nffa trieste

Introduction to Magnetocatalysis

Piero Torelli

CNR - Istituto Officina dei Materiali, ss 14 km 163.5, 34149 Trieste, Italy

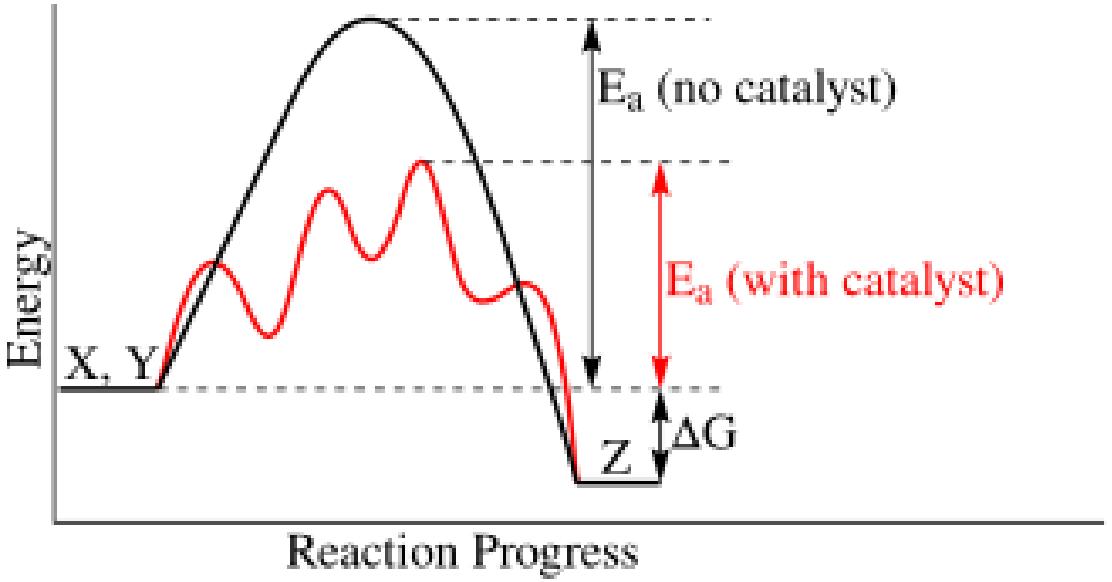
ISTITUTO OFFICINA DEI MATERIALI

Introduction to……Catalysis

Catalysis is the increase in rate of a chemical reaction due to an added substance known as a catalyst. Catalysts are not consumed by the reaction and remain unchanged after the reaction. If the reaction is rapid and the catalyst is recycled quickly, a very small amount of catalyst often suffices; mixing, surface area, and temperature are important factors in reaction rate. Catalysts generally react with one or more reactants to form intermediates that subsequently give the final reaction product, in the process of regenerating the catalyst.

-homogeneus (where catalysts and products are in the same phase)

-**heterogeneous** (where catalysts and products are in the same phase)



