



Cu–Cu₂O–SiO₂ NANOCOMPOSITE: A SIMPLE, EFFICIENT AND GREEN PROCEDURE FOR KNOEVENAGEL CONDENSATION REACTION

Ramdas K. Dhokale

Department of Chemistry, Arts, Science and Commerce College,
Naldurg, Dist. Osmanabad (MS), INDIA.

Corresponding author: rkdhokale@gmail.com

ABSTRACT:

A Knoevenagel condensation reaction between 4-Chlorobenzaldehyde and different active methylene compounds was performed in the aqueous medium under mild conditions using a Cu–Cu₂O–SiO₂ nanocomposite. The highest reaction rates and yields were obtained by using this catalyst. There is evidence to suggest that the reaction proceeds via an autocatalytic pathway, as an induction period was observed before the observed catalytic activity. It was also found that both surface acidic and basic sites are necessary to obtain high rates of the catalytic reaction.

KEYWORDS: Knoevenagel condensation, autocatalytic pathway.

1 INTRODUCTION

Knoevenagel condensation is an industrially important C–C bond formation reaction in organic synthesis, with widespread applications in the synthesis of fine chemicals [1] and pharmaceuticals [2, 3]. In recent years, chemical industries have seen an increased drive towards more environmentally acceptable processes, involving green chemistry methods in order to eliminate/ reduce chemical waste at the source and reduce the use of hazardous reagents in the synthesis. One of the key technologies utilised in green chemistry is heterogeneous catalysis. In general, Knoevenagel condensation through a heterogeneous catalytic pathway is largely base-catalysed, utilising materials such as alkaline exchanged zeolites [4, 5] mesoporous molecular sieves [6], non-porous oxides, mixed oxides, and doped oxides [7, 8]. Studies have also included organic–inorganic hybrid catalysts [9, 10]. Others have posited that the reaction may be acid-catalysed [11, 12].

In the investigation presented here, the Knoevenagel condensation reaction was performed using Cu–Cu₂O–SiO₂ catalyst. The use of these types of catalyst provides a wide range of overall acidity and basicity which allows for comparison of the catalytic activity with the surface acid–base properties, where the surface of such oxide supports reduces the support acidity and generates new basic sites [13, 14]. It is observed that a combination of Cu–Cu₂O–SiO₂ shows enhanced catalytic activity due to well dispersion of catalytic centres. With this aim, a series of Cu–Cu₂O–SiO₂ nanocomposites, having different concentrations of copper, has been synthesized and studied its

catalytic activity for the Knoevenagel condensation at room temperature.

2 EXPERIMENTAL DETAILS

All chemicals used were of AR grade. For the synthesis of Cu–Cu₂O–SiO₂ nanocomposites, the different chemical such as copper acetate, sodium dodecyl sulphate as a capping agents, hydrazine hydrate as a reducing agent, commercial silica were used. The 4-Chlorobenzaldehyde and different active methylene compounds were used for Knoevenagel condensation.

2.1 Preparation of Cu–Cu₂O–SiO₂ nanocomposites.

Cu–Cu₂O–SiO₂ nanocomposites were synthesized by chemical reduction followed by impregnation method. The copper nanoparticles were synthesised by using chemical reduction method. 5 mL (1x10⁻² M) copper acetate solution and 5 mL (1x10⁻² M) sodium dodecyl sulphate were mixed together. The mixture was stirred at 60°C for 30 min. 3 mL hydrazine hydrate solution was added drop by drop with constant stirring in oil bath keeping the temperature at 60°C. The dark coloured slurry/residue was obtained. The content was centrifuged, washed with distilled water, ethanol and

dried.

For making composite, the copper nanoparticles were dispersed into 100 mg silica powder with 5 mL distilled water. The resulting mixture was stirred for 2-3 hours at room temperature. In the nanocomposites, the amount of copper was varied from 5 wt %, 25 wt % and 50 wt%. The obtained residue was centrifuged, washed with water and dried. The product was used as a catalyst for Knoevenagel condensation.

