

Non-noble metal driven catalysis : An exploration of the materials and applications

Magesh Ganesan^{2§}, Jeremy P. Krogman^{1§}, Tatyana Konovalova^{1§}, Leilani Lotti Díaz¹, Chia-Wei Hsu^{1*}

¹Chemical Abstracts Service, a Division of the American Chemical Society, Columbus, Ohio 43202, U.S.A.

²ACS International India Private Limited, Pune, Maharashtra, India 411045

*Corresponding Author: Chia-Wei Hsu; Email: chsu@cas.org

§ Magesh Ganesan, Jeremy P. Krogman, and Tatyana Konovalova contributed equally to this work.

Abstract

Noble metals, which form a significant proportion of catalysts at present, are not sustainable, which necessitates the need for non-noble metal alternatives. This report contains a thorough analysis of data obtained from the CAS Content CollectionTM, pertaining to the recent development of non-noble metal catalysts, their usage, and applications. We herein identify the research trends since 2012 in four subfields: electrocatalysts, homogeneous catalysts, photocatalysts, and biocatalysts. Within the subfields, we present: the most reported catalysts; emerging catalyst substances; significant reactions, and applications; map of the cooccurrence of catalyst substances with their reactions and applications. With this article, we aim to provide a data driven overview of the complex publication landscape and unique scientific insights for a deeper understanding of the field.

Introduction

In 1987, the United Nations (UN) released the report, *Our Common Future*, which defined the concept of sustainable development as “*development that meets the needs of the present without compromising the ability of future generations to meet their own needs.*”¹ Sustainability consists of three aspects: economy, society, and environment.² In turn, sustainable chemistry can be evaluated by three metrics: renewable percentage, optimum efficiency, and waste percentage.³ Catalysts are one of the tools that accommodate these parameters to achieve sustainability.

Noble metals such as platinum, palladium, iridium, and ruthenium feature desired catalytic properties, such as high temperature tolerance and good catalytic activity. For instance, Sonogashira coupling,^{4, 5} Suzuki–Miyaura coupling,^{6, 7} Heck reaction,^{8, 9} and Stille coupling^{10, 11} need palladium as catalysts that result in good yields under various conditions. Iridium and ruthenium also possess catalytic capabilities for arylation, allylation, and other cross-coupling reactions.^{12, 13} Obtaining these noble metals catalysts presents a challenge when it comes to sustainability and the prices are subject to market fluctuations.¹⁴ Noble metals are mostly extracted from low grade ores for which a large amount needs to be mined to extract a small

amount of metal, resulting in environmental damage and high refining cost. For example, around 12 tons of ore is used to produce approximately 31 grams of platinum.¹⁵ In addition, refining of these low-grade ores requires a large amount of energy that is obtained typically via fossil fuels. The high cost and low abundance of noble metals are limiting factors in many key technologies such as fuel cells,¹⁶ zinc-air batteries,¹⁷ water splitting to produce hydrogen,^{18, 19} and hydrogenation.²⁰ Due to their sustainable cost and minimum environmental impact, noble metal replacement in catalytic applications has attracted the attention of scientists.

The chemical properties which cause noble metals to excel as catalysts are their resistance to corrosion, ability to undergo 2-electron oxidation state changes²¹ common in catalytic processes, affinity toward π -bonds, and high product selectivity (Table 1). Ideal candidates for the replacements of noble metal catalysts are the 1st row transition metals namely titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper because of their high availability in the Earth's crust. In addition, many non-noble metal catalysts are more tolerable in the human body compared to noble metal catalysts.²² Unfortunately, the stability under reaction conditions of non-noble metal catalyst presents a major challenge.²³

Table 1: Properties of noble metals and transition metals

Property	Noble metal	1 st row transition metal	Notes
Stability	High	Prone to corrosion	
Availability in earth crust	Scarce	Very high	
Tolerance in human body	Low	High	1300ppm of iron is permitted in pharma products vs 10ppm in case of noble metals, ²⁴ which needs more energy to achieve
Mining process	Polluting and energy intensive	Less pollution and energy consumption	
Ability to undergo 2-electron oxidation stage changes	Yes	Prefer 1-electron oxidation state change	Most catalytic processes involve 2-electron transfer reactions
Selectivity of products	High	Low	

With the help of a search query (See SI for more details), documents related to non-noble metal-based catalysts were identified and the related data was extracted from the CAS Content Collection™, the largest collection of human curated scientific knowledge. The bibliographic analysis and curated data presented in this manuscript aims to provide an enhanced landscape

view on this research topic, helping researchers and decision makers understand the progress in this specific area of study.

As previously mentioned, the CAS Content Collection™ was used to retrieve information regarding the use and application of non-noble metal catalysts / catalysis from the documents published 2012 onwards, resulting in around 50,000 publications (51,286 journals and 5978 patents). In general, the publication trend of non-noble metal catalysts/catalysis manifests a steady growth, and the journal articles dominate the publication volume (82%) between 2012 and 2024 (Figure 1).

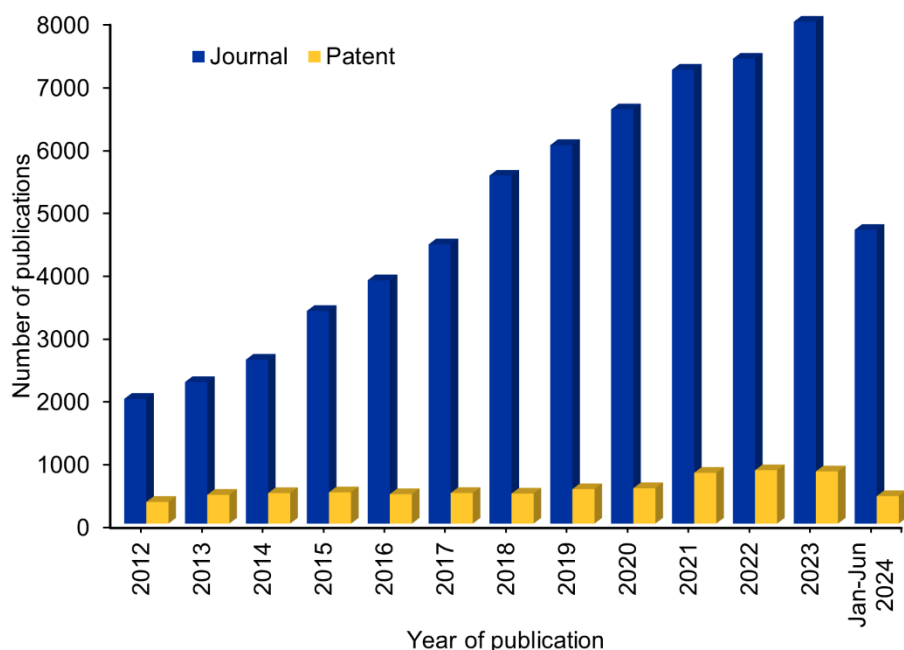


Figure 1. General journal and patent publication trend of non-noble metal catalysts/catalysis. When it comes to journal publications, the countries with the highest number of publications in descending order are China, United States, India, Germany, and South Korea (Figure 2A). The countries with the greatest number of patent publications are China, the United States, Japan, South Korea, and Germany. (Figure 2B).

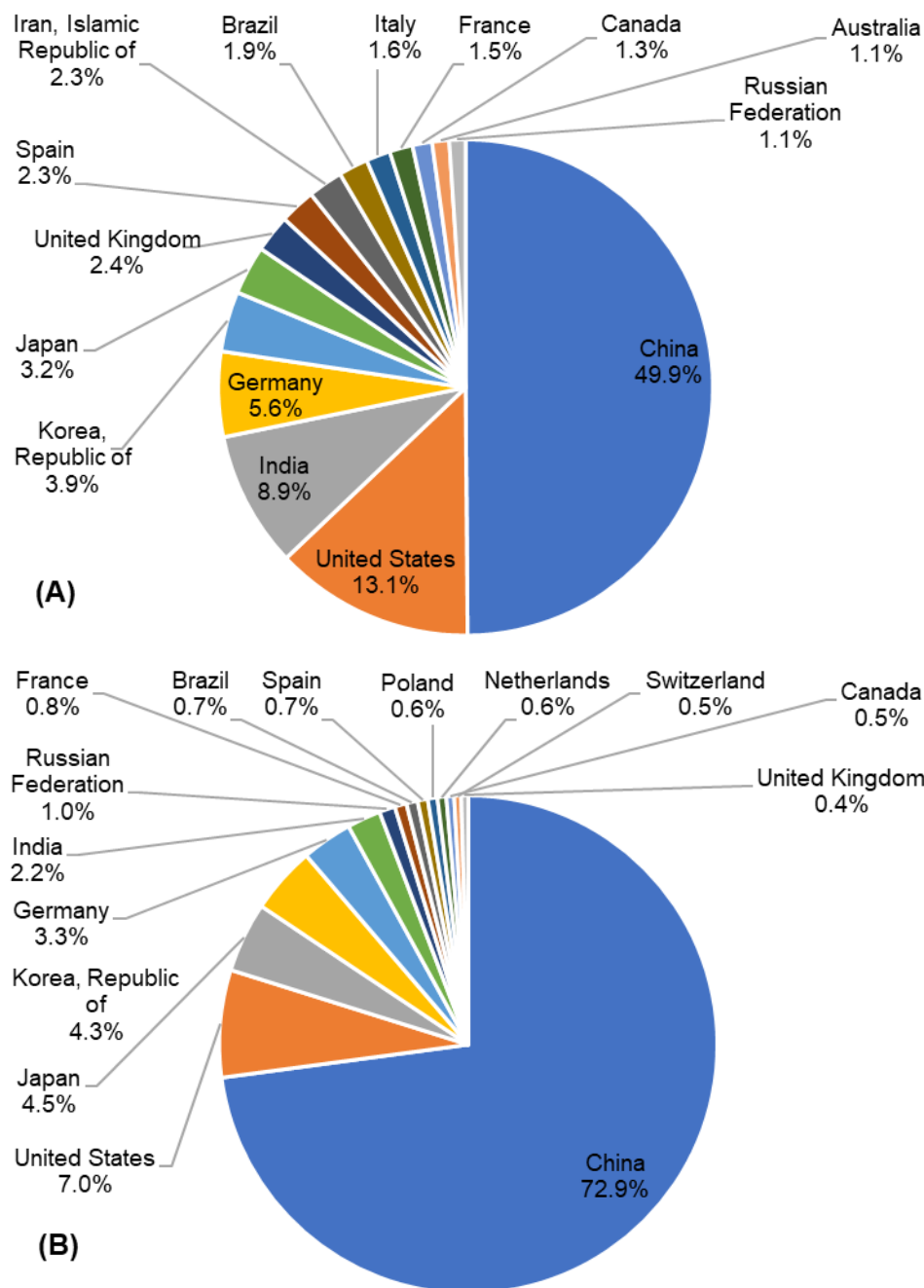


Figure 2. Top countries or regions in terms of journal (A) and patent (B) publications related to non-noble metal catalysts / catalysis.

The top 15 institutions with the highest number of journal publications among all countries are only from China (Figure 3 top left). Upon excluding China, Singapore and the United States have 2 institutions each in the top institutions with the most journal publications (Figure 3 top right). The top 15 institutions with the highest number of patent publications contain 14 institutions from China, and 1 from Germany. Upon excluding China, the top 15 institutions are from 7 different countries, with 4 from the United States, 3 from Germany, 3 from South Korea, and 2 from India.

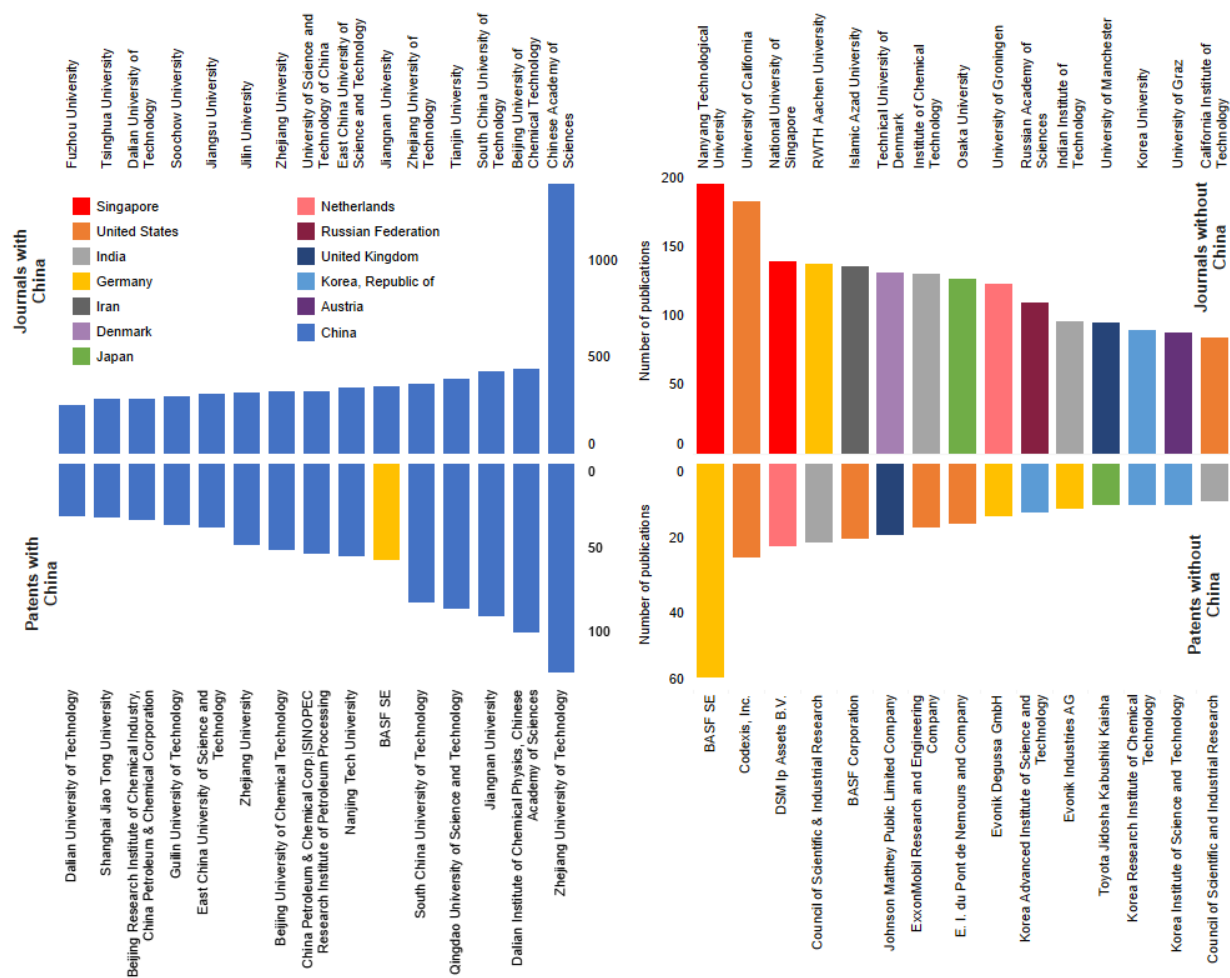


Figure 3. Institutions with the highest number of journal and patent publications reporting non-noble metal catalysts.

We further separated the institutions with the highest number of patents into commercial and non-commercial categories (Figure 4). In the commercial category, BASF SE has the highest number of patents, mostly reporting new inventions for the catalytic synthesis of chemicals.²⁵ Institutions belonging to China Petroleum and Chemical Corporation (SINOPEC) has the next highest number of patents in commercial category. Codexis Inc which develops enzymes has patented biocatalysts for various synthetic applications related to pharmaceutical, food, medical applications.²⁶

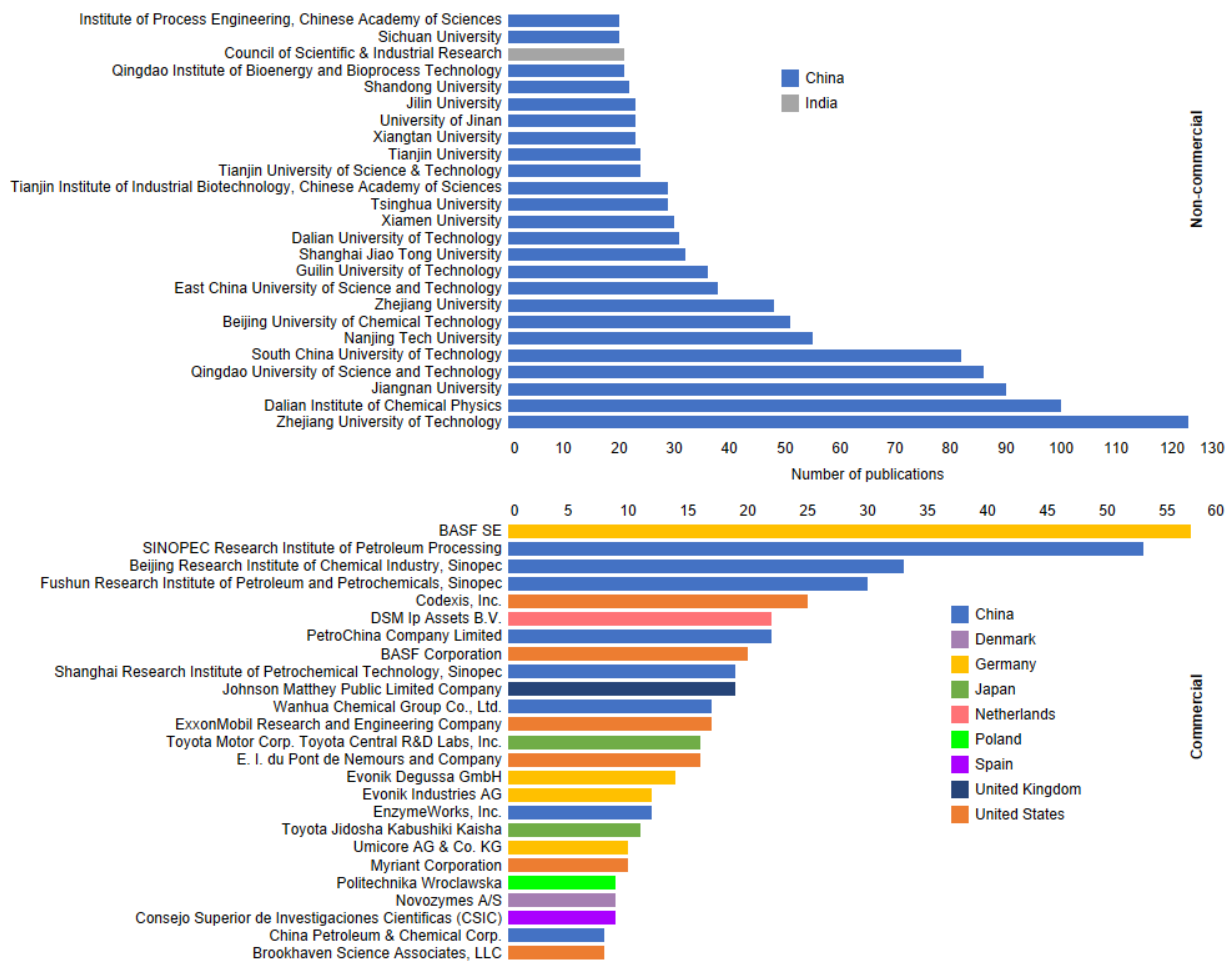


Figure 4. Commercial (bottom) and non-commercial (top) institutions with the highest number of patents reporting non-noble metal catalysts.

In this report, we focus on looking into bibliometric data on sustainable chemistry using non-noble metal catalysts in four research fields: electrocatalysts, photocatalysts, homogeneous catalysts, and biocatalysts. Data regarding these subfields was obtained by further narrowing the original search query (See **SI for more details**). Figure 5 shows the number of publications in the selected fields, where electrocatalyst-related publications are highest followed by biocatalysts, homogeneous catalysts and photocatalysts. Numbers of patents published were similar for biocatalysts, electrocatalysis and homogeneous catalysts, whereas relatively lesser patents were published using photocatalysts. We provide analysis of the developments and publications in these subfields in the sections that follow.

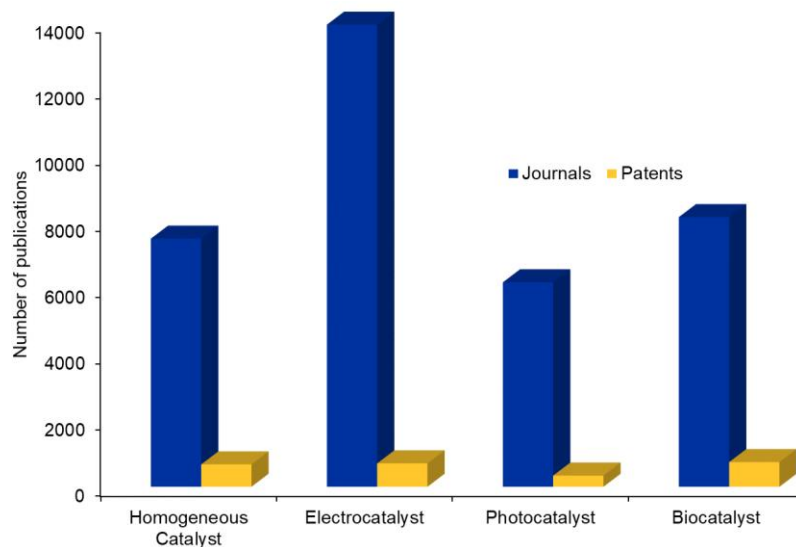


Figure 5. Publication volumes for the four subfields: Homogeneous Catalyst, Electrocatalyst, Photocatalyst, and Biocatalyst in journals and patents.

