ISGC 2022

N°1248 / PC
TOPIC(s) : Homogenous, heterogenous and biocatalysis / Mechanism investigations

Understanding the Reactivity of Isolated Iridium Sites in Covalent Triazine Frameworks for Formic Acid Dehydrogenation

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PURPOSE OF THE ABSTRACT

In the context of various global crises, renewable energy and their storage possibilities are of ever-increasing importance. Green hydrogen attracts growing attention as a secondary chemical energy carrier but requires reversible storage solutions. A promising candidate for storing molecular hydrogen is formic acid (FA), which releases carbon dioxide upon dehydrogenation.[1]

This chemical transformation needs suitable catalysts. Both, homogeneous and heterogeneous catalysts have been reported. In addition, heterogeneous catalysts that contain isolated metal sites are a highly promising material class for this kind of reaction, as they combine high activities and easy process control.[2] In this light, a recent example for a very efficient FA dehydrogenation catalyst consists of isolated iridium sites immobilized on nitrogen-rich covalent triazine frameworks (CTFs).[3] For this Ir/CTF catalyst, a surprisingly high stability against agglomeration of the metal species under reductive conditions was found for temperatures up to 400 °C. Compared to the Ir/CTF prior to reductive treatment, the reduced catalyst shows an increased activity for FA dehydrogenation to CO2. Nevertheless, both materials have a high selectivity due to very little CO formation. However, despite extensive analytical investigations the understanding of the processes on a molecular level remains scarce.

In this work, density functional theory calculations are performed to elucidate the dehydrogenation of FA to CO2 and H2 on the Ir/CTF system used in experiment. The active site of the catalyst is investigated by systematically probing anchoring sites of Ir and modeling of the metal environment. Furthermore, potential mechanisms and activation barriers of the FA dehydrogenation are examined for the most probable catalyst model (Fig. 1). These results are compared to analytical results in order to explain the particular stability of the isolated Ir sites and excellent activity for the release of hydrogen from FA. The findings for this specific catalyst model will improve the understanding of contributions to the catalyst activity and provide insights into the in silico design of efficient future catalysts.

This work was performed as part of the Cluster of Excellence Fuel Science Center (EXC 2186, ID: 390919832) funded by the Excellence Initiative by the German federal and state governments to promote science and research at German universities.

FIGURES

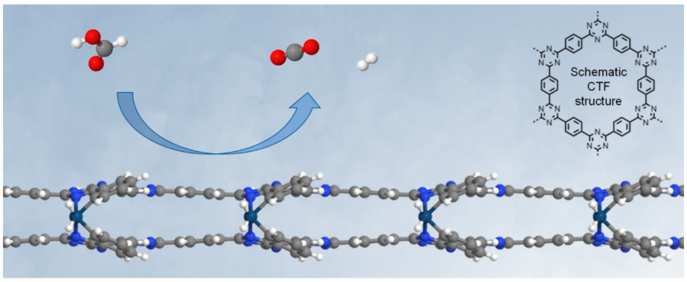

FIGURE 1

Schematic illustration of formic acid dehydrogenation on iridium immobilized on CTF.

Color code: gray = C, white = H, red = O, blue = N, dark blue = Ir.

FIGURE 2

KEYWORDS

Formic Acid Dehydrogenation | Isolated Sites | Covalent Triazine Framework | DFT

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