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CuO Nanoparticles as an Efficient Catalyst for the Synthesis of Flavanones

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ABSTRACT

CuO nanoparticle was found to be an efficient catalyst for the synthesis of flavanones derivatives from the reactions between 2-hydroxyacetophenones and aromatic aldehydes at room temperature. The protocol offers advantages in terms of higher yields, short reaction times, and mild reaction conditions, with reusability of the catalyst. The structures of the synthesized substituted flavanones were confirmed by their Melting point, FT-IR, ^{1}HNMR, ^{13}CNMR and mass spectral analysis.

Key words: Flavanone, CuO, Nanoparticle, Solid Catalyst, Heterogeneous.

INTRODUCTION

Flavonones are known to exhibit numerous useful biological properties including antimicrobial, antitumor, antioxidant, and anti-inflammation.[1-5]The methodology most widely used to prepare flavanones involves the isomerization of appropriately substituted 2-hydroxy chalcones, in turn achieved by an aldol condensation reaction between a 2-hydroxyacetophenone and an aldehyde. These cyclizations have been performed under numerous conditions using acids,[6] bases,[7] silica gel,[8] heat,[9] light,[10] electrolysis,[11] Ni/Zn/K halides[12] and others.[13] Other alternative processes to synthesize flavanones contain oxidation of flavan-4-ol.[14] Reacting benzaldehydes with 1-(2-hydroxyphenyl)-3-phenyl propane- 1,3-diones in basic medium[15] and transformation of 3-bromo-1-phenylprop-2-ynyl aryl ethers in the presence of mercury(II) trifluoroacetate.[16]

In recent years, nano-catalysis has emerged as a sustainable and inexpensive alternative to conventional catalysis since the nanoparticles possess a high surface-to-volume ratio, which improves their activity and selectivity, while at the same time preserving the essential features of a heterogeneous catalyst.[17-20]Nanocrystalline metal oxides find excellent applications as active adsorbents for gases and destruction of hazardous chemical.[21]They are also gaining tremendous importance due to their distinct catalytic activities for various organic transformations.

In continuation of our studies on nanotechnology[17-20,22-24], herein, we wish to report a method for synthesis of flavanones at a strong basic media using CuO nanoparticles as an efficient nanocatalyst.

EXPERIMENTAL

Materials and methods

All chemicals and solvents were purchased from Sigma Aldrich. Merck silica gel F254 plates wereused foranalytical TLC. Melting points were determined and analyzed in open capillary tubes in an Electrothermal IA 9100 melting point apparatus.The IR spectra were obtainedon a Shimadzu 470 spectrophotometer (potassium bromide disks).The ^{1}HNMR and ^{13}CNMR spectra were recorded using Bruker 400spectrometer. XRD (Philips PW 1800) and TEM (LEO 912AB) were used to characterize the copper oxide nanoparticles.

Preparation of CuO nanoparticle

For the synthesis of nano copper oxide,copper(II) nitrate trihydrate (Merck A G. For synthesis) wasused as the precursor. Preparationof CuO took place in a stainless steel autoclave thatwas able to endure working temperature and pressure of 550°Cand 610 atm, respectively. Concentration of $Cu(NO_3)_2$ was0.05 mol dm^{-3}, and heating period about 2 h. Synthesis was carriedout at 500°Cto accelerate the hydrolysis reactions. After removing from furnace, the autoclave was quenched bycold water and CuOnano particles were recovered from dischargedsolution by high speed centrifugation at 14,000 rpm for about60 min. The produced nanoparticles were then three times washedin the same centrifuge with ultra-pure water, and then dried atambient temperature.[25]

Synthesis of flavanones

General procedure for the synthesis of flavanone derivatives

A general procedure for the synthesis of flavanone derivatives was carried out bymixing of 1 mmol of 22 -hydroxyacetophenoneand 1.4mmol of aromatic aldehyde in 10 mL ethanol. CuO nanoparticle (5mmol%) was added and the reaction was stirred at room temperature and monitored by TLC. After completion of the reaction as indicated in table 1,the nanocatalystwas separated by high speed centrifugation. The product was precipitated by addition of the water drop by drop into the remaining solution.