We investigated the general trends among the catalysts substance to get a broader view. Figure 6 illustrates the number of publications in the various substance classes to which the catalysts belong to in journals(left) and patents(right). Elements and organic/inorganic small molecules are the biggest class of catalysts. This is followed by complex and unknown substances (called as 'manual registration' in CAS substance classes)²⁷ which can be defined as: substances without known compositions like commercial catalysts; substances with known but large/complex structures such as enzymes. The fourth biggest category of catalysts are the 'tabular inorganic', which are inorganic substances which are mixtures of compounds such as mixed or doped metal oxides, and sulfides. The chart also shows the further distribution of the catalyst substance classes to the major types of catalysts. The obvious trends are the high contribution of elements, small molecules, and enzymes to the electrocatalysts, homogeneous catalysts, and biocatalysts respectively.

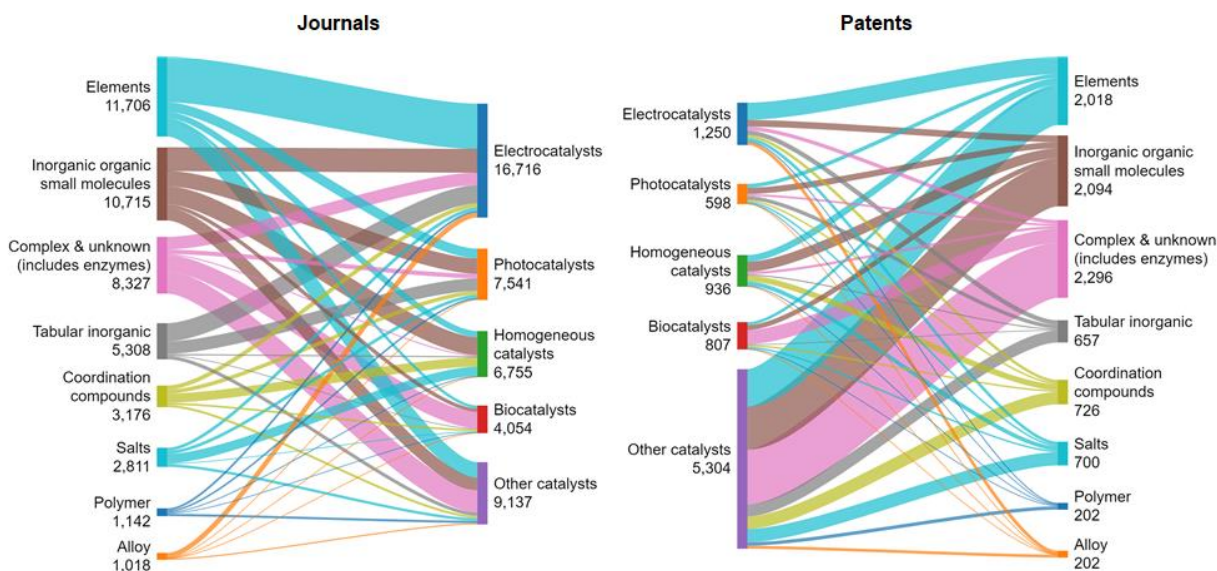


Figure 6. Number of publications in the various substance classes of the catalysts and their distribution among the types of catalysis in journals (left) and patents (right)

Electrocatalysts

Electrocatalysts participate in electrochemical reactions as the electrodes, or the catalytic materials coated on the surface of electrodes. Platinum is the most used electrode material in electrochemical devices because of its catalytic activity. However, its limited abundance and high costs are hurdles that impede the advancement of certain vital electrochemical applications.²⁸ In this section, we further analyze of non-noble metal electrocatalysts data related to sustainability, which was retrieved from our primary search query data using a more narrow electrocatalyst specific search query (See **SI for more details**).

In general, electrocatalyst-related publications show a steady growth in journals and a slower growth in patents (Figure 7). Volume of publications in journals is considerably higher than patents, which demonstrates that much of the research in this area is yet to reach the point of commercialization. We anticipate that there will be more innovative ideas to be commercialized in the future, resulting in a higher growth in patents.

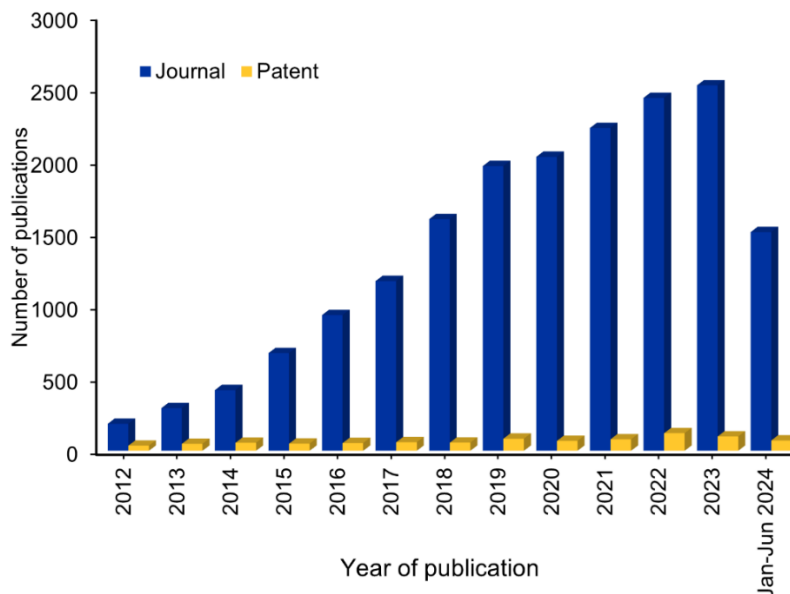


Figure 7. Annual publication trends of electrocatalysts in journals and patents.

The Most Used Substances

To further reveal the trend of substances used as electrocatalysts, herein we selected substances whose CAS indexed role is catalyst. Figure 8 shows that the top two substances are carbon and platinum. Carbon based materials are utilized as support to produce non-noble metal electrodes, while platinum based electrodes are used as a benchmark for comparison.²⁹ Nickel, graphene, cobalt, nitrogen, and iron are also frequently used for electrocatalyst research. Nitrogen is present in N-doped carbon materials which possess active sites for catalytic reactions.³⁰ Single atom catalysts of transition metals such as iron, copper, and manganese loading on nitrogen doped carbon supports perform efficiently as oxygen reduction reaction catalysts in fuel cells. Cobalt, nickel, copper containing core-shell catalysts made of Co-Ni carbonate hydroxides (CoNiCH) and $\text{Cu}(\text{OH})_2[\text{Cu}(\text{OH})_2@\text{CoNiCH}]$ was found to be efficient for oxygen evolution reaction.³¹ Copper, nickel, and phosphorus composites enable urea electrolysis to produce hydrogen at low overpotentials.³² Similar to platinum ruthenium dioxide (RuO_2) and iridium oxide (IrO_2) are used as benchmark for comparison with non-noble metal-based electrocatalysts for oxygen evolution reaction applications.

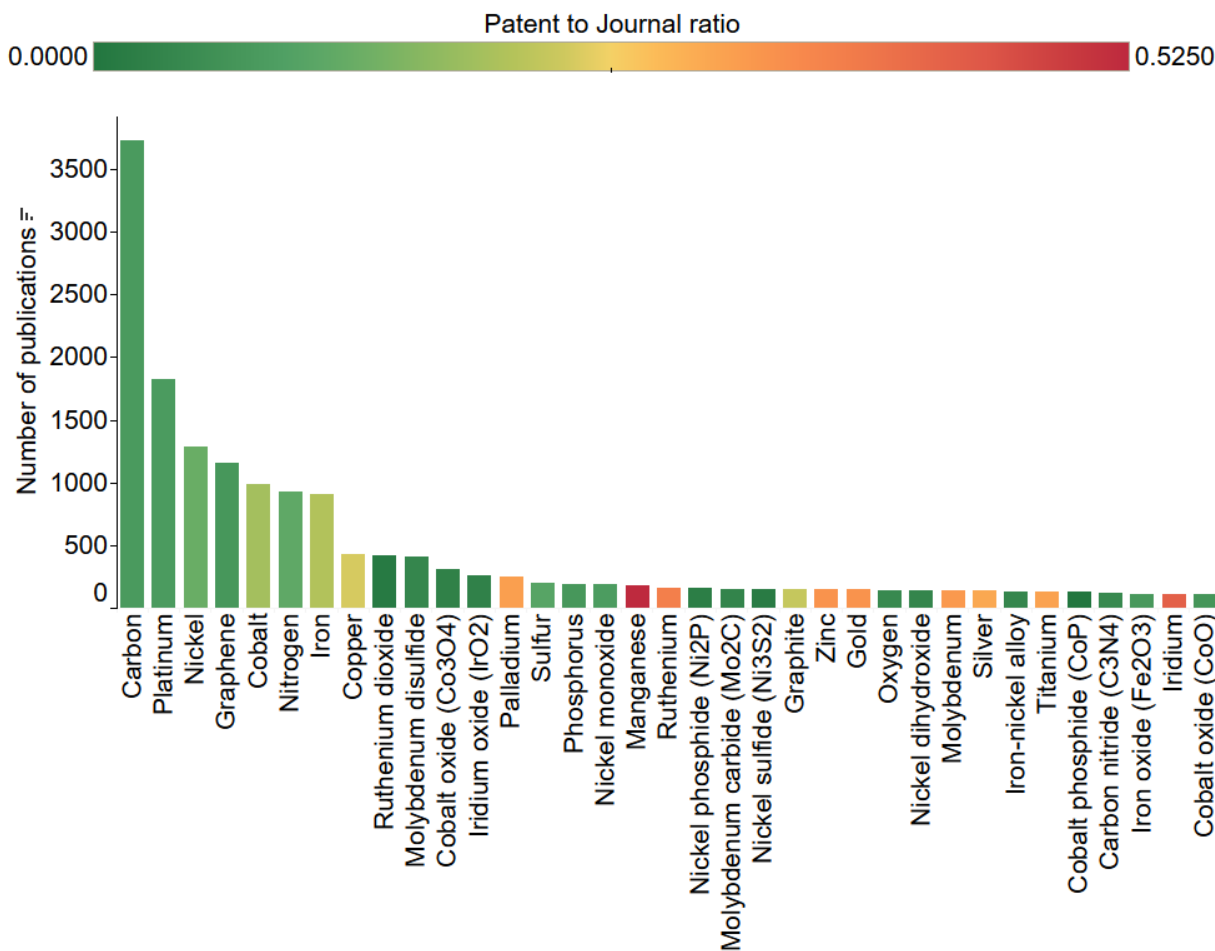


Figure 8. Mostly used catalyst substances in electrocatalyst related publications.

The Emerging Trends of Substances in Electrocatalysts

Catalyst substances that grew significantly in recent years are presented in the Figure 9 alongside their growth trends. Co-Fe alloy, Fe-Ni alloy, vanadium, niobium, zinc, nickel selenide, cobalt diselenide, nickel sulfide, MoO₂, and MoO₃ are identified as the emerging catalysts. Co-Fe alloy and Fe-Ni alloy are efficient bifunctional catalysts capable of performing both oxygen evolution (OER) and oxygen reduction (ORR) used in applications such as zinc-air batteries³³⁻³⁵ and water splitting.³⁶ Nickel selenides are efficient for hydrogen evolution due to their low overpotential.^{37, 38} Cobalt diselenide is an efficient non-noble metal based bifunctional catalyst capable of performing both oxygen evolution and hydrogen evolution (HER), used mostly in HER studies.^{39, 40} Composites containing various nickel sulfides are bifunctional catalysts capable of performing both OER and HER reactions with low overpotentials.^{41, 42} The growth of molybdenum dioxide in recent years is due to its low cost, high stability, and low overpotential for HER applications.⁴³⁻⁴⁵ Due to its stability in alkaline medium and efficient HER catalytic performance, there is increase in research interest in molybdenum trioxide recently.⁴⁶

47 Vanadium doping has been found to increase the durability of phosphide and sulfide catalysts used for OER and HER reactions, which has been attributed to the high valency of vanadium.^{48,}
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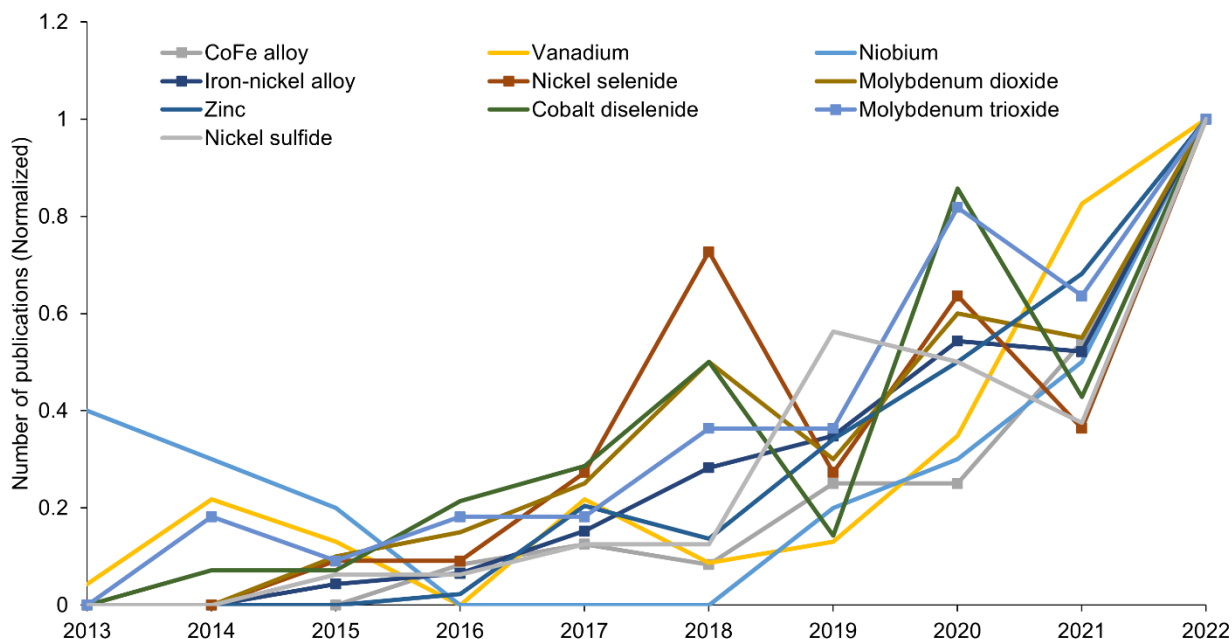


Figure 9. Emerging substances as electrocatalysts in publications from 2013-2022. In Figure 9, the emerging trend of electrocatalysts are shown.

To develop a broader perspective of the substances used as electrocatalysts and to find use of substances with varying composition such as layered double hydroxides (LDH) and MXenes, we delved into the prevalent substance classes and their patent to journal ratios (Figure 10). LDH, transition metals, transition metal phosphides, and noble metals are among the top substances used as catalysts. Due to its high surface area, tunable and variable composition, stability, and ease of doping and intercalation, LDH and composites containing LDH are studied for HER,⁵⁰ OER,⁵¹ and ORR,⁵² which are applied in fuel cells, overall water splitting, and zinc-air batteries. Other carbon-based substances, and polymers in the list are used as supports, binders, and fillers. MXene is another substance class like LDH, that did not appear in the top catalyst substances due to its variable composition. MXenes are layered substances which possess multiple sites known for their catalytic activity such as metal nitride, metal carbide, and carbon nitride within their structure. These favorable properties have driven studies using MXenes as catalysts and co-catalysts for water splitting reactions.⁵³⁻⁵⁵ The figure also presents the patent to journal ratio, which is high among the metallic catalysts compared to the other catalysts.

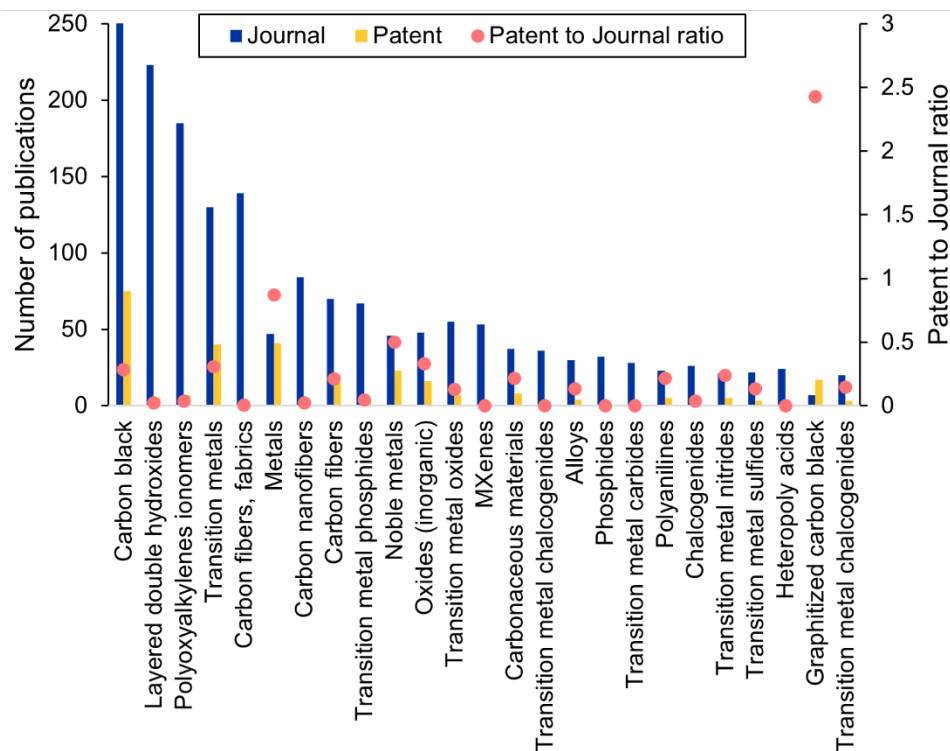
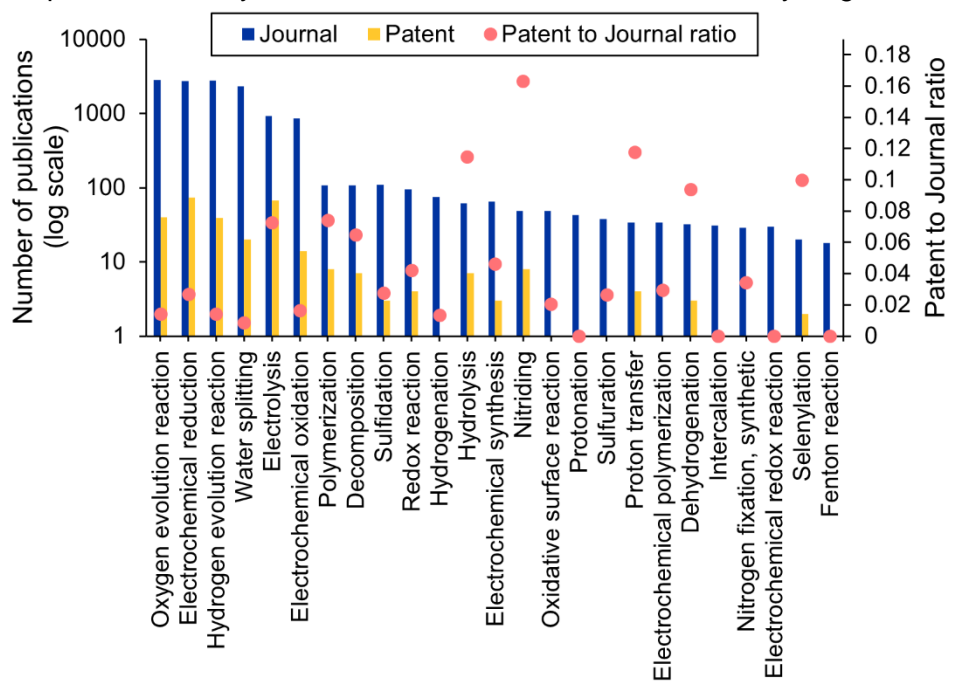


Figure 10: Substance groups which are used as electrocatalysts and their patent to journal ratio.

We then delved into reaction related topics and their patent to journal ratio (Figure 11). The publication volumes of the top 25 reaction topics show oxygen evolution reaction (OER), electrochemical reduction, hydrogen evolution reaction (HER), and water splitting as the top reaction types. OER is a well-known half reaction in the overall water splitting process used to produce hydrogen. OER also plays a significant role in zinc-air batteries; these batteries hold a higher energy density than lithium batteries, hence their emergence as an alternative for applications requiring less voltage. Due to the efforts to generate hydrogen, a potential green fuel, hydrogen evolution reaction has gained significance. Platinum is considered as the best HER catalyst; any breakthrough in finding sustainable alternative to Pt will have significant impact in the green hydrogen production industry.⁵⁶

The co-occurrence between catalysts and reactions is shown in Figure 12. One of the observations is the use of layered materials such as graphene, graphite, sulfur, and molybdenum sulfide in intercalation reactions. Molybdenum sulfide, cobalt, copper,

molybdenum, nickel phosphide, and molybdenum carbide also co-occur with the hydrogen



evolution reaction.

