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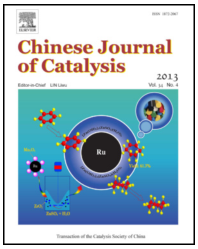

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Article

Combustion-derived CuO nanoparticles: An effective and environmentally benign catalyst in the synthesis of aromatic nitriles from aromatic aldehydes

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ABSTRACT

CuO nanoparticles were synthesized using an energy-efficient and rapid solution combustion technique with malic acid employed as a fuel. The combustion-derived CuO nanoparticles were used as catalysts in a one-pot synthesis of aromatic nitriles from aromatic aldehydes and hydroxylamine hydrochloride. The catalyst was characterized by X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray analysis, transmission electron microscopy, and Brunauer-Emmett-Teller surface area analysis. The catalytic activity of the CuO nanoparticles in the synthesis of aromatic nitriles from aromatic aldehydes was evaluated. The present protocol offers the advantages of a clean reaction, simple methodology, short reaction duration (1–2 min), and high yield (85%–98%). The catalytic activity of the CuO nanoparticles was found to be higher than that of bulk CuO powder under the same conditions. The catalyst can also be recovered and reused up to four times with no significant loss of catalytic activity. The present approach is inexpensive and is a convenient technique suitable for industrial production of CuO nanoparticles and nitriles.

1. Introduction

The advanced properties of nanoscale metal oxide particles have encouraged wide-ranging research activity on their application in electronics, optics, and catalysis [1]. Within the field of green chemistry, nanometal oxide catalyzed reactions are recognized as being attractive and environmentally benign methods of organic synthesis. Among the known varieties of metal oxides, copper oxide nanoparticles (NPs) possess unique physicochemical properties such as small particle size, large surface area, and unusual reactive morphology and surface active sites. In addition to their high thermal stability, strong basic characteristics mean that copper oxide NPs are promising catalysts for organic synthesis [2–5]. There have thus far been numerous methods developed for the preparation of copper oxide NPs, including via solid-state reactions [6]; sol-gel [7], sonochemical [8], solvothermal, alcohothermal [9], hydrothermal [10], and vapor deposition template methods [11]; wet chemistry routes [12]; and alkoxide-based preparations [13]. All of these methods require expensive precursors and high temperatures, are time-consuming, and consume significant amounts of energy for completion. However, among the methods reported in the literature, solution combustion (SC) has proved one of the more successful methods for the synthesis of metal oxide NPs and this method is relatively simple and environmentally benign. The advantages of this method over the

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synthesis approaches mentioned vide supra are shorter reaction time (< 5 min), lower cost (with the potential to scale up), and the possibility of using a one-pot synthesis. In addition to this, the SC method is useful for producing homogenous, porous, and fine crystalline powders [14]. To the best of our knowledge, the synthesis of CuO NPs using SC method has not been extensively reported [15].

In the present study, we focus on the synthesis of CuO NPs via an SC route using malic acid as a fuel. The combustion-derived CuO NPs possess a high surface area with high porosity. A large surface area results in the potential for more active sites such as low-coordinate oxide sites (edges and corners) and lattice defects (anions and cations) [16]. The porous structure also facilitates the adsorption and diffusion of reactant molecules. Both the high surface area and high porosity enhance the catalytic performance. Although homogeneous organic basic catalysts are desirable because of their high activity and selectivity, the separation of such catalysts from the products of the reaction and/or catalyst recovery are inherent problems.

Use of heterogeneous basic catalysts has advantages related to easy separation, efficient recycling, and only minimum traces of metal oxide remaining in the product. This is particularly beneficial to industrial processes in the domain of green chemistry. Thus, heterogeneous basic catalysts have been recognized as potential alternatives to the more commonly used homogeneous catalysts.