RESULT AND DISCUSSION

The XRD pattern of nano-sized is shown in Fig. 1. All diffractionpeaks of X-ray are indexed to the monoclinic crystal system of CuO.No characteristic peaks are observed for other possible impurities,such as $Cu(OH)_2$,Cu_2O or $Cu(OH)_3NO_3$.

Average size of the obtainedCuO particle shown in Fig. 2 is 10 nm. The crystallite size was alsocalculated by X-ray line broadening analysis using the Scherrerequation.It was found that the

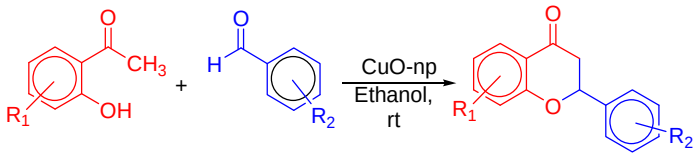
Table 1: Optimization of the catalyst amount

Entry	CuO-np (mmol%)	Time (h)	Yield(%)
1	0	8	Trace
2	1	6	45%
3	2	4	70
4	5	2	87%

Table 2. Synthesis of flavanone by using of different catalyst

Entry	Catalyst(mmol%)	Time (h)	Yield(%)
1	CuO-np (5%)	2	87
2	Bulk CuO (5%)	4	40%
3	Al_2O_3 (5%)	6	60
4	MgO (5%)	4	78%

Table 3: Synthesis of flavanone derivatives by using of nanoCuO as efficient catalyst



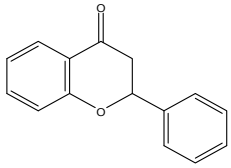
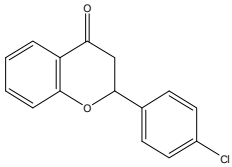
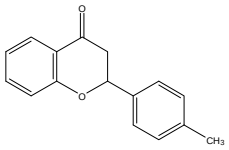
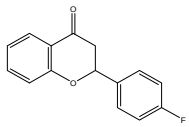
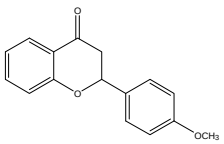
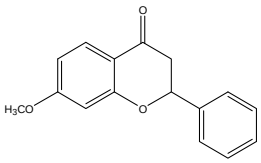
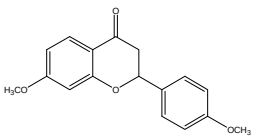
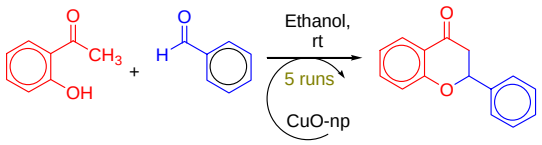
Entry	R_1	R_2	t (h)	Product	Yield (%)
1	H	H	2		87
2	H	4-Cl	2		79
3	H	4-CH_3	3		61
4	H	4-F	2.5		73
5	H	4-OCH_3	4		75
6	4-OCH_3	H	3		66
7	4-OCH_3	4-OCH_3			73

Table 4. The reusability study of nanoCuO catalyst



Run	1	2	3	4	5
Yield(%)	88	89	86	84	84

average CuO crystallite size is15 nm.The mean value of surface area of CuO catalyst was 37.58 m^2/ gfrom BET analysis.

In an initial reaction, we tried to synthesize the flavanone starting with benzaldehyde and 22 - hydroxyacetophenone by using 1mmol% of CuOnano particles inethanol in which the reaction was monitored by TLC. The isolatedproduct was obtainedin good yield (Scheme 1).