Figure 11. Most reported reactions in electrocatalysts and their patent to journal ratio

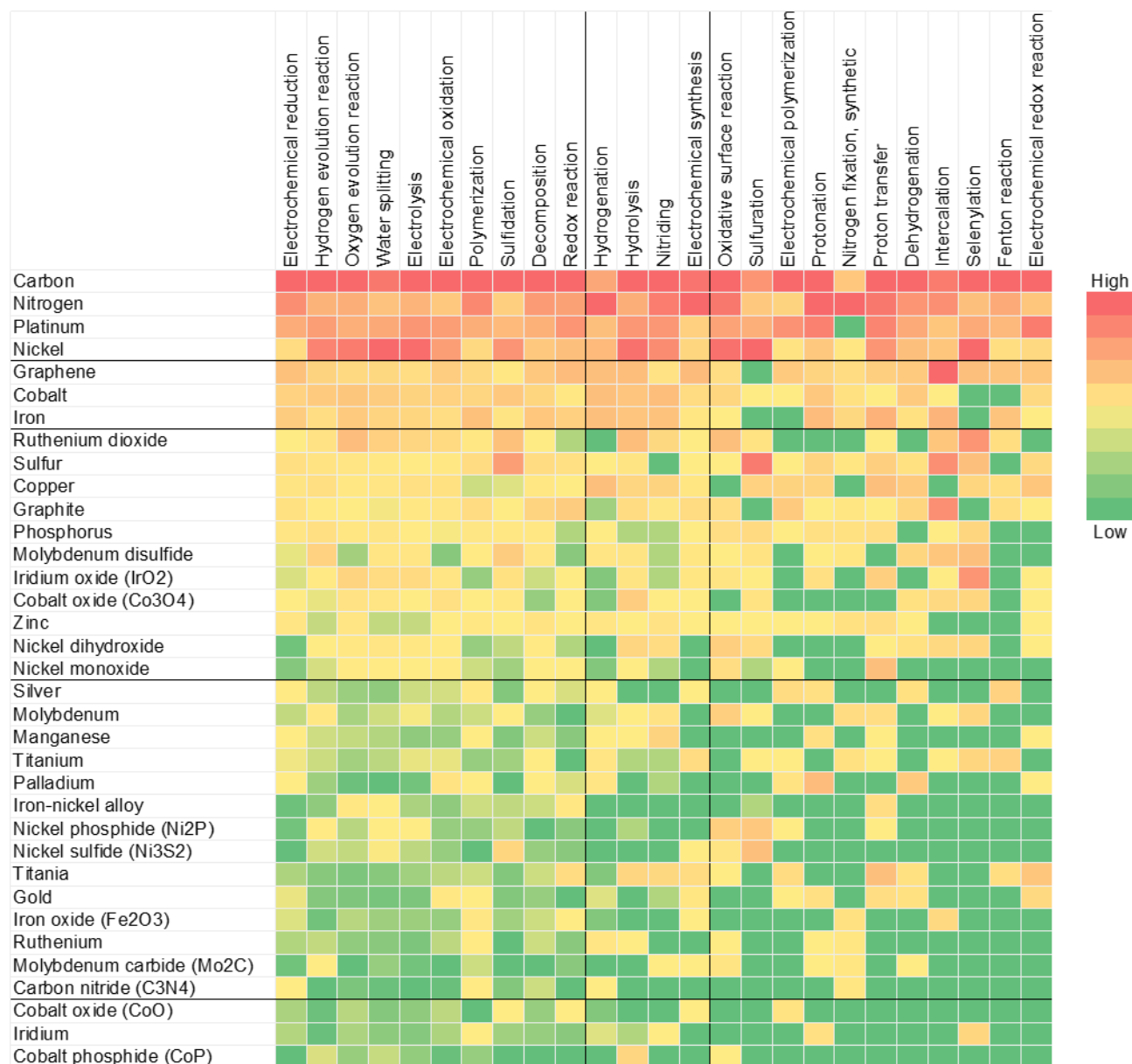


Figure 12. Co-occurrence of catalyst substances and reactions in electrocatalyst publications.

The most indexed uses and their patent to journal ratio are presented in Figure 13. As seen in the indexed reactions, uses related to water splitting are present in most publications. A notable usage is the bifunctional catalysts, which are capable of catalyzing both the anode and cathode reactions in overall water splitting,⁵⁷ and zinc-air battery.⁵⁸ A variety of transition metal based sulfide,⁵⁹ phosphide,⁶⁰ oxide,⁶¹ and alloy⁶² catalysts have displayed bifunctional capabilities. Lastly, reduction reaction catalysts have the highest patent to journal ratio among of the various uses, which seems to be due to the high commercial interest in oxygen reduction reaction catalysts having applications in fuel cells.⁶³ An analysis of cooccurrence of the usage and catalyst substances (Figure 14), shows that carbon, graphite, graphene, and nitrogen are the primary non-metal substances that co-occurred with catalysts/catalysis-based usage concepts; nickel, cobalt, iron, copper, molybdenum disulfide, and zinc are the metal substances that reveal high to moderate co-occurrence in electrocatalyst-related research documents.

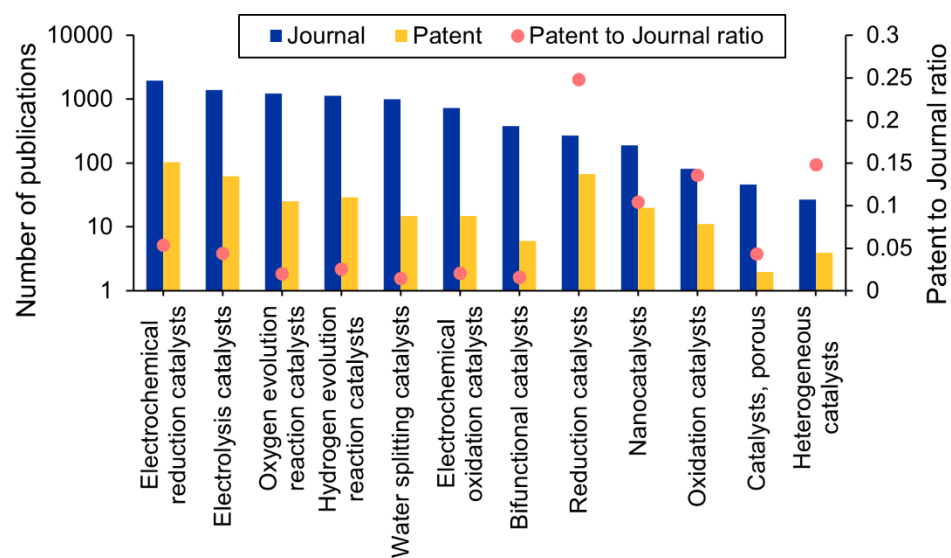


Figure 13. Most reported uses in electrocatalyst publications and their patent to journal ratio

	Electrochemical reaction catalysts	Electrochemical reduction catalysts	Electrolysis catalysts	Oxygen evolution reaction catalysts	Hydrogen evolution reaction catalysts	Water splitting catalysts	Electrochemical oxidation catalysts	Bifunctional catalysts	Reduction catalysts	Nanocatalysts	Oxidation catalysts	Catalysts, porous	Heterogeneous catalysts
Carbon	█	█	█	█	█	█	█	█	█	█	█	█	█
Nitrogen	█	█	█	█	█	█	█	█	█	█	█	█	█
Platinum	█	█	█	█	█	█	█	█	█	█	█	█	█
Nickel	█	█	█	█	█	█	█	█	█	█	█	█	█
Graphene	█	█	█	█	█	█	█	█	█	█	█	█	█
Cobalt	█	█	█	█	█	█	█	█	█	█	█	█	█
Iron	█	█	█	█	█	█	█	█	█	█	█	█	█
Sulfur	█	█	█	█	█	█	█	█	█	█	█	█	█
Copper	█	█	█	█	█	█	█	█	█	█	█	█	█
Graphite	█	█	█	█	█	█	█	█	█	█	█	█	█
Ruthenium dioxide	█	█	█	█	█	█	█	█	█	█	█	█	█
Phosphorus	█	█	█	█	█	█	█	█	█	█	█	█	█
Molybdenum disulfide	█	█	█	█	█	█	█	█	█	█	█	█	█
Zinc	█	█	█	█	█	█	█	█	█	█	█	█	█
Cobalt oxide (Co ₃ O ₄)	█	█	█	█	█	█	█	█	█	█	█	█	█
Iridium oxide (IrO ₂)	█	█	█	█	█	█	█	█	█	█	█	█	█
Nickel dihydroxide	█	█	█	█	█	█	█	█	█	█	█	█	█
Nickel monoxide	█	█	█	█	█	█	█	█	█	█	█	█	█
Manganese	█	█	█	█	█	█	█	█	█	█	█	█	█
Palladium	█	█	█	█	█	█	█	█	█	█	█	█	█
Silver	█	█	█	█	█	█	█	█	█	█	█	█	█
Molybdenum	█	█	█	█	█	█	█	█	█	█	█	█	█
Titanium	█	█	█	█	█	█	█	█	█	█	█	█	█
Gold	█	█	█	█	█	█	█	█	█	█	█	█	█
Titania	█	█	█	█	█	█	█	█	█	█	█	█	█
Iron-nickel alloy	█	█	█	█	█	█	█	█	█	█	█	█	█
Iron oxide (Fe ₂ O ₃)	█	█	█	█	█	█	█	█	█	█	█	█	█
Carbon nitride (C ₃ N ₄)	█	█	█	█	█	█	█	█	█	█	█	█	█
Nickel phosphide (Ni ₂ P)	█	█	█	█	█	█	█	█	█	█	█	█	█
Molybdenum carbide (Mo ₂ C)	█	█	█	█	█	█	█	█	█	█	█	█	█
Nickel sulfide (Ni ₃ S ₂)	█	█	█	█	█	█	█	█	█	█	█	█	█
Ruthenium	█	█	█	█	█	█	█	█	█	█	█	█	█
Cobalt oxide (CoO)	█	█	█	█	█	█	█	█	█	█	█	█	█
Cobalt phosphide (CoP)	█	█	█	█	█	█	█	█	█	█	█	█	█
Iridium	█	█	█	█	█	█	█	█	█	█	█	█	█

Figure 14. Co-occurrence of catalyst substances and uses in electrocatalyst publication.

The most prevalent devices or parts of the devices indexed from non-noble metal electrocatalyst related publications are fuel cells and batteries (Figure 15). Hydrogen based fuel cells play a major role in the proposed hydrogen economy, and research on fuel cells is driven by the need for efficient, stable, and cost effective catalysts⁶⁴ for ORR⁶⁵ and hydrogen oxidation reactions.⁶⁶ Batteries have become essential for storing the various forms of green energy, solving the issue that arises due to their intermittent nature. However, the primary driver behind the need for non-noble metal alternatives in battery research are the zinc-air batteries. Zinc-air batteries involve ORR and OER which traditionally need expensive platinum catalysts, hence need alternatives.⁶⁷

Solar cells, supercapacitors, and photoelectrochemical cells are other popular devices. To bring down the cost of solar cells, there is a need for alternatives to the platinum counter electrodes.^{68, 69} Figure 16 shows the prevalence of the catalyst substances within different apparatus types. Zinc and ruthenium dioxide have high co-occurrence with batteries due to the battery technologies such as zinc-air and zinc-ion, where ruthenium dioxide is used as oxygen evolution reaction catalyst. Palladium is widely used as catalyst in fuel cell related applications. Owing to their photocatalytic activity, titania is prevalent in the solar cells and photoanodes. Photoanodes are part of photoelectrochemical cells for overall water splitting, where ferric oxide⁷⁰ is used as the photocatalyst, and NiO,⁷¹ cobalt phosphide,⁷² and nickel dihydroxide⁷³ are used as cocatalysts for oxygen evolution reaction.

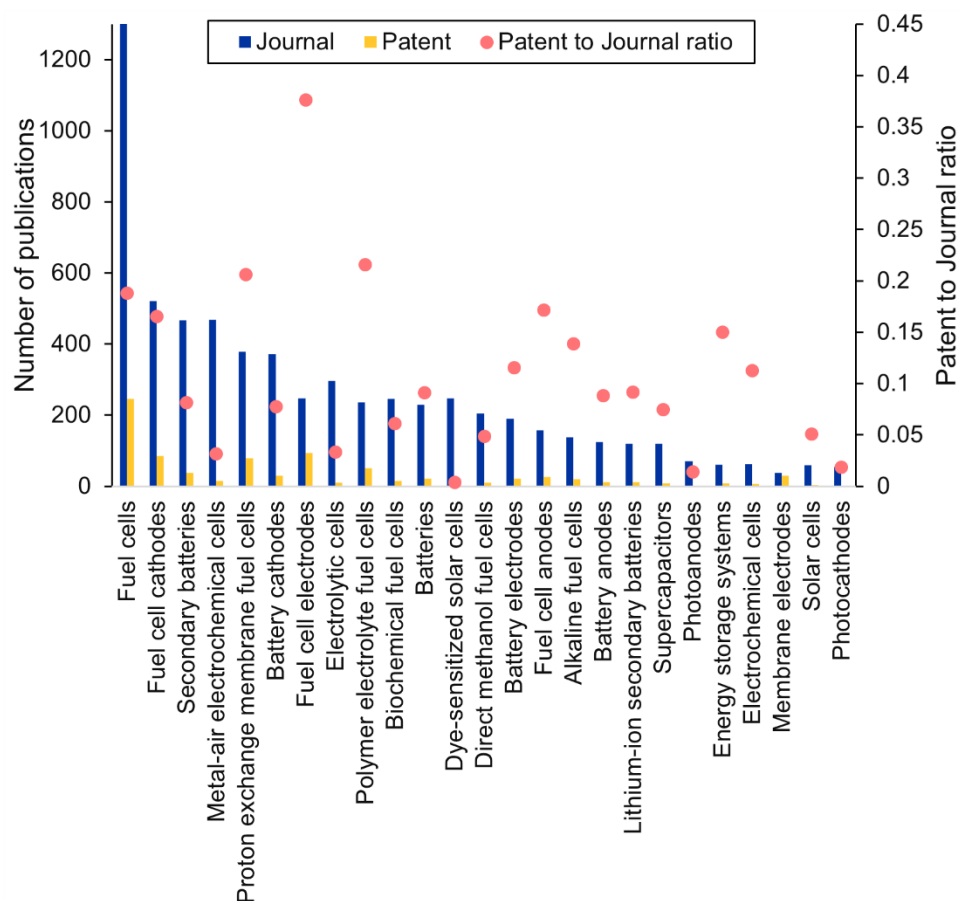


Figure 15. Most prevalent devices in electrocatalyst publications

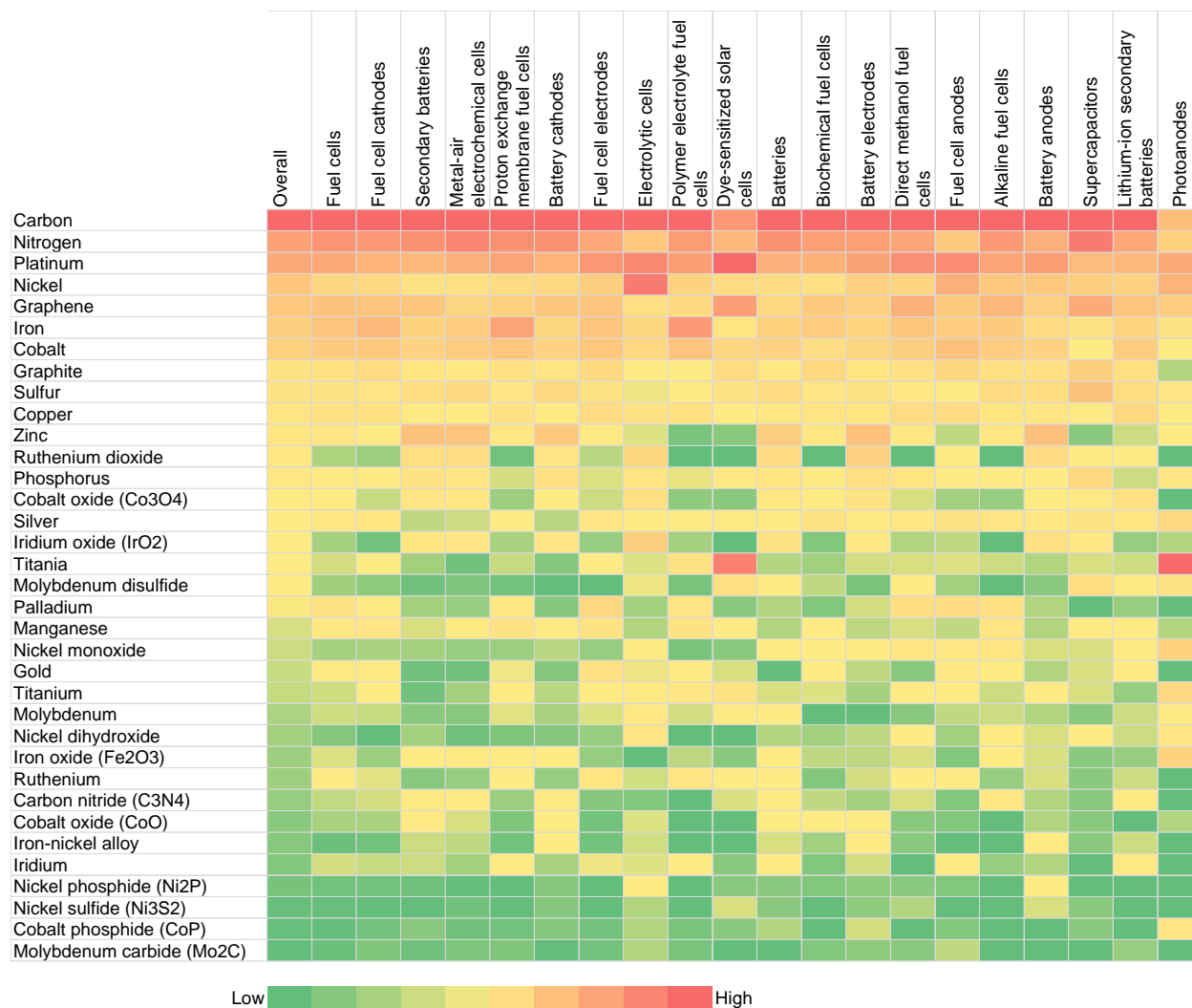


Figure 16. Cooccurrence between the most reported apparatuses and catalysts substance in electrocatalyst publications

Selected Articles in Electrocatalysts from the Dataset

Selected articles from the dataset of electrocatalysts reflecting the major types of substances and their function are summarized below.

Multimetallic systems, such as bimetallic systems have better electronic conductivity than monometallic catalysts.^{74, 75} First-row transition metal-based trimetallic oxide-hydroxide electrocatalysts have shown advanced catalytic properties when compared to mono- and bimetallic-based catalysts.⁷⁶⁻⁷⁸ For instance, Nanda et al. reported porous nanosheets composed of cobalt, nickel and manganese oxide-hydroxide that manifest higher catalytic activity than bimetallic systems (Ni-Mn, Co-Mn or Co-Ni).⁷⁹ This trimetallic nanosheet showed 0% loss of current density after 8000 cycles and performed better than commercially available RuO₂ catalysts in terms of durability and catalytic activity.

Cobalt oxides demonstrate efficient catalytic properties as anode materials for oxygen evolution reaction (OER) in acidic media, but their structural stability is limited under open circuit or high potential applications.⁸⁰⁻⁸² A nitrogen-doped carbon coated Co₃O₄ (Co₃O₄@C) was reported by

Galán-Mascarós et al. showing performance consistency towards OER.⁸³ This scalable electrode composite ($\text{Co}_3\text{O}_4@\text{C}/\text{GPO}$) was made by mixing $\text{Co}_3\text{O}_4@\text{C}$, graphite (G), and paraffin oil (PO) in a specific ratio by weight. This type of anode composite sustains OER performance in 1M H_2SO_4 solution for over 40 hours.

Due to the high porosity and large surface area of metal-organic frameworks (MOFs), they are applied for water splitting applications.⁸⁴ Heteroatom doping and nanofabrication are utilized to enhance the catalytic properties of MOFs. Yun et al. revealed a bifunctional electrocatalysts, V doped Ni-Fe MOFs@graphene oxide, synthesized by vanadium doping and carbonization of bimetallic Ni-Fe MOFs.⁸⁵ The V-Ni_{0.06}Fe_{0.06} MOF/GO performed as a bifunctional electrocatalyst for HER and OER in the presence of an acidic or alkaline solution.

