Journal of Molecular Catalysis A: Chemical 359 (2012) 28–34

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Green synthesis of predominant (1 1 1) facet CuO nanoparticles: Heterogeneous and recyclable catalyst for *N*-arylation of indoles

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ARTICLE INFO

Article history:
Received 21 January 2012
Received in revised form 12 March 2012
Accepted 15 March 2012
Available online 28 March 2012

Keywords:
Nanoparticles
CuO
N-Arylation
Starch
Indoles

ABSTRACT

Well faceted CuO nanoparticles were synthesized by thermal-assisted green strategy at reflux temperature in a short period of time. A possible growth mechanism of such highly faceted nanostructures based on typical biomolecule-crystal interactions in aqueous solution is tentatively proposed. The large surface area (223.36 m^2/g) and rich exposed active sites are expected to endow such nanostructures with excellent performances in catalysis as demonstrated here for remarkable catalytic activity with respect to the *N*-arylation of indoles. Nanoparticles were characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Both the activity and selectivity of the *N*-arylation reactions could be tuned by varying the concentration of CuO nanoparticles. Nanoparticles catalyst were recycled and reused for further catalytic reactions with minimal loss in activity. A variety of indole derivatives afforded corresponding *N*-arylation product with excellent yields (up to 98%).

1. Introduction

Catalyst plays a significant role in the production of chemicals today and nanomaterials have the potential for improving efficiency, selectivity, and yield of catalytic process. The higher surface to volume ratio means that much more catalyst is actively participating in the reaction. The potential for cost saving is tremendous from a material, equipment, labour, and time standpoint. Higher selectivity means less waste and fewer impurities, which could lead to safer and reduced environmental impact. It was reported that catalytic performance of nanocrystals finely tuned either by their composition or by their shape which mediates the electronic structure [1,2]. The composition of nanocrystals was useful in determination of surface atomic arrangement and coordination [3–5]. When nanocrystals with different shapes were applied to electron transfer reaction the average rate constant of reaction increased exponentially with the percentage of surface atoms at the corners and edges increases [6,7]. Several groups intensively investigated the effect of shape of nanocrystals on their catalytic activity and stability and found that some specific facets are believed to be most catalytically active [8,9].

CuO nanoparticles as a catalyst for C–N, C–S, C–O cross-coupling reactions and *C*-arylation reaction have been well-documented because it is safe, cheap, having high theoretical capacity and environmental benignity [10–12]. How to improve catalytic performance is become more important and ranks as one of the hot topic. A fundamental goal of materials science is to design and synthesize materials with controllable shape, size and tailored functionality. The preparation of high purity, monodispersed nanocrystalline CuO using sonochemical [13], microwave irradiation [14], and precipitation-pyrolysis [15] methods were well reported. Major drawback of these methods was the formation of multifaceted CuO nanoparticles. Hence, in this paper, a facile one-step synthetic route is describe to construct face-centred-cubic (fcc) CuO nanostructures assisted by starch as a stabilizer at reflux temperature in a short reaction time. In comparison with reported protocols our method is green, environment-friendly, facile and time-saving. These particles have spherical morphology having predominant (1 1 1) facets, which are expecting to be chemically and dynamically active, therefore catalytically active. To the best of our knowledge, no studies have investigated the catalytic activity of predominant (1 1 1) facet nanometre sized CuO in *N*-arylation of indoles.

2. Experimental

2.1. Preparation of predominant (1 1 1) facet spherical shape CuO nanoparticles

All the reagents used in this synthesis were of analytical grade and used without further purification. CuO nanoparticles were prepared by decomposition of copper ammonia complex. The experimental procedure is briefly described as follows. The blue

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doi:10.1016/j.molcata.2012.03.017

Table 1
Optimization of reaction condition for the *N*-arylation of indole with iodobenzene.

Entry	CuO quantity (mol%)	Base (1 equiv.)	Solvent	Reaction time (h)	Yield[a] (%)
1	10	K_2CO_3	CH_2Cl_2	24	31
2	10	K_2CO_3	CH_3CN	24	59
3	10	K_2CO_3	DMSO	9	97
4	10	K_2CO_3	Toluene	24	76
5	2.5	K_2CO_3	DMF	12	65
6	05	K_2CO_3	DMF	8	98
7	05	–	DMF	24	13
8	00	K_2CO_3	DMF	24	00
9	05	KOH	DMF	24	65
10	05	DBU	DMSO	10	81
11	05	Et_3N	DMSO	10	73
12	03	K_2CO_3	DMSO	10	88

[a] Isolated yield.

solution of copper ammonia complex was stirred with 4 g starch as a stabilizing agent for 1 h followed by addition of 100 ml of 0.25 M $NaBH_4$ solution and resultant solution was refluxed for 1 h. During reflux the color of solution changed from blue to colorless and then it turned slowly to brick red which indicated the formation of CuO nanoparticles. The nanoparticle separated out by centrifuge at 3000 rpm and washed with water two to three times.