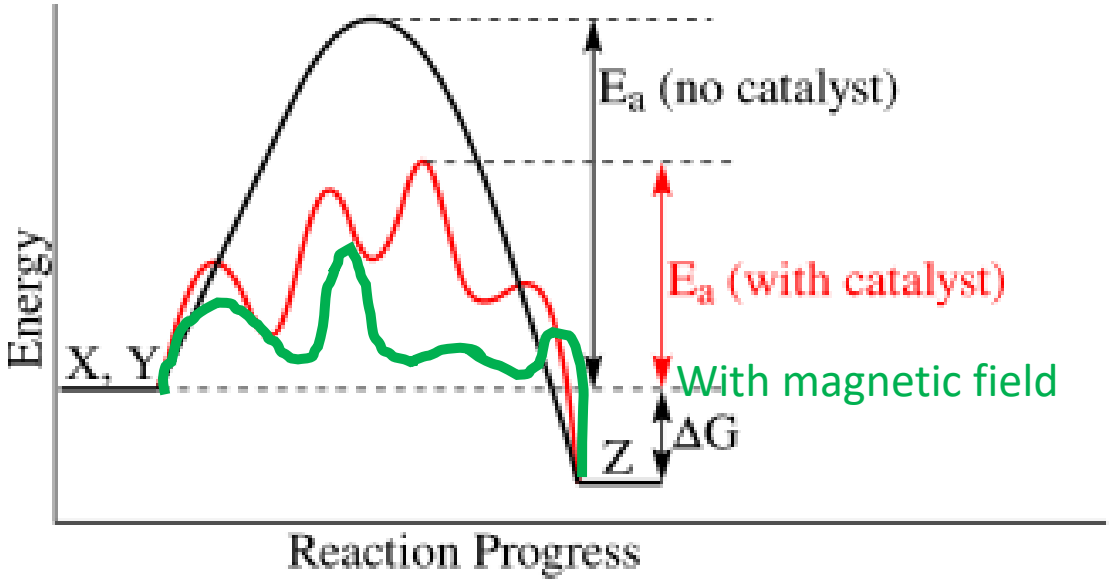
Credits: Wikipedia

Magnetocatalysis or Magnetochemistry

Magnetocatalysis: not found on wikipedia

Magnetochemistry is concerned with the magnetic properties of chemical compounds and elements.

The Magnetocatalysis study the way in which magnetic field or the catalysts magnetization influences the parameter of a chemical reaction (rate or selectivity); in the end the energy landscape of the reaction path.



The origin of magnetocatalysis (or spin-catalysis)

Few years ago it has been proposed that the use of ferromagnetic catalysts could help in lowering the overpotential of the oxygen evolution reaction (OER). The OER is a fundamental step in the water splitting process Is one of the two half reaction of the water electrolysis. Due to the technological and economical importance of the water electrolysis (for the hydrogen production) this has generated a great hype on the possible effect of magnetic catalyst on the water electrolysis.

In the presence of acid, the equations are:

Cathode (reduction): $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Anode (oxidation): $H_2O(l) \rightarrow 1/2\ O_2(g) + 2\ H^+(aq) + 2e^-$

In the presence of base, the equations are:

Cathode (reduction): $2\ H_2O(l) + 2e^- \rightarrow H_2(g) + 2\ OH^-(aq)$

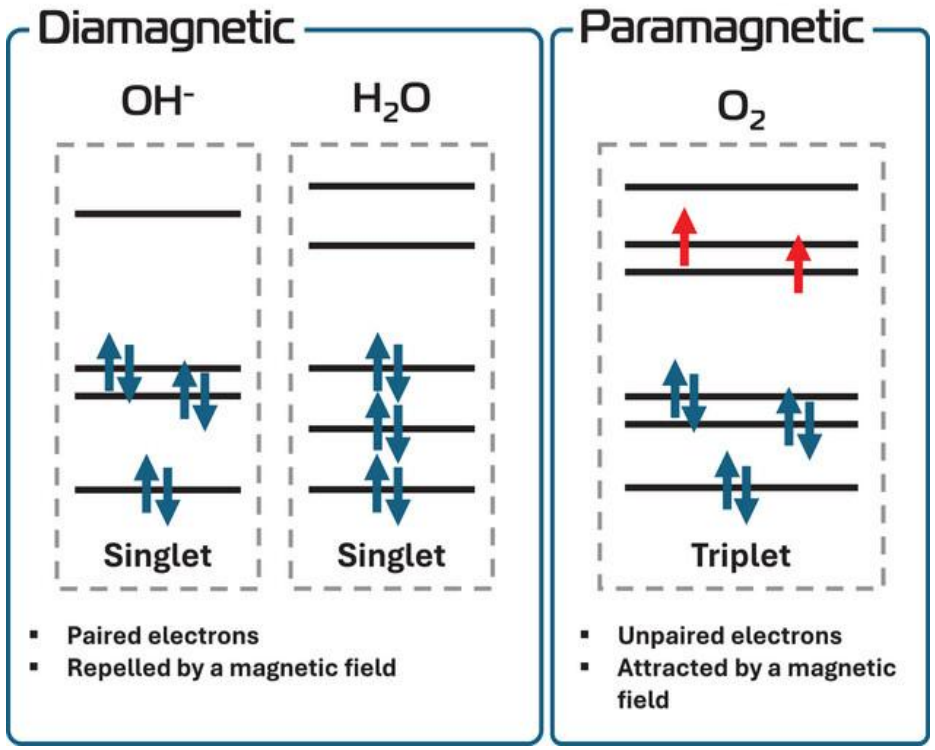
Anode (oxidation): $2\ OH^-(aq) \rightarrow 1/2\ O_2(g) + H_2O(l) + 2\ e^-$