Due to the low cost and earth abundance, molybdenum sulfide (MoS_2) has been identified as a promising electrocatalyst for HER.^{86, 87} However, MoS_2 shows poor oxygen evolution activity because of its insufficient binding with the reaction intermediate on the catalytic site. Liu et al. utilized 3d transition metal doping to modify the active site of MoS_2 . 3d-TMO₆@ MoS_2 (TM = Mn, Fe, and Co) shows better OER catalytic activity than the standard catalyst, IrO_2 . This catalyst also possesses structural stability.⁸⁸

Electrochemical synthesis of H_2O_2 via 2-electron oxygen reduction is challenging due to the high cost of noble metal-based catalysts such as Au-Pd⁸⁹ and Au-Pt-Ni.⁹⁰ Nickel oxide possess unsaturated metal centers that facilitate proper *OOH binding for electrochemical synthesis of hydrogen peroxide,⁹¹ whereas amorphous metal oxides possess better catalytic properties due to their coordinately unsaturated open sites.⁹² Zhang et al. displayed amorphous nickel oxides coated on carbon nanosheets ($\text{NiO}_x\text{-C}$).⁹³ This scalable composite $\text{NiO}_x\text{-C}$ selectively catalyzes 2-electron oxygen reduction (~91%) in 0.1M KOH between 0.15–0.60 V to produce H_2O_2 due to high $\text{NiO}_x\text{-C}$ -*OOH binding strength.

Photocatalysts

In photocatalysis, semiconductor materials absorb light energy and produce electron-hole pairs which drive reduction, and oxidation reactions respectively. The use of photocatalysis to split water and produce hydrogen only using solar energy is considered an ideal solution to energy and environmental problems. Solar energy is primarily composed of visible light and infrared radiation. Most of the photocatalysts known till date either function only under UV light irradiation, do not have sufficient efficiency under visible light irradiation for practical applications, or suffer from low long term stability issues. The challenge and the primary focus in the field of photocatalysis has been to find semiconductor materials which are capable of splitting water using only solar energy and remain stable under the operating conditions. To scale up the production of hydrogen to levels that meet global energy needs, an enormous amount of photocatalysts will be needed, and hence it is necessary that they are made of earth abundant elements to become cost effective.

The search query resulted in 6507 documents out of which 6159 were journal publications and 338 were patents. We found a total of 676 review articles within the journal publications.

Figure 17 shows the number of publications in the from 2012. The number of publications in the journals and patents shows a steady increase over the years, demonstrating the continuous

rising interest in this field. The huge difference between journal publications and the patents is an indication that research in this area of sustainable photocatalysts has still not reached the point of commercialization.

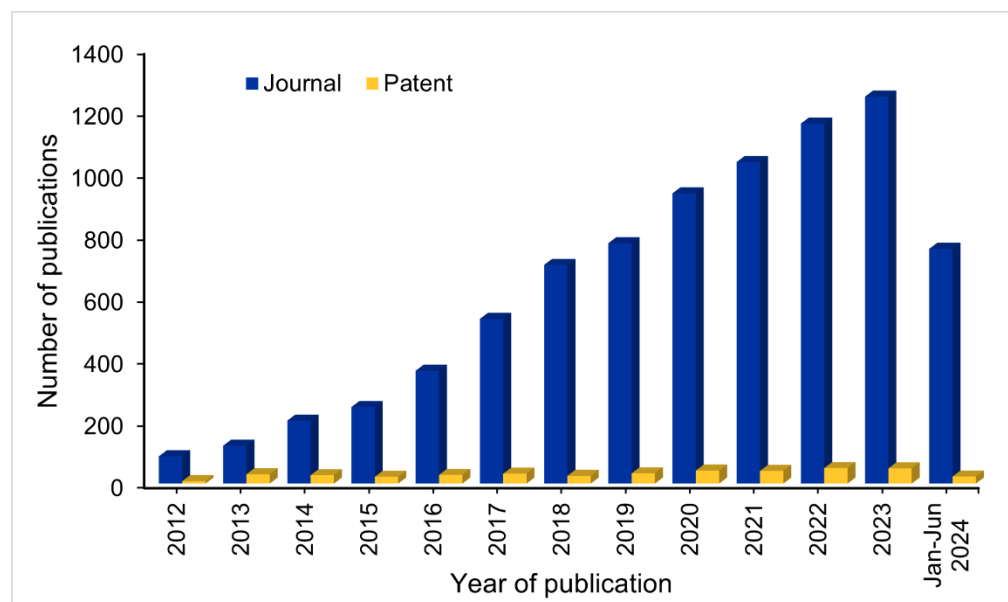


Figure 17. Year-wise number of publications related to photocatalysts.

As expected, the 15 topmost cited documents were reviews of the existing literature and they cover various aspects such as co-catalysts for photocatalysts,⁹⁴ catalytic water treatment,⁹⁵ hydrogen evolution, silver nanoparticles, Cu based nanoparticles,⁹⁶ noble-metal free nanoparticles,⁹⁷ semiconductors for photocatalytic water splitting, transition-metal based co-catalysts for photocatalytic water splitting, carbon nitride photocatalysts, MXene photocatalysts,⁹⁸ nano and microstructured catalysts,⁹⁹ non-noble metal plasmonic photocatalysts,¹⁰⁰ and single-atom catalysts on 2D nanomaterials. 6 out of the top 25 most cited photocatalyst related documents were about graphitic carbon nitride, highlighting the interest and the potential of this specific photocatalyst.

Frequently Used Substances and their Growth Trend

An analysis of the substances with the catalyst role showed that carbon nitride (C_3N_4), titania, cadmium sulfide, and molybdenum sulfide are among the most reported catalysts (Figure 18). The other catalysts in the top 15 are zinc oxide, Co_3O_4 , tungsten oxide, indium zinc sulfide, Fe_2O_3 , $BiVO_4$, cadmium zinc sulfide, and nickel phosphide. Carbon nitride is a promising photocatalyst due to its visible light absorption, stability in alkaline and acidic conditions, and organic composition.¹⁰¹ Cadmium sulfide has bandgap and band positions suitable for overall water splitting using visible light irradiation. However, it is unstable due to photocorrosion and the potential for environmental pollution due to the presence of toxic cadmium. Despite these concerns, studies on CdS continue due to hopes of stabilizing it and containing the environmental damage at a later stage.¹⁰²

The most reported photocatalysts were also color coded according to their patent-to-journal ratio. In general, oxide photocatalysts such as tungsten trioxide, zinc oxide and titanium dioxide have high contribution from patents, compared to nitride and sulfide photocatalysts. Due to its visible light activity and stability, films of WO_3 has been patented for applications such as air purification^{103, 104} and refining.¹⁰⁵

In addition, from the pool of 100 photocatalysts with the highest number of publications, we selected 10 catalysts that demonstrated the highest growth within the last five years (Figure 19). Carbon nitride stands out from the rest of the catalysts due to its relatively very high number of publications along with rapid growth in recent years. Factors such as band gap suitable for visible light absorption, band positions suitable for overall water splitting, metal-free composition and ease of preparation contribute to the high interest in carbon nitride photocatalysts. Most of the other catalysts with higher number of publications are also growing rapidly, due to the recent interest in finding sustainable alternatives to the existing catalysts. It is also worthwhile to note that titanium dioxide continues to draw interest more than 5 decades after the first report of using it for photocatalytic water splitting.

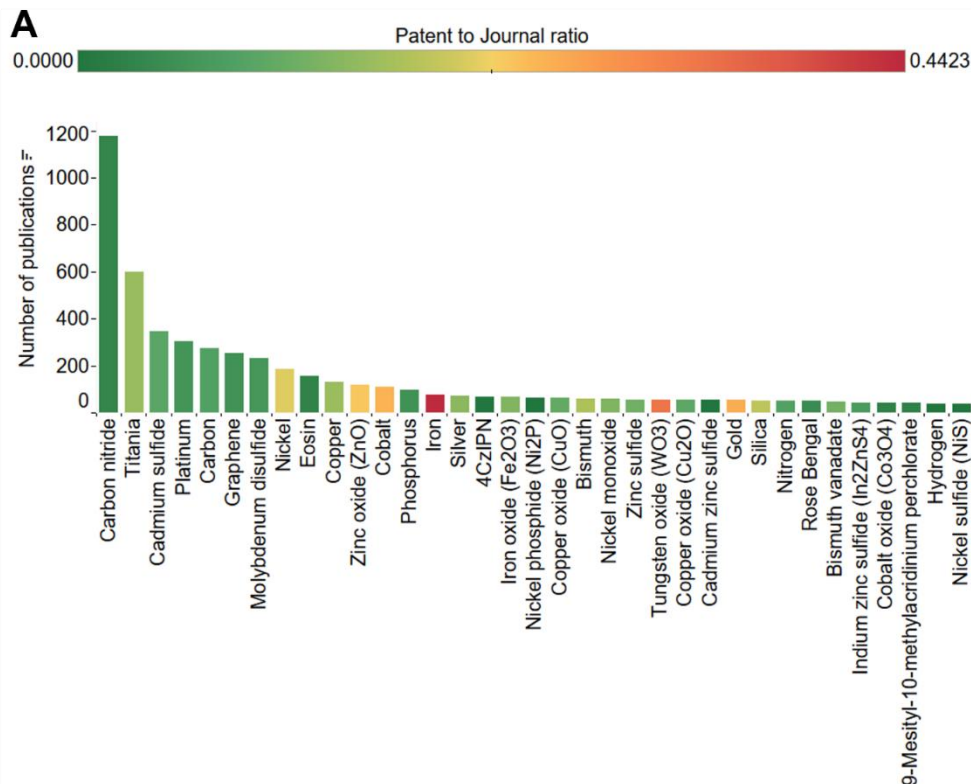


Figure 18. Catalysts substance with the highest number of publications color coded according to their patent to journal ratio.

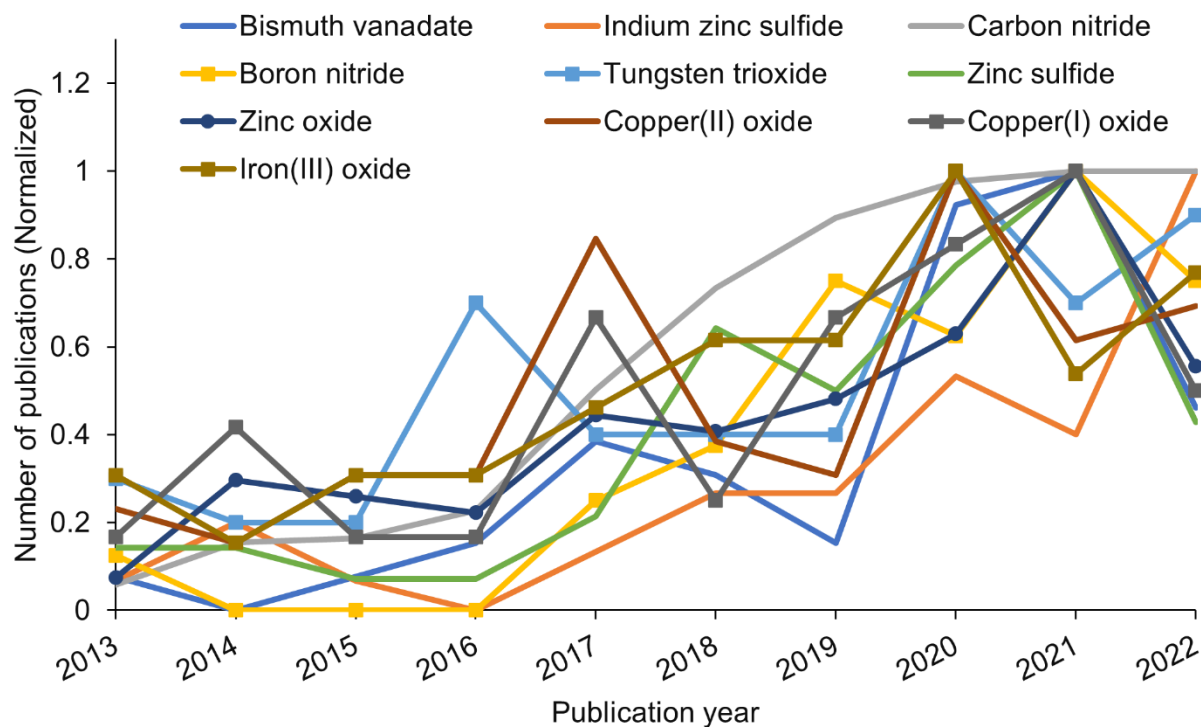


Figure 19. Emerging photocatalysts with the high growth in publications

We then analyzed the data to find the reactions which are facilitated using photocatalysts. Figure 20 presents the most reported reactions along with their patent to journal ratios. Photocatalysts are most used for water splitting to produce hydrogen, and for the decomposition of pollutants. The electron-hole pairs generated can be used for carrying out both the reduction and the oxidation reactions, as seen by the presence of both photooxidation and photochemical reduction. Due to the limited availability of photocatalysts capable of performing overall water splitting, a combination of two different photocatalysts each capable of performing only water oxidation or water reduction in a tandem reaction is widely studied.¹⁰⁶ Electrochemical reduction and oxidation are other important reactions in the publications reporting photocatalysts. Electrocatalysts which enhance the hydrogen evolution or oxygen evolution reaction, referred to as co-catalysts, are loaded on to the surface of the photocatalysts.^{107, 108} To a lesser extent, photocatalysts are also studied for organic reactions such as regioselective synthesis,¹⁰⁹ and diastereoselective synthesis.¹¹⁰

Figure 21 shows the cooccurrence between the reactions and the most used catalysts within the photocatalyst dataset. Due to their band positions suitable for hydrogen evolution reaction and low cost, sulfide photocatalysts such as molybdenum disulfide,^{111, 112} cadmium sulfide, zinc sulfide, and cadmium zinc sulfide have higher contribution to this reaction type. Despite their favorable properties, stability is a common drawback in the sulfide photocatalysts constraining their success. Sulfide based materials such as MoS_2 are also widely explored as co-catalysts to enhance the hydrogen evolution properties of stable photocatalysts such as C_3N_4 .^{113, 114} Despite its large bandgap capable of absorbing only UV light, ZnO continues to be explored as photocatalysts, due its benign nature and low cost, especially for photocatalytic decomposition of pollutant molecules.¹¹⁵ The visible light activity of ZnO is increased by doping it with metals, non-metals, and creating heterojunctions¹¹⁶ with other small bandgap semiconductors.^{115, 117}

The presence of iron in decomposition and photooxidation studies can be attributed to the use of photo Fenton reaction, which involves iron and hydrogen peroxide, and iron containing metal organic frameworks^{118, 115, 117}. The presence of iron in decomposition and photooxidation studies can be attributed to the use of photo Fenton reaction, which involves iron and hydrogen peroxide, and iron containing metal organic frameworks¹¹⁸ for the oxidation of pollutant substances.¹¹⁹ In the oxygen evolution reaction type, bismuth vanadate and cobalt have high contribution due to their high photocatalytic¹²⁰ and co-catalytic¹²¹ activity respectively towards this reaction type. Another catalyst with high contribution is eosin, which has high presence in organic conversion reactions,^{122, 123} due to its use as a photosensitizer in these reactions. 2,4,5,6-Tetrakis(9H-carbazol-9-yl) isophthalonitrile also called as 4CzIPN and rose bengal are other organic photocatalysts widely used in various organic conversion reactions.^{122, 124}

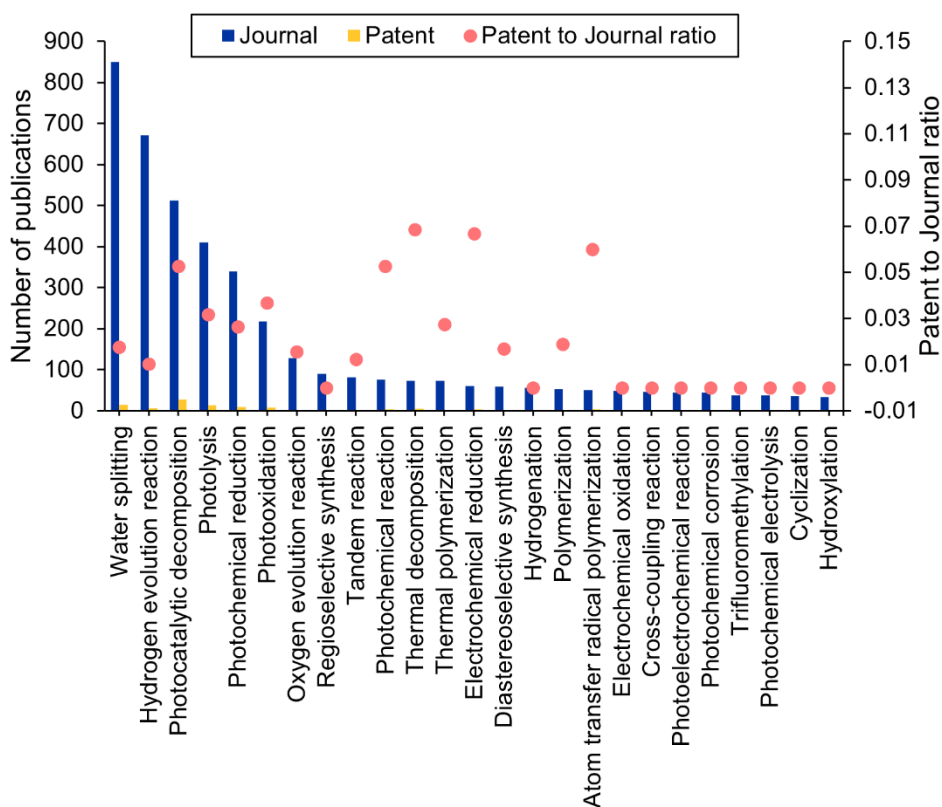


Figure 20. Most reported reactions in the photocatalyst publications

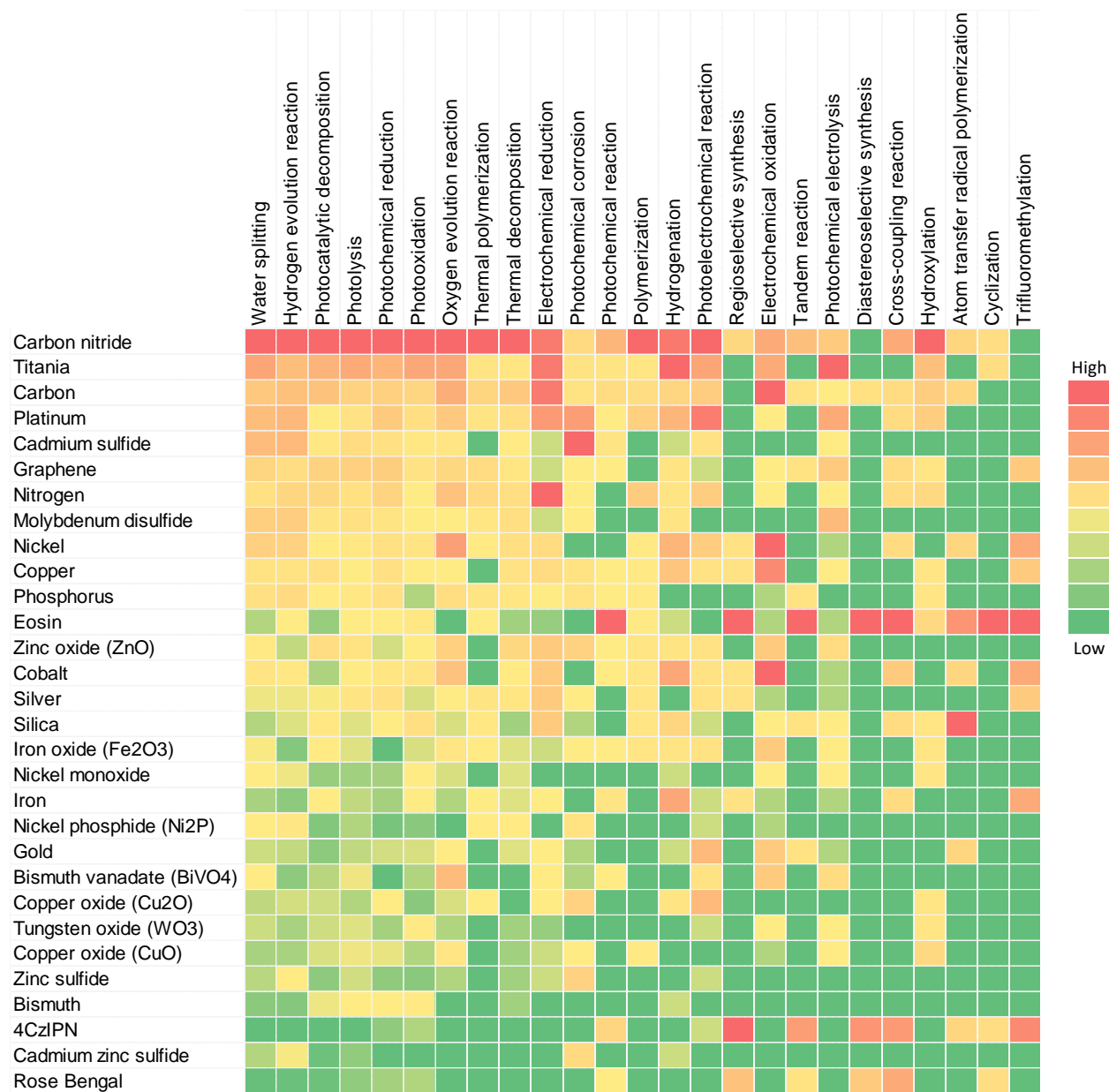


Figure 21. Co-occurrence between the top reactions and the most reported catalyst substance in the photocatalysis related publications.

Figure 22 lists the most reported usage within the photocatalyst dataset. The cooccurrence between the usage and the catalysts within the photocatalyst dataset is presented in Figure 23. The trend among the usage is like the reaction types (Figure 20), with water splitting, and the related catalysts being the predominant ones.

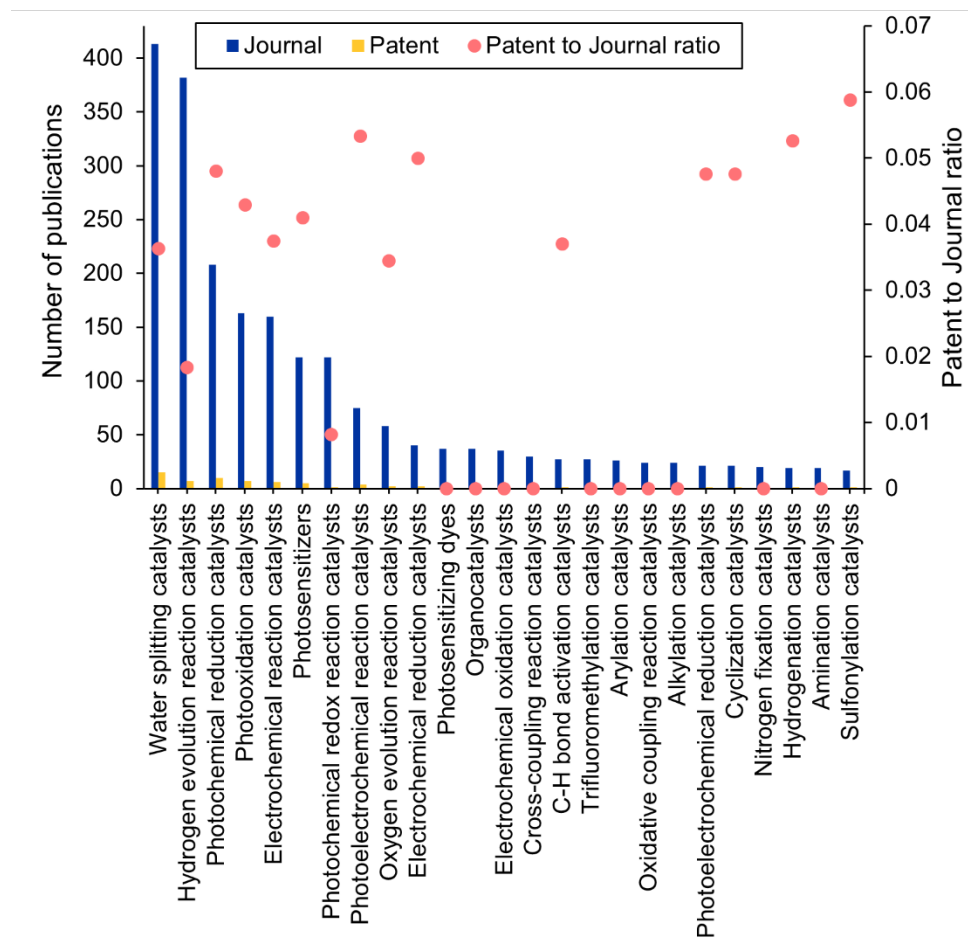


Figure 22. Most prevalent usage in the photocatalyst related publications

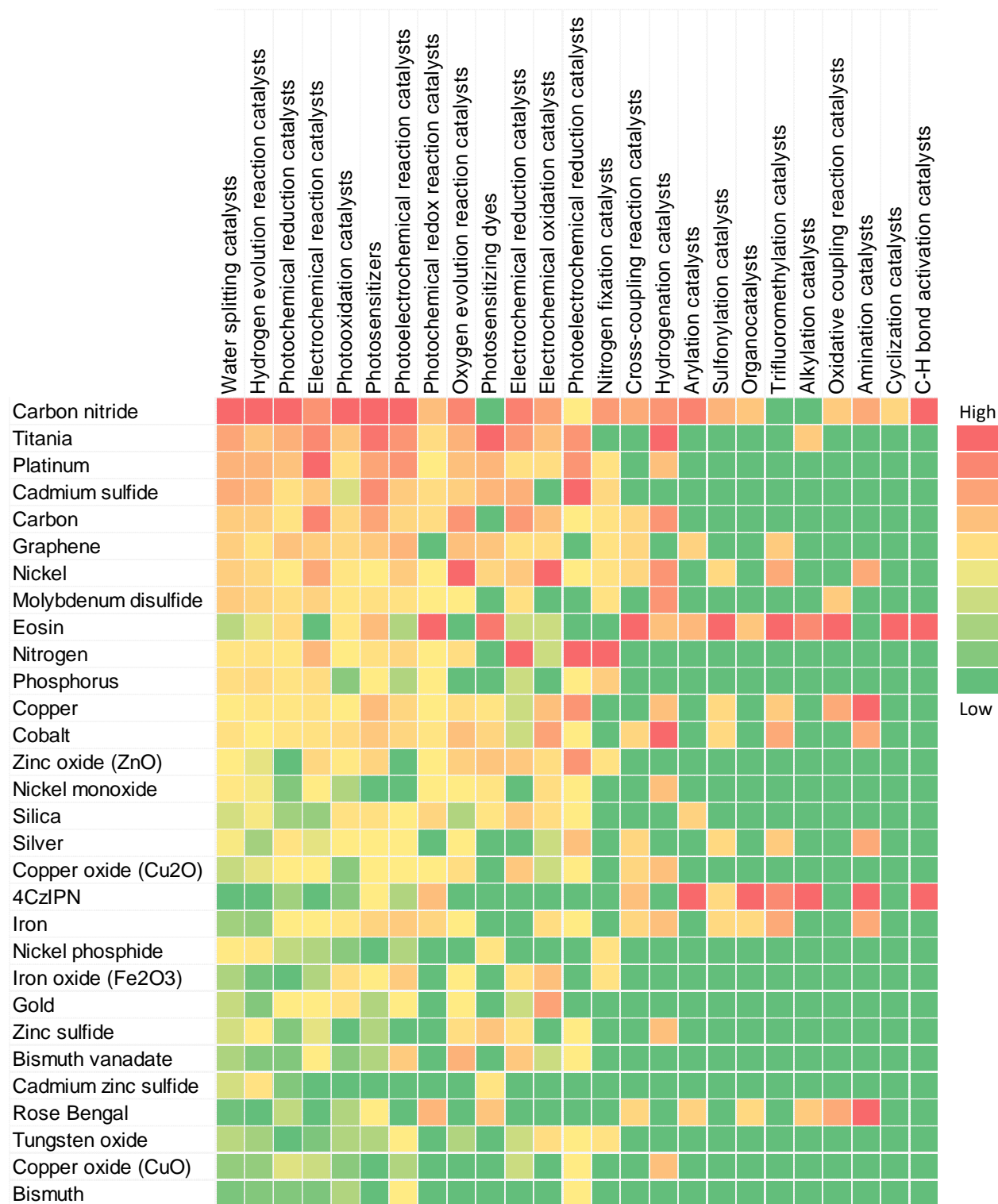


Figure 23. Co-occurrence between the top usage and the most reported catalyst substance in the photocatalyst publications.

In addition to their usage directly as photocatalysts in powder or film form, photocatalysts are also used to fabricate devices or parts of the devices to study the properties of either the photocatalyst or the entire device. By analyzing the CAS Content Collection™ data, a list of the most reported devices or parts of devices was generated and are listed in Figure 24.

Photocatalysts are fabricated as photocathodes, photoanodes, which are either part of photoelectrochemical cells used for water splitting to produce hydrogen or as solar cells. Photocatalysts are also part of various types of solar cells where the photogenerated electrons and holes are used to produce electricity instead of carrying out chemical reactions. Among these devices, patent to journal ratio is high among the solar cells, electroluminescent devices, photochemical reactors, and photoelectric devices.

We further analyzed the cooccurrence between the various devices and the most reported photocatalysts (Figure 25). Bismuth vanadate and tungsten trioxide have a higher than usual contribution to the photoanodes category, as they are predominantly used for the oxidation of water. Molybdenum disulfide, cupric oxide, cuprous oxide, and cadmium sulfide are the photocatalysts used in photocathodes for the reduction of water to produce hydrogen, whereas nickel monoxide is co-catalyst used to enhance the hydrogen production.

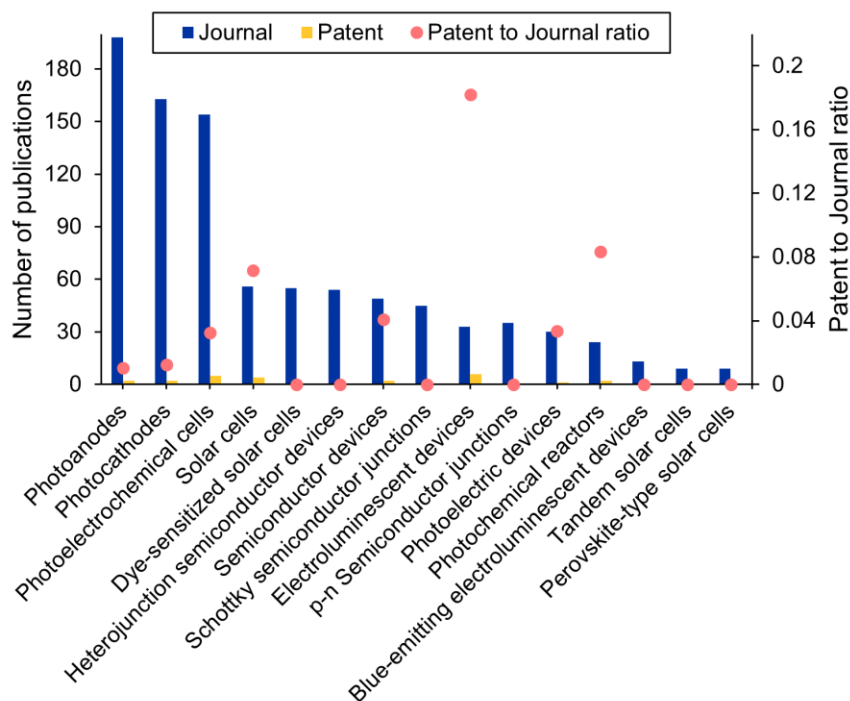


Figure 24. Most reported apparatuses in the photocatalyst related publications

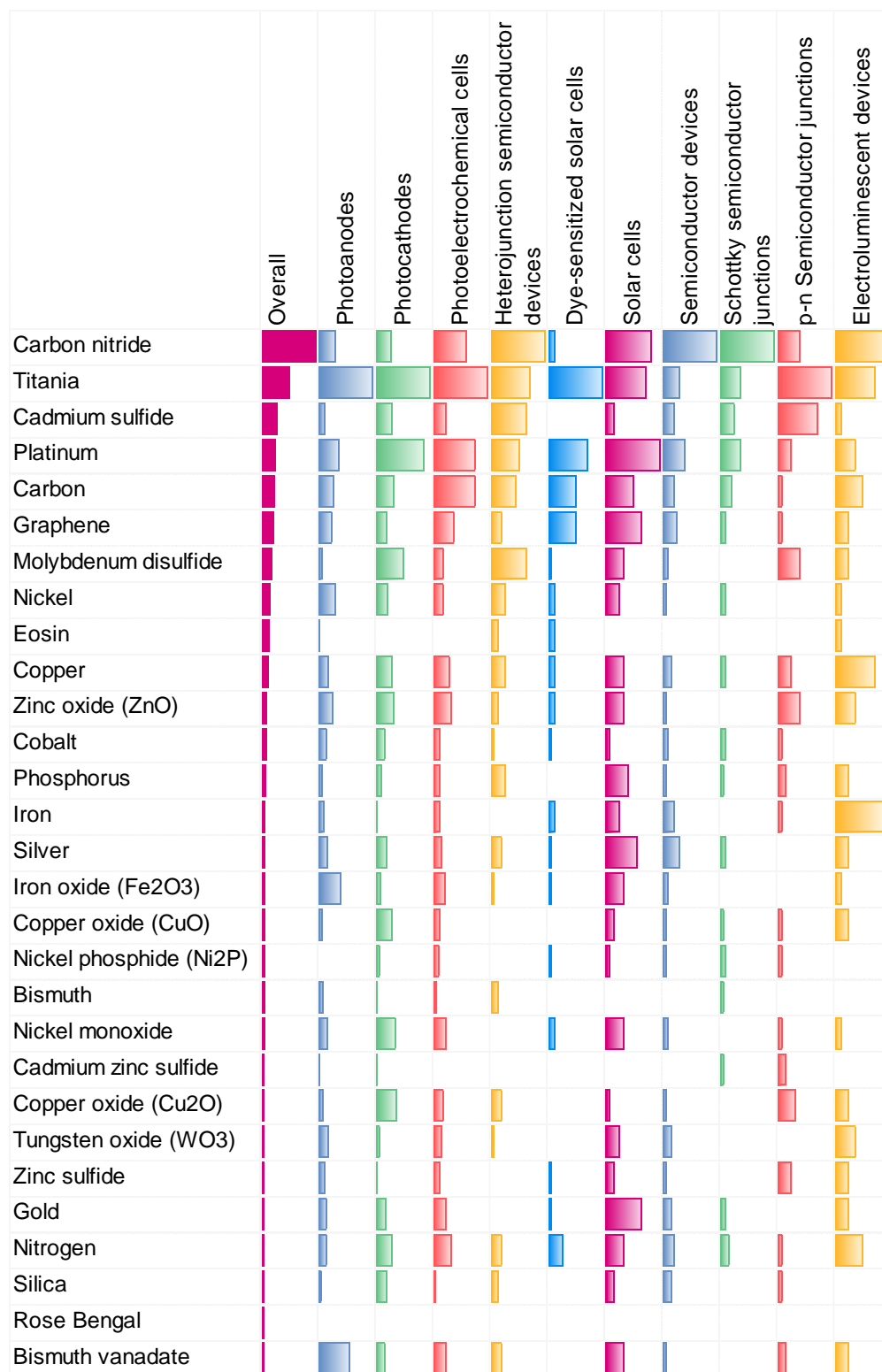


Figure 25. Co-occurrence of the most reported catalyst substances and the apparatuses in the photocatalyst publications.

Selected Journals in Photocatalysts from the Dataset

In the efforts to achieve sustainability in photocatalysis, nonmetal-based catalysts such as graphitic carbon nitride (CN) are getting more attention due to their catalytic activity towards photosynthesis.¹²⁵ Microporous organic polymers (MOPs) are also studied due to their gas separation properties¹²⁶ and potential photocatalytic properties, for example, CO₂ photoreduction.^{127, 128} Kung et al. reported a covalently linked graphitic carbon nitride-melamine—resorcinol—formaldehyde (MRF) microsphere polymers, which possesses photocatalytic properties for CO₂ reduction to methanol.¹²⁹ This material has efficient charge separation due to its covalent C-N bond between CN and MRF, which results in higher photocatalytic properties than CN and MRF alone by 21 and 10 times respectively.

Titania and zirconia are both known for their chemical stability and photocatalytic properties.^{130, 131} The wide band gap of these two types of catalysts (TiO₂: ~3.2 eV; ZrO₂: >5 eV) resulted in limited photocatalytic activity under visible light.^{131, 132} The graphitic carbon nitride (CN) possesses a lower band gap (2.7 eV) and has been proven to form composite materials with titania. This binary TiO₂–CN composite material becomes the visible light photocatalyst.¹³³ Herein, Chen et al. reported a ternary nanocomposite formed by titania, zirconia, and CN that has high specific surface area and bandgap falling in the visible light region.¹³⁴ This nanocomposite photocatalyst further displays its high catalytic efficiency in photodegradation of the antibiotic, berberine hydrochloride (BH).

Boron nitride (BN) is another type of nonmetal photocatalysts due to good thermal stability.¹³⁵ Doping heteroatoms and building hierarchical structures are two promising strategies that could enhance catalytic properties of BN-based materials.^{136, 137} Herein, Lee et al. revealed a hierarchical BN-like flower catalyst with B–O active site that facilitates the photocatalysis of CO₂ reduction.¹³⁸ This as-prepared catalyst has 26.7 and 7.3 times of CO production rate more than the bulk BN and bulk CN for the CO₂ reduction reaction.

Synthetic dyes like methylene blue are major water pollutants, resulting in the degradation of methylene blue to be widely studied.¹³⁹ TiO₂ and ZnO have been studied to remove dyes and other pollutants.¹⁴⁰ Majority of their light absorption falls in UV light region.^{141, 142} Doping tungsten into ZnO makes the light absorption extend to visible light region and improves the photocatalytic efficiency.¹⁴³ Ibupoto et al. developed a low temperature method for the synthesis of tungsten-doped ZnO photocatalysts that perform highly efficient methylene blue degradation.¹⁴⁴ These tungsten-doped ZnO can catalyze the complete degradation of methylene blue to a weakly acid aqueous solution within an hour.

As previously mentioned, hydrogen production from water splitting catalyzed by photocatalysts has become attractive in the past few decades.¹⁴⁵⁻¹⁴⁸ ZnS, ZnCdS, MoS₂, and their composite materials have been studied for the photocatalytic hydrogen production.¹⁴⁹⁻¹⁵¹ MoS₂/ZnS,¹⁵² MoS₂/Zn_xCd_{1-x}S,¹⁵³ and Zn_xCd_{1-x}S/ZnS¹⁵⁴ generally performed better than the single component materials in photocatalytic hydrogen evolution. Few layers of MoS₂ cocatalysts loaded on the surface of CdS photocatalysts have been found to drastically enhance photocatalytic hydrogen generation.¹⁵⁵ Similarly, Shangguan et al. reported few-layered MoS₂/Zn_xCd_{1-x}S/ZnS heterostructures with high efficiency for photocatalytic hydrogen evolution.¹⁵⁶ A supernatant MoS₂ colloidal solution was used to react with Zn_xCd_{1-x}S/ZnS(en)_{1/2} to form the catalyst. This kind of heterostructures possess superior performance in photocatalytic hydrogen production over other ZnCdS@MoS₂ catalysts.

Homogeneous Catalysts

Platinum group metals (PGMs) are predominant in homogeneous catalysis because of their high activity, stability, and versatility. They can activate various bonds and form stable complexes with different ligands. They can also catalyze a wide range of reactions such as hydrogenation, oxidation, coupling, cyclization, polymerization and asymmetric synthesis.¹⁵⁷ They can also exhibit multiple oxidation states and redox behavior that can facilitate catalytic cycles. Table 2 highlights some of the significant reactions that PGMs are used as catalysts.

Table 2. Examples of PGM-based homogeneous catalysts.

Metal	Applications
Platinum(II)	hydrosilylation of alkenes and alkynes, silane etherification, Wacker oxidation of alkenes and Heck coupling of aryl halides.
Palladium(II)	Suzuki cross-coupling of aryl halides, Sonogashira coupling of alkynes, carbonylation of aryl halides and allylic alkylation.
Rhodium(I)	hydroformylation of alkenes, hydroboration of alkenes, asymmetric hydrogenation of ketones and olefin metathesis.
Iridium(I)	asymmetric hydrogenation of imines, transfer hydrogenation of ketones, water oxidation and C-H borylation.
Ruthenium(II)	olefin metathesis, ring-closing metathesis, Grubbs-Hoveyda cross-metathesis and Noyori asymmetric hydrogenation of ketones.
Osmium(VIII)	dihydroxylation of alkenes, Sharpless asymmetric dihydroxylation and Jacobsen-Katsuki epoxidation

As an expert-curated resource, the CAS content is utilized here for the quantitative analysis of publications against variables including time, country/region, research area, and substance details. Homogeneous catalysts query (see SI for more details) was used to retrieve documents that are specific to reports discussing using sustainable catalysts for homogeneous catalysis and/or the studies for the replacement of noble-metal catalysts. A total of 7865 documents were used for the analysis described below.

Figure 26 provides the annual publication trend in this area with a breakdown of journal and patent publications. Like the general search described above there has been significant growth in the area since 2012 where there were less than 400 total publications and more than 1000 in 2023.

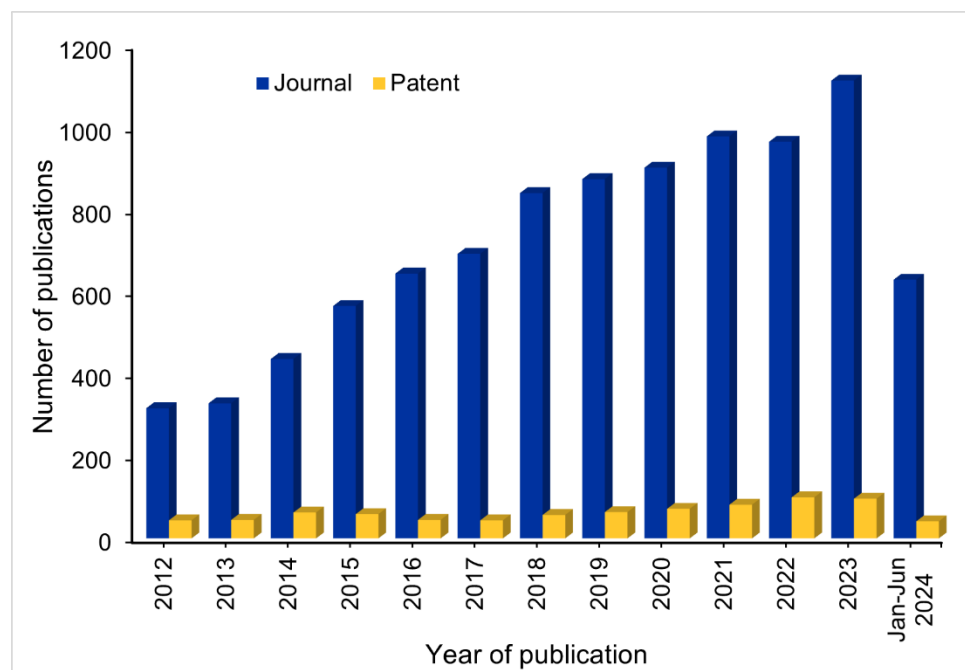


Figure 26. Annual number of publications in homogeneous catalysts among journals and patents.

Coupling Reaction Concepts

Table 3. The top 10 coupling reaction concepts from the publications analyzed.

Reaction concept	Number of publications
Cross-coupling reaction	292
Coupling reaction	247
Suzuki coupling reaction	148
Sonogashira coupling reaction	88
Heck reaction	54
Oxidative cross-coupling reaction	38
Cross-coupling reaction, regioselective	21
Cross-coupling reaction, stereoselective	19
Buchwald-Hartwig reaction	15
Stille coupling reaction	10

Coupling and cross-coupling ranks among the most studied reactions from our search and among the hetero-coupling reactions Suzuki coupling is the most studied (Table 3). This is sensible as Suzuki coupling is a widely used method for making carbon-carbon bonds between organoboron compounds and organic halides or triflates, using a palladium catalyst and a base. It has many advantages over other coupling methods, such as easy availability and stability of organoboron compounds, mild reaction conditions, high functional group tolerance, and low toxicity and environmental impact. Suzuki coupling plays a prominent role in medicinal chemistry.¹⁵⁸ For these reasons Suzuki coupling has been a prime target in the search for more sustainable catalysts. Famously, there have been examples of reports where authors claimed to demonstrate palladium-free Suzuki coupling that were later shown to be catalyzed from palladium contamination.

Leadbeater et. al. reported the first example of transition-metal free Suzuki coupling reactions in 2003.¹⁵⁹ The group later discovered that the Na₂CO₃ used for the reaction contained palladium contamination. The group subsequently published an updated procedure for the reaction to include parts-per-billion levels of palladium as a catalyst.¹⁶⁰ In 2021 Xu et al. claimed that bis(o-tolyl)amine organocatalysts¹⁶¹⁻¹⁶⁴ However, several groups independently reinvestigated their claims and found that the amine catalysts were contaminated with palladium complexes that were entrained during the chromatographic purification of the amine.¹⁶²⁻¹⁶⁴ The paper was retracted by the authors in 2021.

Given these instances, it is crucial to employ rigorous methods to rule out palladium contamination in new catalysts. Ensuring the purity and identity of the catalyst involves performing rigorous purification and characterization, which may include recrystallization, distillation, sublimation, chromatography, mass spectrometry, nuclear magnetic resonance spectroscopy, infrared spectroscopy, X-ray crystallography, and elemental analysis. Sensitive and accurate analysis of the catalyst and the reaction mixture for trace amounts of palladium can be achieved using techniques such as inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence spectroscopy (XRF), energy-dispersive X-ray spectroscopy (EDX), or electrochemical deposition. Additionally, performing control experiments using different sources of the catalyst, solvents, bases, substrates, reaction conditions, and palladium scavengers helps rule out any possible sources of palladium contamination or interference. Finally, mechanistic studies using isotopic labeling, kinetic analysis, intermediate trapping, or spectroscopic monitoring are essential to elucidate the reaction pathway and identify the active species. Employing these methods ensures that the reported catalyst performance is not compromised by unnoticed palladium contamination.

The Most Used Substances

We further analyzed the frequency of the substance use in the field of homogeneous catalysts (Figure 27). Iodine is the most frequently used catalyst substance. Various studies suggest that iodine catalysis primarily happens by activation of reactant through halogen bonding.^{165, 166} For example, iodine is used for oxidative cyclization and oxo-acyloxylation of alkenes and enol ethers.^{167, 168} Nickel,^{169, 170} cobalt,^{171, 172} iron,¹⁶⁹ and copper¹⁶⁹ usually catalyze coupling reactions, C–H functionalization, asymmetric hydrogenation, and direct arylation with their metal-complex forms. Eosin,¹⁷¹⁻¹⁷⁴ iron,¹⁶⁹ and copper¹⁶⁹ usually catalyze coupling reactions, C–H functionalization, asymmetric hydrogenation, and direct arylation with their metal-complex forms. Eosin,^{173, 174} tetrabutylammonium iodide,^{175, 176} and 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile^{177, 178} perform like iodine by creating radical species to initiate the reaction.

Tris(pentafluorophenyl)borane play the role as a Lewis acid catalyst to promote hydroarylation¹⁷⁹ and hydrosilylation.¹⁸⁰ p-toluenesulfonic acid (pTSA)^{177, 178, 181, 182} perform like iodine by creating radical species to initiate the reaction. Tris(pentafluorophenyl)borane play the role as a Lewis acid catalyst to promote hydroarylation¹⁷⁹ and hydrosilylation.¹⁸⁰ p-toluenesulfonic acid (pTSA)^{181, 182} and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)^{183, 184} also perform catalytic reactions as metal-free catalysts.

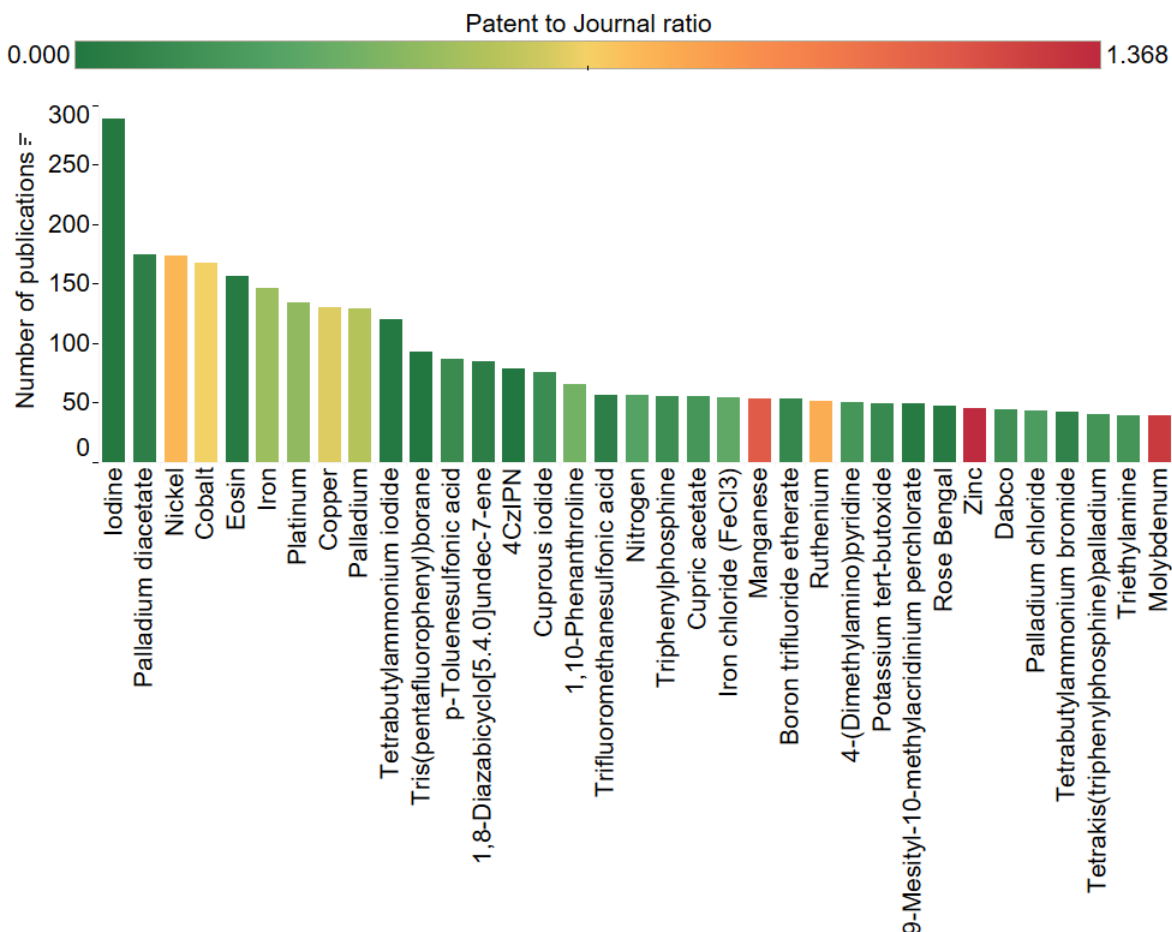


Figure 27. Top 35 substance mostly used as homogeneous catalysts.

In Figure 28, the emerging trend of homogeneous catalysts are shown. Transition metal based catalysts, zinc, nickel, copper, cobalt, manganese, and molybdenum emerge in the period of 2013–2022.¹⁸⁵⁻¹⁸⁷ 2,4,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN) is a visible light driven homogeneous photocatalyst capable of functioning under visible light for organic transformations^{124 185-187} 2,4,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN) is a visible light driven homogeneous photocatalyst capable of functioning under visible light for organic transformations¹²⁴ such as difunctionalization of alkenes and alkynes,¹²² and cyanoalkylation.¹²³ Acridinium, 10-methyl-9-(2,4,6-trimethylphenyl)-, perchlorate (9-Mesityl-10-methylacridinium perchlorate) is another visible light active organic photocatalyst¹⁸⁸ known for its high efficiency in generating radical initiators due to its long lived electron transfer state.¹⁸⁹ Boron trifluoride etherate is a metal-free Lewis acid catalyst for various reactions such as reductive aldol

reaction,¹⁹⁰ vinylation of carbonyl oxygen,¹⁹¹ and electrophilic addition/cyclization of 1,3-enynes.¹⁹²

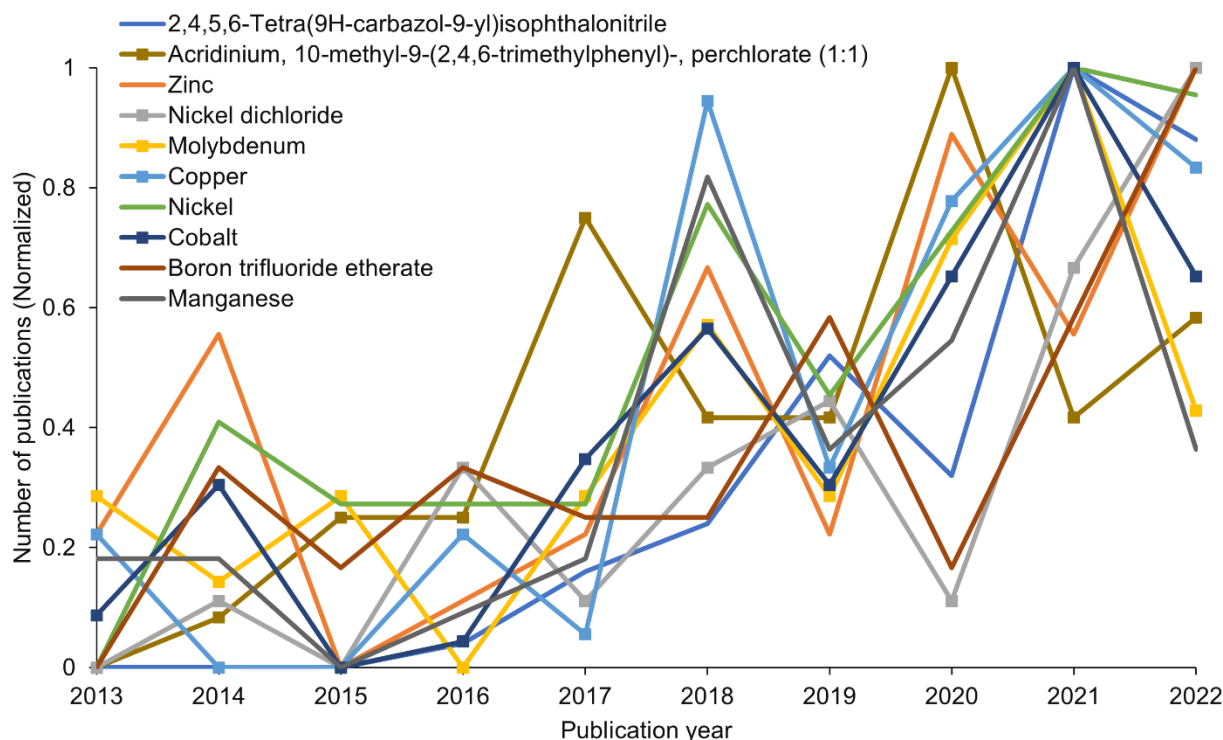


Figure 28. Sustainable homogeneous catalysts which grew significantly between 2013-2022.

In addition to individual catalyst substances, we analyzed the data for substance classes used as homogeneous catalysts (Figure 29). The top substance groups to which the homogeneous catalysts belonged to are transition metals, Lewis acids, N-heterocyclic carbenes, transition metal complexes, and Bronsted acids. Most common Lewis acids catalysts are organoboron catalysts,¹⁹³ which can form frustrated Lewis pairs (FLP) capable of catalyzing a range of organic reactions including hydrogenation, dehydrogenation and cycloisomerization.¹⁹⁴ Metals, noble-metals, and bases have high patent to journal ratio indicating high commercial interest in these substances.

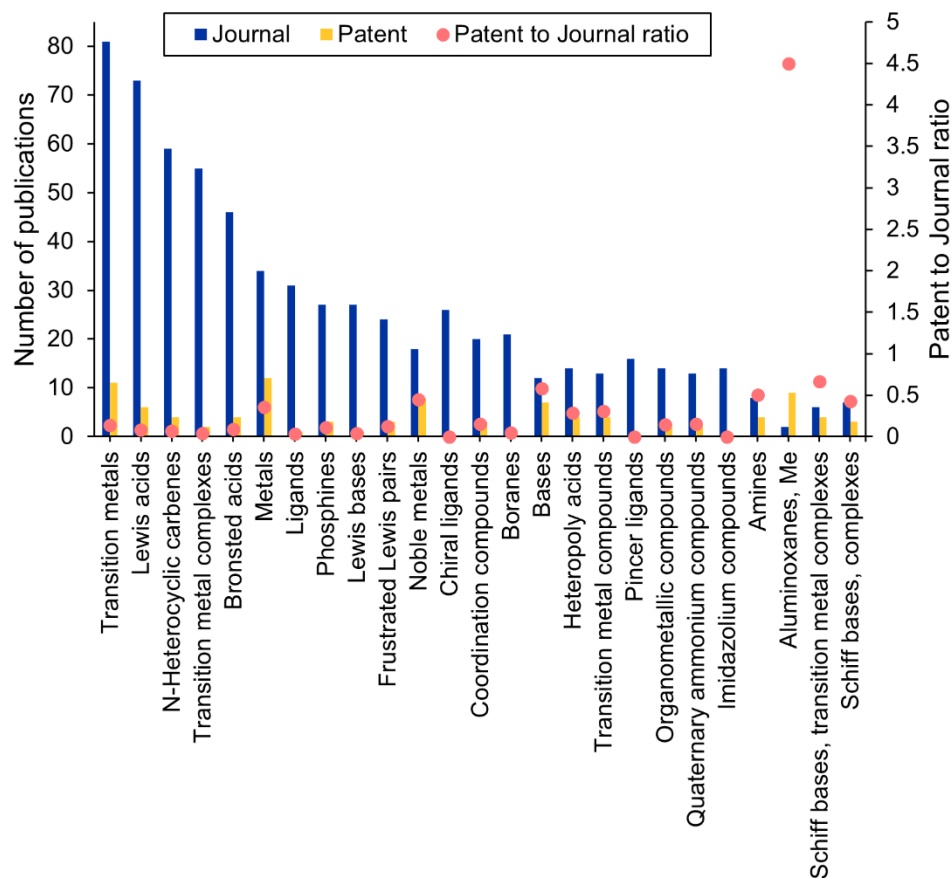


Figure 29. Substance classes reported as homogeneous catalysts.

Figure 30 shows the types of reactions reported using sustainable homogeneous catalysts and their patent to journal ratio. Reactions to synthesize a specific isomer are the most reported reaction types. The other most reported reactions include tandem reaction, cyclization, and oxidation reactions. Reaction types with high patent to journal ratio are hydrogenation, heterocyclization, reduction, oxidation, and condensation reactions.

Non-metal substances such as iodine, eosin, tetrabutyl iodide, and 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile, which are radical initiators in homogeneous catalysis, possess high frequency of co-occurrence with regioselective synthesis, diastereoselective synthesis, and cross-coupling reactions (Figure 31). Metal substances like cobalt, iron, nickel, and copper mainly co-occurred with cross-coupling reactions, oxidation, reduction, hydrogenation, and electrochemical reactions.

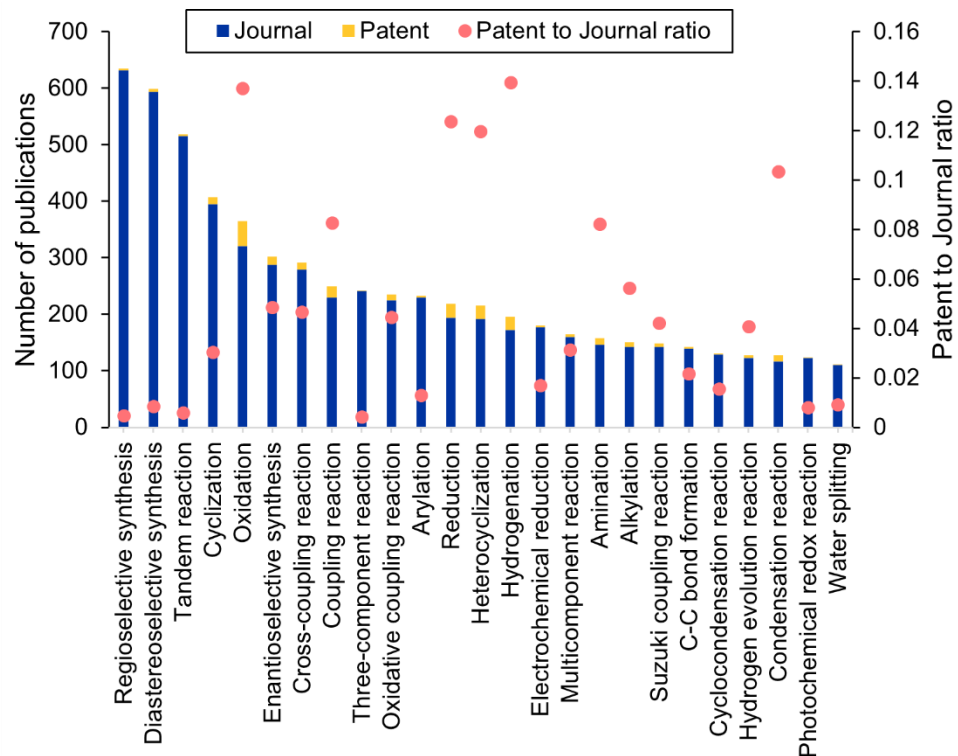


Figure 30. Reactions in high numbers within the homogeneous catalysts publications

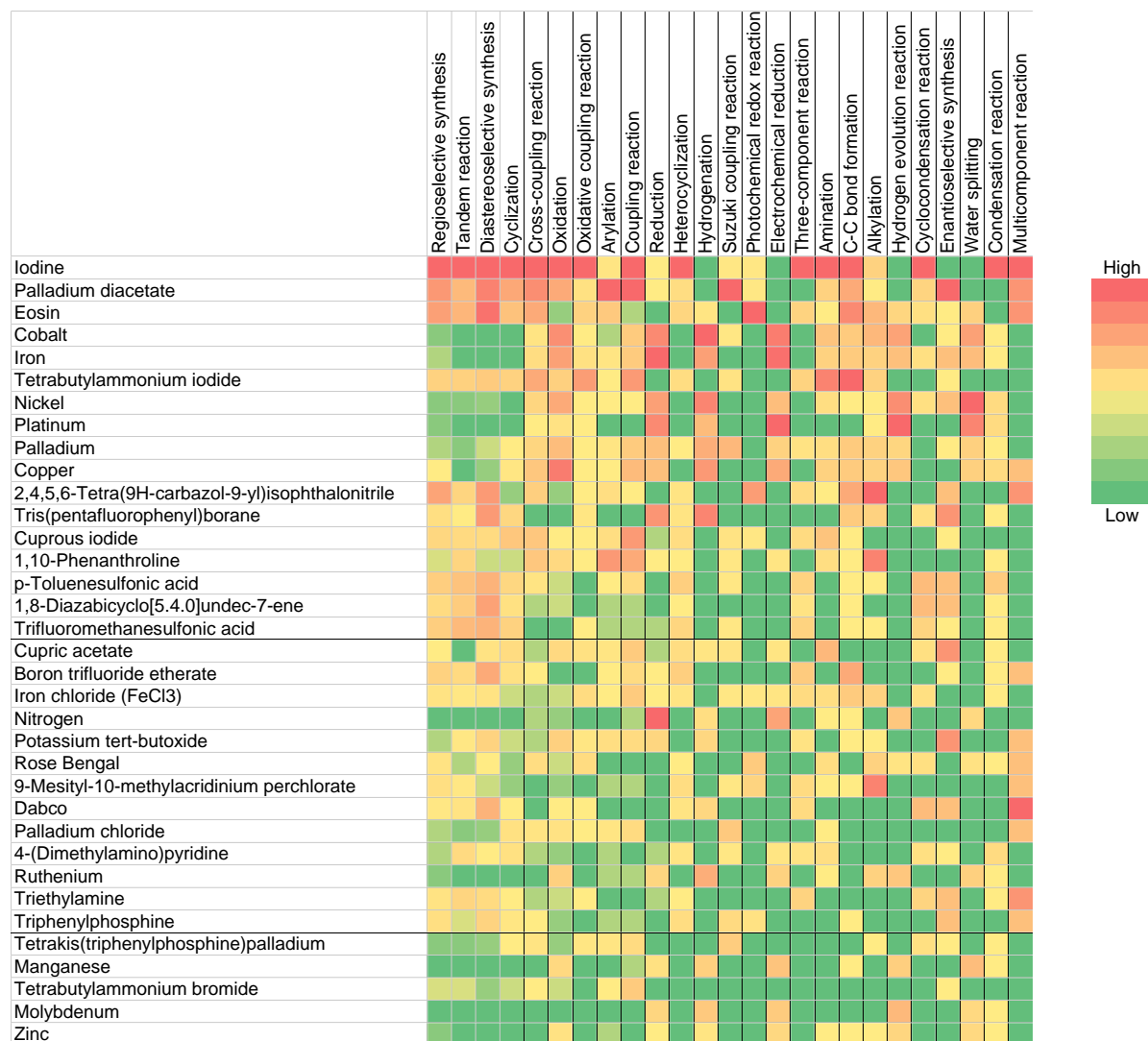


Figure 31. Co-occurrence between catalyst substances and reactions in homogeneous catalyst publication.