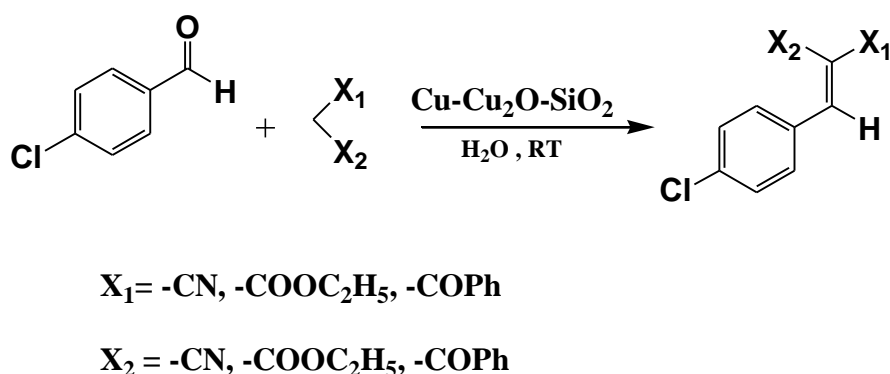
2.2 Characterization of Cu-Cu₂O-SiO₂ nanocomposites

X-ray diffractometer (Philips model PW-1710) was used to identify the structural properties of the samples using Cu K α radiation. Energy-dispersive spectroscopy technique (JSM-JEOL 6360) was used for the elemental analysis of the Cu-Cu₂O-SiO₂ nanocomposites. Particle morphology was measured using a transmission electron microscope (TEM) (Philips, CM200, operating voltages 20–200 kV). The UV-visible (UV-visible) spectra of the powders were recorded using a (JASCO model V-670) spectrophotometer equipped with an integrating sphere accessory. Barium sulphate was used as reference for the reflectance spectra. Fourier transform Infra-red (FT-IR) spectra of the catalysts were recorded in a Perkin-Elmer spectrometer using KBr pellets. The photoluminescence (PL) measurements of the samples were carried out by using Spectrofluorimeter (JASCO FP-750).

2.3 Catalytic activity

The catalytic properties of Cu-Cu₂O-SiO₂ system were examined by Knoevenagel condensation. This condensation was conducted between 4-Chlorobenzaldehyde and different active methylene compounds in water as a solvent. In this reaction, the mixture of 4-Chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), Cu-Cu₂O-SiO₂ (10 mg) catalyst with distilled water was taken in RB flask and stirred continuously at room temperature. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was treated with ethanol for separating the desired product and catalyst by filtration. The products were recrystallized by ethanol and thereafter the various experimental parameters such as melting points, reaction-time and yield of the products were noted. NMR spectra were taken in CDCl₃ using a Bruker Spectrospin Avance II-300MHz spectrophotometer and Jeol-400MHz spectrophotometer with TMS as an internal standard. The catalyst exhibited a clean reaction profile with excellent yields in a short reaction time. The experimental data of all the products were consistent with the proposed structure. Same procedure was adopted for different active methylene compounds.

The general route for Cu-Cu₂O-SiO₂ catalysed Knoevenagel condensation is given below:



3. RESULTS AND DISCUSSION

3.1 X-ray diffraction studies

Fig. 1.1 shows the powder X-ray diffraction patterns of Cu-Cu₂O and Cu-Cu₂O-SiO₂ nanocomposites. All samples show peaks corresponding to well crystallized phase of metallic copper particles [JCPDS card no. 85-1326, 04-0836, 70-3038, 89-2883] with the presence of small intensity peaks for Cu₂O particles [JCPDS No. 78-2076, 05-0667]. This observation reveals the presence of copper particles with Cu₂O particles due to

partial oxidation of surface copper particles [15]. The diffraction peaks with strong intensities appear at $\sim 43.41^\circ$, $\sim 50.36^\circ$, $\sim 74.16^\circ$ are corresponds to (111), (200) and (220) planes of copper particles, respectively. These diffraction peaks corresponds to face-centered cubic structure of elemental copper with the space group of Fm3m [JCPDS No. 85-1326]. The diffraction peaks at $\sim 36.27^\circ$ and $\sim 61.34^\circ$ indicates the presence of Cu₂O, which corresponds to the (110) and (211) plane. In the composites, the broad and diffuse diffraction peak of SiO₂ is observed at $\sim 21.44^\circ$, which is attributed to amorphous silica [16]. The crystallite size of copper as well as Cu₂O NPs was calculated by using Scherrer's equation.

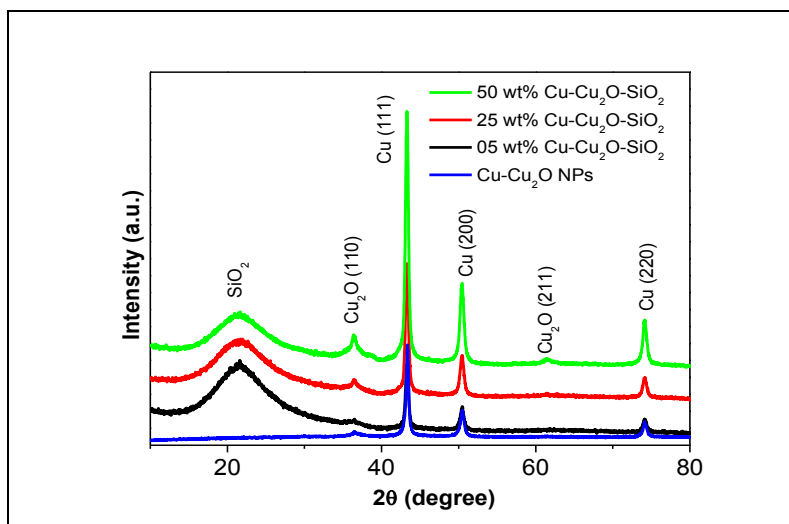


Fig. 1.1: Powder XRD patterns of (a) Cu-Cu₂O nanoparticles, (b) Cu-Cu₂O-SiO₂ (5 wt%), (c) Cu-Cu₂O-SiO₂ (25 wt %), and (d) Cu-Cu₂O-SiO₂ (50 wt %)

3.2 TEM and EDAX studies

Fig. 1.2 (a–b) depicts the transmission electron micrographs of Cu-Cu₂O and Cu-Cu₂O-SiO₂ samples. It is evident from Fig. 1.2(a) that the average particle size of copper nanoparticles is found in the range of 10–15 nm. Fig. 1.2(b) clearly shows the presence of a dispersed phase of Cu-Cu₂O particles in the matrix of SiO₂. The compositions of 5 wt% Cu-Cu₂O-SiO₂, 25 wt% Cu-Cu₂O-SiO₂ and 50 wt% Cu-Cu₂O-SiO₂ samples were determined by using the energy dispersive X-ray analysis (EDAX). Typical EDAX spectrum of 50 wt% Cu-Cu₂O-SiO₂ sample is shown in Fig.1.3. The quantitative analysis of the EDAX spectrum revealed that the relative atomic ratios of Cu and Cu: Si are close to the initial values taken for three nanocomposites samples.

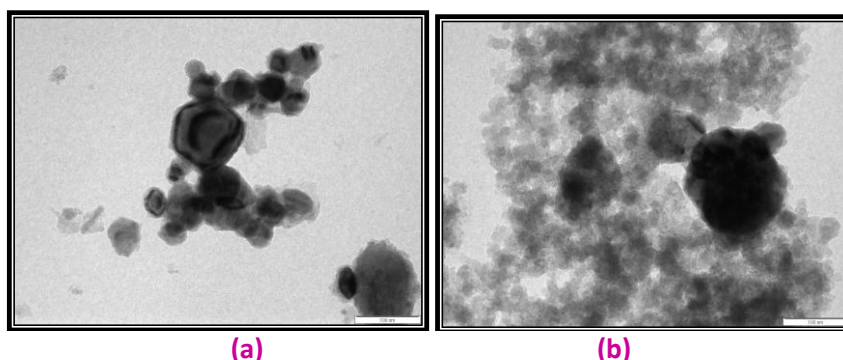


Fig. 1.2: TEM micrographs of (a) Cu-Cu₂O, (b) Cu-Cu₂O-SiO₂ (50 wt%).