Combining either half reaction pair yields the same overall decomposition of water into oxygen and hydrogen:

$2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$

When the spin comes in

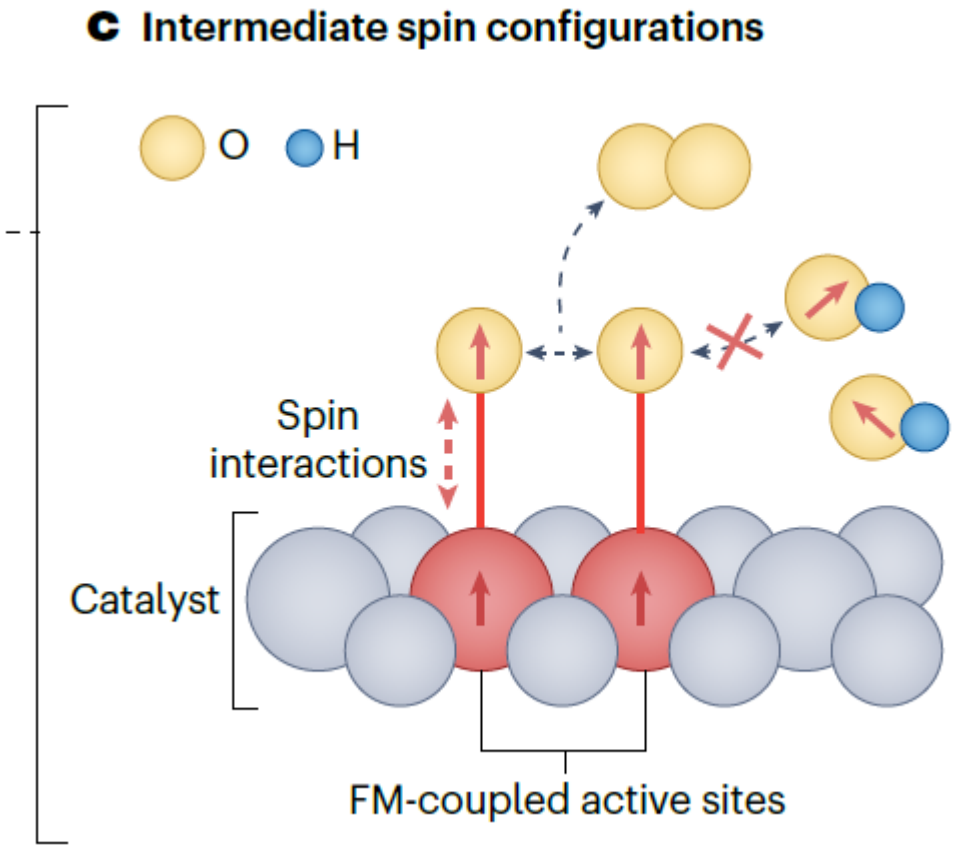
Maybe not everyone knows that……



One important factor contributing to these high overpotential and sluggish kinetics of the OER is the spin-state mismatch between reactants and products; while the reactants (OH− or H2O, depending on the electrolyte pH) are DM, the final product, molecular oxygen (O2), is a PM species in its triplet ground state. Spin is thus not conserved between reactants and products, and this process would, in principle, be forbidden by the spin selection rule. To be more specific, we can assume that, although the reaction is complex and involves at least four steps of electron transfer (typically considered as proton coupled electron transfer steps), there will be a step in the mechanism that involves the transition from a singlet intermediate to a triplet one.

The “hypothesis”

In a simplistic picture the idea is that the spin polarization of the catalyst is transferred to the intermediates of the reaction which afterwards can with less energy create the desired product of the reaction by creating a paramagnetic molecule with the right spin configuration



A more complete description

PCCP

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Phys. Chem. Chem. Phys.*, 2017, **19**, 20451

Spin dependent interactions catalyse the oxygen electrochemistry

J. Gracia [ab]

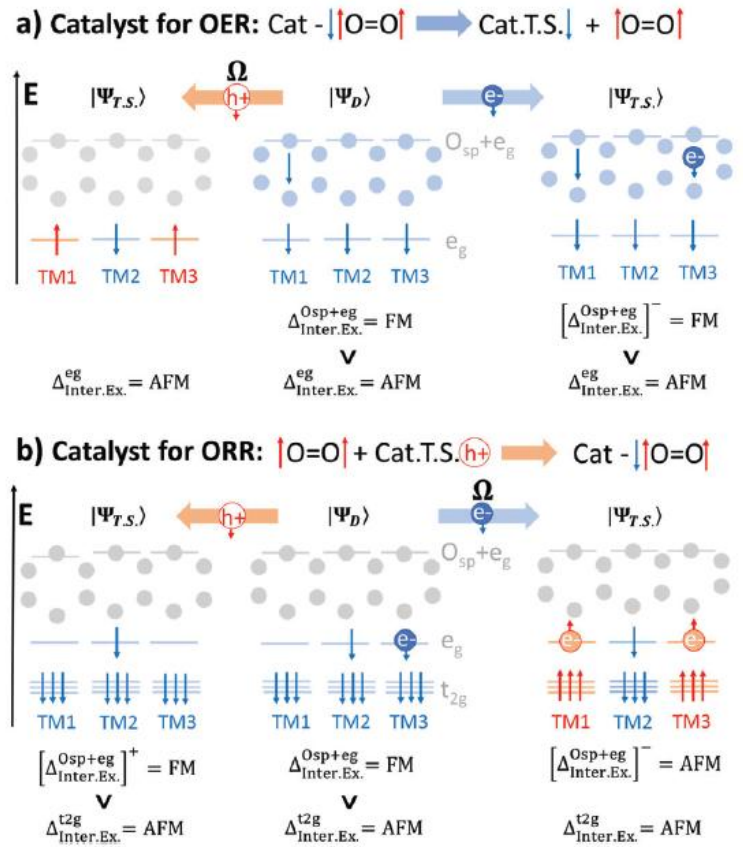


Fig. 3 Possible TS present during e-spin transfer in optimum catalysts for (a) the OER and (b) ORR. The hexagons made from circles symbolise the octahedral crystal field created by the oxygen sp-orbitals connecting the metal atoms.

A bit more of catalysis

Langmuir–Hinshelwood Mechanism:

Reactants adsorb onto the same active

species and thus compete for available active sites

Mars–van Krevelen Mechanism:

Reactants adsorb onto different sites, and the

two surface intermediates interact and reaction occurs. Since each

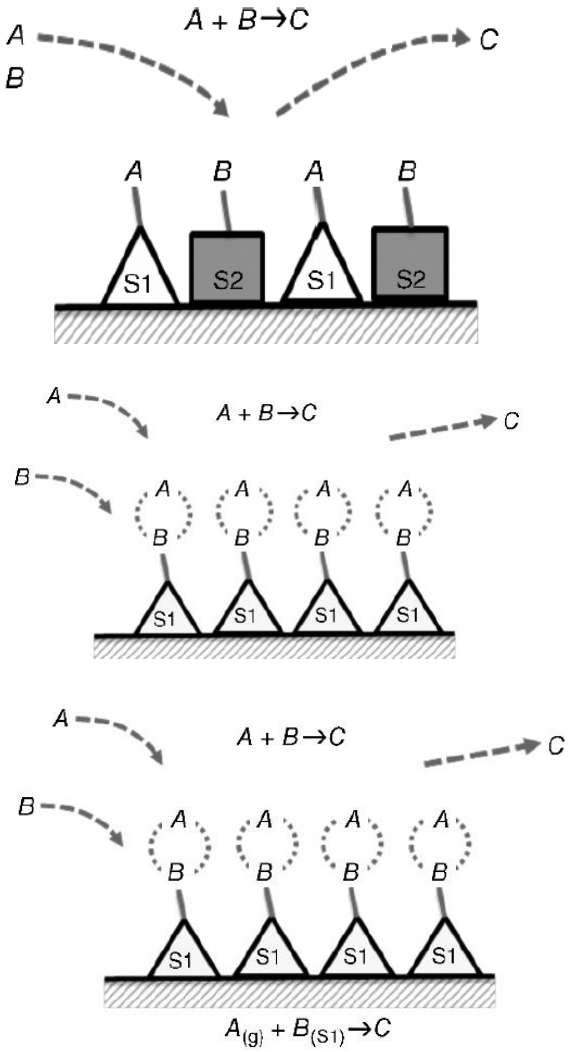
reactant adsorbs onto different surface species, there is no competition

Eley–Rideal Mechanism:

One reactant adsorbs onto the catalyst surface forming

an intermediate surface species, which then reacts with a gas-phase

reactant. Thus, there is no competition for catalytic sites.



The quest for the holy grail……..

NANO LETTERS

pubs.acs.org/NanoLett Letter

Magnetic Field Enhanced Cobalt Iridium Alloy Catalyst for Acidic Oxygen Evolution Reaction

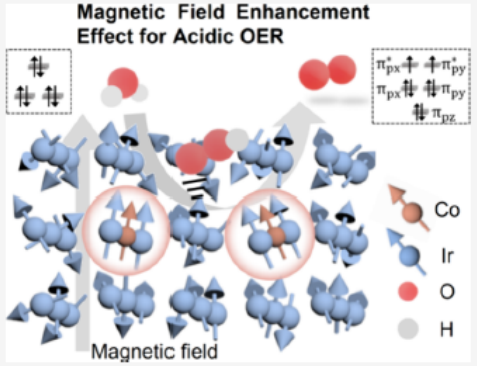
Lamei Li,[‖] Yue Wang,[‖] Renat R. Nazmutdinov, Rustem R. Zairov, Qi Shao,* and Jianmei Lu*

Cite This: *Nano Lett.* 2024, 24, 6148–6157 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Magnetic field mediated magnetic catalysts provide a powerful pathway for accelerating their sluggish kinetics toward the oxygen evolution reaction (OER) but remain great challenges in acidic media. The key obstacle comes from the production of an ordered magnetic domain catalyst in the harsh acidic OER. In this work, we form an induced local magnetic moment in the metallic Ir catalyst via the significant 3d−5d hybridization by introducing cobalt dopants. Interestingly, CoIr nanoclusters (NCs) exhibit an excellent magnetic field enhanced acidic OER activity, with the lowest overpotential of 220 mV at 10 mA cm^{-2} and s long-term stability of 120 h under a constant magnetic field (vs 260 mV/20 h without a magnetic field). The turnover frequency reaches 7.4 s^{-1} at 1.5 V (vs RHE), which is 3.0 times higher than that without magnetization. Density functional theory results show that CoIr NCs have a pronounced spin polarization intensity, which is preferable for OER enhancement.

KEYWORDS: *Iridium, Spin polarization, Alloy, Oxygen evolution reaction (OER)*



Time for questions….where are the critical points?

? **What happens to the material during reaction? How does this affect the magnetic properties of the catalyst?**

? **What is the role of the long range magnetic order?**
On which scale the spin must be aligned to obtain an energetic effect?