The synthesis of nitriles from aldehydes is one of the most important reactions in organic chemistry. The nitrile group is a useful functional group and is an important key intermediate in organic synthesis [17]. Furthermore, nitrile functionality frequently appears in pharmaceutical products. For example, the cyano group is present in HIV protease inhibitors, 5-lipoxygenase inhibitors, and in many other bioactive molecules [18,19]. Nitriles also serve as useful precursors in the synthesis of carboxylic acids [20,21], ketenes [22], amines [23,24], amides [25], and heterocyclic compounds [26].

Over the years, methods have been developed for the synthesis of nitriles, including the nucleophilic displacement of groups such as halogens, aryl sulfonates, alcohols, esters, ethers, and of nitro, amino, and diazonium groups in substrates with inorganic cyanide ions [27,28]. Alternative methods for the synthesis of nitriles involve dehydration of amides [29,30] and aldoximes [31–33]. Conversion of aldehydes [34–41], alcohols [42–44], and carboxylic acids [45–48] to nitriles using various reagents and the direct conversion of amines [49–52] are also documented in the literature. However, these methods of synthesizing nitriles suffer from limitations such as prolonged reaction time, low yield, the necessary use of toxic reagents and solvents, a requirement for excess reagents/catalysts, laborious work-up procedures, or harsh reaction conditions. Thus, the development of an alternate, milder, and cleaner procedure is highly desirable.

Organic syntheses involving greener processes under solvent-free conditions have been investigated as a consequence of stringent environmental and economic regulations [53]. In this context, microwave-assisted reactions are significant for synthetic organic chemistry because of their rapid reaction rate and ease of manipulation [54]. Simple experimental procedures, high yields, improved selectivity, and cleaner reactions of many microwave-induced organic transformations offer additional advantages. Our ongoing research program is aimed at developing environmentally benign synthetic methodologies suitable for organic compounds that are widely used [55,56]. We were therefore inspired to attempt the microwave-assisted synthesis of aromatic nitriles from aromatic aldehydes under solvent-free conditions using catalytic amounts of copper oxide NPs. The catalytic activity of bulk CuO in comparison with the combustion-derived CuO NPs was also evaluated.

2. Experimental

2.1. *Materials*

Copper(II) nitrate trihydrate (98.8% purity) and DL-malic acid (99% purity) were purchased from Merck Chemicals (India) Pvt. Ltd. All organic chemicals used were of commercial grade and procured from Merck Chemicals (India) Pvt. Ltd. All solid aldehydes were used without further purification; liquid aldehydes were distilled before use.

2.2. *Synthesis of CuO nanoparticles*

An aqueous solution containing a mixture of copper(II) nitrate as an oxidizer (O) and malic acid as a fuel (F) (corresponding F/O ratio = 1:1) was placed in a petri dish [57,58]. Excess water was allowed to evaporate by heating on a hot plate until it decomposed with frothing as a result of formation of viscous gel. The petri dish was then placed in a muffle furnace maintained at (450 ± 10) °C. Initially, the viscous gel underwent dehydration and commenced smoldering combustion, which appeared at one end and propagated through the mass within 1 min. Voluminous and porous nanocrystalline black-colored product was obtained. This non-carbonaceous powder is hereafter referred to as CuO NPs.

2.3. *General procedure*

A mixture of aldehyde (2 mmol), hydroxylamine hydrochloride (3 mmol), and copper oxide NPs (5 mol%) was placed in a Pyrex cylindrical tube and then homogenized and irradiated at 250 W in a MILESTONE microwave reactor. After irradiation (1–2 min), the mixture was cooled to 25 °C and extracted with dichloromethane (5 ml × 2). The solvent was filtered under vacuum and the organic layer dried over fused calcium chloride. The crude product was then subjected to short-column silica gel chromatography using light petrol as an eluent to produce pure product.

