Current Developments in Immobilised Homogeneous CO2 Electrocatalysts in Intrinsically Electron Conducting Metal-Organic-Frameworks and Concepts for Electrocatalytic Systems
J.J. Peek

Abstract

Electrocatalysis has made enormous leaps forward in the last decade and can now be considered a serious potential system for the efficient conversion of electrical energy into chemical energy. One of the most interesting applications for electrocatalysis is the reduction of carbon dioxide to high-grade chemicals such as carbon monoxide, formic acid, oxalic acid, formaldehyde, methanol and methane. These substances can then be used in industry or transportation, creating a closed cycle. This idea originates from a regenerative economy, which states the waste emission can be limited by recovering and re-using it. Recently, solid support for catalysis has been at the centre of attention, electrocatalysis is no exception. In general, solid carriers ensure a simplified separation process of the product and medium. In addition, catalysts on solid supports can in theory be recycled, which reduces catalysis costs. Metal-organic frameworks (MOFs) are structures made of metal nodes with organic struts linked between them, forming a vast framework. MOFs are a sophisticated solid support design and is one of the most attractive materials for catalyst immobilisation. MOFs have additional benefits besides the general solid support advantages. MOFs have an extremely high porosity that is unprecedented among other solid carriers, which grants them a high degree of mass transport and surface area. This makes the MOF structure extremely suitable for catalysis, where mass transport and surface area ensure optimal substrate/catalyst contact and thus the most efficient conversion to product can be achieved. This porosity is, however, a complication in the context of electrocatalysis. Charge transport through the MOF is complicated by large distances. Nevertheless, several examples of good electrical conductivity in MOFs have appeared in recent years and the concepts underlying this have been discovered. In this review, the concepts and foundations required for a complete electrocatalytic system with homogeneous catalysts immobilised on MOFs are examined. This is done on the basis of the research question: What are the current developments for immobilised homogeneous CO2 electrocatalysts in intrinsically electron conducting metal-organic-frameworks and which concepts are essential for a good electrocatalytic system? The proposed ideas are placed in context with the help of scientific examples, with the aim to highlight the most recent developments and give researchers a clear picture of the current progressions, challenges, and prospects in this multidisciplinary research field. The most important findings for electro conductive MOFs are the redox matching between metals and organic linkers and the advantage of high energy minority spin electrons for the charge density. Homogeneous electrocatalysis has discovered the importance of the second coordination sphere for effective CO2 catalysis and has proven first-row transition metals can compete with second and third-row metal complexes in terms of activity, selectivity and stability. In catalyst immobilisation techniques, cation exchange and atomic layer deposition (ALD) are the latest developments that can provide more diversity. In addition, pyrolysis is a good tool for obtaining carbonised MOF structures. The latest developments have mainly focused on single-atom catalysts whether or not immobilised in porphyrins or directly in the MOF via pyrolysis. These examples show the most essential required characteristics for its use in a catalytic system, namely; long-term stability, high activity, and good selectivity.