A possible solution: magnetic domains walls

nature communications

Article

https://doi.org/10.1038/s41467-023-38212-2

The origin of magnetization-caused increment in water oxidation

Received: 22 November 2022

Accepted: 21 April 2023

Published online: 29 April 2023

Check for updates

Xiao Ren[1,2,3,7], Tianze Wu[1,7], Zizhao Gong[1,2], Lulu Pan[2], Jianling Meng[4], Haitao Yang[2], Freyja Bjork Dagbjartsdottir[5], Adrian Fisher[5], Hong-Jun Gao[2] & Zhichuan J. Xu[1,6]

Magnetization promoted activity of magnetic catalysts towards the oxygen evolution reaction (OER) has attracted great attention, but remains a puzzle where the increment comes from. Magnetization of a ferromagnetic material only changes its magnetic domain structure. It does not directly change the spin orientation of unpaired electrons in the material. The confusion is that each magnetic domain is a small magnet and theoretically the spin-polarization promoted OER already occurs on these magnetic domains, and thus the enhancement should have been achieved without magnetization. Here, we demonstrate that the enhancement comes from the disappeared domain wall upon magnetization. Magnetization leads to the evolution of the magnetic domain structure, from a multi-domain one to a single domain one, in which the domain wall disappears. The surface occupied by the domain wall is reformatted into one by a single domain, on which the OER follows the spin-facilitated pathways and thus the overall increment on the electrode occurs. This study fills the missing gap for understanding the spin-polarized OER and it further explains the type of ferromagnetic catalysts which can give increment by magnetization.

One possible answer to the question regarding the influence of the long range magnetic order lies in the presence of the domain walls seen as region of the surface where the spin are disordered and thus not able to promote the enhanced spin catalysis.

Trying to summarize

REVIEW
ADVANCED ENERGY MATERIALS
www.advenergymat.de

Spin Matters: A Multidisciplinary Roadmap to Understanding Spin Effects in Oxygen Evolution Reaction During Water Electrolysis

Emma van der Minne, Priscila Vensaus,* Vadim Ratovskii, Seenivasan Hariharan, Jan Behrends, Cesare Franchini, Jonas Fransson, Sarnjeet S. Dhesi, Felix Gunkel, Florian Gossing, Georgios Katsoukis, Ulrike I. Kramm, Magalí Lingenfelder, Qianqian Lan, Yury V. Kolen'ko, Yang Li, Ramsundar Rani Mohan, Jeffrey McCord, Lingmei Ni, Eva Pavarini, Rossitza Pentcheva, David H. Waldeck, Michael Verhage, Anke Yu, Zhichuan J. Xu, Piero Torelli, Silvia Mauri, Narcis Avarvari, Anja Bieberle-Hütter, and Christoph Baeumer**

A central challenge in water electrolysis lies with the oxygen evolution reaction (OER) where the formation of molecular oxygen (O_2) is hindered by the constraint of angular momentum conservation. While the reactants OH^- or H_2O are diamagnetic (DM), the O_2 product has a paramagnetic (PM) triplet ground state, requiring a change in spin configuration when being formed. This constraint has prompted interest in spin-selective catalysts as a means to facilitate OER. In this context, the roles of magnetism and chirality-induced spin selectivity (CISS) in promoting the OER reaction have recently been investigated through both theoretical and experimental studies. However, pinpointing the key principles and their relative contribution in mediating spin-enhancement remains a significant challenge. This roadmap offers a forward-looking perspective on current experimental trends and theoretical developments in spin-enhanced OER electrocatalysis and outlines strategic directions for integrating incisive experiments and operando approaches with computational modeling to disentangle key mechanisms. By providing a conceptual framework and identifying critical knowledge gaps, this perspective aims to guide researchers toward dedicated experimental and computational studies that will deepen the understanding of spin-induced OER enhancement and accelerate the development of next-generation catalysts.