Figure 32 lists the most reported uses in the homogeneous catalysis dataset. In addition to the general use cases such photocatalysts and organocatalysts, cyclization, cross-coupling, and oxidation catalysts are among the most reported uses. Polymerization, ring-opening, hydrosilylation, and oxidation in particular have a high patent to journal ratio indicating commercial interest.

Co-occurrence between the catalyst substances and their uses is presented in Figure 33. Trends such as the use of palladium diacetate as coupling catalysts, eosin in photocatalysts, cobalt, nickel, and iron in hydrogen and oxidation catalysts, are evident from this map. Other notable uses are 2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile in alkylation and bond formation catalysts, p-toluenesulfonic acid in polymerization catalysts, and copper in oxidative cyclization catalysts.

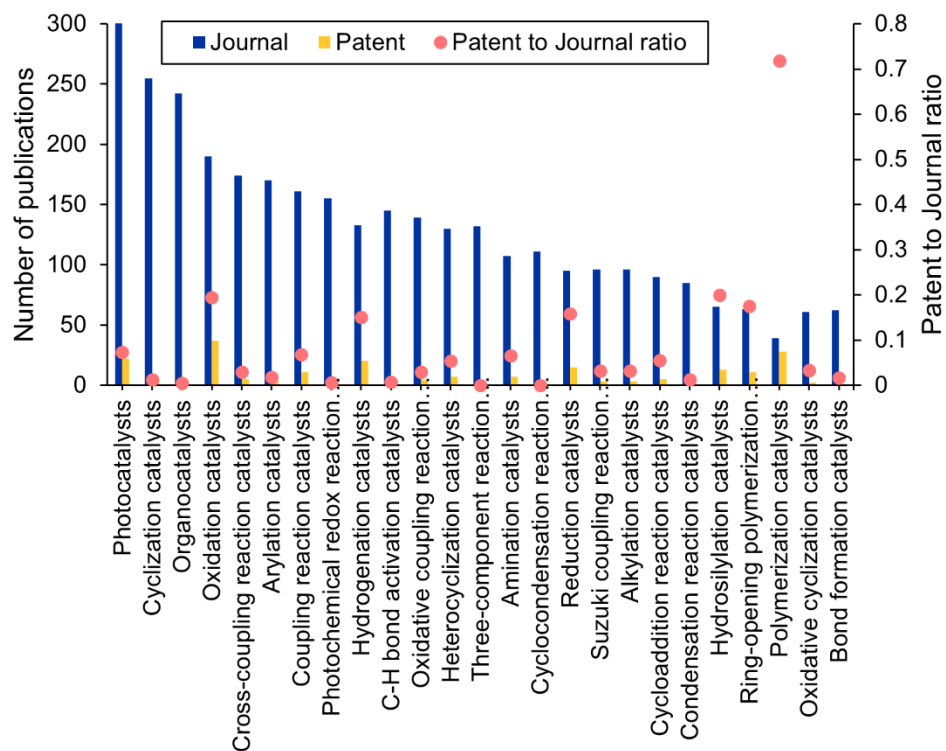


Figure 32. Most prevalent usage in homogeneous catalyst publications

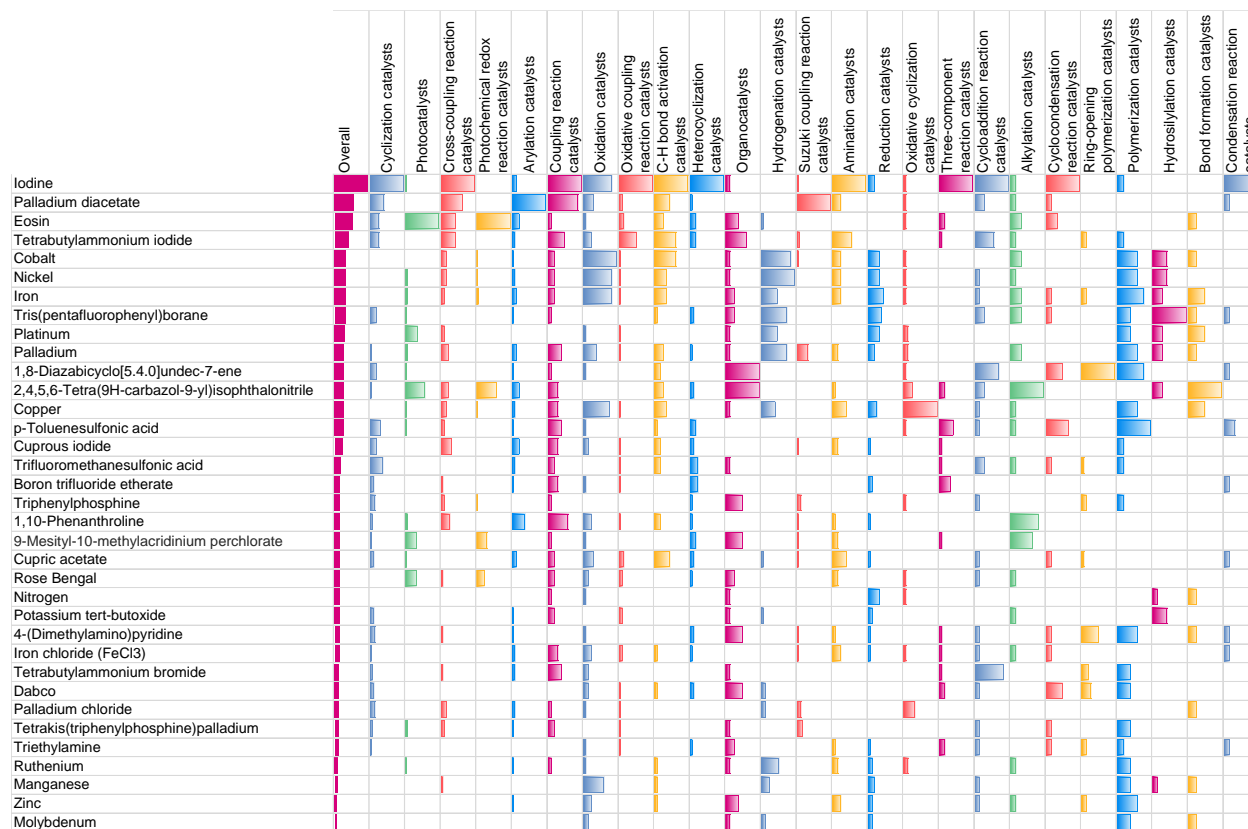


Figure 33. Co-occurrence between most reported usage and the catalyst substances in homogeneous catalyst publications

Biocatalysts / enzymes

Biocatalysts are based on natural proteins, enzymes, which can catalyze specific chemical reactions outside the living cells. Enzymatic biocatalysts are true green and sustainable catalysts. Produced from available renewable feedstocks (plants, animal tissues, bacteria, yeast, and fungi), they are organic, biodegradable, non-toxic and can function under mild reaction conditions (aqueous medium, pH ~7, normal temperature and pressure).¹⁹⁵ Other advantages of biocatalysts include reduced number of byproducts and toxic waste. They also provide shorter and more selective synthetic pathways. All these benefits give a boost to the global biocatalyst market which is expected to reach 170 kilotons by 2026 if it continues to grow at a projected rate of 6.4%.¹⁹⁶

In Figure 34, between 2012 and 2023, the number of journal publications on biocatalysts almost doubled. The rapid growth of biocatalyst patents from 2012 to 2014 was replaced by a slow climb up to 2021 with downs in 2018 and 2020. Although the fraction of patent documents makes up only a tenth of the total publication volume, the number of patents increased overall.

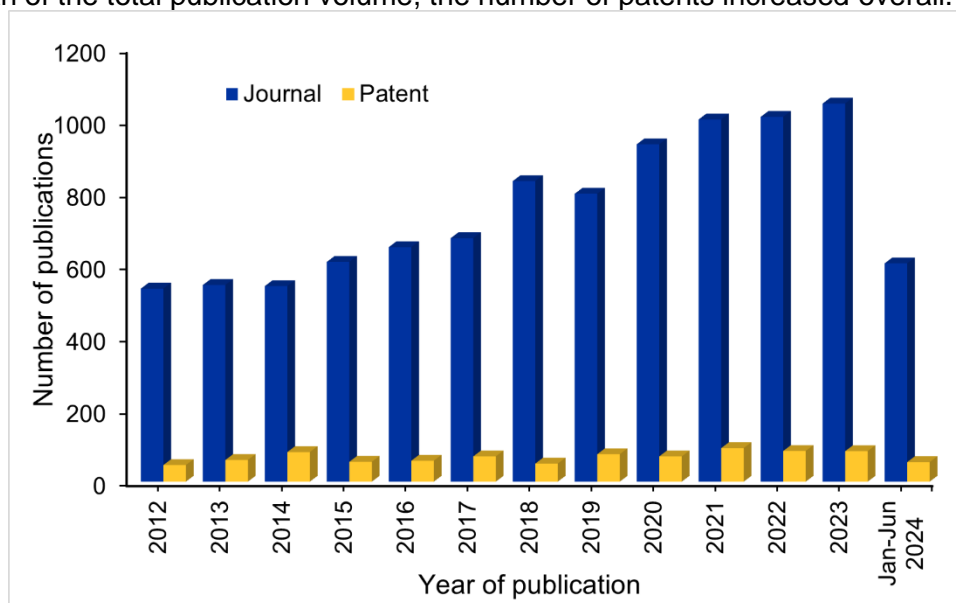


Figure 34. Annual publication trend of biocatalysts from 2012 to 2024.

Enzyme Class

Enzymes can be classified into 6 main classes according to the type of reaction they catalyze: oxidoreductases (peroxidase, laccase, tyrosinase, glucose oxidase), transferases (phosphorylase, glycosyltransferase, acyltransferase), hydrolases (cellulase, amylase, xylanase, lipase, protease), lyases (decarboxylase, aldolase, dehydratase), isomerases (racemase, epimerase, isomerase), and ligases (ligase, synthase, acyl CoA synthase). Among them the three classes, oxidoreductases, transferases, and hydrolases, are the most abundant types of enzymes.¹⁹⁷

Hydrolases occupy more than 50% of the total biocatalysts market followed by oxidoreductases and transferases.¹⁹⁶ The major application of these three enzymes is shown in Table 4.

Table 4. Three major enzyme classes and their applications.

Enzymes	Hydrolases	Oxidoreductases	Transferases
Major application	Synthesis of pharmaceutical compounds ¹⁹⁸⁻²⁰⁰ , polymer synthesis ²⁰¹ ¹⁹⁸⁻²⁰⁰ , polymer synthesis ²⁰¹	Biofuel cells, oxidation polymerization of aromatic compounds ¹⁹⁷	Transferring functional groups ¹⁹⁷

Top Substances Used in Biocatalysts

The combination of metal-based catalysts and enzymes represents an inexpensive and environmentally attractive research area²⁰². Also, combining transition metal catalysts with engineered or artificial metalloenzymes expands the range of catalyzed reactions and improves their reactivities.²⁰³ The use of olefin metathesis catalyst (Ru complex) in combination with a cytochrome P450 enzyme greatly improved the epoxidation selectivity.²⁰⁴ Transition metal complexes biocompatible with living organisms were reported to be efficient biocatalysts. For example, iron(III) phthalocyanine facilitates olefin cyclopropanation in the presence of *E. coli* living microorganisms.²⁰⁵

Enzymes that attracted the most attention as potential biocatalysts are shown in Figure 35. Among them are triacylglycerol lipase and lipase CaLB. The hydrolases and oxidoreductases such as peroxidase, laccase, glucose oxidase, alcohol/glucose dehydrogenase, and carbonyl reductase contribute to this field significantly. Carbon-based materials and transition metals (Ni, Fe, Pt, Cu, Co) are widely used to optimize enzymatic systems which makes them attractive.^{202, 206} Nickel and cobalt coordinated covalent organic frameworks were found to exhibit oxidase like properties. Nickel and iron containing metal organic framework nanozymes showed peroxidase like activity for biosensing applications.²⁰⁷ NiFe hydrogenase catalysts which are immune to inhibition by oxygen were studied recently for hydrogen oxidation reactions, which are traditionally catalyzed by expensive Pt catalysts.²⁰⁸ This trend shows that the hydrolases and oxidoreductases are two primary types of biocatalysts and the combination between biocatalysts and metal catalysts is another approach in this field.²⁰⁹ Nickel and iron metal organic frameworks containing nanozymes showed peroxidase like activity for biosensing applications.²⁰⁷ Successful application of NiFe hydrogenase enzymes for hydrogen oxidation reaction traditionally catalyzed by expensive Pt had been reported.²⁰⁸

The substance classes used in biocatalysis are presented in Figure 36. Enzymes dominate other classes of compounds in both journal and patent publications. Immobilized enzymes are in second place. Immobilizing enzymes provide several benefits such as minimizing enzymes inhibition by the products, reusing the catalysts without the need for separation of the used biocatalysts, and enables establishing continuous flow biocatalysis.^{210, 211} Most of the patents

involve the application of enzymes and encapsulated enzymes for the synthesis of organic and biomolecules^{212, 213} Most of the patents involve the application of enzymes and encapsulated enzymes for the synthesis of organic and biomolecules^{212, 213} and conversion of biomass.²¹⁴

The other substances broadly used as biocatalysts are porphyrins, enzyme mimics, hemoglobins, and co-enzymes. Porphyrins including metalloporphyrins, their analogues and derivatives exhibit enzyme like properties.^{215, 216} Porphyrins are commonly used in electrocatalytic applications.²¹⁷ The visible light absorption ability of porphyrin-based compounds enables their application in photocatalytic and photosensitizer applications.^{218, 219} Vitreoscilla hemoglobin has been reported as an efficient biocatalyst for organic synthesis.^{220, 221} The class of coenzymes represents a special case. Coenzyme includes an organic molecule that binds to the active sites of certain enzymes assisting catalytic reactions. The patent to journal ratio for coenzymes is the highest among the substance classes, showing high commercial interest towards these biocatalysts.

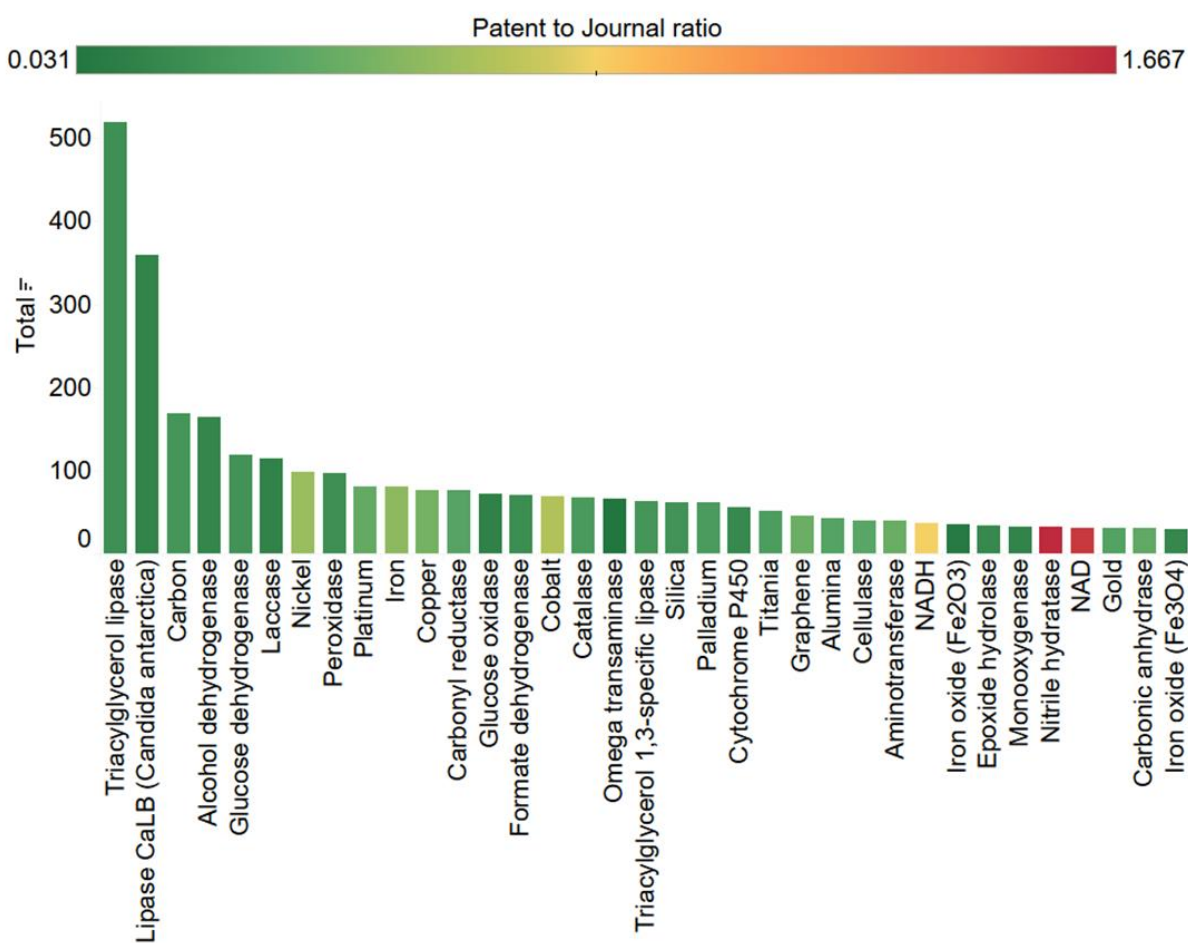


Figure 35. Most reported catalyst substances in biocatalyst publications

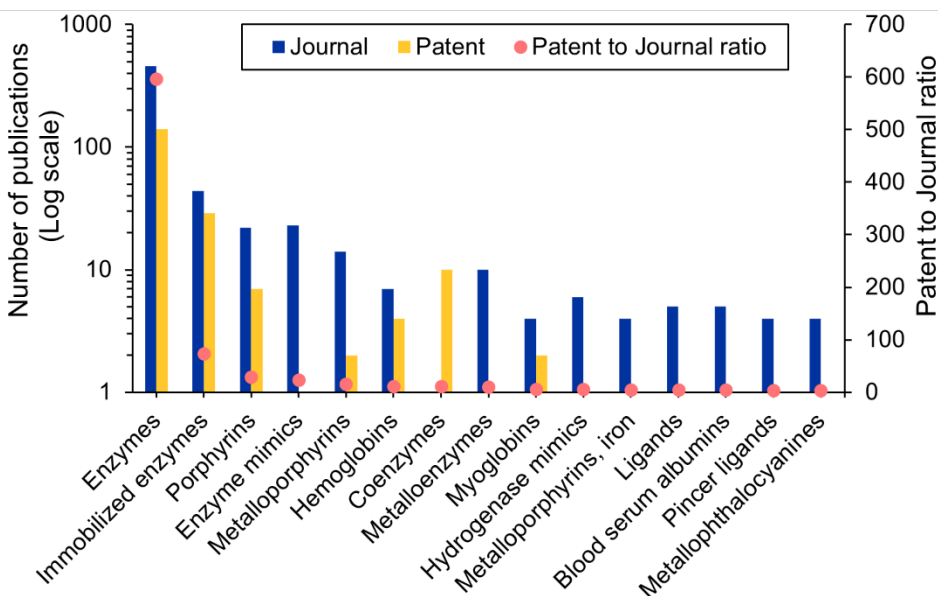


Figure 36. Most reported substance classes used as catalysts in the biocatalysis dataset.

