



Review Of Research



ENVIRONMENTALLY BENIGN KNOEVENAGEL CONDENSATION REACTION BY NANOPARTICLES

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ABSTRACT

Selective catalytic Knoevenagel condensation is achieved with catalytic amounts of Cu–Cu₂O–SiO₂ supports. In this phase reaction, quantitative yields were obtained under mild reaction conditions. Cu–Cu₂O–SiO₂ catalysts showed efficiency of 100% conversion and 100% selectivity. With smaller quantities of Cu–Cu₂O–SiO₂ took less duration for the completion of reaction than other catalysts in this environmentally benign process.

KEYWORDS: Selective catalytic Knoevenagel, quantitative yields, environmentally benign process.

1 INTRODUCTION

There is an increasing focus on the development of environmentally friendly solid acid/base catalysts to minimize the effluents and pollution in the chemical industry due to the increasing anxiety of the legislation. It is challenging to develop heterogeneous catalyst leading to C–C formation, which are very widely applied in organic synthesis [1–2]. The versatile Knoevenagel condensation reaction is classically catalysed by bases [3–4] in the liquid phase systems, with known combinations of amines and carboxylic or Lewis acid under homogeneous conditions. This has copious applications for elegant synthesis of fine chemicals [5–6]. The main problems associated with the usage of bases and acids in the reactions are huge organic waste generated due to the formation of unwanted by products resulting from polymerization, bis-addition and self-condensation, and the total dissolved salts resulting from the neutralization of the soluble bases or acids. Literature survey reports various heterogeneous catalysts mediated reactions using aluminium oxide [7], xanolate/potassium-tert-butoxide [8–9], cation-exchanged zeolites [10], alkali containing MCM-41 [11], AlPO₄–Al₂O₃ catalysts [12], clays as KSF, K10 [13–16],

hydrotalcites [17–23], anionic resins [24] and diamino-functionised mesoporous materials [25–26], to mention a few. Solid supported reagents are exceptional acid catalysts which have become popular in the past two decades. Their application in organic synthesis forms a viable alternative to the use of conventional acids/bases and homogeneous catalysts. Low toxicity, moisture, air tolerance and low price are other common features make the use of solid supported reagents as attractive alternate to the conventional Lewis acid and triflates. Many researchers reported the efficacy of Cu–CuO₂–SiO₂ catalyst in highly selective reactions [27–29]. In this communication we report the scope use of Cu–CuO₂–SiO₂ for Knoevenagel condensation, which proved to be excellent. 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-Nitrobenzaldehyde 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. The synthetic route is as shown in Fig.1.1.



Fig. 1.1: Synthetic route of Cu–Cu₂O–SiO₂ nanocomposites.

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

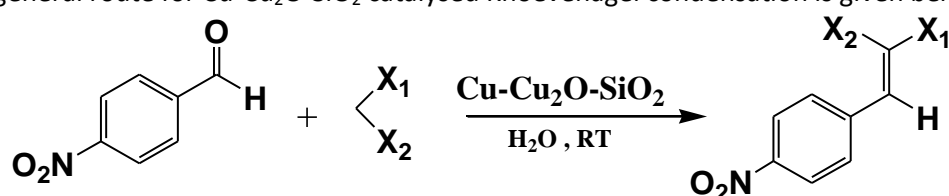
X-ray diffractometer (Philips model PW-1710) was used to identify the structural properties of the samples using Cu K α radiation. Energy-dispersive spectroscopy technique (JSM-JEOL 6360) was used for the elemental analysis of the Cu–Cu₂O–SiO₂ nanocomposites. Particle morphology was measured using a 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-Nitrobenzaldehyde and different active methylene compounds in water as a solvent. In this reaction, the mixture of 4-Nitrobenzaldehyde (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. 1.2 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 [30]. The diffraction peaks with strong intensities appear at ~43.41°, ~50.36°, ~74.16° 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 ~36.27° and ~61.34° 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 ~21.44°, which is attributed to amorphous silica [31]. The crystallite size of copper as well as Cu₂O NPs was calculated by using Scherrer's equation.