NMR spectra of the organic compounds were obtained on a 400 MHz Bruker AMX spectrometer in DMSO-d6 using TMS as a standard. Gas chromatography-mass spectroscopy (GC-MS) patterns were obtained using a Shimadzu GC-MS QP 5050A instrument equipped with a 30-m long and 0.32-mm diameter BP-5 column at temperatures from 80 to 250 °C with an interval of 15 °C. IR spectra were recorded using a Shimadzu FT-IR-8400s spectrometer with KBr pellets used for solids and with thin films between NaCl plates in the case of liquids.

2.4. *Characterization of catalysts*

Powder X-ray diffraction (PXRD) data were recorded on a Philips X'pert PRO X-ray diffractometer using graphite monochromatized Cu K_α radiation (λ = 0.1541 nm) operated at 40 kV and 30 mA. The morphologies of the products were examined using a Quanta-200 scanning electron microscope equipped with an energy-dispersive X-ray spectroscope. Samples were gold-coated prior to scanning electron microscopy (SEM) analysis. The nano/microstructure of the products was observed by transmission electron microscopy (TEM) and selected-area electron diffraction (SAED), which was performed using a Hitachi model H-600 instrument operating at 100 kV. Surface area measurements and pore size distribution analyses were carried out after degassing the sample under high vacuum at 300 °C for 4 h, and nitrogen adsorption measurements were carried out at –196 °C using gas sorption analyzer (Quantachrome Corporation NOVA 1000).

3. Results and discussion

3.1. *Catalyst characterization results*

Figure 1 shows the XRD pattern recorded for the CuO NPs, where all diffraction peaks have been indexed to the pure monoclinic crystalline phase of CuO. These values are consistent with those reported in the literature and with the respective JCPDS card No. 45-0937. The broadness of the peaks indicates the nanocrystalline nature of the CuO NPs and the particle size calculated from the Scherrer's formula ($D = K\lambda/\beta\cos\theta$) is in the range of 20–30 nm.

The morphologies of the bulk CuO powder and combustion-derived CuO nanopowder were investigated by SEM. The SEM image of bulk CuO powder (Fig. 2(a)) reveals that the powder has less porosity compared with the combustion-derived CuO nanopowder. The SEM micrograph (Fig. 2(b)) reveals that the latter powder is porous and agglomerated with polycrystalline NPs. The pores and voids can be attributed to the amount of gases that escaped during combustion. The process of agglomeration takes place because of an increase in the rate of nucleation of the particles at higher temperatures.

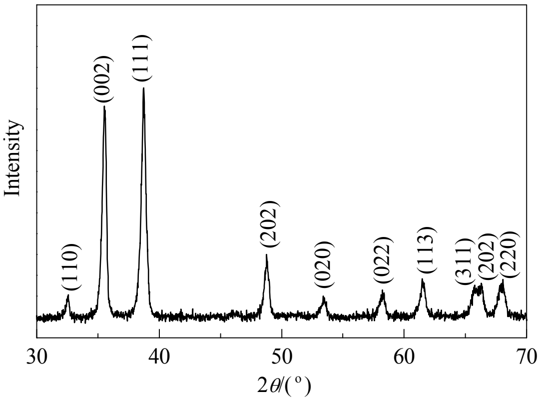


Fig. 1. XRD pattern of the CuO nanoparticles synthesized in this work.

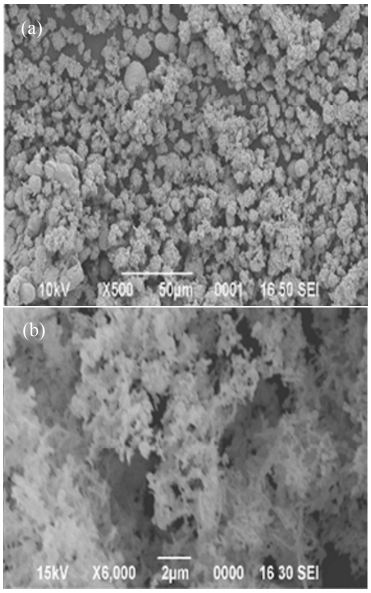


Fig. 2. SEM image of bulk CuO powder (a) and the CuO nanoparticles (b).

