Synthesis and Characterization of Transition Metal based Nanocatalysts for Energy Efficient Electrochemical H_2 production

Santosh Semwal (santoshs@rgipt.ac.in)

Department of Sciences and Humanities

Rajiv Gandhi Institute of Petroleum Technology Jais, Amethi, Uttar Pradesh, India

Abstract

The development of efficient and durable catalysts for hydrogen production mediated by various oxidation reactions is crucial for enabling clean and sustainable hydrogen energy technologies. Transition metal (TM) compounds have emerged as promising heterogeneous catalysts for oxidizing sulfur compounds, water, and methanol to generate hydrogen gas and valuable chemicals via thermochemical and electrochemical routes. Hydrogen has emerged as a promising energy carrier for a sustainable and low-carbon future. However, the development of economical and scalable production methods from abundant feedstocks remains a significant challenge. The electrochemical oxidation of sulfur-based compounds is a crucial process in various industrial applications, such as the desulfurization of fuels, production of sulfuric acid, elemental sulfur and hydrogen. TM-based catalysts have been extensively studied for Sulfion Oxidation Reaction (SOR) due to their unique electronic properties, high conductivity, and ability to facilitate electron transfer reactions. These catalysts can significantly enhance the reaction kinetics, selectivity, and overall efficiency of the SOR process. The choice of TM, its composition, nanostructure, and support material play a vital role in determining the catalytic performance. The electrochemical water oxidation reaction is a key half-cell reaction in many nonconventional energy conversion and storage technologies, such as electrochemical water splitting is pollution-free approach to produce hydrogen fuel and used in metal-air batteries. But, the sluggish kinetics of the OER

present a significant bottleneck that requires effective catalysts to facilitate the multi-electron transfer process. TM-based heterogeneous catalysts have emerged as promising candidates due to their high activity, stability, and earth abundance compared to noble metal catalyst. The electrochemical conversion of methanol to value-added chemicals has gained significant attention due to the increasing demand for sustainable energy storage and chemical production. Among the potential products, formate (HCOO) is a valuable chemical feedstock with applications in various industries, including agriculture, pharmaceuticals, and energy storage. The electrocatalytic oxidation of methanol to formate offers an attractive alternative to traditional chemical processes, as it can be conducted under mild conditions and potentially utilize renewable electricity. TM-based catalysts have shown great promise in facilitating the selective oxidation of methanol to formate. These catalysts can be designed and tailored to achieve high activity, selectivity, and stability through careful selection of metal centers, ligand environments, and nanostructured architectures.

Chapter 1: In this chapter, we have elaborated the detailed introduction and literature survey of TM-based catalyst for sulfion, water and methanol oxidation reaction. TM-based catalysts have high electrocatalytic activity, high surface area with high active sites for MOR, OER and HER.

Chapter 2: In this chapter, the synthesis of the NiFeOOH-Co_9S_8 heterojunction catalyst represents a promising approach for sustainable hydrogen production and waste valorization. This bifunctional catalyst leverages the synergy between the nickel-iron oxyhydroxide (NiFeOOH) and cobalt sulfide (Co_9S_8) components to facilitate the sulfur oxidation reaction (SOR) coupled with the hydrogen evolution reaction (HER). The SOR involves the oxidation of sulfur-containing compounds, such as sulfion (a mixture of sulfur-containing waste from industrial processes and petroleum refining), to produce valuable chemicals like sulfuric acid and elemental sulfur. Simultaneously, the HER occurs, generating hydrogen gas as a clean energy carrier.

Chapter 3: In this chapter, the Co_3O_4@NiCu-Polymer nano cubes synthesized using polyacrylolyl hydrazide as a reducing and capping agent on a nickel foam surface represent a versatile and efficient catalyst system for both methanol oxidation and water oxidation reactions. The selective production of formate from methanol and the ability to operate without a membrane system make this catalyst promising for various energy-related applications, such as fuel cells, chemical synthesis, and water splitting processes.

Chapter 4: In this Chapter, the trimetallic CoCeFe catalyst was synthesized via a reducing sugar method, likely involving the reduction of metal precursors by a carbohydrate like glucose to form the mixed metal oxide/sulfide nanoparticles. This catalyst is being explored for the water splitting reaction, which produces hydrogen gas as a clean fuel. Here we used cerium with Co and Fe because cerium itself can act as both a catalyst and a catalyst promoter. Its flexible coordination environments and excellent redox properties (ability to cycle between Ce^{3+} and Ce^{4+} oxidation states) make it advantageous. The redox cycling of Ce can facilitate charge transfer processes involved in catalytic cycles.

Chapter 5: In this chapter, we have concluded the important aspect of TM based nano catalyst for efficient electrochemical H_2 production. Future perspectives of the work are also discussed, along with some key recommendations.