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First Report on Silicate Intercalated Monometallic Cobalt Hydrotalcite (Co-HT) Materials: Preparation and Its Applications

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Monometallic cobalt hydrotalcite having interlayer silicate anions were prepared for the first time by the simple sol–gel method. The FT-IR spectra and powder XRD patterns revealed the presence of silicate anions in the interlayer space. The DR-UV-Vis spectra were evidence of the presence of cobalt in Co^{3+} and Co^{2+} in the octahedral environment. The resultant silicate anions intercalated cobalt hydrotalcite materials possessing high surface area, exposed active sites and found to be promising activity for the oxidation of primary and secondary alcohols under solvent-free conditions.

Keywords: Layered Compounds, Catalytic Properties, Sol–Gel Chemistry, Oxides, Nanostructures.

1. INTRODUCTION

Layered cobalt hydroxide constitutes an important class of materials and has shown immense potential in various research fields such as catalysts, supercapacitors, electrocatalysts, biosensors, electrochromic electrodes and optical devices, water treatment agents etc.[1–5] Hydroxides of cobalt are well known to crystallize in two different polymorphs: α-$Co(OH)_2$ and β-$Co(OH)_2$. The α-$Co(OH)_2$ is reported to be isostructural with hydrotalcite-like material with a residual positive charge owing to the presence of cobalt partially in the Co^{3+} oxidation state ($Co(OH)_{2-x}$), which results in a layered structure possessing charge balancing anions (e.g., NO_3^-, CO_3^{2-}, Cl^-, etc.).[6–12] However, the layered α-$Co(OH)_2$ is converted into spinel upon calcination at high temperature.[6–10] Although the resultant α-$Co(OH)_2$ has shown immense potential as a supercapacitor, biosensor etc., the catalytic applications are limited. It is speculated that the introduction of hard anions such as silicate and phosphate anions might result in the stabilization of layered HT-type α-$Co(OH)_2$ structures and have exposed cobalt species, which may have potential for catalytic applications. The presence of interlayer silicate anions might stabilize the layered structure of α-$Co(OH)_2$ and provide both a redox and Lewis acid centre. In this regard, it is worth mentioning here that we have recently developed the silicate anions stabilized hydrotalcite materials and shown their potential as catalysts for various organic transformations.[6–10] The oxidized products of alcohols to aldehydes and ketones are valuable intermediates in the organic synthesis, fine chemical, pharmaceutical and agricultural sector industries.[9, 13] The use of noble metals such as Ru, Pd, Pt, Au and metal oxide catalysts have been reported for selective oxidation; however, the higher cost, scarcity and toxic nature of noble metals limit their applications.[14] To the best of our knowledge, this is the first report on the synthesis of cobalt-based monometallic hydrotalcite with an interlayer silicate anion. The developed materials were used in the oxidation of various primary and secondary alcohols into aldehydes and ketones under mild conditions.

2. EXPERIMENTAL SECTION

2.1. Preparation of α-$Co(OH)_2$

The synthesis of α-cobalt hydroxide has been carried out in round bottom (RB) flask by simple sol–gel method.[6–10, 15] In a typical procedure involve dissolving calculate amount of cobalt acetate ($Co(CH_3COO)_2 \cdot 4H_2O$ (5.0 mmol)) and hexamethylenetetramine HMT (60.0 mmol) in 200 ml of solution containing 9:1 mixture of deionized water and ethanol. The resultant reaction mixture was allowed to stir for 17 h at 90 °C, which yielded α-$Co(OH)_2$ precipitate.

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