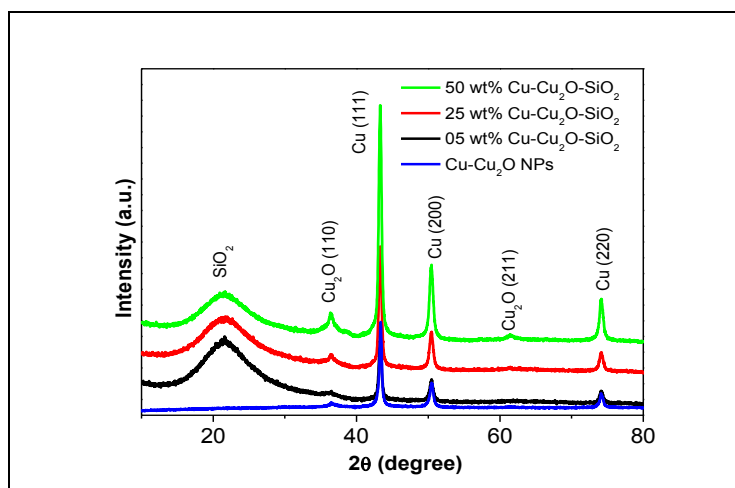


Fig. 1.2: Powder XRD patterns of (a) Cu-Cu₂O nanoparticles, (b) Cu-Cu₂O-SiO₂ (5 wt%), (c) Cu-Cu₂O-SiO₂ (25 wt %), and (d) Cu-Cu₂O-SiO₂ (50 wt %)

3.2 TEM and EDAX studies

Fig. 1.3 (a–b) depicts the transmission electron micrographs of Cu-Cu₂O and Cu-Cu₂O-SiO₂ samples. It is evident from Fig. 1.3(a) that the average particle size of copper nanoparticles is found in the range of 10-15 nm. Fig. 1.3(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.1.4. 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.

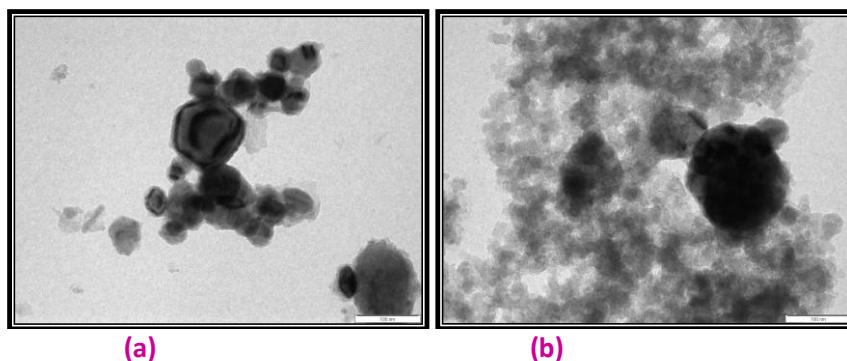


Fig. 1.3: TEM micrographs of (a) Cu-Cu₂O, (b) Cu-Cu₂O-SiO₂ (50 wt%).

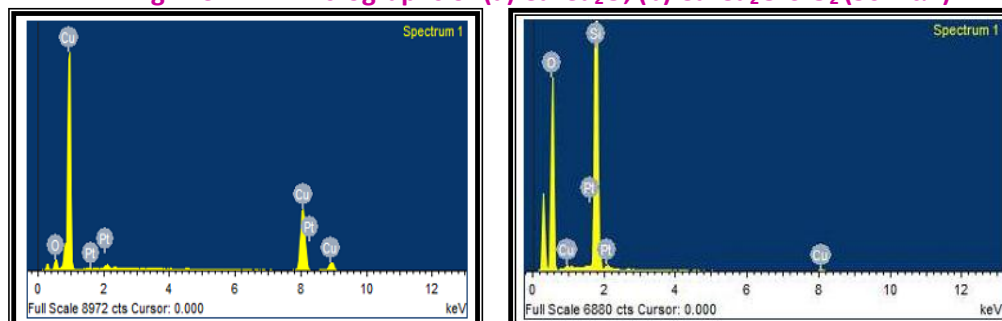


Fig. 1.4: EDAX patterns (a) Cu-Cu₂O nanoparticles and (b) Cu-Cu₂O-SiO₂ (50 wt %).

3.3 Optical absorption properties

Fig. 1.5 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 [32]; while the broad absorption edge from 450 to 550 nm is noted for Cu₂O and SiO₂ particles [33]. Earlier literature reported that the UV/Vis absorption spectrum of Cu₂O was characterized by a broad absorption band from 400 to 600 nm with intercepts to wavelength-axis at 500 nm [34]. Yeshchenko et al. synthesized copper nanoparticles embedded in SiO₂ matrix, which exhibited surface plasmon resonance (SPR) absorptions in the visible-light region. As shown in figure, the SPR peak of copper nanoparticles at 592 nm is more intense compared to the absorption edge of Cu₂O particles. This also confirms the ratio of copper nanoparticles is more than that of Cu₂O particles.

