Supporting Information

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Free-ZnO nanoparticles: An efficient green catalyst for the one-pot multicomponent synthesis of tetrahydrobenzo[b]pyran and dihydropyrimidone derivatives

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ESI-1: Method for the Preparation of ZnO NPs:1

Procedure: ZnO NPs have been synthesized by dissociation of Zn(OAc)₂·2H₂O in a basic medium at temperatures 60-75°C. For synthesizing nanoparticles ZnO NPs, 100 ml 3M NaOH solution in ethanol is slowly added in 50 ml 1M solution of Zn(CH₃COO)₂·2H₂O in ethanol kept at 65 °C. The final solution was stirred and heated at 65 °C for 1 h. When the reactions were completed, the solid and solution phases were separated by centrifugation and the solids were washed free of salts with de-ionized water (3x5 ml) and ethanol (2x5 ml). This method allows precipitation of ZnO nanoparticles and avoids precipitation of hydroxides if the temperature is more than 60°C. The formation of nano-sized particles were confirmed by UV-Vis and TEM studies.

ESI-2: Method for the Preparation of SiO₂ NPs:2

Procedure: A mixture of 20 ml of ethanol and 20 ml water was stirred for few minutes then 4 ml of tetraethyl orthosilicate (TEOS) followed by 4 ml of aqueous ammonia solution (NH₄OH) were added with continuous stirring by the mechanical stirrer machine for 5 hours. After that the mixture was kept to settle down and washed thoroughly with water and ethanol, centrifuged and white colloidal part was used for reactions.
ESI-3: Method for the Preparation of Fe₃O₄ NPs:\(^3\)

**Procedure:** The magnetic Fe₃O₄ nanoparticles were synthesized by co-precipitation method. Briefly, co-precipitating aqueous solutions of (NH₄)₂Fe₂(SO₄)₃ and FeCl₃ mixtures, in alkaline medium. (NH₄)₂ Fe₂(SO₄ )₃and FeCl₃ solutions are mixed in their respective stoichiometry *(i.e. Ratio Fe : Fe =1:2).* The mixture is kept at 80 °C. This mixture is added to the boiling solution of NaOH (0.5 mol. is dissolved in 200 ml of distilled water) within 10 second under constant stirring. The solution was maintained at 90-95 °C for 1.5 h. The Fe₃O₄ nanoparticles were washed several times by distilled water and used for reaction. The separation of Fe₃O₄ nonoparticles by an external magnet shown in figure below.

ESI-4: Method for the Preparation of CuO NPs:\(^4\)

**Procedure:** To prepare CuO NPs NaOH (0.5M) solution added drop by drop to a 0.1 M copper nitrate solution (100 ml) in a 500 ml beaker till the pH of the solution reaches to 12 (checked by pH paper). The blue green gel was formed. It was then filtered and washed several time with distilled water to free nitrate. It was then dried in a hot oven at 100 °C for 10 hours to decompose Cu(OH)₂ to CuO NPs.

Method for the Preparation of Metal Oxide Supported Lewis-Acid Catalyst:

**ESI-4: Preparation of Al₂O₃-FeCl₃ Lewis Acid Catalyst:**

**Procedure:** A mixture of anhydrous iron(III) chloride (1 g) in two drops of conc. HCl, aluminium oxide (10 g) and chloroform (30 ml) was refluxed for 3 h with continuous stirring and then cooled to room temperature. The white silica turned yellow due to absorption of
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FeCl$_3$ on surface of alumina (Al$_2$O$_3$). The solid residue was separated by filtration and then catalyst (SiO$_2$-FeCl$_3$) was completely dried in oven before use. The same experimental procedure has been adopted for the preparation of SiO$_2$-FeCl$_3$, Al$_2$O$_3$- and Al$_2$O$_3$-ZnCl$_2$ catalysts.

References:


