction (A) and after 5 catalytic cycles (B) was carried out. The diffractograms obtained are shown in Figure S11.

In the diffractogram Figure S11a, the appearance of low-intensity diffraction signals around (2θ (degree)) 35.5 and 38.7 can be noticed, together with other characteristic signs of the diffraction of metallic copper at (2θ (degree)) 43.3 and 50.5.[53,54] These results indicate that a small amount of CuO is formed after the first reaction. Although a fraction of Cu(0) was converted to Cu(II), the catalyst efficiency was not affected. However, when the XRD analysis of the tablet was carried out after 5 catalytic cycles, Figure S11b, it was possible to observe essentially amorphous characteristics, corresponding to glasses.

Subsequently, the SEM analysis was performed after 5 catalytic cycles, and the micrographs are shown in Figure S12. Therefore, in the images from the SEM analysis, it is possible to observe notable differences in the quantity and morphology of the copper nanoparticles after the reactions.

Catalytic Reduction of 4-Nitrophenol by Sodium Borohydride. To extend the application scope and due to the successful application of the catalyst on the synthesis of propargylamines, the Cu(0)NPs@waste-glass-tablet was used as a catalyst for the catalytic reduction of 4-nitrophenol by sodium borohydride. In a basic medium, the hydride ions (H^-) adsorb on metallic nanoparticles, converting 4-nitroenolate ions to 4-aminophenol. The intensity reduction of the initial absorbance (A_0) at 400 nm over time (A) can be associated with the reaction progress.

The presence of $NaBH_4$ plays a crucial role in the reduction of 4-nitrophenol. Usually, the catalytic runs are performed with high concentrations of $NaBH_4$ compared to 4-nitrophenol for catalyst evaluation, possibly aiming to achieve a higher reaction rate and to adjust the kinetic curve to a pseudo-first-order reaction. However, apart from acting as a reducing agent, $NaBH_4$, depending on the concentration, can be toxic due to the presence of boron. According to the Environmental Protection Agency (EPA), the boron limit should be lower than 2.4 μg/mL to avoid further purification processes.[57,58]

The thermal treatment under a hydrogen atmosphere results in the reduction of CuO and the growth of metallic copper nanoparticles (Figures 1iii and 3c,d). Thus, the catalytic reduction proceeds by the transference of hydride ions adsorbed on the copper nanoparticles to 4-nitroenolate. A schematic representation of the mechanism is presented in Figure S14. The evolution of gas, i.e., hydrogen gas, just after the immersion of the copper-based waste glass catalyst in sodium borohydride solution, can be associated with a heterogeneous reaction mechanism for the reduction of 4-nitrophenol.

The use of glass waste as a support for ordinary copper oxide (Cu_2O) shows a straightforward and green route to obtain a supported copper catalyst. The immobilization of commercial copper (I) oxide without a wet route (or any solvent) and stabilizing agents provides an alternative to obtain heterogeneous catalysts by annealing the raw materials and powdered glass waste. Figure 7a shows the catalyst performance of the copper-based glass waste catalyst for the catalytic reduction of 4-nitrophenol. The catalyst obtained in tablet form can be reused easily, without the need for centrifugation and filtration steps. The copper-based catalyst in tablet form can be removed with tweezers, and after washing with distilled water, the copper catalyst can be reused three times with a slight increase in the time required from 40 min (first run) to 60 min (third run, Figure 7d) to complete the reaction. As expected, due to the chemical stability of the soda-lime glass waste, characteristic of silica-based glasses, the tablet without copper oxide shows no catalytic activity (Figure 7e).

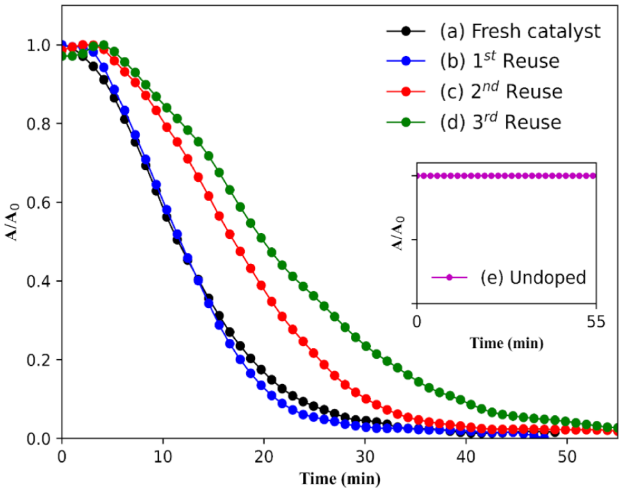

Figure 7. Normalized absorbance (A/A_0) against time (min) for copper-based waste glass catalyst. (a) Fresh catalyst (first run) and (b) first, (c) second, and (d) third reuse runs. Inset graphic: (e) undoped waste glass.