1. Introduction

Shifting away from fossil fuels to renewable energy sources is essential to reduce carbon emissions and mitigate climate change. The intermittent nature of renewable electricity and the industrial and agricultural need for carbon-neutral feedstocks necessitate production of green energy carriers, such as hydrogen.[1,2] The "power-to-hydrogen" strategy therefore aims at splitting water into O_2 and H_2 via the oxygen and hydrogen evolution reactions. However, this remains an energy-inefficient process because of the complex reaction pathway and resulting high overpotentials of the OER.[3]

One important factor contributing to these high overpotential and sluggish kinetics of the OER is the spin-state mismatch between reactants and products; while the reactants (OH^- or H_2O, depending on the electrolyte pH) are DM,

nature energy

Review article

https://doi.org/10.1038/s41560-025-01744-6

Spin-related and non-spin-related effects of magnetic fields on water oxidation

Received: 11 March 2024

Accepted: 21 February 2025

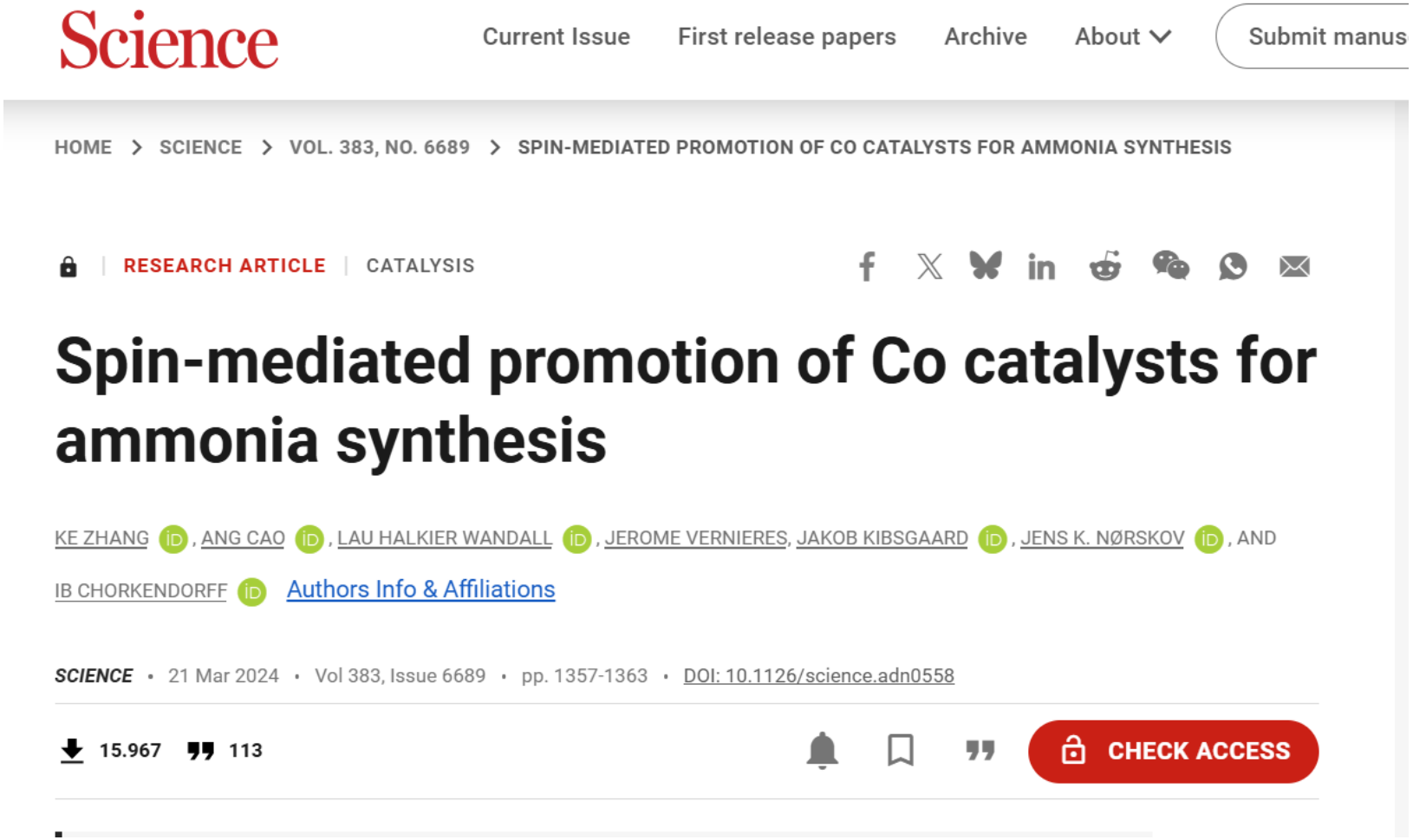
Published online: 24 April 2025

Check for updates

Anke Yu[1], Yuwei Zhang[1], Siyuan Zhu[1], Tianze Wu[1] & Zhichuan J. Xu[1,2]

Water electrolysis is hindered by the slow kinetics and high overpotentials associated with the oxygen evolution reaction (OER), which takes place at the anode. Spin manipulation in the OER is a promising approach by which to modulate the reaction pathway to improve the energetics and kinetics. To that end, application of magnetic fields in the OER has been shown to enhance performance; however, whether the underlying promotional mechanisms are spin-related or non-spin-related remains a topic of ongoing debate. In this Review we explore OER enhancement under magnetic fields and elucidate both spin-related and non-spin-related effects, examining key fundamentals and experimental practices to distinguish these effects. For spin-related mechanisms, we highlight the key effects of spins on the catalyst bulk, catalytic interface and reaction intermediate. We provide guidance for understanding whether enhancements are spin-related or not.

Other application



Science

Current Issue First release papers Archive About Submit manus

HOME > SCIENCE > VOL. 383, NO. 6689 > SPIN-MEDIATED PROMOTION OF CO CATALYSTS FOR AMMONIA SYNTHESIS

RESEARCH ARTICLE | CATALYSIS

Spin-mediated promotion of Co catalysts for ammonia synthesis

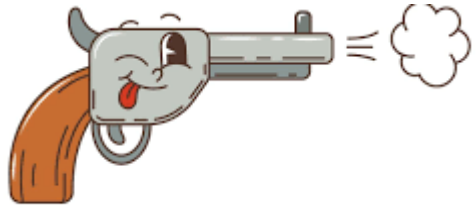
KE ZHANG, ANG CAO, LAU HALKIER WANDALL, JEROME VERNIERES, JAKOB KIBSGAARD, JENS K. NØRSKOV, AND IB CHORKENDORFF Authors Info & Affiliations

SCIENCE • 21 Mar 2024 • Vol 383, Issue 6689 • pp. 1357-1363 • DOI: 10.1126/science.adn0558

15.967 113 CHECK ACCESS

The concept of magnetocatalysis is not restricted to water electrolysis but can be applied to all reaction in which the formation of a final products or intermediates of reaction which are paramagnetic (i.e. with a net spin moment)

The smoking gun



We need an experiment in which the application of a magnetic field can change the yield (or even better the selectivity) of a reaction without changing other parameter of the experiment (bubbles, circuit resistivity, etc.). For this reason gas phase heterogeneous catalysis is more suited then electrochemistry. We need to find the best reaction which involves the most suited molecules to demonstrate our hypothesis.

We need an experimental approach that can follow the evolution of the chemical and magnetic properties of the catalyst during the reaction. I.e. we need a very advanced operando technique.

We need an very special catalyst, this is a great challenge from material science point of view:
We have to find a material that:
-Is catalytically active
-Present a magnetic transition or a sharp Tc in the Temperature range of interest.
-Or a material that has a disordered spin structure at remanence that become ordered with small fields

We want you!



Many thanks

Organizers:
Giovanni Carlotti & **Marco Madami** – UniPG
Gianluca Gubbiotti & **Silvia Tacchi** – CNR-IOM

and thank you for your attention!



Premio Roberta Ciprian 2025

Deadline for submission 01/12/2025