The most reported reactions in the biocatalyst publications and their patent-to-journal ratio are shown in Figure 37. The top reported biocatalyzed reactions are enantioselective synthesis, transesterification, and oxidation. Enantioselective reactions play a crucial role in synthesis of specific organic molecules, whereas transesterification has applications in biodiesel and food industry. Biomass hydrolysis and electrochemical reduction are also top reactions catalyzed by enzymes.

The cooccurrence between catalysts and reactions in biocatalysts publications is presented in Figure 38. Triacylglycerol lipase, lipase CaLB (*Candida antarctica*), and alcohol dehydrogenase have high cooccurrence with enantioselective synthesis, hydrolysis, reduction, and hydrogenation. Laccase, peroxidase, glucose oxidase, NADH, NAD, and NADPH frequently appeared with oxidation and reduction.

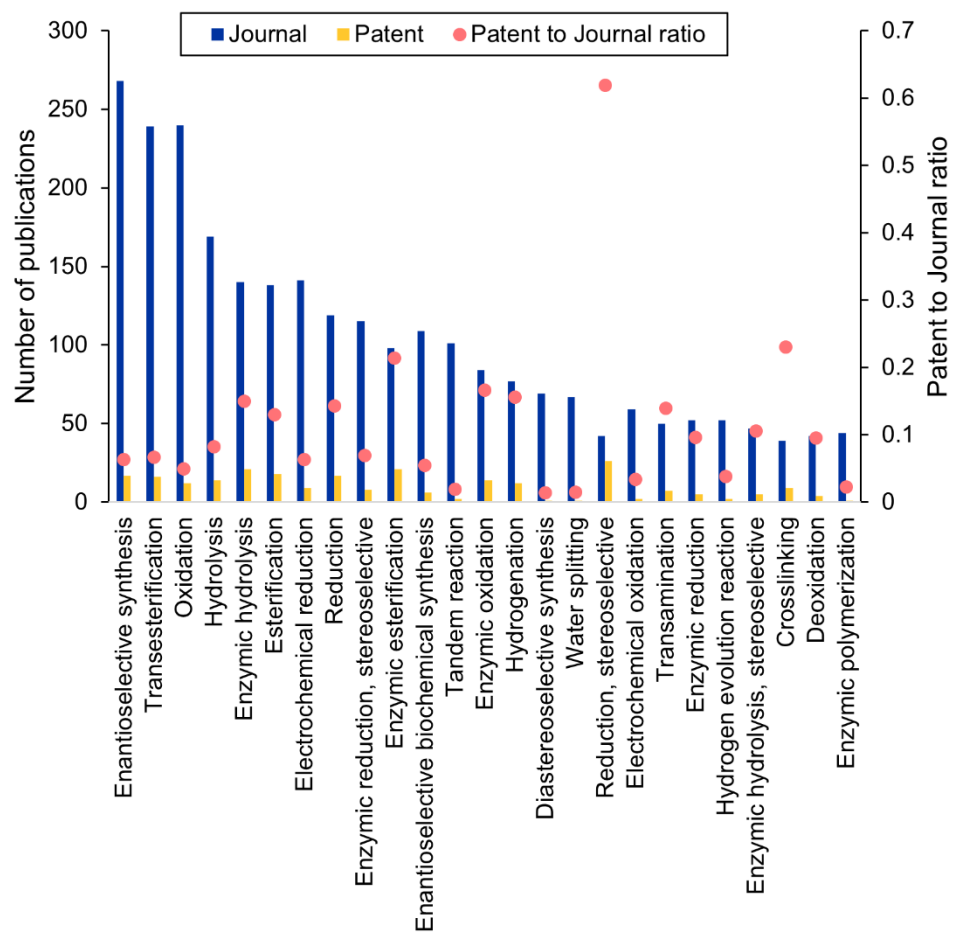


Figure 37. Most reported reactions in biocatalyst publications



Figure 38. Co-occurrence between the reactions and catalyst substances in the publications reporting biocatalysis.

Figure 39 list the most reported uses in biocatalyst publications. Photocatalysts and electrochemical reaction catalysts are the major uses as a wide variety of applications which involve light and electrochemical studies respectively are ascribed to these two categories. Figure 40 maps the co-occurrence of usage with catalyst substances providing further insights.

Triacylglycerol lipase and lipase CaLB (*Candida antarctica*) cooccurred with immobilized enzymes, transesterification catalyst, esterification catalysts, and nanocatalysts. Alcohol dehydrogenase, laccase, peroxidase, glucose oxidase, NADH and NAD co-occurred with photocatalysts and electrochemical reaction catalysts. Alcohol dehydrogenase, NADH, NAD, and NADPH showed up with coenzymes, as they are either coenzymes themselves (ex. NADH, NAD and NADPH) or enzymes which benefit from these coenzymes.

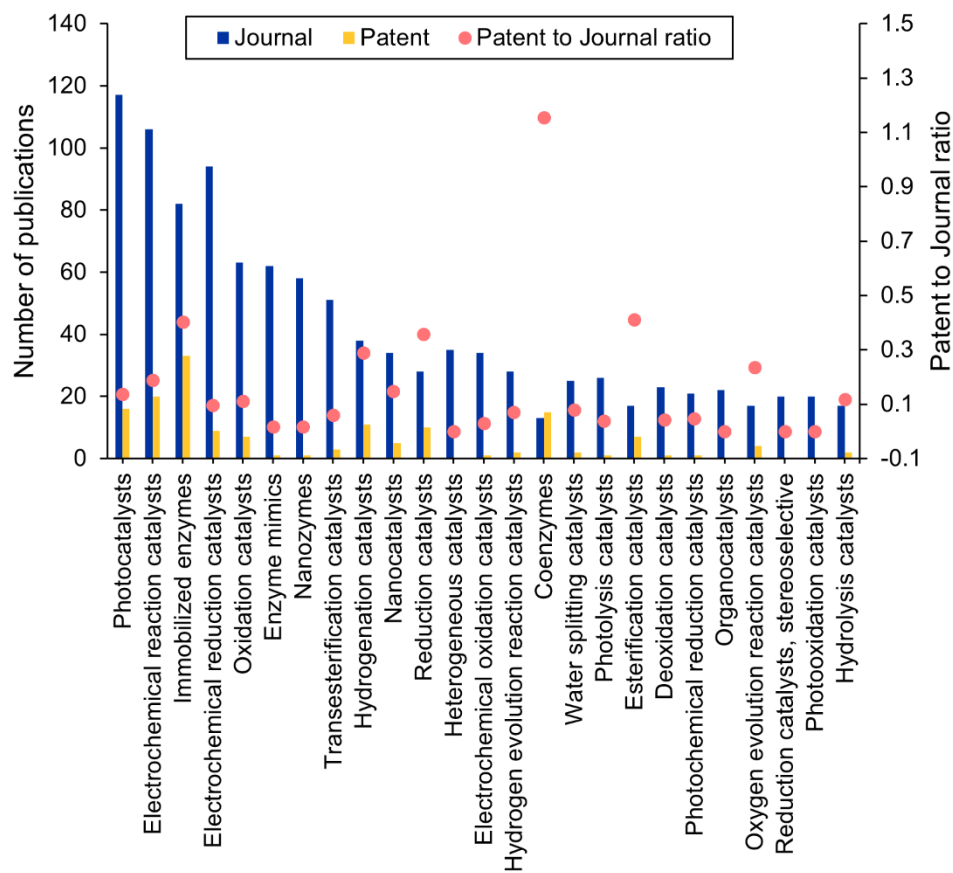


Figure 39. Most reported uses in biocatalyst publications



Figure 40. Co-occurrence of the uses and catalyst substances in biocatalyst publications

Biochemical fuel cells, biosensors, bioreactors, and their individual components such as electrodes are the most reported apparatuses within the biocatalysis publications (Figure 41). The high patent to journal ratio of bioelectrodes and electrodes for the biochemical fuel cells shows commercial interest in these devices. The cooccurrence of the catalysts and apparatuses is showing in Figure 42. Due to its ability to facilitate oxygen reduction reaction, laccase is the most used substance in biochemical fuel cells.^{222, 223} Triacylglycerol lipase and carbon are the most used catalysts in bioreactors and fuel cell cathodes respectively. Glucose oxidase is the most used substance in biosensors due to the need for glucose monitoring in healthcare.

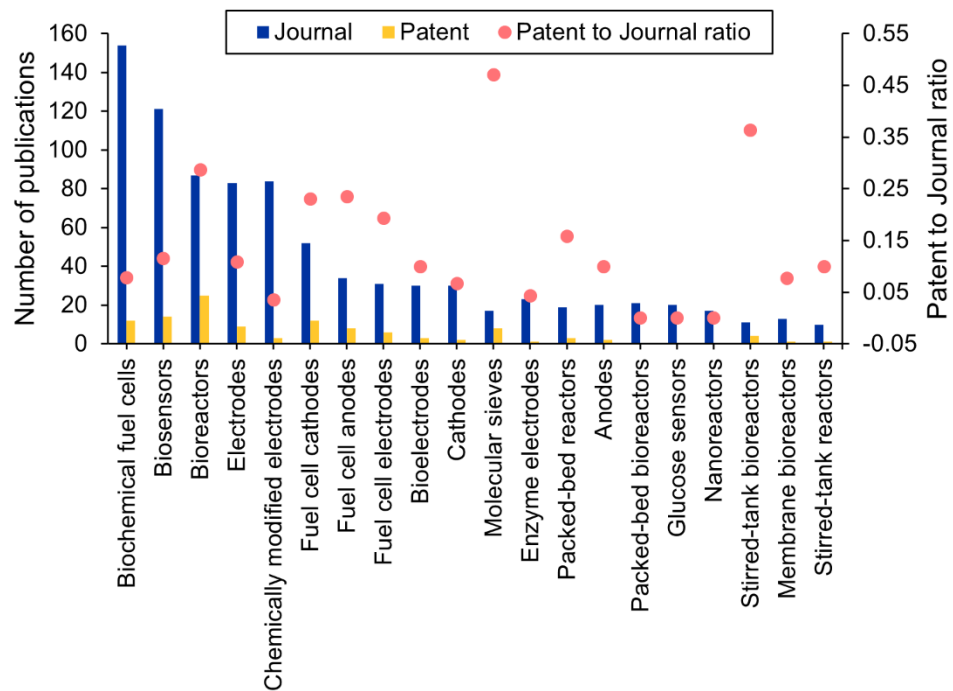


Figure 41. Most reported apparatuses in the biocatalyst publications

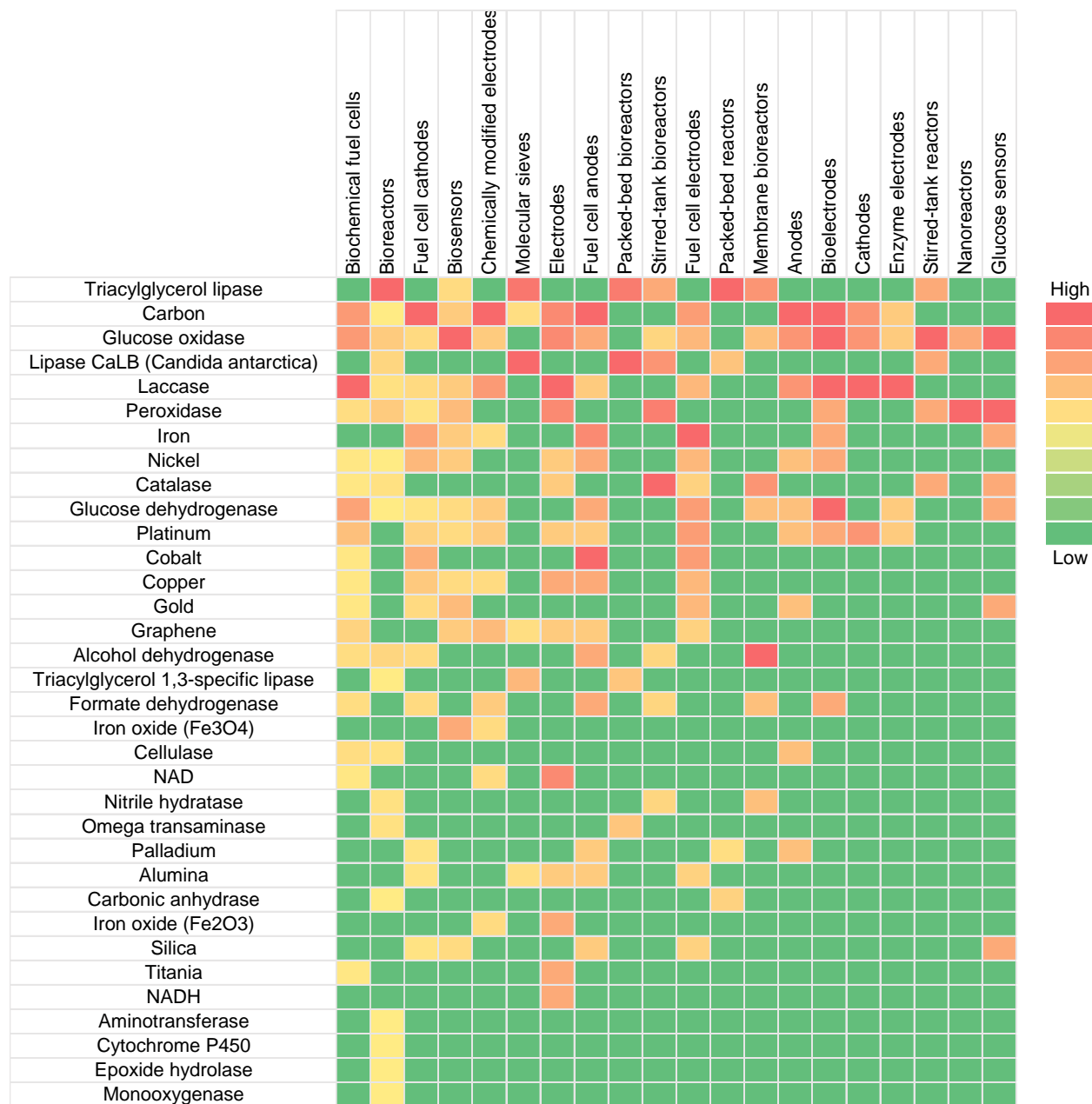


Figure 42. Co-occurrence of apparatus and catalyst substances biocatalysis publications.

Selected Journals in Biocatalysts from the Dataset

Herein research articles in biocatalysts that elucidate the types of enzymes, their combinations, advanced modifications, and formation of biocomposites with artificial materials are described.

Synthesis of α -chiral amines with high stereoselectivity and efficiency challenging.²²⁴ Biocatalysis have become one of the major approaches to obtain optically pure chiral amines.²²⁵ Many bioactive compounds such as alkaloids have more than one stereocenter and a biocatalytic cascade helps to achieve stereoselectivity throughout the synthesis of alkaloids and chiral amines.²²⁵ Many bioactive compounds such as alkaloids have more than one stereocenter and a biocatalytic cascade helps to achieve stereoselectivity throughout the

synthesis of alkaloids and chiral amines.^{224, 226, 227} Herein, Mutti et al. revealed a one-pot biocatalytic system composed of ene-reductases (EReds) and imine reductases (IReds) to facilitate the stereoselective synthesis of amines with two stereocenters from α,β -unsaturated ketones (conversion rate: >99%; diastereomeric ratio: up to 99.0:1.0; enantiomeric ratio: up to >99:<1).²²⁸

Catalytic conversion of cyclic compounds into expanded/shrunk cyclic compounds is of great importance for pharmaceutical research.^{229, 230} Transition metal-catalyzed ring expansion via carbon-carbon bond activation has been well-studied.²³¹⁻²³³ N-heterocycles, especially the azetidines, are very important moieties/building blocks of biologically active compounds, which have limited synthetic options.²³⁴ Arnold et al. reported a novel synthesis of azetidine via one-carbon ring expansion of aziridines using engineered cytochrome P450, called P411-AzetS.²³⁵ P411-AzetS enables highly enantioselective [1,2]-Stevens rearrangement resulting in highly enantiopure azetidine derivatives (enantiomeric ratio, 99:1).

Regulation of carbon dioxide has been a paramount topic in relation to control of global warming. Carbon capture, utilization, and storage (CCUS) technologies are rapidly emerging and attract considerable research interest.²³⁶ Conversion of CO₂ into bicarbonate or carbonate is one of the methods to store CO₂ in aqueous solution. Carbonic anhydrases (CA) can catalyze CO₂ hydration and bicarbonate dehydration.²³⁷ Amao et al. developed a bienzymatic system composed of CA and formate dehydrogenase (CbFDH) that catalyzes CO₂ conversion at a wide range of pH.²³⁸ Addition of CA promotes the CbFDH catalyzed CO₂ reduction to formate in higher pH region (>9.5) conditions. At lower pH (6.3–6.5), CA primarily converts CO₂ into bicarbonate. This CA/CbFDH system facilitates CO₂ storage at a wide range of pH by alternatively using one of the enzymes.

The obstacles of the application enzymes in industry are stability, long term storage, reusability, and recovery.^{239, 240} Immobilization of enzymes removes these disadvantages and enables the application.^{241, 242} Dos Santos et al. utilized Taguchi method to optimize the immobilization of lipase A from *Candida antarctica* (CALA) onto halloysite nanotubes (Hal) for *p*-nitrophenyl butyrate hydrolysis.²⁴³ In this study, CALA-Hal displays better stability at 50–90 °C and higher catalytic activity at pH 9 compared to original lipase A.

As mentioned in the previous paragraph, enzyme immobilization can also be carried out using porous organic frameworks such as metal-organic frameworks (MOFs) and hydrogen-bonded organic frameworks (HOFs) to form biocomposites with high activity, stability, reusability, and recyclability.²⁴⁴⁻²⁴⁶ Nidetzky et al. reported a D-amino acid oxidase (DAAO)-immobilized on tetraamidine/tetracarboxylate-based HOFs (BioHOF-1). They applied polypeptide chain to functionalize DAAO (Z-DAAO) and enhance the immobilization of DAAO on BioHOF-1 (Z-DAAO@BioHOF-1).²⁴⁷ This functionalized biocomposite, Z-DAAO@BioHOF-1 displayed higher enzyme loading (2.5 fold) and activity (6.5 fold) compared to non-functionalized DAAO biocomposite (DAAO@BioHOF-1). Z-DAAO@BioHOF-1 demonstrates better activity than other carriers such as zeolite-based frameworks biocomposite, Z-DAAO@ZIF-8, and it retains the activity after 10 cycles of D-methionine oxidation.

These selected journals reveal the broad interests that researchers have in biocatalyst. Using single or various enzymes and supporting materials, like porous materials to form stable biocomposites, facilitates organic reactions.

Conclusions

Sustainable catalysts using non-noble metal catalysts to replace noble metals has advanced a lot in the last 11 years. The general publication trends show a steady growth of novel ideas in this field. With subject-specific search queries, we further analyzed the publications of electrocatalysts, photocatalysts, homogeneous catalysts, and biocatalysts. Detailed analysis in these subfields of catalysts include publication trends; most prevalent catalysts, reactions, uses, and apparatuses; cooccurrence of catalysts with reactions, uses, and apparatuses; extent of commercial interest in substances and applications.

In electrocatalysts, the primary contributors to non-noble metal alternative catalysts are transition metals, metal oxides, metal phosphides, metal chalcogenides, layered double hydroxides, alloys, and mXenes. Water splitting, oxygen evolution reaction, hydrogen evolution, oxygen reduction reaction which have applications in fuel cells, hydrogen generation, batteries, and solar cells are the major drivers of research in electrocatalysts. Driven primarily by the need for energy and its storage, a widely variety of catalysts continue to emerge in electrocatalysts.

Research publications in photocatalysis continues to increase over the years and the focus is on finding a suitable photocatalyst with enough efficiency for commercial solar hydrogen production from water and for pollutant degradation rather than on replacing any noble metal. Due to its visible light absorption capability, carbon nitride has replaced TiO_2 as the most studied photocatalyst and continues to grow rapidly. Though the reactions and uses in photocatalysts are mostly related to hydrogen production and pollutant degradation, a small but considerable number of them are related to light driven organic reactions and organic photocatalysts.

Homogeneous catalysts analysis demonstrates that publications distributed to various organic reactions, such as cyclization, cross-coupling reaction, arylation, etc. Suzuki coupling reaction is the top named reaction focused by researchers. Transition metals, acids, bases, metal complexes, are some of the major classes of substances used as homogeneous catalysts. These catalysts, some of which are photoactive, are used for a range of reactions used in organic synthesis with emphasis on stereoselectivity.

Our analysis of biocatalysts shows that there is considerable interest in using biocatalysts as a sustainable way of catalyzing various reactions. The consistent increase in the number of publications shows growing interest in this area. The combination of biocatalysts and metal catalysts is also an emerging approach to achieve the sustainability of valuable molecule production. In addition to the highly prevalent enzymes, organometallic substances which mimic enzymes, and other bioderived molecules are also studied as biocatalysts. Biocatalysts have wide variety of applications such as organic synthesis, fuel cells, and sensors.

Overall, non-noble metal-based catalysts made of organic, inorganic, and bio-based substances continues to attract interest in the efforts to achieve the same catalytic performance as the noble metals and to replace them. The continued increase in such publications is an indication of the progress made in these efforts.

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