Recent Advances in Sustainable Catalysts and Catalysis with Non-noble Metals

Tatyana Konovalova[1], Jeremy P. Krogman[1], Leilani Lotti Díaz[1], Magesh Ganesan[2], Chia-Wei Hsu[1]

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

[2]ACS International India Private Limited, Pune, Maharashtra, India 411004

Abstract

This report displays data analysis pertaining to the recent development of non-noble catalysts and their application in catalysis. With the CAS Content Collection™, we elucidated the overall annual publication from 2012 to 2022, and investigated the advances in four sub-fields, electrocatalysts, homogeneous catalysts, photocatalysts, and biocatalysts. Herein we not only reveal the top concepts that appeared in non-noble metal catalysts but also disclose the top substances and categorized concepts that appeared in sub-fields, followed by the global participation.

Introduction

In 1987, UN announced a report, *Our Common Future*, which defined the concept of sustainable development as "*Sustainable development is 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] Sustainable chemistry can be evaluated by three metrics: renewable percentage, optimum efficiency, and waste percentage.[3] Catalysts are one of the methods that accommodates these parameters to achieve sustainability. Noble metals like platinum, palladium, iridium, ruthenium, etc. usually 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 resulted in good yields under various conditions. Iridium and ruthenium also perform their catalytic capabilities in arylation, allylation, and other cross-coupling reactions.[12, 13] However, the high cost and abundancy of noble metals become the burdens in their catalytic applications. To eliminate the economic concerns in sustainable chemistry, noble metal replacement in catalytic applications attracts attention among scientists.

Since the noble metals are mostly extracted from low graded ores, a large amount of low-grade ore is mined to extract a small amount resulting in environmental damage. For example, to produce around 31 gm of platinum, around 12 tons of ore is used.[14] In addition, refining of these low-grade ores requires a large amount of energy.

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The chemical properties which make the noble metals excel as catalysts are their resistance to corrosion, ability to undergo 2-electron oxidation state changes[15] which is common in catalytic process, affinity toward π-bonds, high product selectivity, and the ease of isolation and characterization due to their stability.

The 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 global availability. In addition, many of these metals are more tolerable in the human body compared to noble metals.

Table 1: Properties of noble metals and transition metals

Property	**Noble metal**	**1st 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,[16] 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	
Easy of characterization	Easy due to stability	Difficult due to stability. Inert conditions may be needed.	

In this review, the CAS (Chemical Abstracts Service) Content Collection was utilized to retrieve chemical information regarding the use and application of non-noble metal catalysts/catalysis published during 2012–2022. In general scope, the publication trend of non-noble metal catalysts/catalysis manifests a steady growth, and the journal dominates the publication volume (82%) between 2012 and 2022 (Figure 1).

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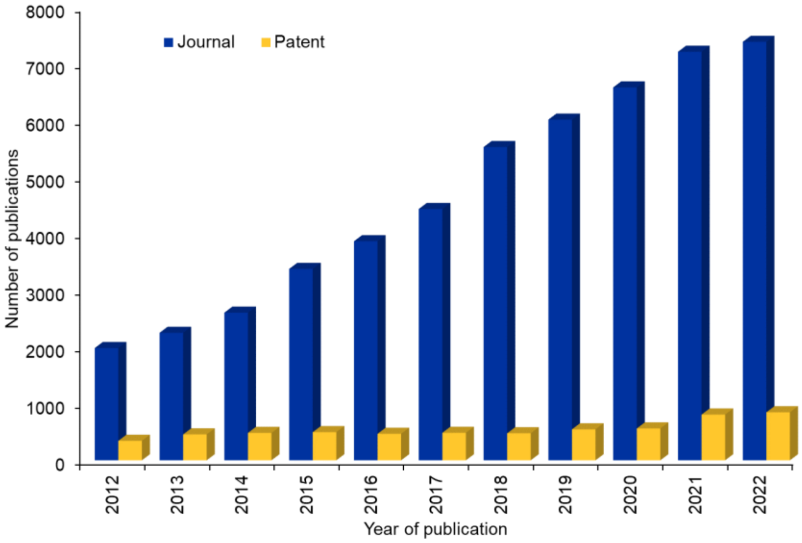

Figure 1. General journal and patent publication trend of non-noble metal catalysts/catalysis during 2012–2022.

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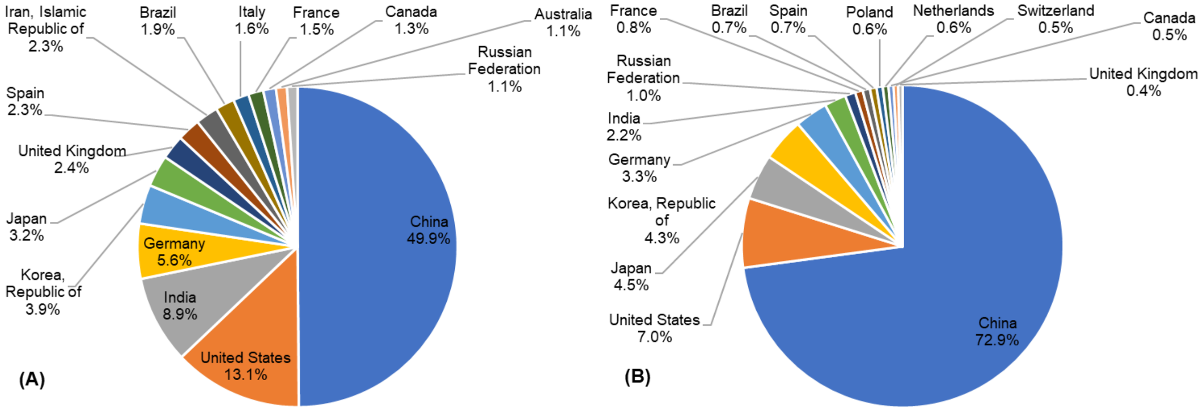

Figure 2. Top countries or regions in terms of journal (left) and patent (right) publications related to non-noble metal catalysts/catalysis.

The top countries which published the largest number of journals are China, the United States, India, Germany, etc.; regarding the patent publication, the top countries are China, the United States, Japan, Korea, etc. (Figure 2 and Table S1).

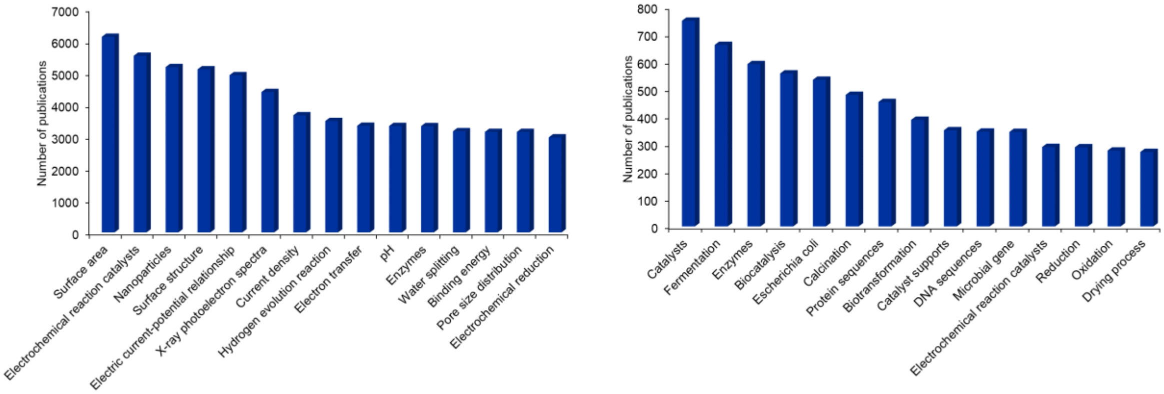

Figure 3. Top 15 concepts appeared in non-noble metal catalysts/catalysis-related research as journals (Left) and patents (Right) during 2012–2022.

The CAS content curations team evaluate the publications and index the various concepts that are being reported. Top concepts that appeared in journals and patents are shown in Figure 3. In journals, electrochemical reaction catalysts, water splitting, and hydrogen evolution reaction represent the electrocatalysts-related reactions/applications; enzymes are related to biocatalysts. In patents, the top 15 concepts are mostly bio-related, and electrochemical reaction catalysts appeared as well. This trend shows that biocatalysts and electrocatalysts are both prominent concepts in patent publications. In addition to top concepts, photocatalysts and homogeneous catalysts are also important concepts of sustainable catalysts.

In this review, we aim at sustainable chemistry using non-noble metal catalysts in four search fields: electrocatalysts, photocatalysts, homogeneous catalysts, and biocatalysts/enzymes. We further narrow the search query to screen the data for these four fields. In Figure 4, electrocatalyst-related research shows its relative significance among the subfields in journals and patents. Each subfield has a similar patent publication volume in the past decade (Homogeneous catalyst: 675; electrocatalyst: 694; photocatalyst: 338; biocatalyst: 745).

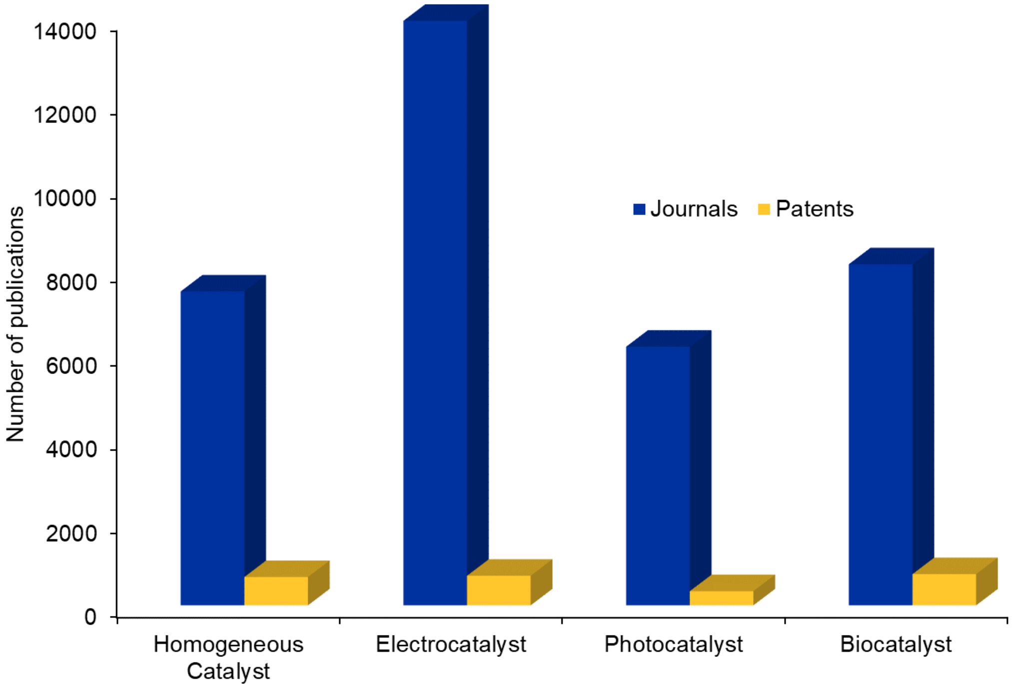

Figure 4. Publication volume of four sub-field: Homogeneous Catalyst, Electrocatalyst, Photocatalyst, and Biocatalyst in journals and patents.

Electrocatalysts

Electrocatalysts participate in electrochemical reactions as the electrodes, or the catalytic materials coated on the surface of electrodes. Platinum is the mostly used electrode material in electrochemical devices because of its catalytic activity. However, its limited abundance and high costs usually become a hurdle that impedes the development of electrochemical applications.[17] In this section, we further reveal the publication trends in electrocatalysts using non-noble metals as the replacement of noble metals.

Electrocatalyst-related concepts are retrieved from our original raw data with a narrow search query. In general, electrocatalyst-related publication pertains a steady growth both in journal and patent (Figure 5). Publication volume of journal is remarkably higher than patents in the

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past decade (2012–2022). We can anticipate there will be more innovative ideas to be commercialized in the future.

