

Investigation of catalytic properties of green synthesized copper oxide nanoparticles in Biginelli reaction

P. A. S. H. Perera and H. I. C. De Silva*

Department of Chemistry, University of Colombo, Sri Lanka

* *hicdesilva@chem.cmb.ac.lk*

Biginelli-type synthesis is an efficient one-pot synthesis method for preparation of 3,4-dihydropyrimidine derivatives, which have many pharmaceutical properties. Use of a Lewis acidic earth abundant transition metal oxide such as nano-copper oxide rather than concentrated HCl, as the catalyst, allows Biginelli reaction to be conducted in a greener approach. The catalytic potential of green synthesized copper oxide nanoparticles was studied in two Biginelli type reactions. Black tea leaf waste powder-aqueous extract (BTLE) was prepared by heating the tea waste powder (5 g) with double distilled water (100 ml) at 60 °C for two hours. Synthesis of copper oxide nanoparticles was done by mixing $[\text{Cu}(\text{CH}_3\text{COO})_2] \cdot \text{H}_2\text{O}$ (2.795 g), dissolved in double distilled water (70 ml), with BTLE (20 ml). The calcination temperature was 320 °C. Based on the powder-XRD of the synthesized nanoparticles, the copper (I) oxide was majorly present with a lower fraction of copper (II) oxide. SEM image analysis revealed nanoparticle (50-100 nm) aggregates of few micrometers (1-5 μm). To study the catalytic activity of the nanoparticles in the Biginelli reaction, the reaction between urea, ethyl acetoacetate, and benzaldehyde was conducted with variation of time from one, two, and eight hours with the reagent stoichiometry controlled

at 1.0: 1.1: 1.1 equivalents of benzaldehyde, ethyl acetoacetate, and urea, respectively, in refluxing ethanol. In each trial, a constant amount of copper oxide catalyst (30 mg) was used. The obtained crude was recrystallized with ethanol. When the reaction time was increased from one hour to two hours, the Biginelli product yield increased from 26.0 % to 29.0 %. At the end of eight hours, the Biginelli product was obtained at a 31.8 % yield. The ^1H NMR and the FTIR analysis confirmed the formation of the pure product, ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate. The reaction between urea, ethyl acetoacetate, and 4-methoxybenzaldehyde, conducted under the same reaction conditions for eight hours, yielded the methoxy derivative of Biginelli product in 8.7%. Formation of the product was confirmed by FTIR and ^1H NMR analysis. The lesser yields in the Biginelli type reactions indicate that green synthesized copper oxide nanoparticles with high copper (I) oxide content do not act as an efficient catalyst in Biginelli type reactions.

Key words:

Green synthesis, Copper (I) oxide, catalysis, Biginelli reactions