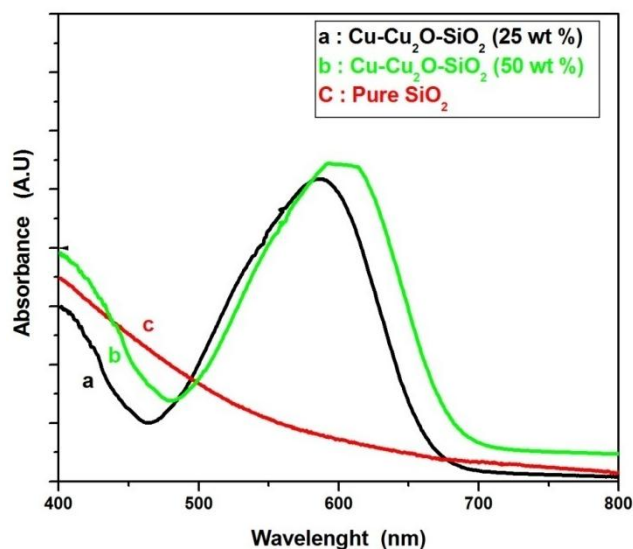


Fig. 1.5: UV-Visible spectra of pure SiO₂ and Cu-Cu₂O-SiO₂.

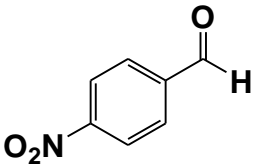
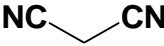
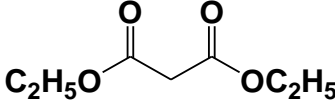
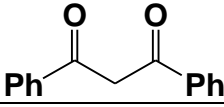
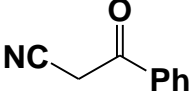
4 CATALYTIC STUDIES

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

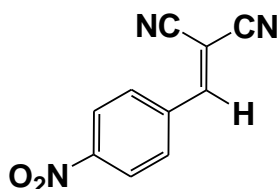
To determine the appropriate composition of the catalysts, we investigated the reaction at different composition of copper nanoparticles such as 5, 25 and 50 wt% supported on SiO₂ matrix. It is noted that 50 wt% copper NPs supported on SiO₂ yields large amount of products than that of other compositions. 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 88-95 %, 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-Nitrobenzaldehyde and different substituted active methylene compounds.

Sr. No.	Aldehyde	Different Active Methylene Compounds	Time (min)	Yield (%)	M.P. (°C) Observed
1			2	95	160 – 162
			3	90	158-160
			4	88	162-164
			3	92	162-164

5. SPECTRAL DATA OF SELECTED COMPOUNDS



2-(4-Nitrobenzylidene) malononitrile: solid; M.P.: 160-162°C (Lit³⁵. 160-161°C);

IR (KBr): 3116, 3039, 2359, 2230, 1578, 1556, 1413, 934, 779 cm⁻¹;

¹H-NMR (CDCl₃): δ 7.90 (s, 1H), 8.10 (d, 2H, J = 8.0 Hz), 8.41 (d, 2H, J = 7.9 Hz).

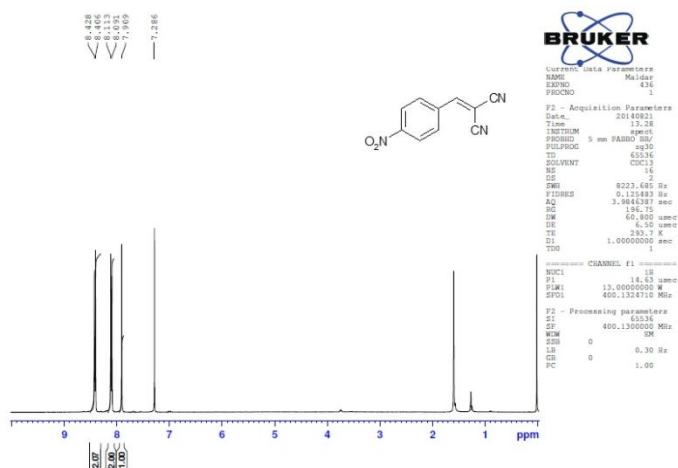


Fig. 1.6: ¹H Spectra of 2-(4-Nitrobenzylidene) malononitrile

6. CONCLUSIONS

A new catalytic process is developed with higher order of activity for the conversion of C–C bonds by Knoevenagel condensations with high degree of selectivity using small amounts of catalyst. This new heterogeneous catalyst is a practical alternative for application of Knoevenagel reactions in view of the following advantages: (a) use of non-toxic and inexpensive catalysts (b) involvement of environmentally

benign processes and (c) reusability of catalyst (d) high catalytic activity under very mild conditions (e) easy separation of the catalyst by simple filtration.

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