

UNPRECEDENTED NICKEL CENTERED H⁺ REDUCTION CATALYSIS: ACCURATELY MODELLING MULTIPLE STATES OF THE [NiFe]-HYDROGENASE

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Hydrogen production through water splitting appears to be the best solution in the long run for the storage of renewable energies. Hydrogenases are organometallic enzymes containing iron and/or nickel metal centers, whose catalytic performances rival that of platinum for hydrogen evolution. Their fascinating properties make them the ideal inspiration for the design of new molecular catalysts for technological devices. However, all heterodinuclear NiFe models reported so far do not reproduce the reactivity that occurs at the active site of [NiFe] hydrogenases, a mainly Ni-centered chemistry. We will report on a structural and functional NiFe mimic that displays an unprecedented reactivity at the Ni site. This is attested by the detection of two catalytic intermediates that reproduce structural and electronic features of the Ni-L and Ni-R states of the enzyme during catalytic turnover. Under electrocatalytic conditions, this mimic displays a high turnover frequency for H₂ evolution from mildly acidic solutions.

