Catalysis

Surfactant Intercalated Mono-metallic Cobalt Hydrotalcite: Preparation, Characterization, and its Bi-functional Electrocatalytic Application

Dhanjay Sharma,[a] A. Sakthivel,*[b] S. Michelraj,[c, d] A. Muthurasu,[c, d] and V. Ganesh*[c, d]

A series of surfactants are intercalated into mono-metallic hydrotalcite type α-$Co(OH)_2$ through ion exchange method to produce organic-cobalt hydrotalcite (HT-SDS, HT-TMA and HT-SL). The resultant material maintains its inner laminate structure with increased interlayer spacing. FT-IR spectroscopic studies and powder XRD analysis revealed the successful intercalation of SDS into the interlayers of α-cobalt hydroxides. TEM and N_2 sorption studies further demonstrate the intercalation of organic surfactant in the interlayer spacing of CoHT. XPS studies indicated the presence of surface exposed cobalt in both Co^{2+} and Co^{3+} oxidation states. Furthermore, the applicability of these intercalated materials in electrocatalytic applications specifically for oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) in alkaline medium is explored. Among the various investigated materials, sodium dodecyl sulphate (SDS) intercalated material exhibited better performance in terms of higher catalytic current at a lower overpotential value. Moreover, the kinetic parameters associated with electrocatalysis are determined, and the mechanism behind OER and ORR is elucidated. These results clearly demonstrate the potential bi-functional utility of such layered materials for electrocatalytic applications.

1. Introduction

Chemistry behind the intercalation of organic molecules into layered materials is very interesting and mainly involves host-guest interaction between the layered inorganic materials and organic macromolecules. This strategy often significantly changes the chemical, catalytic, adsorption, magnetic, optical, and electronic properties of the resultant intercalated layered materials.[1] The presence of organics within the interlayer of inorganic materials facilitates the isolation of active sites, which presents many opportunities for industrial applications such as heterogeneous catalysts, adsorbents to remove toxic effluents, and in electrochemical devices such as capacitors, sensors, electrocatalysts and batteries.[2] Nanoporous inorganic materials such as clay (cationic and anionic) and layered zeolites play a major role in the intercalation of several ionic and non-ionic molecules.[3] Hydrotalcite (HT) is one of the attractive candidates that possess exchangeable anions that can intercalate into the interlayer space forming a variety of composite materials.[4,5] The introduction of various anions such as inorganic ions, polyoxo anions, and organic anions, along with macromolecules impart unique properties to the composite, which render them promising applications in various fields namely adsorption, catalysis, polymer additives, drug delivery, supercapacitors, electro-catalysis, bio-sensors, and optical devices.[4,5]

Layered hydrotalcite materials are positively charged, with anionic (e.g. SiO_4^{4-}, CO_3^{2-}, NO_3^{2-}, Cl^-, and OH^-) gallery occupying the interlayer spacing.[5] Different layered materials have been studied with the intercalation of various anionic surfactants. Mg–Al LDH (layered double hydroxide) materials have been reported with intercalating ions, viz.., SDS, sulfate, sulfonate, carboxylate, and phosphate; the resultant materials find various applications as the polymer nanocomposites and lubricant additives.[6] In addition, recent years attention also focused on the preparation of mono-metallic hydrotalcite and explored its applications.[4b,c and 5b,c] In this regard, it is worth mentioning here that, cobalt hydroxide exists in two polymorphs viz., α-$Co(OH)_2$ and β-$Co(OH)_2$, among which α-$Co(OH)_2$ is difficult to synthesize because the α-phase is meta-stable and transforms rapidly into the β-form during synthesis.[5] α-Hydroxides are iso-structural with hydrotalcite-like materials. In general, mono-metallic HT derived from α-$Co(OH)_2$ exhibits superior electrochemical activity as compared to that of the β-form because of its poor or turbo-statically crystallized structure.[7] Hence, the anionic surfactant-intercalated cobalt layered double hydroxides with large interlayer spacing have attracted much interest for the study of electrochemical redox activity, mineral flotation

[a] Dr. D. Sharma
Department of Chemistry, Inorganic Materials & Catalysis Laboratory, University of Delhi (North Campus), Delhi-110007, India
E-mail: dhananjay.ssd@gmail.com
[b] Prof. Dr. A. Sakthivel
Department of Chemistry, School of Physical Sciences, Central University of Kerala, Tejaswini Hills, Periye P.O., Kasaragod-671320, Kerala, India
E-mail: sakthiveldu@gmail.com
sakthivelcuk@cukerala.ac.in
[c] S. Michelraj, Dr. A. Muthurasu, Dr. V. Ganesh
Electrodics and Electrocatalysis (EEC) Division, CSIR – CentralElectrochemical Research Institute (CSIR–CECRI), Karaikudi – 630003, Tamilnadu, India.
[d] S. Michelraj, Dr. A. Muthurasu, Dr. V. Ganesh
Academy of Scientific and Innovative Research (AcSIR), Ghaziabad – 201002, India
E-mail: vganesh@cecri.res.in
ganelectro@gmail.com

Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.202002030