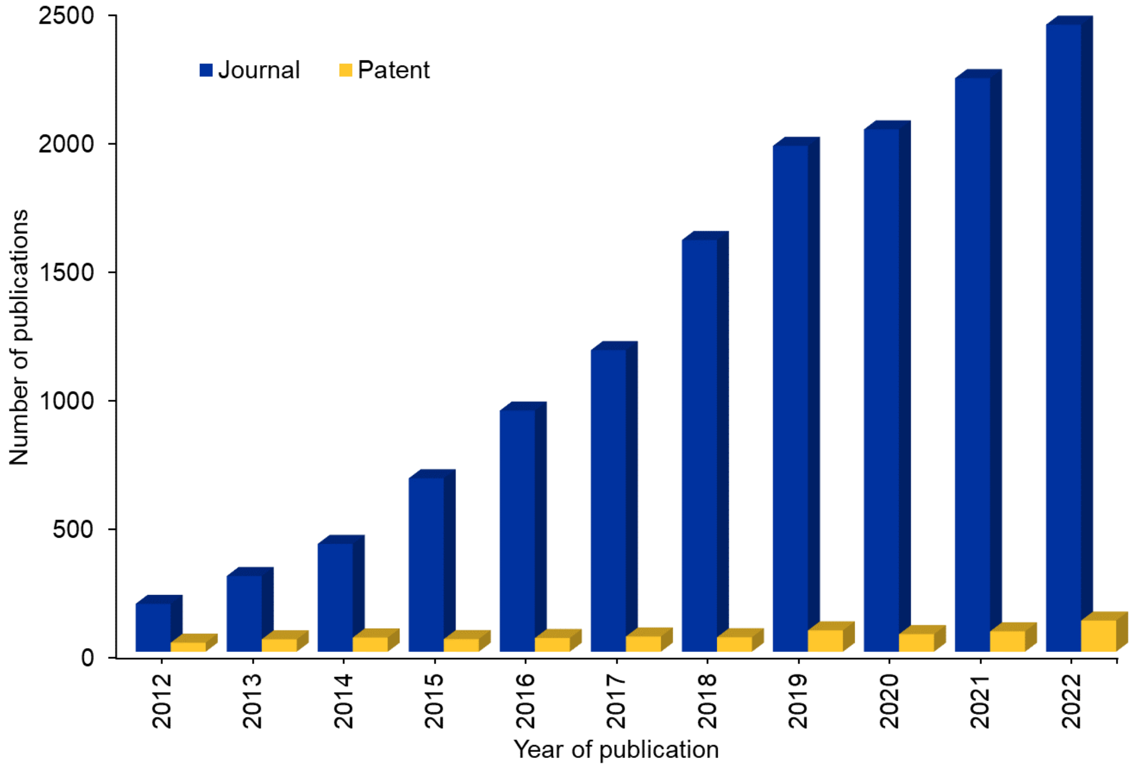

Figure 5. Annual publication trends of electrocatalysts in journals and patents.

The countries which published the most in journals are shown below in Table 2A**.** China is the leading country, followed by United States, India, Korea, Germany, and then Japan. Followed by China, Japan is the patent assignee country with the second largest publication volume in patents (Table 2B).

Table 2. (A) Publication volume of top countries in journals

Coutry or region	Number of journal publications
China	9351
United States	1676
India	879
Korea, Republic of	745
Germany	318
Japan	311

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Australia	215
Iran, Islamic Republic of	173
Singapore	161
Canada	141
United Kingdom	139
Taiwan	120
France	119
Italy	107
Spain	97

Table 2. (B) Publication volume of top countries in patents

Countries or region	Number of patent publications
China	470
Japan	64
United States	52
Korea, Republic of	37
Germany	18
India	12
France	8
Canada	6
Denmark	4
Belgium	3
Italy	3
Australia	2
Austria	2
Saudi Arabia	2
Switzerland	2

Out of the various concepts that are indexed in the electrocatalyst related publications, we filtered the data with the CAS classification code—RXN (reaction). The publication volume of top 15 RXN-classified concepts (Figure 6, Left) elaborate that oxygen evolution reaction (OER), electrochemical reduction, hydrogen evolution reaction (HER), and water splitting play significant roles in electrocatalyst-related research; In the USH (usage) concept category (Figure 6, Right), electrochemical reaction/reduction catalysts and nanoparticles/sheets predominately present in the electrocatalyst related publications, followed by electrolysis, OER, HER, and water splitting catalysts. Carbon based nanomaterials are usually used as conducting supports as well as nanostructured electrocatalysts exhibit high activity due to higher surface area.

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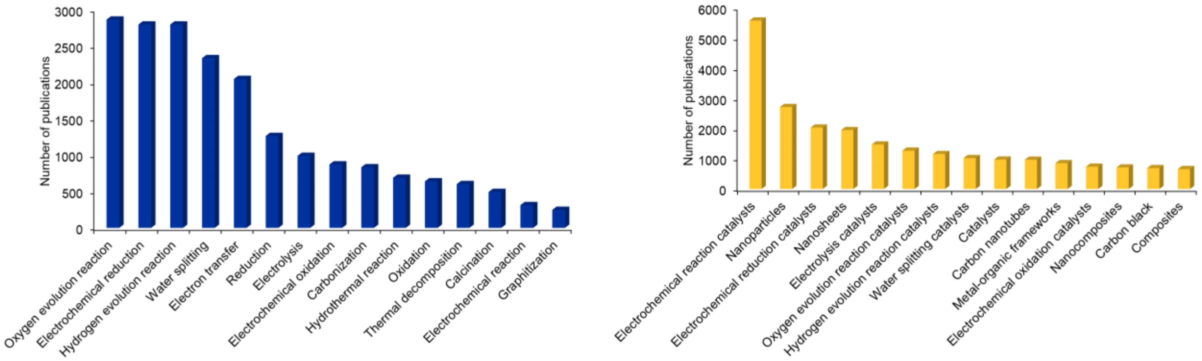

Figure 6. Left: top 15 reaction-related concepts of electrocatalysts frequently appeared in publications; right: top 15 usage-related concepts of electrocatalysts frequently appeared in publications.

The Mostly Used Substances

To further reveal the trend of substances used as electrocatalysts, herein we select substances whose CAS indexed role is the catalyst**.** Figure 7 shows that the top two substances are carbon and platinum; carbon based materials are utilized as support to produce the electrode with non-noble metal electrocatalysts and platinum based electrodes are used for the comparison with the alternative electrodes.[18] Nickel, graphene, cobalt, nitrogen, and iron are also used for electrocatalyst research frequently. Nitrogen is used as the doping agent to form N-doped materials binding with transition metals to form catalysts.[19] Iron–nitrogen–carbon, Iron-copper-N-doped-carbon, and cobalt–nitrogen–carbon form as single/double atom catalysts in electrochemical reactions.[20, 21] Copper and nickel complexed as CoNi carbonate hydroxides and performed the oxygen evolution reaction catalysis.[22] Copper, nickel, and phosphorus composites enable urea electrolysis as electrodes in the electrolysis cell**.**[23] Ruthenium dioxide (RuO_2) and iridium oxide (IrO_2) are used as references for non-noble metal-based catalysts research.[24, 25]

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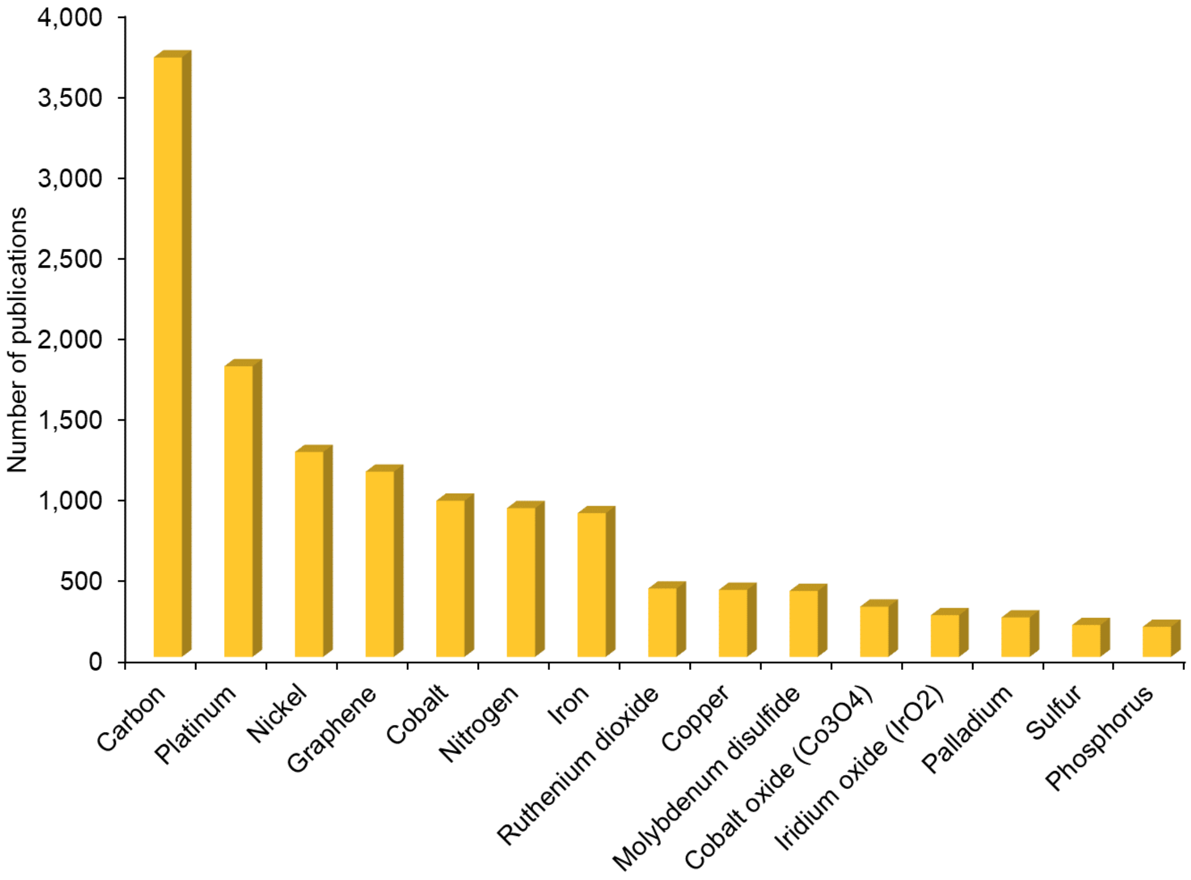

Figure 7. Top 15 mostly used substances in electrocatalysts-related publications.

Electrocatalysts Selected Concepts

We showed the selected concepts in electrocatalysts in journals and patents (Figure 8). Except the electrochemical reaction, the top three reaction concepts appeared in journals are oxygen evolution reaction, hydrogen evolution reaction, and water splitting; In patents, the top concepts are fuel cells, fuel cell related terms (fuel cell electrode/cathode/anode, etc.), doping, and composites, which demonstrates that these applications are primarily commercialized.

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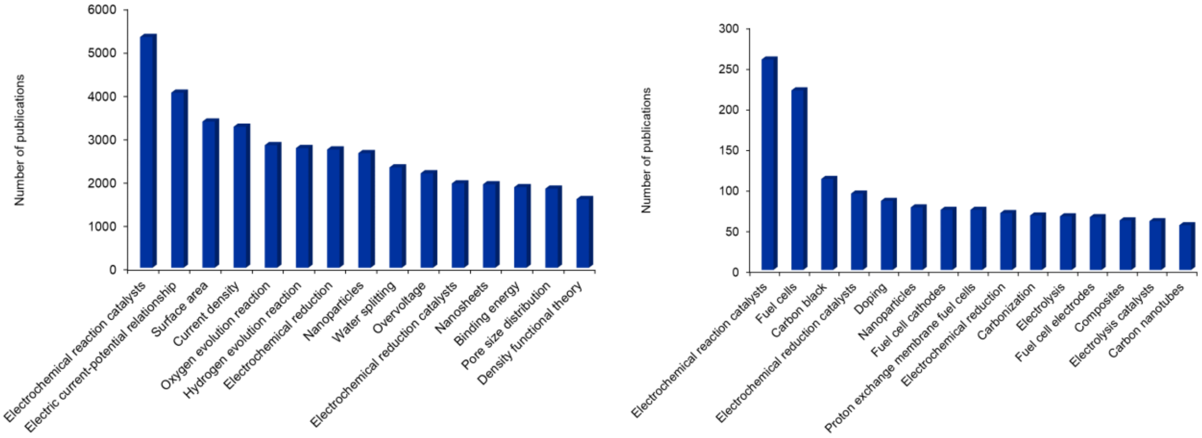

Figure 8. Human intelligence-selected electrocatalyst-related concepts in journals (left) and patents (right).

Fuel Cell Related Concepts

We further reveal the fuel cell-related analysis by manually selecting fuel cell-related concept followed by data analysis. Figure 9 displays that nanomaterials are heavily utilized in fuel cell for both journal and patent publications. Metal-organic frameworks (MOFs) are getting attention among academia and industry. For instance, zeolite imidazolate frameworks (ZIFs, a subcategory of MOFs) and iron complexes are used to produce cathode catalysts[26] as well as ZIFs and Se.[27] Other transition metals, such as cobalt, manganese, tungsten, nickel, etc. are also involved in the production of electrocatalysts via the MOFs, and transform to 3D porous electrodes with catalytic reactivity.[28]

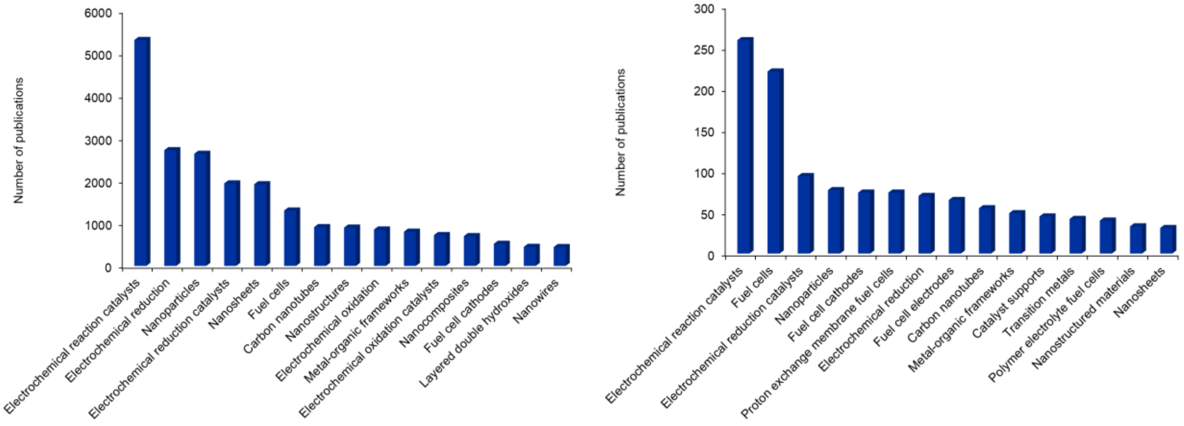

Figure 9. Human intelligence-selected fuel cell-related concepts in journals (left) and patents (right).