The yields of the catalytic process were 98.6%, 99.78%, 97.62%, and 96.66% for the three reuses, respectively, while maintaining their catalytic activity over 96%. The interaction with $NaBH_4$ likely caused the reorganization of the supported nanoparticles on the catalyst surface, leading to enhanced performance in the initial reuse.[59] The slight reduction in the conversion rate could be attributed to the rearrangement of 4-aminophenol on the catalyst surface, reducing the direct interaction of the nanoparticles with 4-NP.[60]

The activity parameter (κ) should be used to evaluate the catalytic performance of the catalyst. Usually, the activity parameter can be mass normalized (κ_m) and/or reaction volume normalized (κ_c), as shown in Table 1. The apparent

Table 1. Kinetic Parameters of the Degradation of 4-Nitrophenol

Catalyst	$\frac{NaBH_4}{4-NP}$	k_{app} (× 10^{-3}) (s^{-1})	κ_m ($s^{-1}.g^{-1}$)	κ_c ($L.s^{-1}.g^{-1}$)	Reference	Supported
Cu(0)NPs@waste-glass-tablet	10	2.26	0.281	0.014	This Work	Y
Cu-carbon	90.9	12.4	10.79	0.034	[61]	N[a]
Cu/carbon	30.5	6.57	4.60	0.014	[61]	N[a]
CuO@C (MOF)	30	6	120	10.5	[62]	Y[a]
CuOnano@glass	25	5.88	67.7	0.203	[29]	Y[a]
CuO@CMK-8	123	22	203	5.6	[63]	Y[a]
CuO/Cu_2O nanowires	200	8.3567	83.57	0.209	[64]	N
Cu on coal-based carbons	41.7	13.0	13.0	0.0424	[65]	Y[a]

[a] Catalyst in powder format. Y = yes; N = not supported.

constant rate (k_{app}) was 2.26, 3.00, 2.26, and 1.28 (10^{-3} s^{-1}) from (a−d) of Figure 7, respectively, which is related to the efficiency of the catalysts. Not only does the Cu(0)NPs@waste-glass-tablet catalyst show comparable activity using the lowest $NaBH_4$/4-NP ratio (considering the effect of $NaBH_4$ concentration on the reaction kinetics), but it can also be recycled without filtration and/or centrifugation steps.

CONCLUSION

In summary, a new catalyst in tablet format was prepared using waste glass as a support for the growth of Cu(0) nanoparticles by H_2-assisted thermal treatment. This ecological tablet was used as an efficient catalyst for the A^3 coupling reaction under solvent-free conditions, affording the synthesis of a variety of propargylamines in excellent yields, in short reaction times, and with low catalyst loading. Furthermore, the catalyst based on glass waste as a support for CuNPs demonstrated high efficiency in the degradation process of 4-nitrophenol with a low concentration of $NaBH_4$. The main advantages of these alternative protocols are a low-cost catalyst; easy and efficient recovery and reuse of the catalyst, which demonstrates the stability of the catalyst; and the reuse of waste.

Of particular note is the reuse of vitreous waste (window glass) obtained from landfills, which can prevent the accumulation of waste in cities, thus reducing environmental disasters and environmental pollution. Furthermore, from a circular economy perspective, recycling this waste can be an interesting alternative from an economic point of view since greater added value is attributed to this undesirable solid waste. It is worth noting that the development of solutions for solid waste, such as glass waste, meets Sustainable Development Goal (SDG) numbers 8, 9, 11, and 12, which are Decent Work and Economic Growth; Industry, Innovation, and Infrastructure; Sustainable Cities and Communities, and Responsible Consumption and Production, respectively.

Finally, the synthetic methodology developed for the preparation of propargylamines fits into principles 1, 2, 3, 4, 5, 7, 8, 9, and 12 of Green Chemistry, which are Prevention; Atomic Efficiency; Safe Synthesis; Development of Safe Products; Use of Safe Solvents and Auxiliaries; Use of Renewable Raw Material Sources; Avoid the Formation of Derivatives; and Catalysis and Intrinsically Safe Chemistry for Accident Prevention, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.4c09871.

General information, material characterization, spectral data, ^1H and ^{13}C NMR and IR spectra for all compounds (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. N.C.: data curation, methodology, and writing—original draft. S.S.: data curation, formal analysis, and visualization. J.R.: conceptualization, investigation, visualization, and editing. F.C.A.: data curation, methodology, and writing—original draft. R.S.: conceptualization, resources, investigation, and writing—review and editing. G.V.B.: conceptualization, funding acquisition, supervision, writing—review and editing.

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■ ABBREVIATIONS

4-NP	4-nitrophenol
XRD	X-ray diffraction
LIBS	Laser-induced breakdown spectroscopy
PSD	Particle size distribution
TLC	Thin-layer chromatography
NMR	Nuclear magnetic resonance
FT-IR	Fourier-transform infrared spectroscopy
SEM	Scanning electron microscopy
EDS	Energy-dispersive spectrometer
EPA	Environmental Protection Agency

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