



Boosting multiple photo-assisted and temperature controlled reactions with a single redox-switchable catalyst: Solvents as internal substrates and reducing agent



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ABSTRACT

An alternative and economically viable process for the synthesis of β-aryl enals, enones and the aryl amines has been developed by partial oxidation of ethanol, isopropanol and *N,N*-dimethyl formamide (DMF). The formation of β-aryl enals, enones and the aryl amines was catalyzed by a mixed metal oxides layer of cobalt and chromium supported on halloysite nanotubes, designated as CoCr₂O₄-HNT. The C–C and C–N bond formation reactions were found to be influenced by temperature and the nature of base. The condensation of aldehyde with *in situ* generated acetaldehyde by ethanol oxidation forming β-aryl enals occurred selectively at 120 °C. The partial oxidation of isopropanol to acetone and its condensation with aldehydes forming β-aryl enones occurred at room temperature. Increase in temperature caused the liberation of hydrogen gas from isopropanol and allowed the reversible reduction of aldehydes to alcohols. Increase in temperature in isopropanol and increase in base concentration in ethanol causes the selective reduction of aldehydes to alcohols. Besides being active for the Claisen-Schmidt type of reactions and the aryl halides amination process, the synthesized catalyst was also found to be highly active for the photocatalytic oxidation of benzyl alcohols in absence of any external oxidizing agent. The positive holes (h⁺) generated at the Co(II) site as evident from EPR analysis was considered to be responsible for high photocatalytic activity of the material reducing the recombination rate of holes and electrons (e⁻). Density Functional Theory calculations were performed to understand the mechanism of ethanol oxidation to acetaldehyde.

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