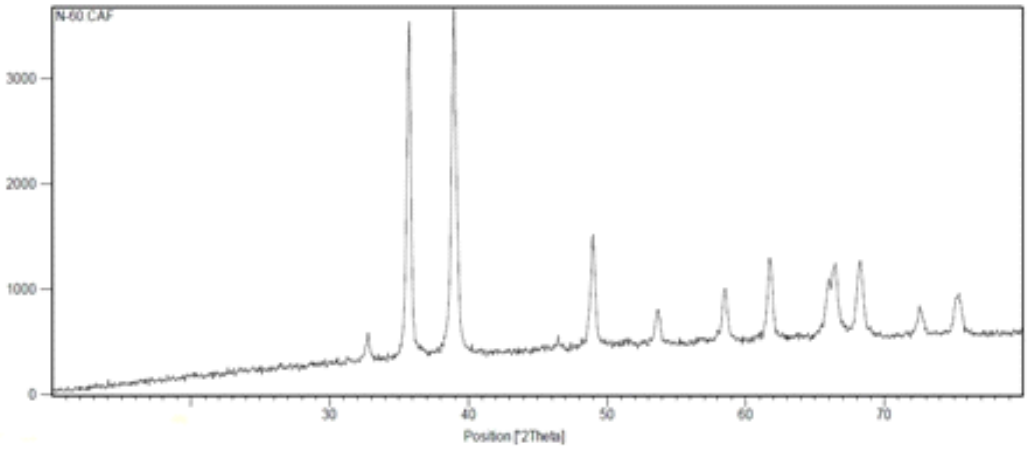


Fig. 1. XRD pattern of synthesized nanoCuO

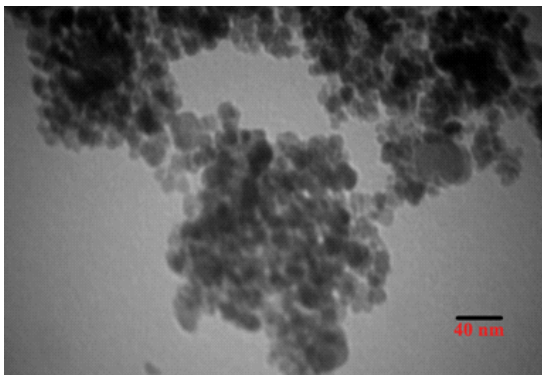
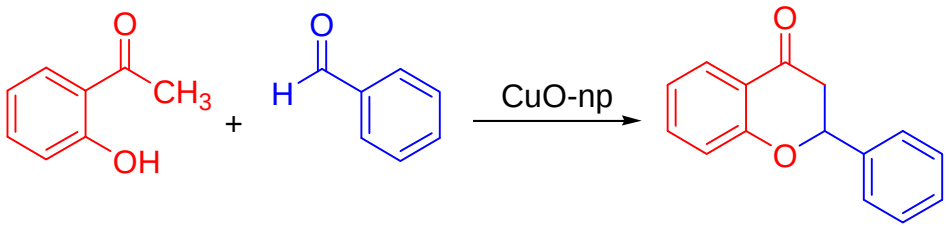


Fig. 2: The TEM image of nanoCuO

In the absence of catalyst, the desired flavanone was obtained in trace yield in 8 h (Table 1).Increasing the loading of CuO nanoparticles to 5mmol% gave the title product in 87% yield in 2 h. Thusan increase in the concentration of catalyst not only promotesthe reaction but also resulted in an increased yield (Table 1).

In order to find the efficiency and the superiority of nanoCuO catalyst, we continued our study by comparing the catalytic activity ofCuO nanoparticles with other traditional solid lewisbase



Scheme 1

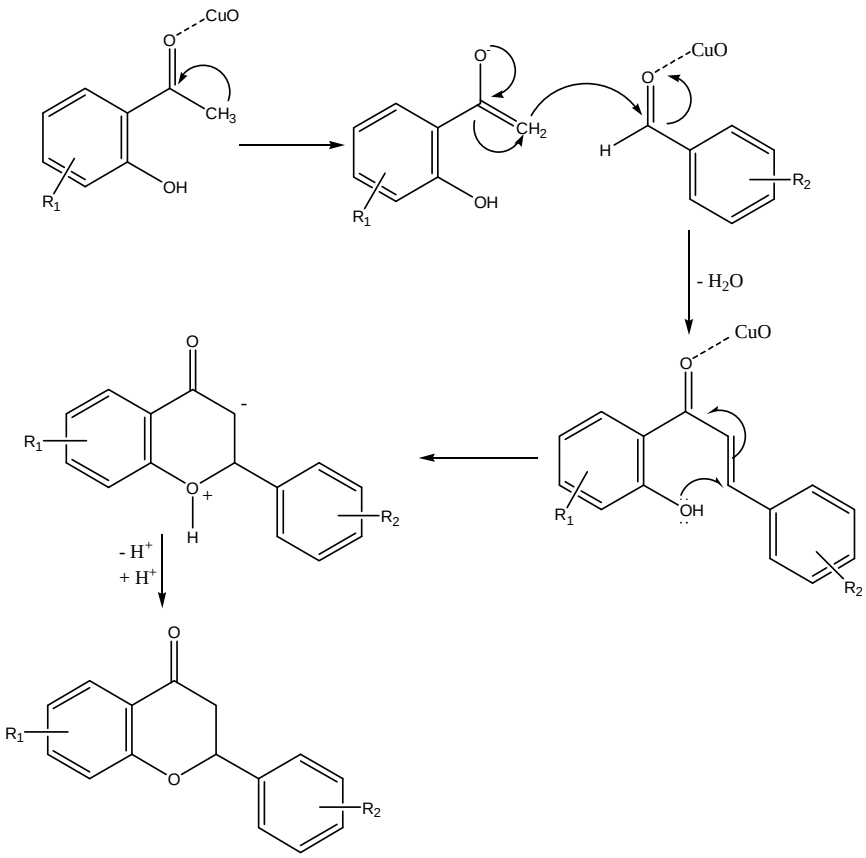
catalyst. The CuO nanoparticle catalyst was used along with other known solid basesas catalysts for the reaction between benzaldehyde and 22 - hydroxyacetophenone in 10 mL of ethanol as a model system for the synthesis of the corresponding flavanone derivative. The results are summarized in Table 2. Amongall of the catalysts tested CuO nanoparticles proved to be the mostefficient (Table 2).

The size of CuO plays an important role in terms of yieldsand reaction times. Changing the size of the particles from nanoparticles to bulk resulted in a drop in the catalytic activity. It isinteresting to note that the CuO nanoparticle catalyst catalyzesthe present reaction in high yield within a short reaction time comparedto the other solid base catalysts.The increased catalytic activity of nanoCuO over commerciallyavailable bulk CuO may be attributed to the higher surface area ofnanoCuO than bulk CuO as well as the higher surface concentration of the reactive sites.

After obtaining best results by using of nanoCuO as catalyst for the preparation of flavanone derivatives, the reaction was extended to other substituted benzaldehyde and 22 - hydroxyacetophenone and the results are depicted in Table 3.

In a mechanistical point of view, it is envisioned that the reaction proceeds through enolate intermediate at the first step followed by aldol-type condensation with bezaldehyde and finally an intramolecular cyclization leads to corresponding flavanone derivative (Scheme 2).

CuO nanoparticle catalyst was found to be reusable, however gradual decline of activity was observed. Better resultswere obtained when, after the first run, the catalyst was separatedby centrifugation, and the remained catalyst was washed with ether and dried at 150°C overnight, and reused. The reusability study applied for the reaction between benzaldehyde and 22 -



Scheme 2

hydroxyacetophenone as model reaction. Table 4represents the comparison ofefficiency of catalyst after five times.

CONCLUSION

In conclusion, CuO nanoparticle catalystwas simply prepared. The prepared heterogeneous catalysts were well characterized. The catalytic efficiency of the prepared catalysts was investigated for the preparation of flavanone derivatives. In the presence of the prepared solid catalyst, all the reactions were performed in short reaction times and gave the corresponding products at high yields. Nanosized particles,with a high surface to volume ratio, simple workup andrecovery, and reusability up to five consecutive runsmake this a new, efficient, and superior catalystfor the synthesis of flavanonederivatives.

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