

Metal-Organic Frameworks and Their Derivatives for Heterogeneous Catalysis

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Abstract

Catalysis has sparked intense interest in both scientific research and industrial applications. A catalyst is a material that speeds up a chemical reaction towards equilibrium while consuming relatively little energy. One or more desirable reactions can proceed more quickly and selectively under generally benign conditions by utilizing the right catalyst. Since catalytic processes are used to produce more than 95% of all modern chemical products, the search for better catalytic materials is an exciting and rapidly developing area of study.

Metal-organic frameworks (MOFs) offer significant potential for the rational design of novel catalytic materials as indicated by the several numbers of publications published in the last ten years. The coordination bonds between metal ions/clusters and organic ligands form the foundation of these novel class of crystalline porous materials. MOFs excel as heterogeneous catalysts due to several characteristics, including their remarkable structural diversity, intrinsic hybrid organic–inorganic nature, unsaturated metal sites, potential voids for host guest interactions etc. However, the broadness of catalytic applications using MOFs are quite limited, as MOFs are considered not stable under harsh acidic or basic conditions. In the present thesis, we have discovered a MOF based heterogeneous system which is chemically and thermally stable under harsh basic conditions.

Electrochemical energy storage and conversion technologies have been acknowledged as the most viable solutions to address the world's mounting energy dilemma due to their high levels of energy efficiency and minimal environmental impact. Redox flow batteries, rechargeable Zn - air batteries, proton exchange membrane fuel cells, water electrolyzers are some of the EESC systems that have received the greatest attention and development. Regardless of their various working theories, these electrochemical systems all aim for the physicochemical properties of materials to determine their ultimate storage capacity and conversion efficiency. These properties include low cost, low overpotential, high electrochemical active surface area, better electronic conductivity or lower charge transfer resistance, well-defined redox couples, long-term stability at higher current density etc.

MOFs are a developing precursor for earth-abundant element-based electrocatalysts. Because of polymeric nature and presence of organic/metal moieties, by calcination/carbonization a MOF can be converted into metal/carbon composite or individually each (refer as MOF-derived materials), depending upon the calcination gaseous environment. Pure MOF electrocatalysts suffer from low stability, nonconductivity, severe environmental sensitivity under extreme acidic/basic electrolytic conditions. Although MOF-derived materials partially address these issues, they nevertheless have certain inherent drawbacks, such as an inability to regulate the pore size during carbonization and dissolution of active sites particularly in acidic media. Therefore, more work is

required in this current research to enhance the functionality of MOF derivatives for application in actual EESC devices in the future.

Chapter 1: In this chapter, we give a brief introduction of MOF and MOF-derived materials. With an emphasis on structure-property relationships, we discuss key elements of creating MOF catalysts, their atomic-level structural information. We also summarize the MOF catalysts used so far for various organic transformation reactions. A detailed study on the working principles of the electrochemical energy storage and conversion devices, along with that we have discussed the methods for creating unique MOF-derived nanostructured materials with functionalities that are specifically suited for electrocatalysis.

Chapter 2: In this chapter, we have developed an earth-abundant Mn based heterogeneous catalyst using the trick of immobilization of homogeneous Mn-Phenanthroline complex into MOF pores. The as synthesized heterogeneous catalysts designated as Mnphen@ZIF demonstrated as first MOF based catalysts for the selective synthesis of functionalized branched ketones where alcohols being used as renewable coupling partner. Superior stability of catalyst under harsh basic conditions well examined by SEM, TEM, BET, PXRD, TGA and EDX elemental mappings. The borrowing hydrogen strategy was validated through mechanistic studies and deuterium labelling experiments. The released hydrogen gas was also measured by water displacement method or quantified by GC. Formation of extra Lewis acid sites, defects, and pore enhancement during catalysis helped in achieving higher activity and selectivity.

Chapter 3: In this chapter, a unique synthetic approach has been introduced where nano structurally grown zinc layered double hydroxide on graphitic carbon felt (CF) is converted into a zeolitic imidazolate framework (ZIF-8), and then, subsequent carbonization resulted in a N/O-functionalized porous carbon electrode (N,O/CF). Because of the presence of N/O-containing functional groups and deposition of ZIF-8-derived nano porous carbon on the CF, the N,O/CF is found to be highly hydrophilic in nature with a large surface area. Cyclic voltammetry measurements with N,O/CF suggest the fast electrochemical kinetics of $V(IV) \leftrightarrow V(V)$ reactions. Polarization curves and electrochemical impedance spectroscopy measurements of the vanadium redox flow battery (VRFB) assembly illustrate the significant decrease in charge transfer resistance at electrode surfaces. At 50 mL/min electrolyte flow rate, N,O/CF delivers energy efficiencies of 83.11 and 76.66% at current densities of 40 and 80 mA/cm², respectively. The values are 82.59 and 76.39%, respectively, at 100 mL/min, showing the negligible effect of the flow rate. The power density of VRFBs at various electrolyte flow rates is also presented, which increases with increasing flow rates and is higher for N,O/CF (~821 mW/cm²) than for bare CF (606 mW/cm²). The stability test confirms the retention of energy, voltage, and coulombic efficiencies after recycling of the electrode. The above-mentioned findings of improved performance of VRFBs with employing the N,O/CF electrode are a cumulative effect of enhanced nano porosity, an increased number of catalytic active sites, high wettability, and low charge transfer resistance.

Chapter 4: In this chapter, we report atomically dispersed Co-Mn dual single atom catalysts anchored on nanostructured N-doped porous carbon polyhedral synthesizing via controlled carbonization of a Co/Mn-doped ZIF-8 MOF. The atomically isolated Co-Mn site in CoMn/NC is recognized by combining microscopic as well as spectroscopic techniques. CoMn/NC exhibited excellent ORR activities in alkaline ($E_{1/2}$, 0.89V) as well as in acidic ($E_{1/2}$, 0.82 V) electrolytes with long-term durability and enhanced methanol tolerance. Density functional theory (DFT) suggests that Co-Mn site is efficiently activating the O–O bond via bridging adsorption, decisive

for the 4e⁻ oxygen reduction process. Though the Co-Mn sites favor O₂ activation via the dissociative ORR mechanism, stronger adsorption of the intermediates in the dissociative path degrades its overall ORR activity. Our DFT studies conclude that ORR on Co-Mn site mainly occurs via bridging side-on O₂ adsorption following thermodynamically and kinetically favorable associative mechanistic pathways with lower overpotential and activation barrier. CoMn/NC performed excellently as a cathode in proton exchange membrane (PEM) fuel cell and rechargeable Zn-air battery with high peak power densities of 970 & 176 mW cm⁻², respectively. This work provides the guidelines for the rational design and synthesis of non-precious DSACs for enhancing the ORR activity as well as robustness of DSACs and opens the door to design the multi-functional robust electrocatalysts for energy storage and conversion devices.

Chapter 5: In this chapter, based on the current studies we have drawn the conclusion. We also discuss the work's potential future directions and important suggestions.