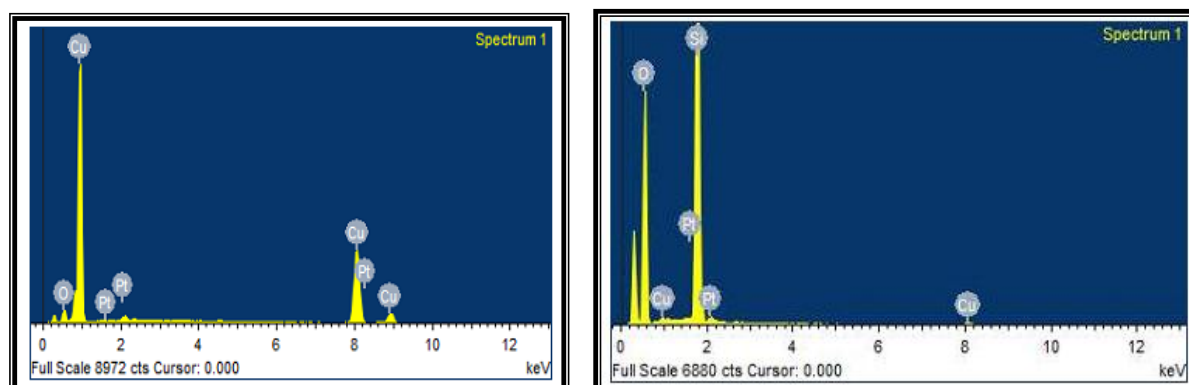


Fig. 1.3: EDAX patterns (a) Cu-Cu₂O nanoparticles and (b) Cu-Cu₂O-SiO₂ (50 wt %).

3.3 Optical absorption properties

Fig. 1.4 shows the UV-visible absorption spectra of the Cu-Cu₂O-SiO₂ nanocomposites in aqueous solution. In all spectra, the surface plasmon resonance (SPR) band is observed at 592 nm for Cu NPs [17]; while the broad absorption edge from 450 to 550 nm is noted for Cu₂O and SiO₂ particles [18].

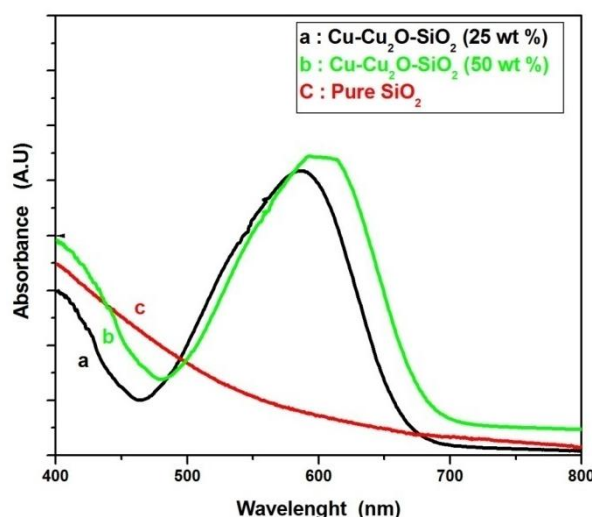


Fig. 1.4: UV-Visible spectra of pure SiO₂ and Cu-Cu₂O-SiO₂.

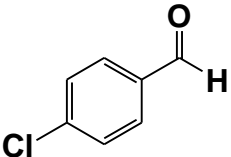
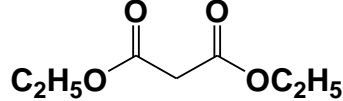
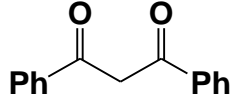
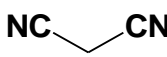
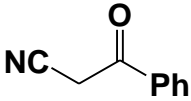
4 CATALYTIC STUDIES

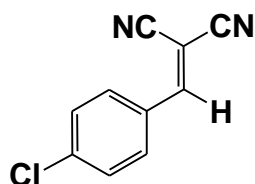
The catalytic activities of Cu-Cu₂O-SiO₂ nanocomposites have been tested towards the Knoevenagel condensation reaction of 4-Chlorobenzaldehyde and different substituted active methylene compounds in water as a solvent. It is observed that all the reactions occurred rapidly and are completed in 2-5 minutes giving excellent yields of the Knoevenagel products.

To determine the appropriate composition of the catalysts, we investigated the reaction at different composition of copper nanoparticles such as 5, 25 and 50 wt% supported on SiO₂ matrix. It is noted that 50 wt% copper NPs supported on SiO₂ yields large amount of products than that of other compositions. Therefore, the further catalytic studies are carried out using 50 wt% of Cu-Cu₂O-SiO₂ nanocomposite. The reactants and products formed with their percentage yield as well as melting point, in this condensation, are summarized in Table 1.1.

The yield of the products was in the range of 85-94 %, which reveals that, Cu-Cu₂O-SiO₂ (50 wt %) gave better yield with better selectivity also. Active methylene compounds with strong electron withdrawing groups (-CN) giving better yields in short time as compared to that of others.

Table 1.1: Cu-Cu₂O-SiO₂ (50 wt %) catalysed Knoevenagel condensation of 4-Chlorobenzaldehyde and different substituted active methylene compounds.

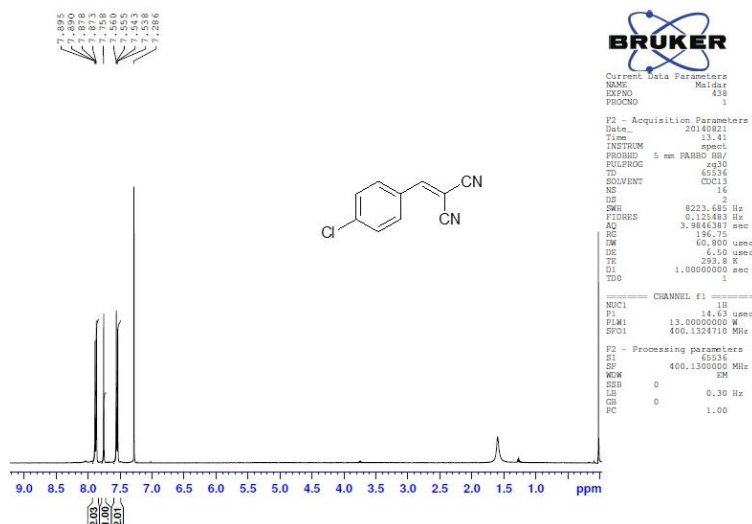
Sr. No.	Aldehyde	Different Active Methylene Compounds	Time (min)	Yield (%)	M.P. (°C) Observed
1			3	90	158-160
			5	85	166-168
			2	94	162 – 164
			3	92	164-166

5. SPECTRAL DATA OF SELECTED COMPOUNDS

2-(4-Chlorobenzylidene) malononitrile: Solid; **M.P.:** 162-164°C (Lit¹⁹.164°C);

IR (KBr): 3033, 2359, 2225, 1580, 1552, 856, 581cm⁻¹;

¹H-NMR (CDCl₃): δ 7.54 (dd, 2H, *J* = 7.5 & 3.2 Hz), 7.75 (s, 1H), 7.88 (dd, 2H, *J* = 7.3 & 3.1 Hz).

**Fig. 1.5: ¹H Spectra of 2-(4-Chlorobenzylidene) malononitrile****6. CONCLUSIONS**

A Knoevenagel condensation reaction performed in the aqueous medium by using Cu-Cu₂O-SiO₂ nanocomposite, demonstrated the highest catalytic activity, producing the highest product yield and overall rate. With this catalyst, no side-products were observed, and hence, the reaction selectivity was 100%.

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