The elemental quantification and stoichiometric ratio of copper oxide NPs were confirmed by energy-dispersive X-ray analysis (EDX), which showed the presence of a uniform distribution of copper to oxygen (atomic ratio of 1:1) in CuO NPs, as shown in Fig. 3. This agrees well with the results obtained via XRD.

The TEM image in Fig. 4(a) shows a network of larger particles that are of moderate size and that are irregularly shaped, formed by the agglomeration of well-dispersed NPs with average sizes of 20–30 nm. The sizes of these NPs are in good agreement with the values obtained from XRD analysis. The phase purity, clear morphology, and crystallinity were confirmed by SAED. SAED (inset) provides supporting evidence for the polycrystalline structure of the CuO NPs.

The surface area of the CuO NPs was measured using the BET method. The CuO NPs have a larger surface area (52 m^2/g) compared with that of bulk CuO (10–12 m^2/g). This can be attributed to the liberation of gaseous products such as H_2O,

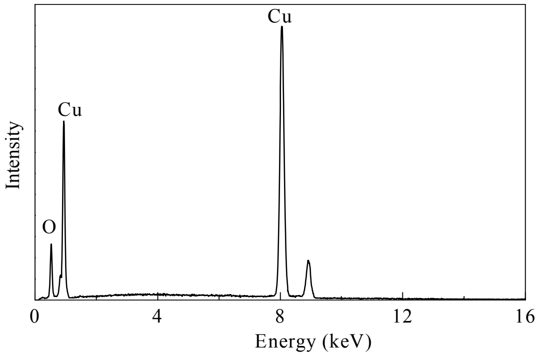


Fig. 3. EDX spectrum of the CuO NPs.

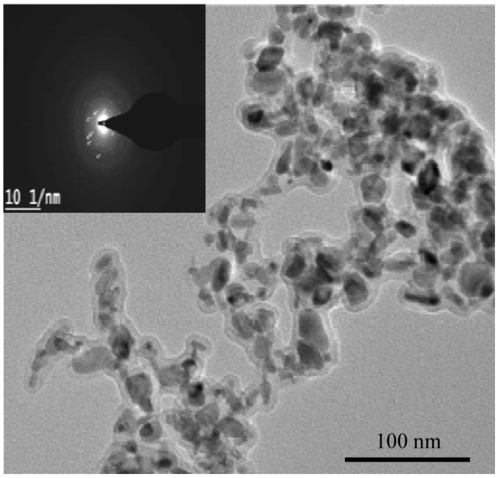


Fig. 4. TEM image of the CuO nanoparticles and SAED pattern of CuO (inset).

CO_2, and N_2 during combustion, whereby the agglomerates disintegrate and most of the heat is carried away from the system, thus hindering particle growth. This larger surface area is important for catalytic/adsorbent applications because the small size of the particles maximizes the surface area that is exposed to the reactant, allowing more reactions to occur. Figure 5 shows a representative adsorption-desorption isotherm of nitrogen obtained at the temperature of liquid nitrogen. This, according to the IUPAC classification, is a type IV isotherm with type H1 hysteresis. Type H1 hysteresis indicates that, for spherical pores, the pore opening is smaller than the diameter of the main cavity. As the desorption portion of the isotherm moves from higher partial pressure to lower partial pressure, a gradual decrease in pore volume is observed. As with the adsorption portion of the isotherm, this is an indication of the broad distribution of mesopores in the CuO NPs. The type IV isotherm suggests the presence of mesopores in the CuO NPs and this was confirmed by the results of pore size distribution measurements. The pore size distribution profile exhibits two peaks for the CuO NPs centered at 45 and 48 nm. This result indicates the formation of dual mesopores, with the peak at 45 nm due to the mesopore opening leading into the main cavity and a large number of mesopores uniformly distributed in the CuO NPs at 48 nm. The pore size distribution, with reference to the average pore diameter range and pore volume range calculated via the Barrett-Joyner-Halenda method, were found to be 44.82–48.36 nm and 0.431–0.441 cm^3/g, respectively. These values are in good agreement with the values obtained from the pore size distribution plot (Fig. 5).