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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 as an ideal solution to the energy and environmental problems. Most of the photocatalysts known till date either function only under UV light irradiation or does not have sufficient efficiency under visible light irradiation for practical applications. 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 not necessarily made of non-noble metals. However, to produce sufficient hydrogen to fulfill the energy requirements of the future, an enormous amount of photocatalyst will be needed and hence it should also be made of earth abundant elements. We further refined our search criteria to filter in only the documents related to both photocatalysis and photoelectrochemistry.

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. As expected, the 15 topmost cited documents were reviews of the existing literature and they cover various aspects such as co-catalysts for photocatalysts,[29] catalytic water treatment,[30] hydrogen evolution, silver nanoparticles, Cu based nanoparticles,[31] noble-metal free nanoparticles,[32] semiconductors for photocatalytic water splitting, transition-metal based co-catalysts for photocatalytic water splitting, carbon nitride photocatalysts, MXene photocatalysts,[33] nano and microstructured catalysts,[34] non-noble metal plasmonic photocatalysts,[35] and single-atom catalysts on 2D nanomaterials. In particular, 6 out of the top 25 most cited photocatalyst related documents were about graphitic carbon nitride, which highlights the interest and the potential of this specific photocatalyst.

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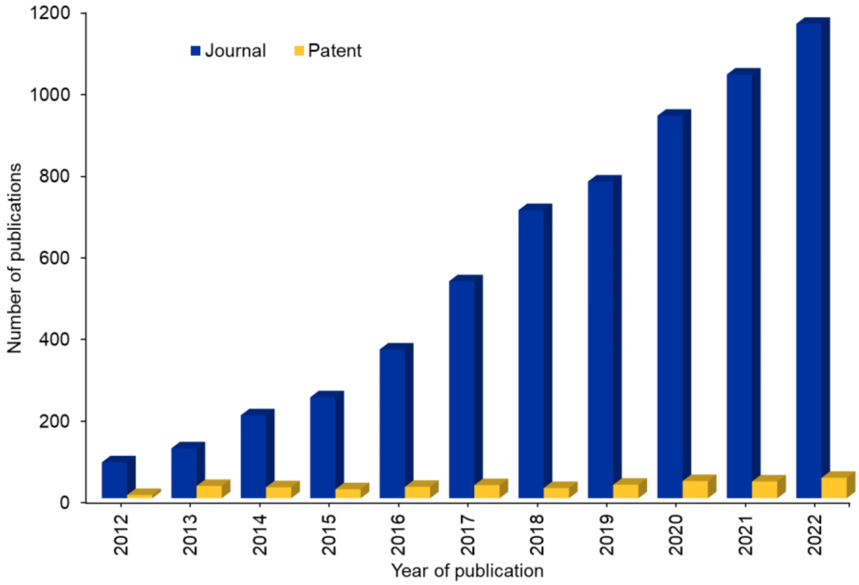

Figure 10. Year-wise number of publications related to photocatalysts

Figure 10 shows the number of publications per in the last 11 years. The number of publications in the journals and patents shows a steady increase over the years. This shows that interest in this field continues to grow on a yearly basis. The huge difference between the number of journal publications and the patents is an indication that research in this area has still not reached the point of commercialization.

Table 3. (A) Country wise distribution of the number of patents in the field of photocatalysis during 2012–2022

Country or region	Number of publications
China	262
Korea, Republic of	21
Japan	11
India	11
United States	7
Germany	3
Latvia	2
France	2
Canada	2
Austria	2
United Kingdom	1
Singapore	1
Netherlands	1

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Brazil	1
Belgium	1

Table 3. (B) Country wise distribution of the number of journal publications in the field of photocatalysis during 2012–2022

Country or region	Number of publications
China	3887
United States	596
India	526
Korea, Republic of	297
Germany	230
Japan	200
United Kingdom	102
Australia	92
Iran, Islamic Republic of	87
Singapore	79
Spain	78
France	75
Taiwan	73
Italy	69
Canada	46

The number of publications related to photocatalysts in the patents and journals are shown in the Table 3. China published the maximum number of patents followed by Republic of Korea, India, and Japan. When it comes to the number of journal publications, the maximum number of publications are from China followed by United States of America, India and Republic of Korea.

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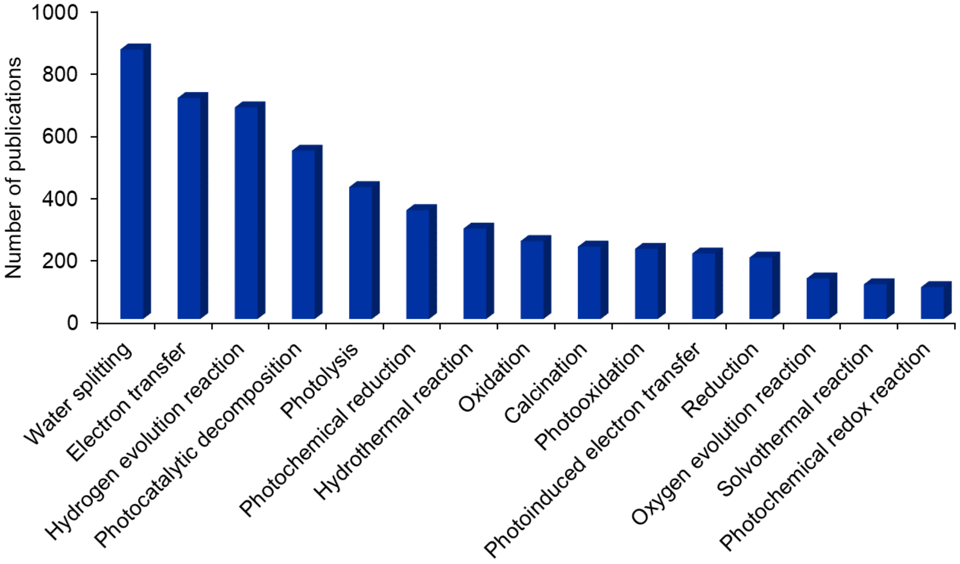

Figure 11. Top 15 reaction concepts to which photocatalysts are applied

The CAS Content Collection^{TM} analyses a document for the concepts involved in the article. Of these, specific interest to us is the type of reaction to which the photocatalysts are applied to. As shown in Figure 11, the photocatalysts are widely used for the splitting of water to produce hydrogen. In addition, it is also used for the photocatalytic decomposition of various pollutants, followed by use in photolysis reactions.

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. Using data analysis of the CAS Content Collection^{TM} a list of the topmost used devices are generated and are listed in Figure 12. Photocatalysts are largely fabricated as photocathodes, photoanodes, photoelectrochemical cells, followed by solar cells.

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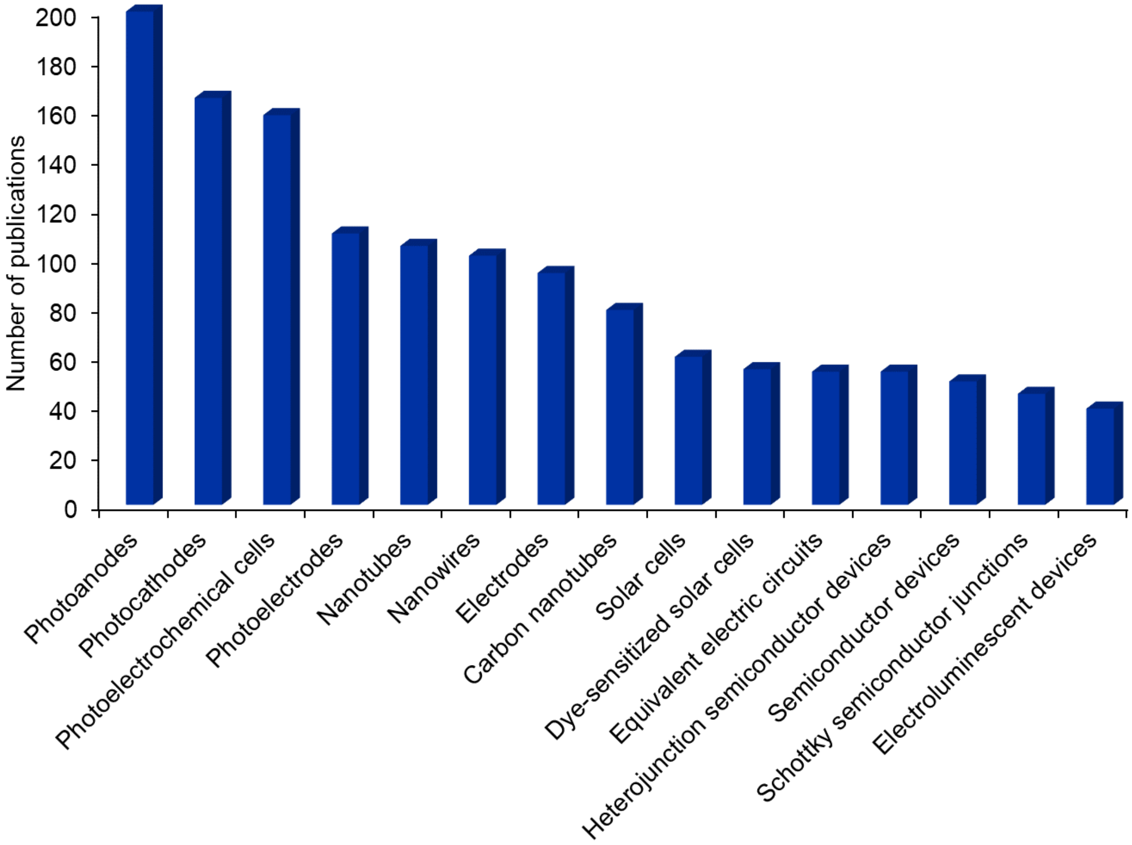

Figure 12. Top 15 device-based concepts using photocatalysts in the CAPLUS database

The substances present in the documents were indexed in the CAS Content Collection^{TM} according to their role. An analysis of the top substances with the catalyst role showed that the carbon nitride (C_3N_4), titania, cadmium sulfide, and molybdenum sulfide consistently remained in the top 4 catalysts (Figure 13). The other catalysts which consistently remained in the top 15 catalysts are zinc oxide, Co_3O_4, tungsten oxide, indium zinc sulfide, Fe_2O_3, $BiVO_4$, cadmium zinc sulfide, and nickel phosphide.

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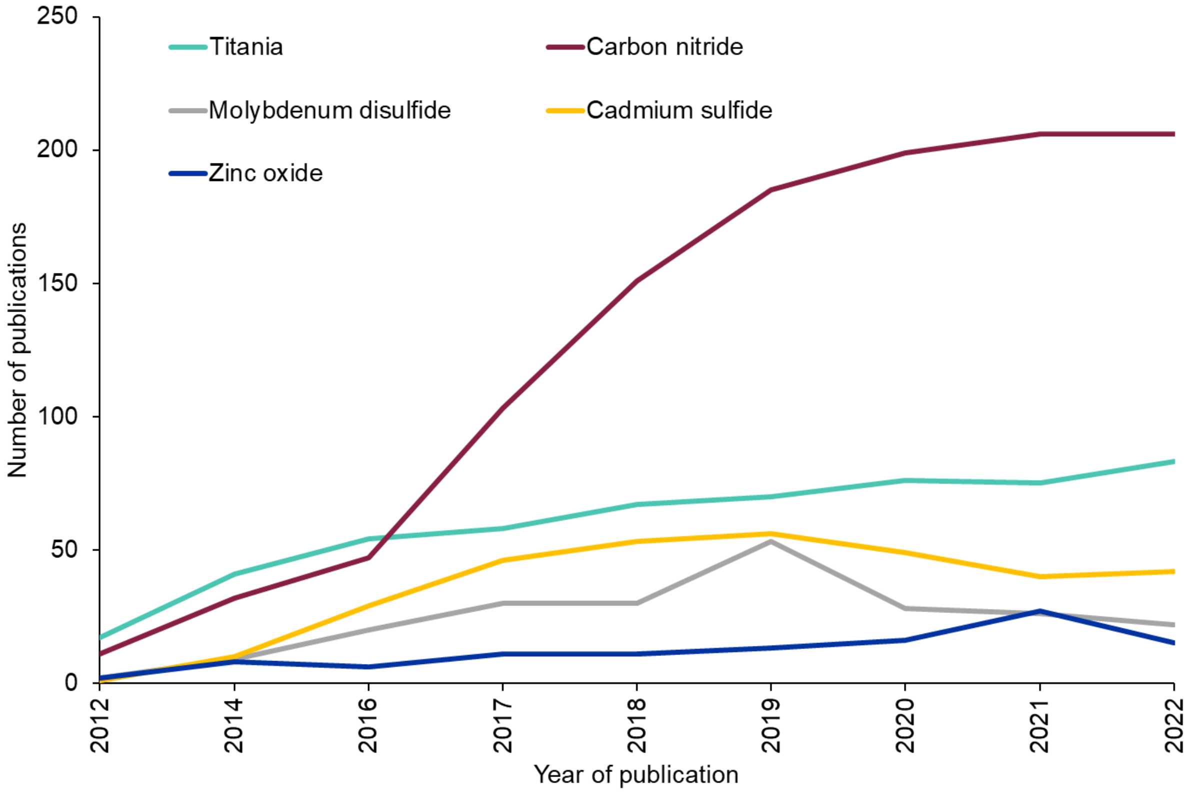

Figure 13. Number of publications using different photocatalysts in the last 11 years

Number of publications using different photocatalysts is shown in the Figure 13. Though titanium dioxide is one of the earliest studied photocatalysts, even now a lot of studies are being carried out on this. Similarly, carbon nitride photocatalysts continue to top the most studied photocatalysts even though it has been studied for a long time. The number of publications on catalysts such as ZnO, CdS, MoS_2, $BiVO_4$, cadmium zinc sulfide, and Cu_2O is showing a decreasing trend in recent years. Indium zinc sulfide is one of the recently studied photocatalysts and there is an increasing trend in the number of publications on this photocatalyst in recent years.

Information related to the institutions conducting research on this topic will be of interest to those researching in this topic, organizations looking for collaboration and organizations looking to commercialize the technology. Chinese universities top the list of publishers in journals and there are universities from Japan, UK, Republic of Korea and Singapore also in the top 30 list (Figure S1). The top 30 publishers of patents list also contains mostly Chinese universities and contain some other institutions from India, Republic of Korea, Germany, and USA (Figure S2).

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Homogeneous Catalysts

Homogeneous Catalysis

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.[36] They can also exhibit multiple oxidation states and redox behavior that can facilitate catalytic cycles. Table 4 highlights some of the significant reactions that PGMs are used as catalysts.

PGMs are scarce, expensive and subject to market fluctuations.[37] The global demand for PGMs exceeds the supply, which leads to high prices and geopolitical risks. The extraction and refining of PGMs also have environmental and social impacts such as energy consumption, greenhouse gas emissions, water pollution and human rights violations. Therefore, there is ongoing research to find alternatives to PGMs for greater overall sustainability.

Table 4. 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.

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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 Method) 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. The time frame for publication was limited to 2012–2022 for our analysis.

Figure 14 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 2021.

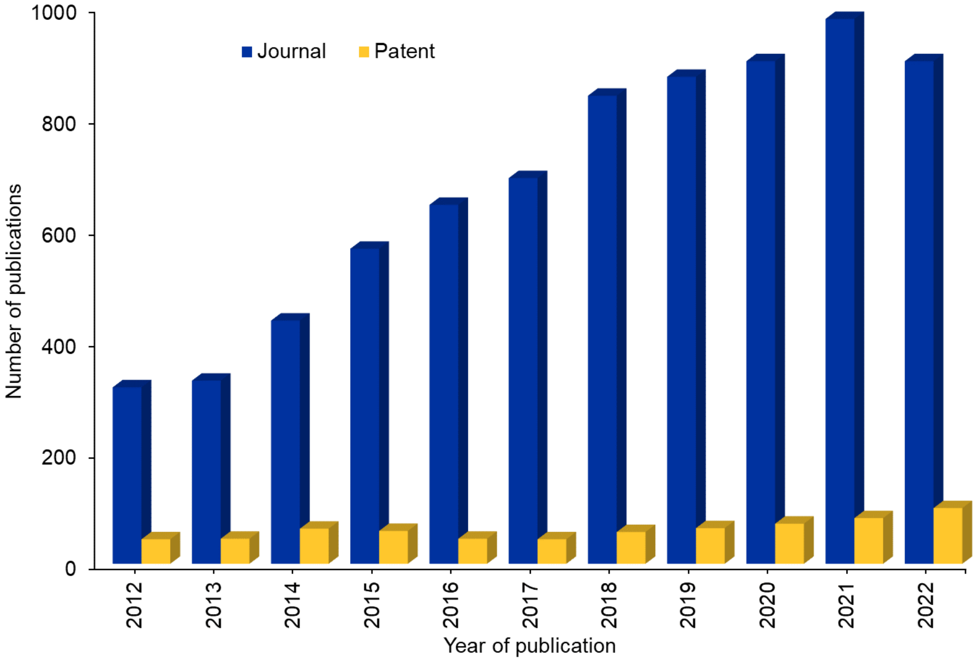

Figure 14. Annual publications for homogeneous catalysts.

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Table 5. The top 20 reaction concepts from the publications analyzed.

Reaction concept	Number of publications
Diastereoselective synthesis	599
Tandem reaction	518
Cyclization	407
Oxidation	361
Enantioselective synthesis	302
Cross-coupling reaction	292
Coupling reaction	247
Three-component reaction	242
Oxidative coupling reaction	235
Arylation	232
Heterocyclization	213
Reduction	212
One-pot synthesis	211
Hydrogenation	193
Electron transfer	183
Electrochemical reduction	180
Multicomponent reaction	165
Amination	158
Alkylation	150
Suzuki coupling reaction	148

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 5). This is sensible as Suzuki coupling is a widely used method for making carbon-carbon bonds between

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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.[38] For these reasons Suzuki coupling has been a prime target for a 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.[39] The group later discovered that the Na_2CO_3 used for the reaction contained palladium contamination. The group later published an updated procedure for the reaction to include ppb palladium catalyst.[40]

- Xu et al. published a paper in Nature Catalysis in 2021 claiming that bis(o-tolyl)amine organocatalysts could catalyze the Suzuki reaction under metal-free conditions.[41] 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.[42-44] The paper was retracted by the authors in 2021.

  Some experimental methods necessary to prove that a new catalyst contains no palladium contamination are:

  - Performing rigorous purification and characterization of the catalyst to ensure its purity and identity. This may include recrystallization, distillation, sublimation, chromatography, mass spectrometry, nuclear magnetic resonance spectroscopy, infrared spectroscopy, X-ray crystallography and elemental analysis.

  - Performing sensitive and accurate analysis of the catalyst and the reaction mixture for trace amounts of palladium 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.

  - Performing control experiments using different sources of the catalyst, different solvents, different bases, different substrates, different reaction conditions and different palladium scavengers to rule out any possible sources of palladium contamination or interference.

  - Performing mechanistic studies using isotopic labeling, kinetic analysis, intermediates trapping or spectroscopic monitoring to elucidate the reaction pathway and identify the active species.

We further analyzed the frequency of the substance use in the field of homogeneous catalysts (Figure 15). Iodine is the most frequently used substance. It usually initiates the radical species, followed by remaining mechanistic steps. For example, iodine is used for oxidative cyclization

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and oxo-acyloxylation of alkenes and enol ethers.[45, 46] Carbons represent active carbon, graphene, graphite, onion like carbon catalysts, etc. and provide selective oxidation of substituted phenol.[47] Nickel,[48, 49] cobalt,[50, 51] iron,[48] and copper[48] usually catalyze coupling reactions, C–H functionalization, asymmetric hydrogenation, and direct arylation with their metal-complex forms. Eosin,[52, 53] tetrabutylammonium iodide,[54, 55]8 and 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile[56, 57] perform like iodine by creating radical species to initiate the reaction. Tris(pentaflurophenyl)borane play the role as a Lewis acid catalyst to promote hydroarylation[58] and hydrosilylation.[59] p-Toluenesulfonic acid (pTSA)[60, 61] and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)[62, 63] also perform catalytic reactions as metal-free catalysts.

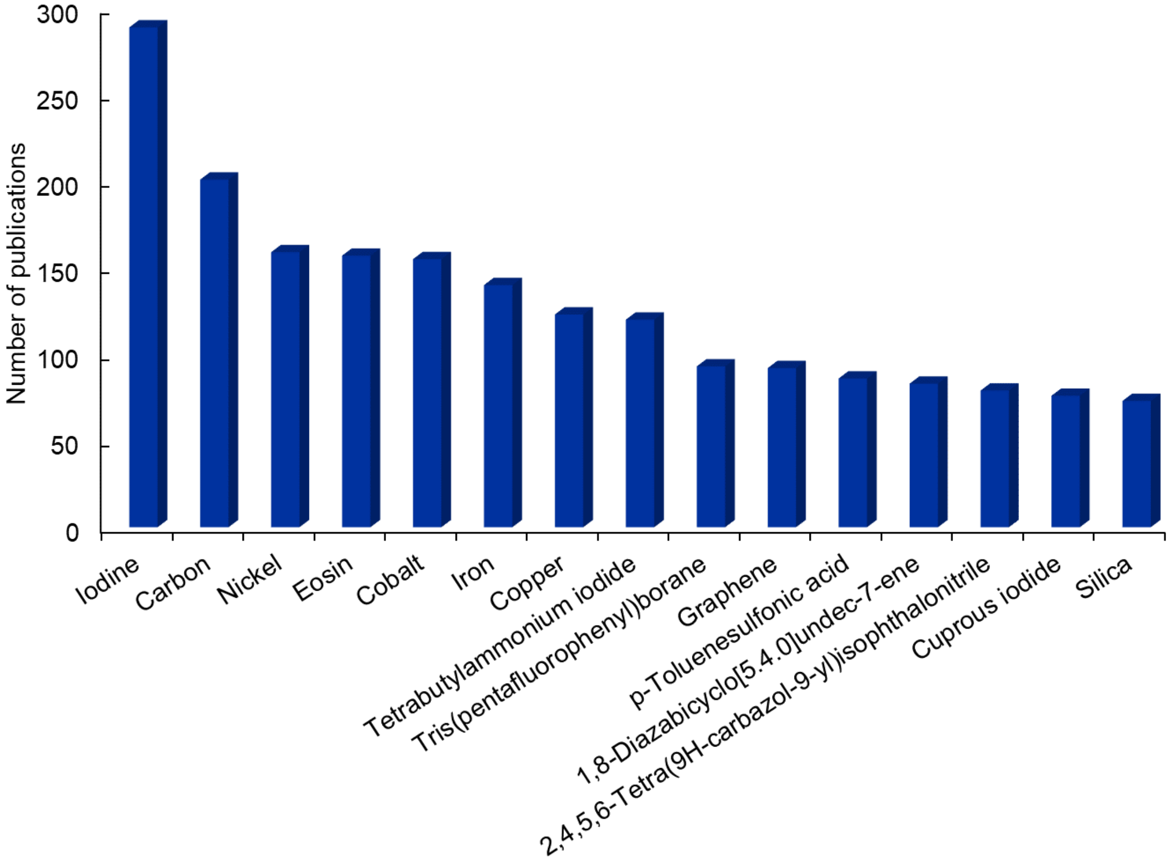

Figure 15. Top 15 substance mostly used as homogeneous catalysts.

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Biocatalysts/enzymes

Biocatalysts are based on natural proteins, enzymes, that can catalyze specific chemical reaction outside the living cells. Enzymatic biocatalysts are true green and sustainable catalysts. Produced from available renewable feedstocks (plants, animal tissues, bacteria, yeast, fungi) they are organic, biodegradable, nontoxic and can function under mild reaction conditions (aqueous medium, pH ~ 7, normal temperature and pressure).[64] 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%.[65]

Current publication landscape on biocatalysts

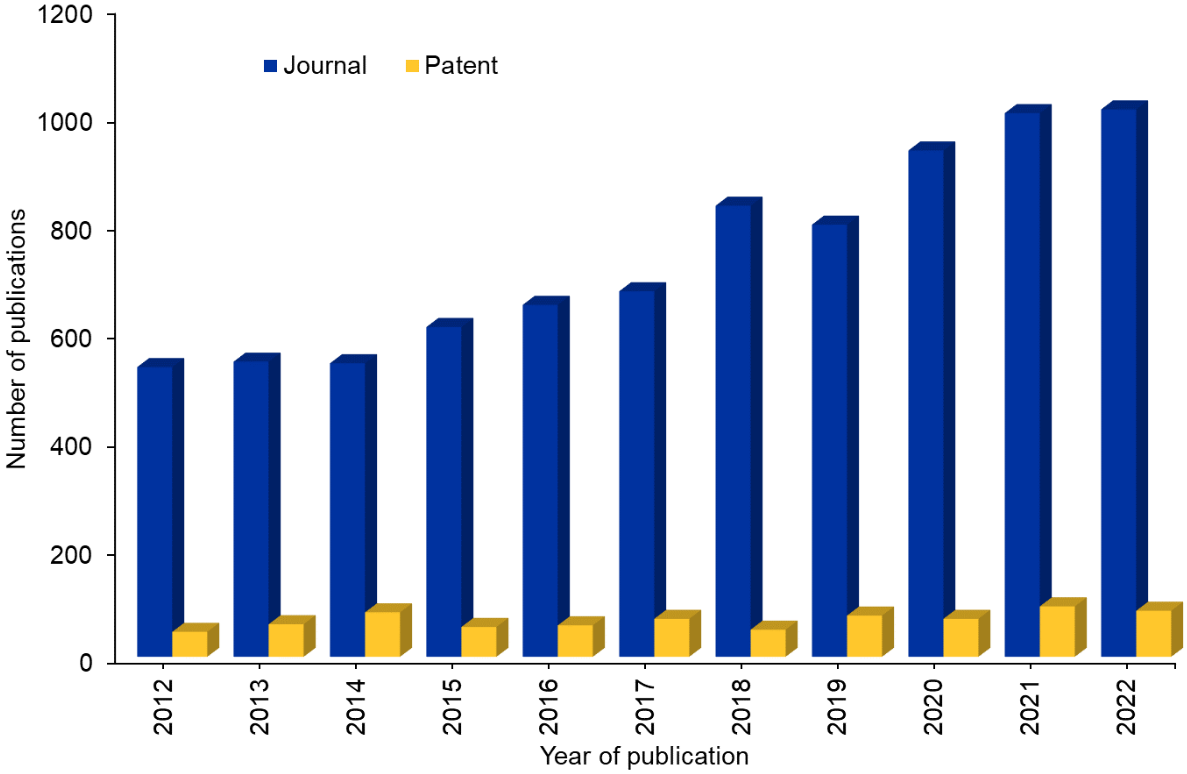

Figure 16. Annual publication trend of biocatalysts from 2012 to 2022.

In Figure 16., between 2012 and 2022, 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 over the decade.

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Biocatalyst top journal organization countries include China, United States, Germany and India followed by Republic of Korea, Brazil, United Kingdom and Spain (Table 6A). Major contributors are Chinese Academy of Science, Zhejiang University of Technology (China), Jiangnan University (China), University of Giaz (Austria), University of Manchester (England), University of Michigan (USA), University of Groningen and Delft University (Netherlands), Bielefeld University (Germany), Technical University of Denmark, University of California (USA), Institute of Chemical Technology (India), RWTH Aachen University (Germany) (Table 6B & 6C).

Table 6. (A) Top countries or regions published with journals from 2012 to 2022.

Country or region	Number of publications
China	2557
United States	1154
Germany	706
India	596
Korea, Republic of	369
Brazil	363
United Kingdom	358
Spain	356
Japan	266
France	193
Italy	193
Russian Federation	146
Iran, Islamic Republic of	125
Canada	115
Australia	64

Table 6. (B) Top organizations published journals including China from 2012 to 2022.

Organization	Number of publications
Zhejiang University of Technology	116
Zhejiang University	52
University of Science and Technology of China	20
Tsinghua University	25
Tianjin University	38
South China University of Technology	90
Soochow University	13
Jilin University	39
Jiangsu University	26
Jiangnan University	106
Fuzhou University	16

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East China University of Science and Technology	63
Dalian University of Technology	20
Chinese Academy of Sciences	149
Beijing University of Chemical Technology	38

Table 6. (C) Top organizations published journals without China from 2012 to 2022.

Organization	Number of publications
University of Graz	63
University of Manchester	52
University of Michigan	51
University of Groningen	50
Delft University of Technology	45
Bielefeld University	44
Technical University of Denmark	41
University of California	39
Institute of Chemical Technology	38
RWTH Aachen University	35
Clarkson University	31
The University of Manchester	30
Russian Academy of Sciences	29
Graz University of Technology	29

Biocatalyst top patent assignee countries include China, United States, Republic of Korea, Germany, India and Japan (Table 7A). The leading patent assignees are Jiangnan University (China) and Zhejiang University of Technology (China) followed by BASF SE (Germany), Korea Advanced Institute of Science and Technology, Samsung Electronics Co., CO2 Solutions (Canada, Quebec), Evonic (Germany), Merck Sharp (New Jersey, USA), Uniwersytet Przyrodniczy We Wrocławiu (Poland), du Pont (Wilmington, DE, USA), Politechnika Warszawska (Poland), Council of Scientific and Industrial Research (India), Embio Limited (India), Orochem Technologies (USA), United States Dept. of Navy (USA) (Table 7B & 7C).

Table 7. (A) Top patent assignees countries

Country or region	Number of publications
China	396

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United States	65
Korea, Republic of	47
Germany	39
India	25
Japan	22
Poland	15
Russian Federation	15
Brazil	12
Spain	11
Switzerland	10
France	8
Canada	7
Finland	5
United Kingdom	5

Table 7. (B) Top patent assignees with China

Patent assignee	Number of publications
Jiangnan University	18
Zhejiang University of Technology	17
BASF SE	15
Nanjing Tech University	15
Dalian Institute of Chemical Physics, Chinese Academy of Sciences	13
South China University of Technology	9
Korea Advanced Institute of Science and Technology	7
Samsung Electronics Co., Ltd.	7
CO2 Solutions Inc.	6
Dalian University of Technology	6
Evonik Industries AG	6
Qingdao University of Science and Technology	6
Beijing University of Chemical Technology	5
EnzymeWorks, Inc.	5
Merck Sharp & Dohme Corp.	5

Table 7. (C) Top patent assignees without China

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Country or region	Number of publications
BASF SE	15
Korea Advanced Institute of Science and Technology	7
Samsung Electronics Co., Ltd.	7
CO2 Solutions Inc.	6
Evonik Industries AG	6
Merck Sharp & Dohme Corp.	5
Uniwersytet Przyrodniczy we Wroclawiu	5
E. I. Du Pont De Nemours and Company	4
Politechnika Wroclawska	4
Council of Scientific & Industrial Research	3
Embio Limited	3
OROCHEM Technologies, Inc.	3
United States Dept. of the Navy	3
Aarti Industries Limited	2
Agentase, LLC	2

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.[66]

Hydrolases occupy more than 50% of the total biocatalysts market followed by oxidoreductases and transferases.[65] Major application of these three enzymes is shown in Table 8.

Table 8. Three major enzyme classes and their applications.

Enzymes	Hydrolases	Oxidoreductases	Transferases
Major application	Synthesis of pharmaceutical compounds[67-69], polymer synthesis[70]	Biofuel cells, oxidation polymerization of aromatic compounds[66]	Transferring functional groups[66]

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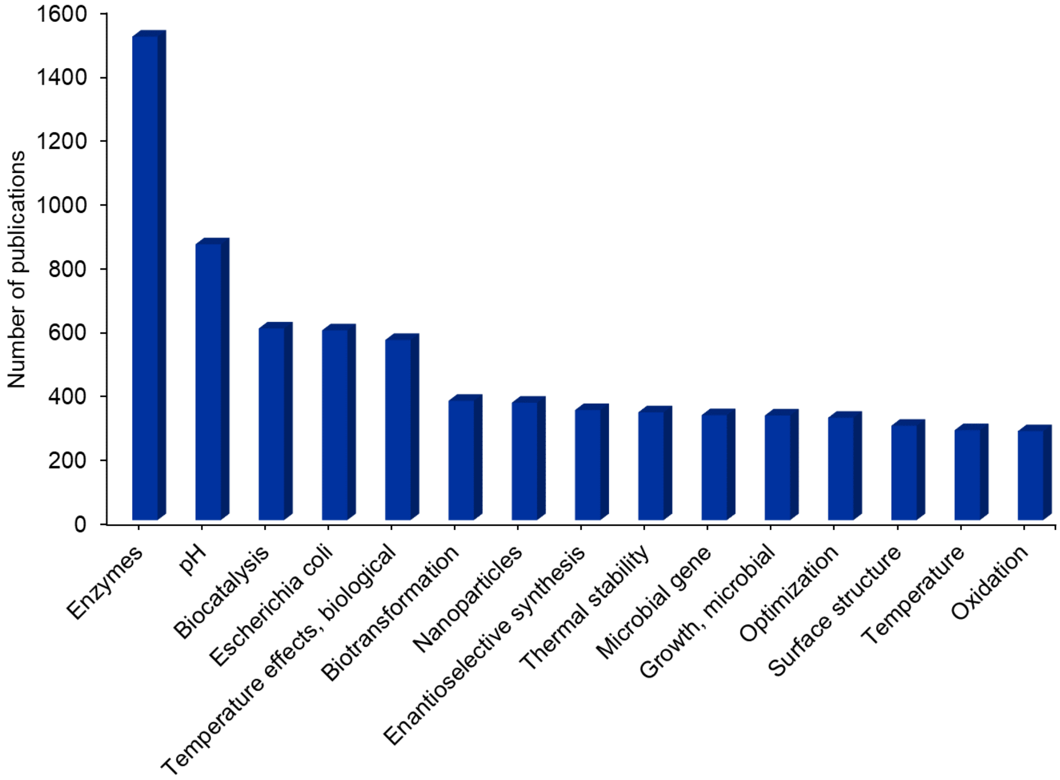

Figure 17. Top 15 concepts of biocatalysts in journals from 2012 to 2022.

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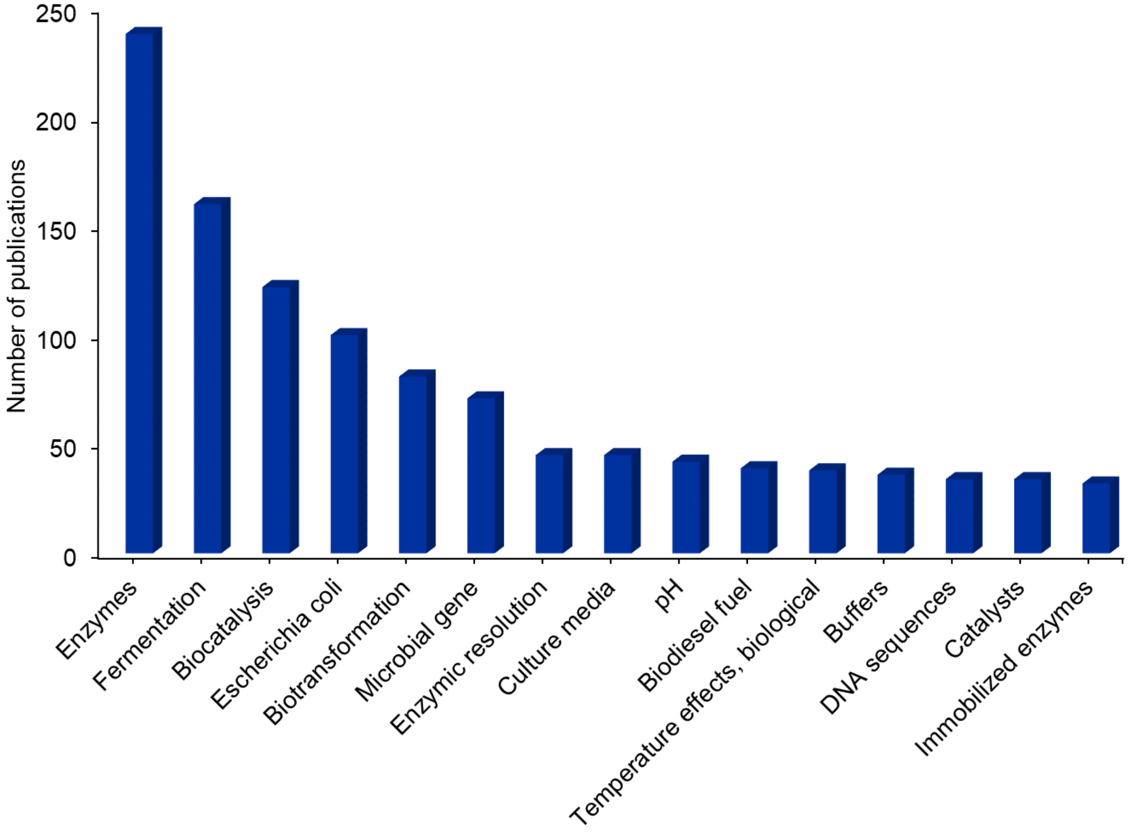

Figure 18. Top 15 concepts of biocatalysts in patents from 2012 to 2022.

Top Concepts

Enzymes and biocatalysis are the top concepts in both journal and patent publications (Figure 17 and 18). Besides those common concepts, journals include biotransformation, fermentation, enantioselective synthesis, transesterification, enzymic hydrolysis, that biocatalysts frequently participate in. Biodiesel fuel, biofuel and biochemical fuel cells present the research interests in the production of biomass-based fuel using biocatalysts.

In patent publications, the major concepts relate to enzyme production, such as fermentation, microbial gene, Escherichia coli, Pseudomonos, mutation, encapsulation. Such concepts as biodiesel fuel, fatty acids, Et esters, enzymic esterification show that patents are focused on biofuel production (Figure 18).

Usage and reaction-sorted concepts displayed more information in this field. Reaction-sorted concepts display that regio/stereoselective reaction, cyclization, polymerization, diastereoselective reaction, etc. are frequently catalyzed using biocatalysts (Figure S3). In the usage-sorted concepts, stereoselective reaction catalysts, polymerization catalysts, transesterification catalysts, etc. appeared in the documents (Figure S4). Publication trend in these two classes reflects to the current biocatalyst applications[66]: enzymes as biocatalysts to

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catalyze various reaction, especially stereoselective/regioselective reactions and polymerizations.

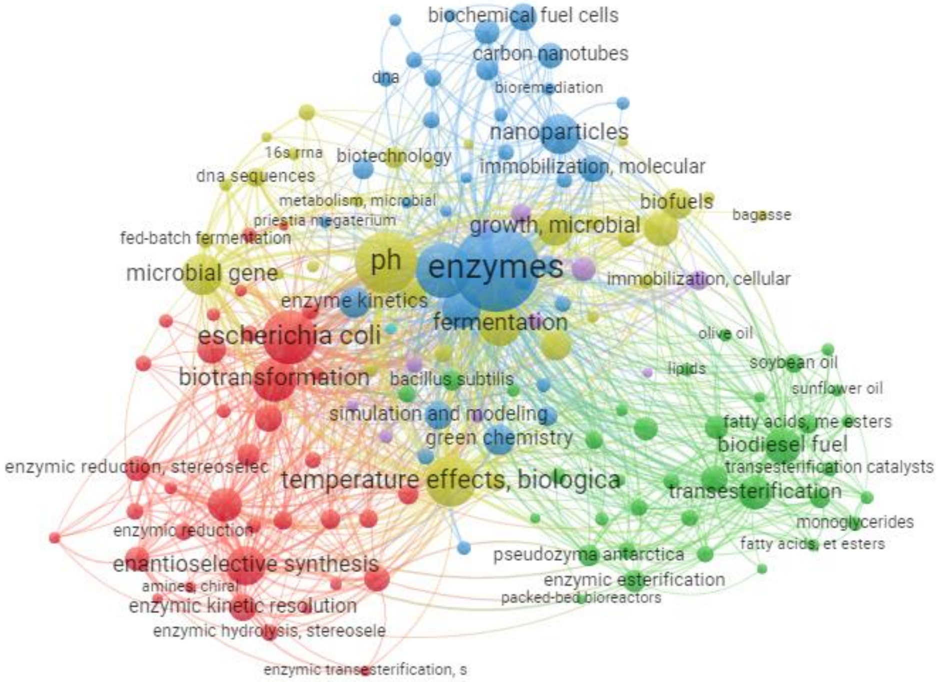

Figure 19. Biocatalyst 150 co-occurring concepts

Figure 19 shows the co-occurring concepts diagram as a combination of 4 clusters with “Enzymes” in the center. “Red” cluster consists of concepts representing reactions such as “enantioselective synthesis”, “enzymic hydrolysis”, “enzymic reduction” and so on. “Green” cluster includes concepts related to biodiesel: “Biodiesel fuel”, “Fatty acids, Me esters”, “Transesterification catalysts”, “Enzymic esterification” and so on. “Blue” cluster includes “Biofuels”, “Biochemical fuel cells”, “Immobilization”. “Yellow” cluster includes enzymes properties “pH” and methods of production “Fermentation”. All clusters show concepts related to the enzyme microbial/bacterial sources “Escherichia coli”, “Bacillus Subtills” and so on. Those microorganisms can be applied to activate reaction on biofuel cell electrodes.

Top Substances Used in Biocatalysts

The combination of metal catalysts and biocatalysts represents an attractive research area[71]. When olefin metathesis catalyst (Ru complex) is used in combination with a cytochrome P450 enzyme the epoxidation selectivity is greatly improved.[72] Combining of transition metal catalysts with engineered or artificial metalloenzymes also widen the range of reactivities and catalyzed reactions.[73] Transition metal catalysts biocompatible with living organisms (E. coli cells) were reported. For example, iron(III) phthalocyanine catalyst is capable of efficient olefin cyclopropanation in the presence of a E. coli living microorganism.[74]

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In Figure 20, triacylglycerol lipase and lispase CaLB—the hydrolase—attracted the most attention from the researchers; oxireductases like peroxidase, laccase, glucose oxidase, alcohol/glucose dehydrogenase, and carbonyl reductase also contribute to this field significantly. Other species, such as carbon and other transition metals like nickel, iron, platinum, copper, and cobalt usually form hybrid materials or participate in one-pot synthesis to synthesize molecules.[71, 75] This trend shows that the hydrolases and oxireductases are two primary types of biocatalysts and the combination between biocatalysts and metal catalysts is another approach in this field.

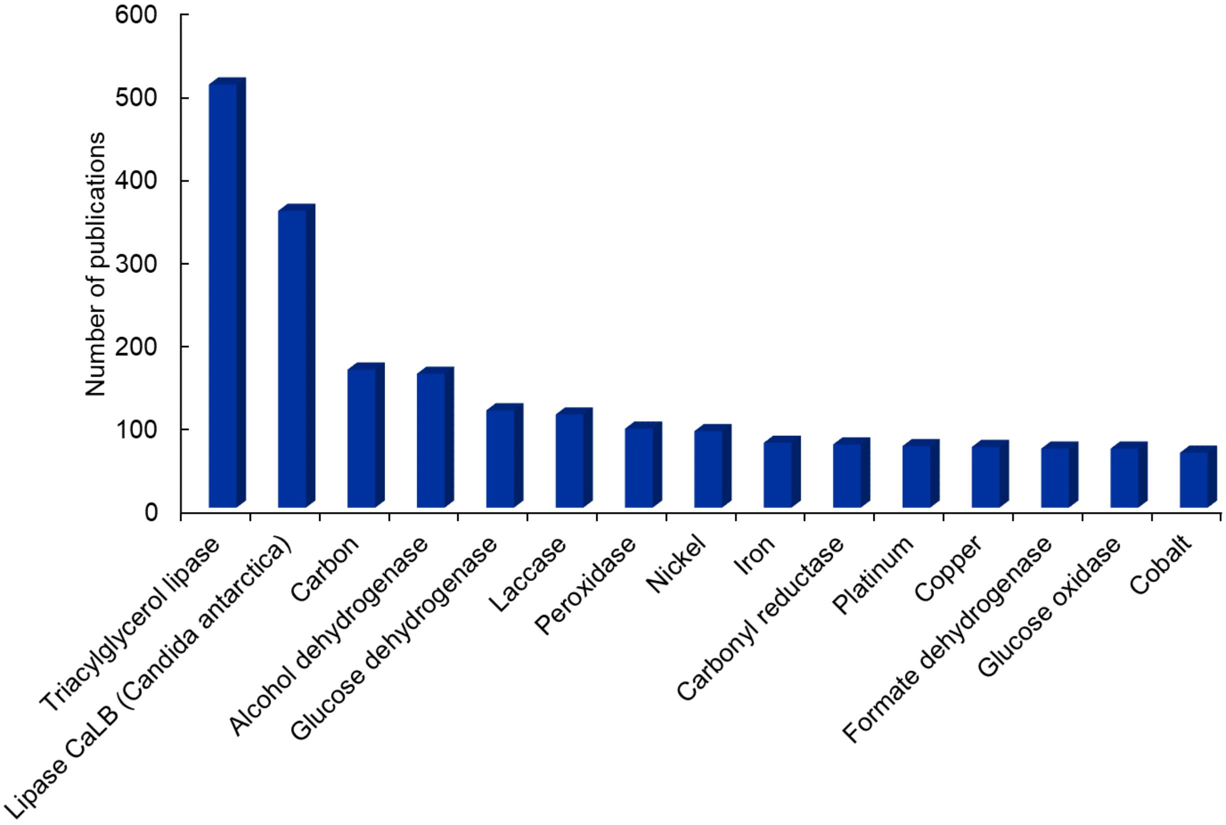

Figure 20. Top 15 substances mostly appeared in the field of biocatalysts.

Conclusion

Sustainable catalysts using non-noble metal catalysts to replace noble metal advanced a lot in the last 11 years. The general publication trend shows 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. In electrocatalysts, water splitting, oxygen evolution reaction, and hydrogen evolution reaction contribute significantly to this subfield. Non-noble metals and nanomaterials form new electrode materials

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with catalytic properties. The fuel cell-related concepts display that the metal-organic frameworks and non-noble metals form porous materials and catalyze reactions. This concept emerges from the research communities recently.

Research in photocatalysis continues to focus on finding a suitable photocatalyst with enough efficiency for commercial solar hydrogen production from water rather than on replacing any noble metal. Our analysis of the non-noble metal based photocatalysts show that the interest in research on this field continues to increase. This is due to the potential this technology holds to solve energy and environmental issues. The trends also show that the various materials have been studied and some well-known materialscontinue to attract interest of the researchers whereas the interest in some materials seems to have decreased. The low number of patents compared to journals publications show that photocatalyst has still not a stage of commercialization.

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. In substance aspect, radical reaction initiator like iodine, eosin, and tetrabutylammonium iodide are the mainstream as the noble metal catalysts replacement in the homogeneous catalysis.

Our analysis of biocatalysts shows that there is considerable interest in using biocatalysts as a sustainable way of catalyzing the 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.

According to our analysis, non-noble metal-based catalysts have a bright future in various fields with organic, inorganic, and bio-based substances to replace noble metals and achieve the same catalytic performance.

Method

This report used data from the CAS Content Collection^{TM}, which covers publications in more than scientific journals from around the world in a wide range of disciplines, 62 patent authorities, and 2 defensive publications (Research Disclosures and IP.com).

The following search query was used to find as many documents related to non-noble metal catalysts/catalysis-related research:

(base metal(3a)?cataly? or replace(a)platinum or substitut?(2a)platinum or replace(a)noble or substitut?(2a)noble or replac?(a)precious or substit?(2a)precious? or non-noble or non-precious or metal free or earth abundant or biocataly? or low cost(2a)?catalyst? or cost effective(2a)?catalyst? or inexpensive(2a)?catalyst? or platinum(2a)free or palladium(2a)free or iridium(2a)free or precious metal?(2a)free or noble metal?(2a)free) and ?cataly? and 2012-2023/py. There are about 65000 documents were retrieved (2012–2023).

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To capture more specific data, four search queries of (1) Homogeneous catalysts; (2) Electrocatalysts; (3) Photocatalysts; (4) Biocatalysts are used to retrieved the data from the original query.

Homogeneous catalysts:

(base metal(3a)?cataly? or replace(a)platinum or substitut?(2a)platinum or replace(a)noble or substitut?(2a)noble or replac?(a)precious or substit?(2a)precious? or non-noble or non-precious or metal free or earth abundant or biocataly? or low cost(2a)?catalyst? or cost effective(2a)?catalyst? or inexpensive(2a)?catalyst? or platinum(2a)free or palladium(2a)free or iridium(2a)free or precious metal?(2a)free or noble metal?(2a)free) and ?cataly? and 2012-2023/py and (homogeneous or nmr or crystal structure or ligand or organocat? or coupl? or pharma? or organometal? or dinuclear or trinuclear or coordination or thf or grignard or medic? or toluene or benzene or arene or complexes or phenyl or chiral or diastereo? or heterocy? or organophotocat? or electrophil? or nucleophile? or aryl? or bond activation or amination or metal-organic framework?) not biocataly? not surface? not semiconduct? not calcin? not nano?

Electrocatalysts:

(base metal(3a)?cataly? or replace(a)platinum or substitut?(2a)platinum or replace(a)noble or substitut?(2a)noble or replac?(a)precious or substit?(2a)precious? or non-noble or non-precious or metal free or earth abundant or biocataly? or low cost(2a)?catalyst? or cost effective(2a)?catalyst? or inexpensive(2a)?catalyst? or platinum(2a)free or palladium(2a)free or iridium(2a)free or precious metal?(2a)free or noble metal?(2a)free) and ?cataly? and 2012-2023/py and (electrocataly? or fuel cell? or water electrolysis or batter? or orr or her or oer) not photocataly? not biocataly?

Biocatalysts:

(base metal(3a)?cataly? or replace(a)platinum or substitut?(2a)platinum or replace(a)noble or substitut?(2a)noble or replac?(a)precious or substit?(2a)precious? or non-noble or non-precious or metal free or earth abundant or biocataly? or low cost(2a)?catalyst? or cost effective(2a)?catalyst? or inexpensive(2a)?catalyst? or platinum(2a)free or palladium(2a)free or iridium(2a)free or precious metal?(2a)free or noble metal?(2a)free) and 2012-2023/py and (?enzym? or hem? or ?oxidas? or hydrolas? or ?reductas? or ?hydrogenas? or transferas? or lipas? or porphyrin? or isomeras? or nitrogenas? or biofuel? or biodiesel) not food not drug? not waste? not peptid? not protein? not human?