2.2. Sample characterization

The powder X-ray diffraction (XRD) measurements were carried out on a PHILIPS HOLLAND, XRD system using Cu Kα radiation ($\lambda = 1.54056$ Å). The morphology of the CuO nanoparticles was investigated via scanning electron microscopy (SEM), (model JSM-5400, JEOL) and transmission electron microscopy (TEM) (Philips CM200). The BET surface area was determined by specific surface area analyzer (ASAP 2000, micrometrics) with nitrogen gas as an adsorbate.

2.3. Catalytic test

Indole (0.351 g, 3 mmol), iodobenzene (0.673 g, 3.3 mmol), CuO nanoparticles (0.0105 g), K_2CO_3 (0.414 g, 3 mmol) and *N*,*N*-dimethyl formamide (10 ml) was taken in a round bottom flask fitted with a reflux condenser. The resulting mixture was refluxed for the time as mentioned in Table 1. The progress of the reaction was monitored by TLC. After completion of reaction, mixture cooled to room temperature and diluted with 10 ml of water and extracted with ethyl acetate (2× 10 ml). The combined organic extracts were washed with brine and dried on anhydrous sodium sulphate. Solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatography on silica gel using ethyl acetate and petroleum ether (1:9) as eluent to yield analytically pure product. Aqueous layer was centrifuged to recover CuO nanocatalyst.

3. Results and discussion

3.1. Structural analysis

The X-ray diffraction analysis of prepared CuO nanoparticles was carried to identify the product (Fig. 1).

All diffraction peaks are index with the corresponding planes of CuO. The XRD spectra showing an intense peak at 36.4 is having plane (1 1 1), which is the crystal plane of CuO. The low intensity peaks at 29.6, 61.7 which match well with the plane (1 1 0), (1 1 3).

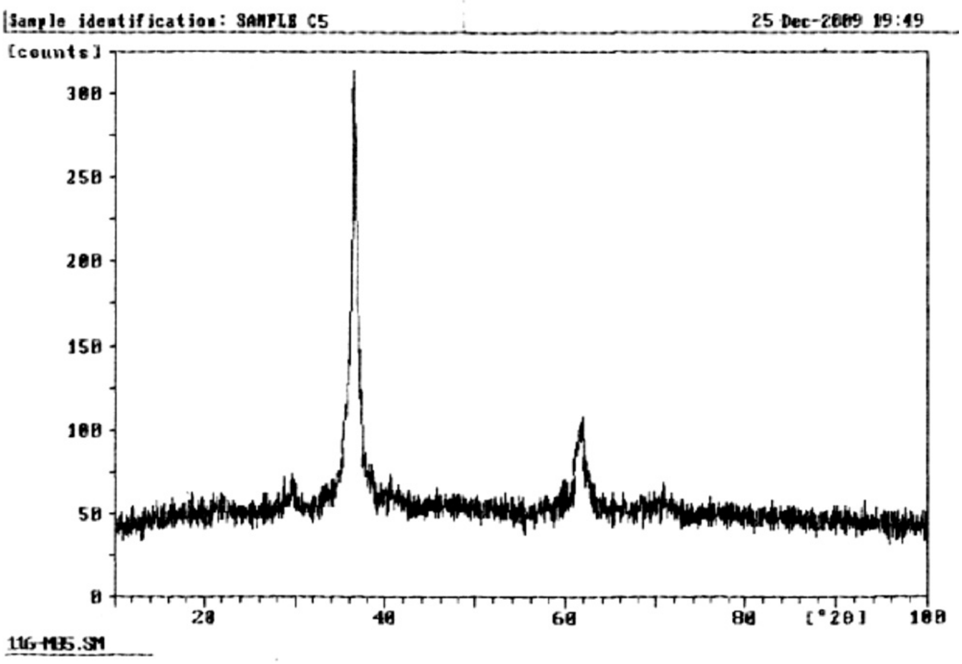

Fig. 1. XRD spectra of CuO nanoparticles.