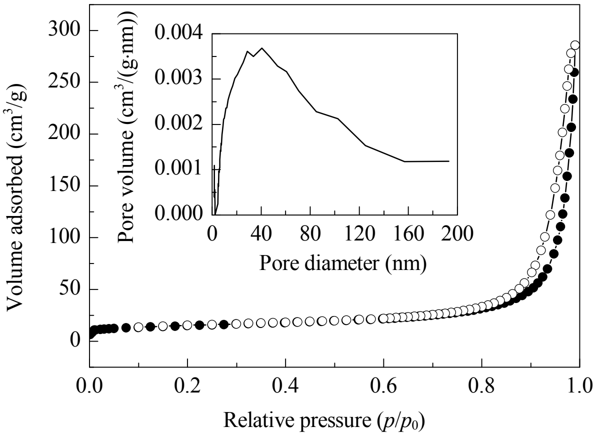


Fig. 5. Nitrogen adsorption-desorption isotherm of the CuO nanoparticles and pore size distribution curve (inset) determined from the N_2-desorption isotherm.

3.2. *Catalytic activity*

In the course of the reaction it was found that, under microwave heating, the reaction of an araldehyde with hydroxylamine hydrochloride in the presence of CuO NPs is rapid, clean, and high yielding. To optimize the reaction conditions, we studied the reaction of 4-methoxybenzaldehyde (2 mmol) with hydroxylamine hydrochloride (3 mmol) in the presence of CuO NPs (5 mol%) under microwave irradiation. The starting material completely reacted within 60 s, as indicated by TLC analysis. After isolation and purification by silica gel column chromatography, 4-methoxybenzonitrile was isolated with a 98% yield.

The effect of catalyst load on the reaction time and yield was studied. The best result was obtained with 5 mol% of the catalyst which gave 98% yield within 60 s. The use of a lesser amount of catalyst (< 5 mol%) resulted in lower yields, but a higher amount of catalyst (> 5 mol%) did not affect the reaction with respect to either duration or yield. However, in the absence of the catalyst, the yield of the nitrile was low (< 5%) and oxime was a major product (> 90%) after 2 min of irradiation at 250 W. Choosing an appropriate solvent is of critical importance for successful microwave-assisted synthesis. To search for the optimal solvent, the reaction of 4-methoxybenzaldehyde (2 mmol), hydroxylamine hydrochloride (3 mmol), and CuO NPs (5 mol%) was examined using water, methanol, ethanol, MeCN, DMF, THF, ethyl acetate, diethyl ether, and hexane as solvents, at 100 °C under microwave irradiation conditions. All of the reactions were carried out at the maximum power of 250 W. The yields of the nitrile as a minor product were 0, 5%, 3%, 8%, 7%, 6%, 4%, 8%, and 5% for the respective solvents listed above, and oxime as a major product was produced in yields of 65%, 70%, 73%, 78%, 69%, 74%, 66%, 71%, and 77%, respectively. Contrastingly, formation of the corresponding nitrile (93%) as a major product was observed when the same reaction was carried out under solvent-free conditions. This study clearly shows that microwave irradiation in conjunction with CuO NPs (5 mol%) as a catalyst results in high yields of nitriles under solvent-free conditions. Therefore, no solvent was used for the remaining microwave-assisted reactions to be discussed because it is environmentally friendly and the use of toxic organic reagents can be avoided.