Photocatalysts:

(base metal(3a)?cataly? or replace(a)platinum or substitut?(2a)platinum or replace(a)noble or substitut?(2a)noble or replac?(a)precious or substit?(2a)precious? or non-noble or non-precious or metal free or earth abundant or biocataly? or low cost(2a)?catalyst? or cost effective(2a)?catalyst? or inexpensive(2a)?catalyst? or platinum(2a)free or palladium(2a)free or iridium(2a)free or precious metal?(2a)free or noble metal?(2a)free) and ?cataly? and 2012-2023/py and (?photocataly? or photo-cataly? or photoelectroc? or photo-electroc?)

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Publications related to these four fields, categorized concepts and frequently used substances, were obtained by searching within this entire document collection using the four search queries shown above.

References

(1) *Report of the World Commission on Environment and Development: Our Common Future*. **https://sustainabledevelopment.un.org/content/documents/5987our-common-future.pdf** (accessed 2023 9th August).
(2) *What is Sustainability? How Sustainabilities Work, Benefits, and Example*. https://www.investopedia.com/terms/s/sustainability.asp (accessed 2023 9th August).
(3) Sustainable Chemistry. *Organic Process Research & Development* **2015**, *19* (7), 685-686. DOI: 10.1021/acs.oprd.5b00200.
(4) Liang, Y.; Xie, Y.-X.; Li, J.-H. Modified Palladium-Catalyzed Sonogashira Cross-Coupling Reactions under Copper-, Amine-, and Solvent-Free Conditions. *The Journal of Organic Chemistry* **2006**, *71* (1), 379-381. DOI: 10.1021/jo051882t.
(5) Eckhardt, M.; Fu, G. C. The First Applications of Carbene Ligands in Cross-Couplings of Alkyl Electrophiles: Sonogashira Reactions of Unactivated Alkyl Bromides and Iodides. *Journal of the American Chemical Society* **2003**, *125* (45), 13642-13643. DOI: 10.1021/ja038177r.
(6) Kirchhoff, J. H.; Netherton, M. R.; Hills, I. D.; Fu, G. C. Boronic Acids: New Coupling Partners in Room-Temperature Suzuki Reactions of Alkyl Bromides. Crystallographic Characterization of an Oxidative-Addition Adduct Generated under Remarkably Mild Conditions. *Journal of the American Chemical Society* **2002**, *124* (46), 13662-13663. DOI: 10.1021/ja0283899.
(7) Dreher, S. D.; Lim, S.-E.; Sandrock, D. L.; Molander, G. A. Suzuki−Miyaura Cross-Coupling Reactions of Primary Alkyltrifluoroborates with Aryl Chlorides. *The Journal of Organic Chemistry* **2009**, *74* (10), 3626-3631. DOI: 10.1021/jo900152n.
(8) Xu, H.-J.; Zhao, Y.-Q.; Zhou, X.-F. Palladium-Catalyzed Heck Reaction of Aryl Chlorides under Mild Conditions Promoted by Organic Ionic Bases. *The Journal of Organic Chemistry* **2011**, *76* (19), 8036-8041. DOI: 10.1021/jo201196a.
(9) Wu, C.; Zhou, J. Asymmetric Intermolecular Heck Reaction of Aryl Halides. *Journal of the American Chemical Society* **2014**, *136* (2), 650-652. DOI: 10.1021/ja412277z.
(10) Del Valle, L.; Stille, J. K.; Hegedus, L. S. Palladium-catalyzed coupling of allylic acetates with aryl- and vinylstannanes. *The Journal of Organic Chemistry* **1990**, *55* (10), 3019-3023. DOI: 10.1021/jo00297a014.
(11) Li, J.-H.; Liang, Y.; Wang, D.-P.; Liu, W.-J.; Xie, Y.-X.; Yin, D.-L. Efficient Stille Cross-Coupling Reaction Catalyzed by the Pd(OAc)2/Dabco Catalytic System. *The Journal of Organic Chemistry* **2005**, *70* (7), 2832-2834. DOI: 10.1021/jo048066q.
(12) Bera, S.; Roy, S.; Pal, S. C.; Anoop, A.; Samanta, R. Iridium(III)-Catalyzed Intermolecular Mild N-Arylation of Aliphatic Amides Using Quinoid Carbene: A Migratory Insertion-Based Approach. *ACS Catalysis* **2021**, *11* (17), 10847-10854. DOI: 10.1021/acscatal.1c02653.
(13) Han, M.; Yang, M.; Wu, R.; Li, Y.; Jia, T.; Gao, Y.; Ni, H.-L.; Hu, P.; Wang, B.-Q.; Cao, P. Highly Enantioselective Iridium-Catalyzed Coupling Reaction of Vinyl Azides and Racemic Allylic Carbonates. *Journal of the American Chemical Society* **2020**, *142* (31), 13398-13405. DOI: 10.1021/jacs.0c01766.
(14) *Platinum Processes & Uses*. https://www.thenaturalsapphirecompany.com/education/precious-metal-mining-refining-techniques/platinum-mining-

https://doi.org/10.26434/chemrxiv-2023-v30kj **ORCID:** https://orcid.org/0000-0002-0645-0622 Content not peer-reviewed by ChemRxiv. **License:** CC BY 4.0

refining/#:~:text=It%20can%20take%20from%20eight,single%20troy%20ounce%20of%20platinum. (accessed 2023 9th August).
(15) Ludwig, J. R.; Schindler, C. S. Catalyst: Sustainable Catalysis. *Chem* **2017**, *2* (3), 313-316. DOI: 10.1016/j.chempr.2017.02.014 (acccessed 2023/08/09).
(16) *GUIDELINE ON THE SPECIFICATION LIMITS FOR RESIDUES OF METAL*

CATALYSTS OR METAL REAGENTS. https://www.ema.europa.eu/en/documents/scientific-guideline/guideline-specification-limits-residues-metal-catalysts-metal-reagents_en.pdf (accessed 2023 9th August).
(17) Mai, H.; Le, T. C.; Chen, D.; Winkler, D. A.; Caruso, R. A. Machine Learning for Electrocatalyst and Photocatalyst Design and Discovery. *Chemical Reviews* **2022**, *122* (16), 13478-13515. DOI: 10.1021/acs.chemrev.2c00061.
(18) Zhang, G.; Su, H.; Zhang, Y. Construction of Glutinous Rice Potpourri-like MOTT−Schottky Ni/CeO2 Heterojunction Nanosheets for Robust Electrochemical Water Reduction. *Energies* **2022**, *15* (24), 9443.
(19) Wang, W.; Wang, Y.; Wang, X.; Jiang, B.; Song, H. Engineering Hollow Core–Shell N–C@Co/N–C Catalysts with Bits of Ni Doping Used as Efficient Electrocatalysts in Microbial Fuel Cells. *ACS Applied Materials & Interfaces* **2022**, *14* (37), 41912-41923. DOI: 10.1021/acsami.2c09230.
(20) Hao, Z.; Ma, Y.; Chen, Y.; Fu, P.; Wang, P. Non-Noble Metal Catalysts in Cathodic Oxygen Reduction Reaction of Proton Exchange Membrane Fuel Cells: Recent Advances. *Nanomaterials* **2022**, *12* (19), 3331.
(21) Ren, L.; Lu, J.; Liu, H. Activated carbon supported Fe–Cu–NC as an efficient cathode catalyst for a microbial fuel cell. *New Journal of Chemistry* **2022**, *46* (45), 21579-21590, 10.1039/D2NJ03939G. DOI: 10.1039/D2NJ03939G.
(22) Guo, B.; Kang, J.; Zeng, T.; Qu, H.; Yu, S.; Deng, H.; Bai, J. 3D Printing of Multiscale Ti64-Based Lattice Electrocatalysts for Robust Oxygen Evolution Reaction. *Advanced Science* **2022**, *9* (24), 2201751. DOI: https://doi.org/10.1002/advs.202201751.
(23) Xu, X.; Ji, S.; Wang, H.; Wang, X.; Linkov, V.; Wang, P.; Pan, L.; Wang, G.; Wang, R. Cu-induced NiCu-P and NiCu-Pi with multilayered nanostructures as highly efficient electrodes for hydrogen production via urea electrolysis. *Nanoscale* **2022**, *14* (44), 16490-16501, 10.1039/D2NR04409A. DOI: 10.1039/D2NR04409A.
(24) Chen, X.; Chen, D.; Li, G.; Sha, P.; Yu, J.; Yu, L.; Dong, L. FeNi incorporated N doped carbon nanotubes from glucosamine hydrochloride as highly efficient bifunctional catalyst for long term rechargeable zinc-air batteries. *Electrochimica Acta* **2022**, *428*, 140938. DOI: https://doi.org/10.1016/j.electacta.2022.140938.
(25) Vishnu, B.; Mathi, S.; Sriram, S.; Jayabharathi, J. Greenly Reduced CoFe-PBA/Nickel Foam: A Robust Dual Electrocatalyst for Solar-Driven Alkaline Water Electrolysis with a Low Cell Voltage. *ChemistrySelect* **2022**, *7* (33), e202201682. DOI: https://doi.org/10.1002/slct.202201682.
(26) Tian, J.; Morozan, A.; Sougrati, M. T.; Lefèvre, M.; Chenitz, R.; Dodelet, J.-P.; Jones, D.; Jaouen, F. Optimized Synthesis of Fe/N/C Cathode Catalysts for PEM Fuel Cells: A Matter of Iron–Ligand Coordination Strength. *Angewandte Chemie International Edition* **2013**, *52* (27), 6867-6870. DOI: https://doi.org/10.1002/anie.201303025.
(27) Zhang, L.; Lu, C.; Ye, F.; Pang, R.; Liu, Y.; Wu, Z.; Shao, Z.; Sun, Z.; Hu, L. Selenic Acid Etching Assisted Vacancy Engineering for Designing Highly Active Electrocatalysts toward the Oxygen Evolution Reaction. *Advanced Materials* **2021**, *33* (14), 2007523. DOI: https://doi.org/10.1002/adma.202007523.
(28) *Nanofiber electrocatalyst*. https://patents.google.com/patent/US20190060888A1/en?oq=US2019%2f0060888 (accessed 2023 9th August).

https://doi.org/10.26434/chemrxiv-2023-v30kj **ORCID:** https://orcid.org/0000-0002-0645-0622 Content not peer-reviewed by ChemRxiv. **License:** CC BY 4.0