We have compared the catalytic activity of CuO NPs with that of bulk copper oxide. When the model reactions between 4-methoxybenzaldehyde (2 mmol) and hydroxylamine hydrochloride (3 mmol) with either CuO NPs (5 mol%) or bulk CuO

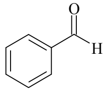
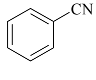
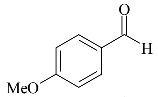
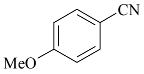
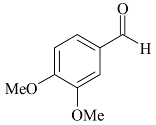
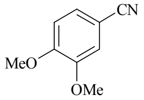
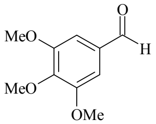
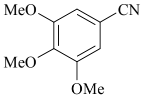
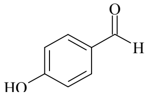
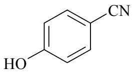
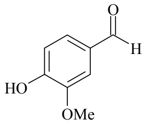
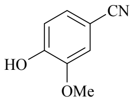
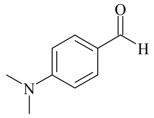
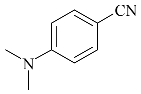
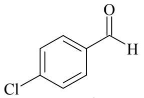
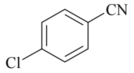
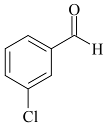
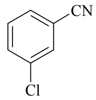
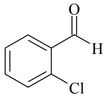
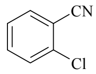
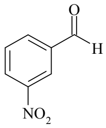
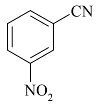
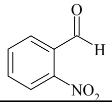
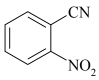
(5 mol%) were conducted under the optimized conditions, yields of 98% and 39%, respectively, were obtained after 60 s. This clearly indicates that CuO NPs enhance the catalytic activity in the synthesis of aromatic nitriles from aromatic aldehydes.

The generality of the above reactions was tested by carrying out the reactions with various substituted araldehydes. It was consequently found that the reactions proceed smoothly irrespective of the substituent (see Table 1). Araldehydes possessing electron donating groups, e.g., –OMe, –OH or –N, N(Me)$_2$, electron withdrawing groups such as –NO$_2$, or halides were found to give the corresponding nitriles with excellent yield (85%–98%).

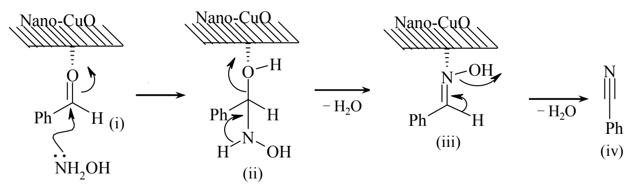
We further explored the effect of increasing the power and reaction time in the conversion of 4-methoxybenzaldehyde to 4-methoxybenzonitrile, but no change in product ratios was observed. The identity of the synthesized compounds was confirmed by IR analysis. In the IR spectra, the characteristic CN stretching mode was observed at 2220–2245 cm^{-1}. The molecular ion peaks (M$^+$) observed in the mass spectra were in agreement with the expected molecular weights. The melting or boiling points of the compounds, as given in Table 1, also

Table 1

Solvent-free synthesis of nitriles from aldehydes under microwave irradiation at 250 W.

Entry	Aldehyde	Product	Time (s)	Isolated yield (%)		m.p. or b.p.*(°C)	
				CuO NPs	Bulk CuO	Found	Reported
1			65	95	34	185*	190* [59]
2			60	98	39	55–56	57–59 [37]
3			45	97	35	60	63 [60]
4			55	96	34	90	92–94 [60]
5			45	93	32	110	110 [59]
6			70	98	38	83	83 [60]
7			85	90	30	71	73–75 [59]
8			80	94	33	92	94 [59]
9			95	95	34	38	37–39 [59]
10			75	96	35	40	43–46 [59]
11			90	92	32	112	115 [59]
12			100	95	33	104–106	107 [59]

Other conditions: aldehyde 2 mmol, hydroxylamine hydrochloride 3 mmol, CuO NPs 5 mol%.



Scheme 1. Proposed mechanism for the catalytic synthesis of aromatic nitriles from aromatic aldehydes.

agree with the literature values. As can be seen from Table 1, CuO NPs can serve as an efficient catalyst in the formation of 4-methoxybenzonitriles with high yields in short reaction times. The size of the CuO plays an important role in terms of yield and reaction time. Changing the size of the particles from nanoparticles to bulk resulted in a drop in the catalytic activity (entry 2 of Table 1). It is interesting to note that the CuO nanoparticles catalyze the present reaction in high yield and within a shorter reaction time compared with the other catalysts.

3.3. Proposed mechanisms for the CuO NP catalyzed synthesis of aromatic nitriles

GC-MS analysis supports a proposed three-step mechanism for this reaction (Scheme 1). In the first step, CuO NPs may complex with the carbonyl oxygen atom of aldehyde (i), thus activating it for the nucleophilic attack of the hydroxylamine and resulting in the formation of a tetrahedral intermediate (ii). In the proceeding step, dehydration of (ii) may take place to produce oxime (iii). During the formation of (iii), the liberated HCl from the hydroxylamine hydrochloride is expected to promote the dehydration of (iii) to nitrile (iv) to complete the final step of the reaction.

3.4. Recyclability of the catalyst

The reusability of the catalyst was examined by employing the reaction listed as entry 2 in Table 1 under identical reaction conditions. The catalyst was easily recovered from the mixture by filtration. It was repeatedly washed with distilled water and ethyl acetate, and dried for 2–3 h under vacuum. The recycled catalyst was used four times and nitrile obtained without any appreciable decrease in the yield, with yields for the four cycles of 93%, 92%, 90%, and 92%, respectively. After every reaction, the catalyst was recovered from the reaction mixture and regenerated in the manner described above.

4. Conclusions

A simple combustion synthesis has been developed for the synthesis of CuO NPs using malic acid as a fuel. CuO NPs are employed as a catalyst in the rapid synthesis of aromatic nitriles from araldehydes, obtained in excellent yield and with high purity under mild reaction conditions. The catalyst can be recovered by simple filtration and be reused for at least four cycles without any significant loss of catalytic activity. The microwave-assisted, rapid, and one-pot synthesis of nitriles from aldehydes and hydroxylamine hydrochloride has been developed. A wide range of nitriles have been synthesized under solvent-free conditions in a short reaction time. This protocol could prove to be a practical alternative for the synthesis of nitriles, especially in difficult cases wherein low nucleophilicity of the aldehydes inhibits the reaction. The proposed method for obtaining aromatic nitriles is an inexpensive, convenient, and environmentally friendly technique that is suitable for industrial production.

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Graphical Abstract

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Combustion-derived CuO nanoparticles: An effective and environmentally benign catalyst in the synthesis of aromatic nitriles from aromatic aldehydes

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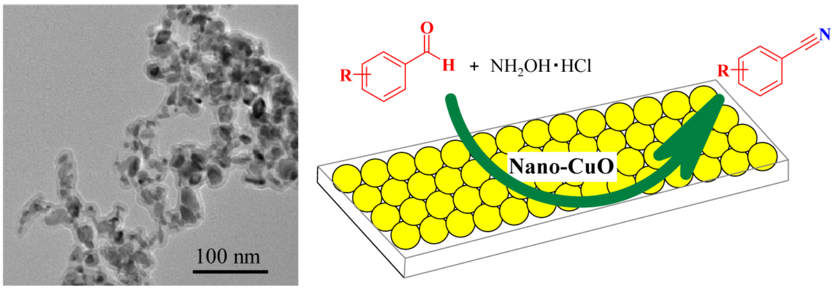

CuO nanoparticles show excellent catalytic activity in the synthesis of aromatic nitriles from aromatic aldehydes. The present approach offers the advantages of a clean reaction, simple methodology, short reaction duration, and high product yield.

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