(29) Li, X.; Yu, J.; Jaroniec, M.; Chen, X. Cocatalysts for Selective Photoreduction of CO2 into Solar Fuels. *Chemical Reviews* **2019**, *119* (6), 3962-4179. DOI: 10.1021/acs.chemrev.8b00400.
(30) Parvulescu, V. I.; Epron, F.; Garcia, H.; Granger, P. Recent Progress and Prospects in Catalytic Water Treatment. *Chemical Reviews* **2022**, *122* (3), 2981-3121. DOI: 10.1021/acs.chemrev.1c00527.
(31) Gawande, M. B.; Goswami, A.; Felpin, F.-X.; Asefa, T.; Huang, X.; Silva, R.; Zou, X.; Zboril, R.; Varma, R. S. Cu and Cu-Based Nanoparticles: Synthesis and Applications in Catalysis. *Chemical Reviews* **2016**, *116* (6), 3722-3811. DOI: 10.1021/acs.chemrev.5b00482.
(32) Lu, H.; Tournet, J.; Dastafkan, K.; Liu, Y.; Ng, Y. H.; Karuturi, S. K.; Zhao, C.; Yin, Z. Noble-Metal-Free Multicomponent Nanointegration for Sustainable Energy Conversion. *Chemical Reviews* **2021**, *121* (17), 10271-10366. DOI: 10.1021/acs.chemrev.0c01328.
(33) Murali, G.; Reddy Modigunta, J. K.; Park, Y. H.; Lee, J.-H.; Rawal, J.; Lee, S.-Y.; In, I.; Park, S.-J. A Review on MXene Synthesis, Stability, and Photocatalytic Applications. *ACS Nano* **2022**, *16* (9), 13370-13429. DOI: 10.1021/acsnano.2c04750.
(34) Prieto, G.; Tüysüz, H.; Duyckaerts, N.; Knossalla, J.; Wang, G.-H.; Schüth, F. Hollow Nano- and Microstructures as Catalysts. *Chemical Reviews* **2016**, *116* (22), 14056-14119. DOI: 10.1021/acs.chemrev.6b00374.
(35) Sayed, M.; Yu, J.; Liu, G.; Jaroniec, M. Non-Noble Plasmonic Metal-Based Photocatalysts. *Chemical Reviews* **2022**, *122* (11), 10484-10537. DOI: 10.1021/acs.chemrev.1c00473.
(36) Kettler, P. B. Platinum Group Metals in Catalysis: Fabrication of Catalysts and Catalyst Precursors. *Organic Process Research & Development* **2003**, *7* (3), 342-354. DOI: 10.1021/op034017o.
(37) Price pressures on metals. *Nature Catalysis* **2019**, *2* (9), 735-735. DOI: 10.1038/s41929-019-0359-7.
(38) Brown, D. G.; Boström, J. Analysis of Past and Present Synthetic Methodologies on Medicinal Chemistry: Where Have All the New Reactions Gone? *Journal of Medicinal Chemistry* **2016**, *59* (10), 4443-4458. DOI: 10.1021/acs.jmedchem.5b01409.
(39) Leadbeater, N. E.; Marco, M. Transition-Metal-Free Suzuki-Type Coupling Reactions: Scope and Limitations of the Methodology. *The Journal of Organic Chemistry* **2003**, *68* (14), 5660-5667. DOI: 10.1021/jo034230i.
(40) Arvela, R. K.; Leadbeater, N. E.; Sangi, M. S.; Williams, V. A.; Granados, P.; Singer, R. D. A Reassessment of the Transition-Metal Free Suzuki-Type Coupling Methodology. *The Journal of Organic Chemistry* **2005**, *70* (1), 161-168. DOI: 10.1021/jo048531j.
(41) Xu, L.; Liu, F.-Y.; Zhang, Q.; Chang, W.-J.; Liu, Z.-L.; Lv, Y.; Yu, H.-Z.; Xu, J.; Dai, J.-J.; Xu, H.-J. RETRACTED ARTICLE: The amine-catalysed Suzuki–Miyaura-type coupling of aryl halides and arylboronic acids. *Nature Catalysis* **2021**, *4* (1), 71-78. DOI: 10.1038/s41929-020-00564-z.
(42) Avanthay, M.; Bedford, R. B.; Begg, C. S.; Böse, D.; Clayden, J.; Davis, S. A.; Eloi, J.-C.; Goryunov, G. P.; Hartung, I. V.; Heeley, J.; et al. Identifying palladium culprits in amine catalysis. *Nature Catalysis* **2021**, *4* (12), 994-998. DOI: 10.1038/s41929-021-00710-1.
(43) Vinod, J. K.; Wanner, A. K.; James, E. I.; Koide, K. Fluorometric study on the amine-catalysed Suzuki–Miyaura coupling. *Nature Catalysis* **2021**, *4* (12), 999-1001. DOI: 10.1038/s41929-021-00711-0.
(44) Novák, Z.; Adamik, R.; Csenki, J. T.; Béke, F.; Gavaldik, R.; Varga, B.; Nagy, B.; May, Z.; Daru, J.; Gonda, Z.; et al. Revisiting the amine-catalysed cross-coupling. *Nature Catalysis* **2021**, *4* (12), 991-993. DOI: 10.1038/s41929-021-00709-8.
(45) Ravi, O.; Shaikh, A.; Upare, A.; Singarapu, K. K.; Bathula, S. R. Benzimidazoles from Aryl Alkyl Ketones and 2-Amino Anilines by an Iodine Catalyzed Oxidative C(CO)–C(alkyl) Bond Cleavage. *The Journal of Organic Chemistry* **2017**, *82* (8), 4422-4428. DOI: 10.1021/acs.joc.7b00165.
(46) Reddi, R. N.; Prasad, P. K.; Sudalai, A. I2-Catalyzed Regioselective Oxo- and Hydroxy-acyloxylation of Alkenes and Enol Ethers: A Facile Access to α-Acyloxyketones, Esters, and Diol Derivatives. *Organic Letters* **2014**, *16* (21), 5674-5677. DOI: 10.1021/ol5027393.

https://doi.org/10.26434/chemrxiv-2023-v30kj **ORCID:** https://orcid.org/0000-0002-0645-0622 Content not peer-reviewed by ChemRxiv. **License:** CC BY 4.0

(47) Lin, Y.; Li, B.; Feng, Z.; Kim, Y. A.; Endo, M.; Su, D. S. Efficient Metal-Free Catalytic Reaction Pathway for Selective Oxidation of Substituted Phenols. *ACS Catalysis* **2015**, *5* (10), 5921-5926. DOI: 10.1021/acscatal.5b01222.
(48) Mousseau, J. J.; Charette, A. B. Direct Functionalization Processes: A Journey from Palladium to Copper to Iron to Nickel to Metal-Free Coupling Reactions. *Accounts of Chemical Research* **2013**, *46* (2), 412-424. DOI: 10.1021/ar300185z.
(49) Du, X.; Huang, Z. Advances in Base-Metal-Catalyzed Alkene Hydrosilylation. *ACS Catalysis* **2017**, *7* (2), 1227-1243. DOI: 10.1021/acscatal.6b02990.
(50) Khan, B.; Dutta, H. S.; Koley, D. Remote C–H Functionalization of 8-Aminoquinolinamides. *Asian Journal of Organic Chemistry* **2018**, *7* (7), 1270-1297. DOI: https://doi.org/10.1002/ajoc.201800276.
(51) Margarita, C.; Andersson, P. G. Evolution and Prospects of the Asymmetric Hydrogenation of Unfunctionalized Olefins. *Journal of the American Chemical Society* **2017**, *139* (4), 1346-1356. DOI: 10.1021/jacs.6b10690.
(52) Roy, V. J.; Sen, P. P.; Raha Roy, S. Visible-Light-Mediated Cross Dehydrogenative Coupling of Thiols with Aldehydes: Metal-Free Synthesis of Thioesters at Room Temperature. *The Journal of Organic Chemistry* **2021**, *86* (23), 16965-16976. DOI: 10.1021/acs.joc.1c02111.
(53) Srivastava, V. P.; Yadav, A. K.; Yadav, L. D. S. Eosin Y Catalyzed Visible-Light-Driven Aerobic Oxidative Cyclization of Thioamides to 1,2,4-Thiadiazoles. *Synlett* **2013**, *24* (04), 465-470. DOI: 10.1055/s-0032-1318158.
(54) Zhang, S.; Guo, L.-N.; Wang, H.; Duan, X.-H. Bu4NI-catalyzed decarboxylative acyloxylation of an sp3 C–H bond adjacent to a heteroatom with α-oxocarboxylic acids. *Organic & Biomolecular Chemistry* **2013**, *11* (26), 4308-4311, 10.1039/C3OB40748A. DOI: 10.1039/C3OB40748A.
(55) Ding, L.; Deng, Y.-H.; Sun, T.-Y.; Jiang, Y.; Xia, X.-F. Merging Hydrogen Atom Transfer and Halogen Atom Transfer for Iodide-Catalyzed Radical Reductive Cyclization of 1,6-Enynes. *Organic Letters* **2022**, *24* (17), 3113-3117. DOI: 10.1021/acs.orglett.2c00552.
(56) Zhu, H.-L.; Zeng, F.-L.; Chen, X.-L.; Sun, K.; Li, H.-C.; Yuan, X.-Y.; Qu, L.-B.; Yu, B. Acyl Radicals from α-Keto Acids: Metal-Free Visible-Light-Promoted Acylation of Heterocycles. *Organic Letters* **2021**, *23* (8), 2976-2980. DOI: 10.1021/acs.orglett.1c00655.
(57) Yuan, X.-Y.; Zeng, F.-L.; Zhu, H.-L.; Liu, Y.; Lv, Q.-Y.; Chen, X.-L.; Peng, L.; Yu, B. A metal-free visible-light-promoted phosphorylation/cyclization reaction in water towards 3-phosphorylated benzothiophenes. *Organic Chemistry Frontiers* **2020**, *7* (14), 1884-1889, 10.1039/D0QO00222D. DOI: 10.1039/D0QO00222D.
(58) Kumar, G.; Qu, Z.-W.; Grimme, S.; Chatterjee, I. Boron-Catalyzed Hydroarylation of 1,3-Dienes with Arylamines. *Organic Letters* **2021**, *23* (22), 8952-8957. DOI: 10.1021/acs.orglett.1c03457.
(59) Blondiaux, E.; Cantat, T. Efficient metal-free hydrosilylation of tertiary, secondary and primary amides to amines. *Chemical Communications* **2014**, *50* (66), 9349-9352, 10.1039/C4CC02894E. DOI: 10.1039/C4CC02894E.
(60) Srivastava, A. K.; Ali, M.; Sharma, K. N.; Joshi, R. K. Metal-free, PTSA catalyzed facile synthesis of β-ketoacetal from β-chlorocinnamaldehyde. *Tetrahedron Letters* **2018**, *59* (33), 3188-3193. DOI: https://doi.org/10.1016/j.tetlet.2018.07.022.
(61) More, S. G.; Rupanawar, B. D.; Suryavanshi, G. Metal-Free, Acid-Catalyzed 1,6-Conjugate Addition of NH-Sulfoximines to para-Quinone Methides: Accessing to Diarylmethine Imino Sulfanone. *The Journal of Organic Chemistry* **2021**, *86* (15), 10129-10139. DOI: 10.1021/acs.joc.1c00869.
(62) Surendra Reddy, G.; Ramachary, D. B. Reaction engineering and photophysical studies of fully enriched C-vinyl-1,2,3-triazoles. *Organic Chemistry Frontiers* **2019**, *6* (21), 3620-3628, 10.1039/C9QO00864K. DOI: 10.1039/C9QO00864K.

https://doi.org/10.26434/chemrxiv-2023-v30kj **ORCID:** https://orcid.org/0000-0002-0645-0622 Content not peer-reviewed by ChemRxiv. **License:** CC BY 4.0

(63) Donikela, S.; Mainkar, P. S.; Nayani, K.; Chandrasekhar, S. Metal Free Domino β-Azidation/[3 + 2] Cycloaddition Reaction for the Synthesis of 1,2,3-Triazole-Fused Dihydrobenzoxazinones. *The Journal of Organic Chemistry* **2019**, *84* (16), 10546-10553. DOI: 10.1021/acs.joc.9b01660.
(64) Kate, A.; Sahu, L. K.; Pandey, J.; Mishra, M.; Sharma, P. K. Green catalysis for chemical transformation: The need for the sustainable development. *Current Research in Green and Sustainable Chemistry* **2022**, *5*, 100248. DOI: https://doi.org/10.1016/j.crgsc.2021.100248.
(65) *Global Biocatalysts Market Outlook*. https://www.expertmarketresearch.com/reports/biocatalysts-market (accessed 2023 9th August).
(66) Shoda, S.-i.; Uyama, H.; Kadokawa, J.-i.; Kimura, S.; Kobayashi, S. Enzymes as Green Catalysts for Precision Macromolecular Synthesis. *Chemical Reviews* **2016**, *116* (4), 2307-2413. DOI: 10.1021/acs.chemrev.5b00472.
(67) Littlechild, J. A. Archaeal Enzymes and Applications in Industrial Biocatalysts. *Archaea* **2015**, *2015*, 147671. DOI: 10.1155/2015/147671.
(68) Wu, S.; Snajdrova, R.; Moore, J. C.; Baldenius, K.; Bornscheuer, U. T. Biocatalysis: Enzymatic Synthesis for Industrial Applications. *Angewandte Chemie International Edition* **2021**, *60* (1), 88-119. DOI: https://doi.org/10.1002/anie.202006648.
(69) Li, G.; Wang, J.-b.; Reetz, M. T. Biocatalysts for the pharmaceutical industry created by structure-guided directed evolution of stereoselective enzymes. *Bioorganic & Medicinal Chemistry* **2018**, *26* (7), 1241-1251. DOI: https://doi.org/10.1016/j.bmc.2017.05.021.
(70) Jiang, Y.; Loos, K. Enzymatic Synthesis of Biobased Polyesters and Polyamides. *Polymers* **2016**, *8* (7), 243.
(71) Gröger, H.; Hummel, W. Combining the 'two worlds' of chemocatalysis and biocatalysis towards multi-step one-pot processes in aqueous media. *Current Opinion in Chemical Biology* **2014**, *19*, 171-179. DOI: https://doi.org/10.1016/j.cbpa.2014.03.002.
(72) Denard, C. A.; Huang, H.; Bartlett, M. J.; Lu, L.; Tan, Y.; Zhao, H.; Hartwig, J. F. Cooperative Tandem Catalysis by an Organometallic Complex and a Metalloenzyme. *Angewandte Chemie International Edition* **2014**, *53* (2), 465-469. DOI: https://doi.org/10.1002/anie.201305778.
(73) Köhler, V.; Turner, N. J. Artificial concurrent catalytic processes involving enzymes. *Chemical Communications* **2015**, *51* (3), 450-464, 10.1039/C4CC07277D. DOI: 10.1039/C4CC07277D.
(74) Wallace, S.; Balskus, E. P. Interfacing Microbial Styrene Production with a Biocompatible Cyclopropanation Reaction. *Angewandte Chemie International Edition* **2015**, *54* (24), 7106-7109. DOI: https://doi.org/10.1002/anie.201502185.
(75) Lau, C.; Adkins, E. R.; Ramasamy, R. P.; Luckarift, H. R.; Johnson, G. R.; Atanassov, P. Design of Carbon Nanotube-Based Gas-Diffusion Cathode for O2 Reduction by Multicopper Oxidases. *Advanced Energy Materials* **2012**, *2* (1), 162-168. DOI: https://doi.org/10.1002/aenm.201100433.

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