Recent advances in sustainable catalysts and catalysis with non-noble metals

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Abstract

This report displays bibliometric data analysis pertaining to the recent development of non-noble metal catalysts and their application in catalysis with a focus on sustainability. Using the CAS Content Collection[TM], we discuss the annual publication trends from 2012 to 2022 in four subfields: electrocatalysts, homogeneous catalysts, photocatalysts, and biocatalysts. Herein we reveal the top concepts that appeared associated with non-noble metal catalyst publications, along with the top substances and categorized concepts in each of the four sub-field. The global participation data is broken down and discussed for the topic of interest.

Introduction

In 1987, the United Nations (UN) announced the 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 tools that accommodate 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 result in good yields under various conditions. Iridium and ruthenium also perform their catalytic capabilities in arylation, allylation, and other cross-coupling reactions.[12, 13]

Noble metals are mostly extracted from low grade ores, a large amount of it needs to be mined to extract a small amount, resulting in environmental damage and contamination. For example, to produce around 31 grams of platinum, around 12 tons of ore is used.[14] 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 can also become impactful burdens in their

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catalytic applications. To eliminate the economic and lower the environmental impact in sustainable chemistry, noble metal replacement in catalytic applications has attracted attention among scientists.

The chemical properties which cause noble metals to excel as catalysts are their resistance to corrosion, ability to undergo 2-electron oxidation state changes[15] that is 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 earth crust. Although even some first-row transition metals such as cobalt may be subject to their own significant mining and environmental challenges. 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	

With the help of a search query (details in the methods section), documents related to non-noble metal based sustainable catalysts were identified and the related data were extracted from CAS Content Collection™. This data was used to identify technologies, materials, applications, types of publications, country wise trends, top institutions, and so on. This perspective article provides different perspective of the field of non-noble metal based sustainable catalysts. These analyses will help researchers know their research better and help decision makers to understand the progress in this specific area.

In this perspective, the CAS Content Collection™ was used to retrieve information regarding the use and application of non-noble metal catalysts / catalysis from the documents published during 2012–2022 (See **Methods**). Overall there are 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 2022 (Figure 1). The top 5 countries with the highest number of publications in journals in the descending order are China, United States, India, Germany, and South Korea. Regarding patent publication, the top countries are China, the United States, Japan, South Korea, and Germany. (Figure 2 and Table S1).

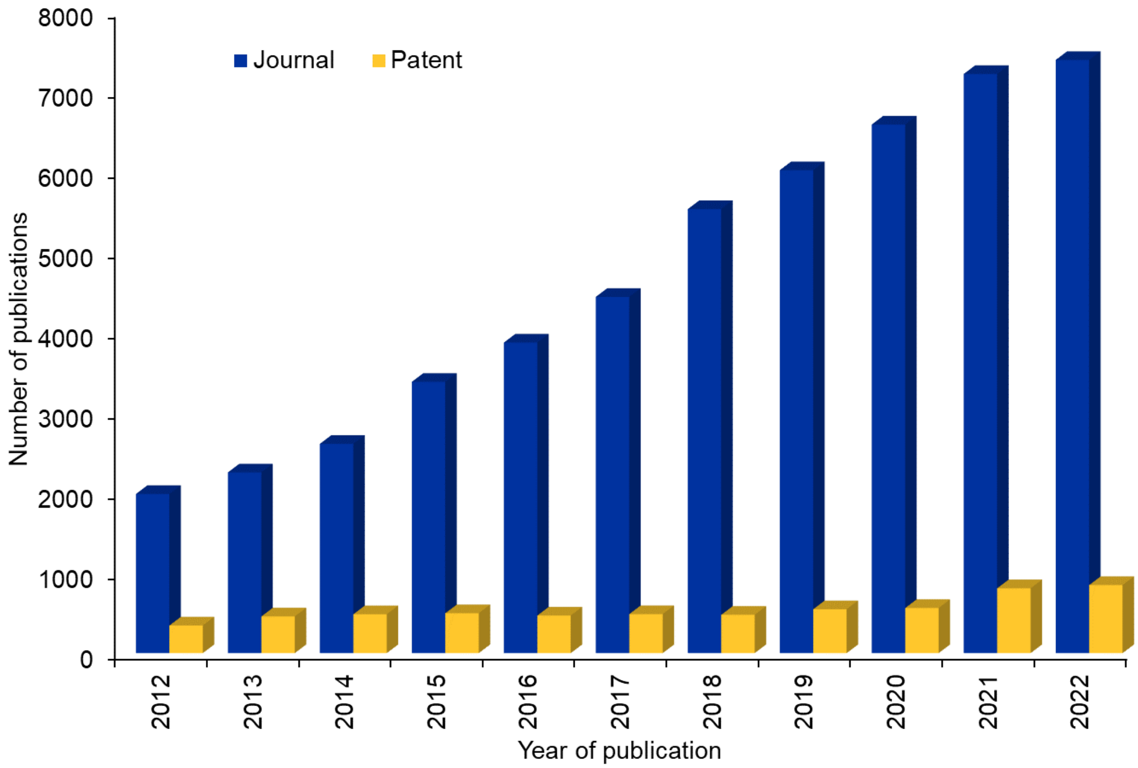


Figure 1. General journal and patent publication trend of non-noble metal catalysts/catalysis during 2012–2022.

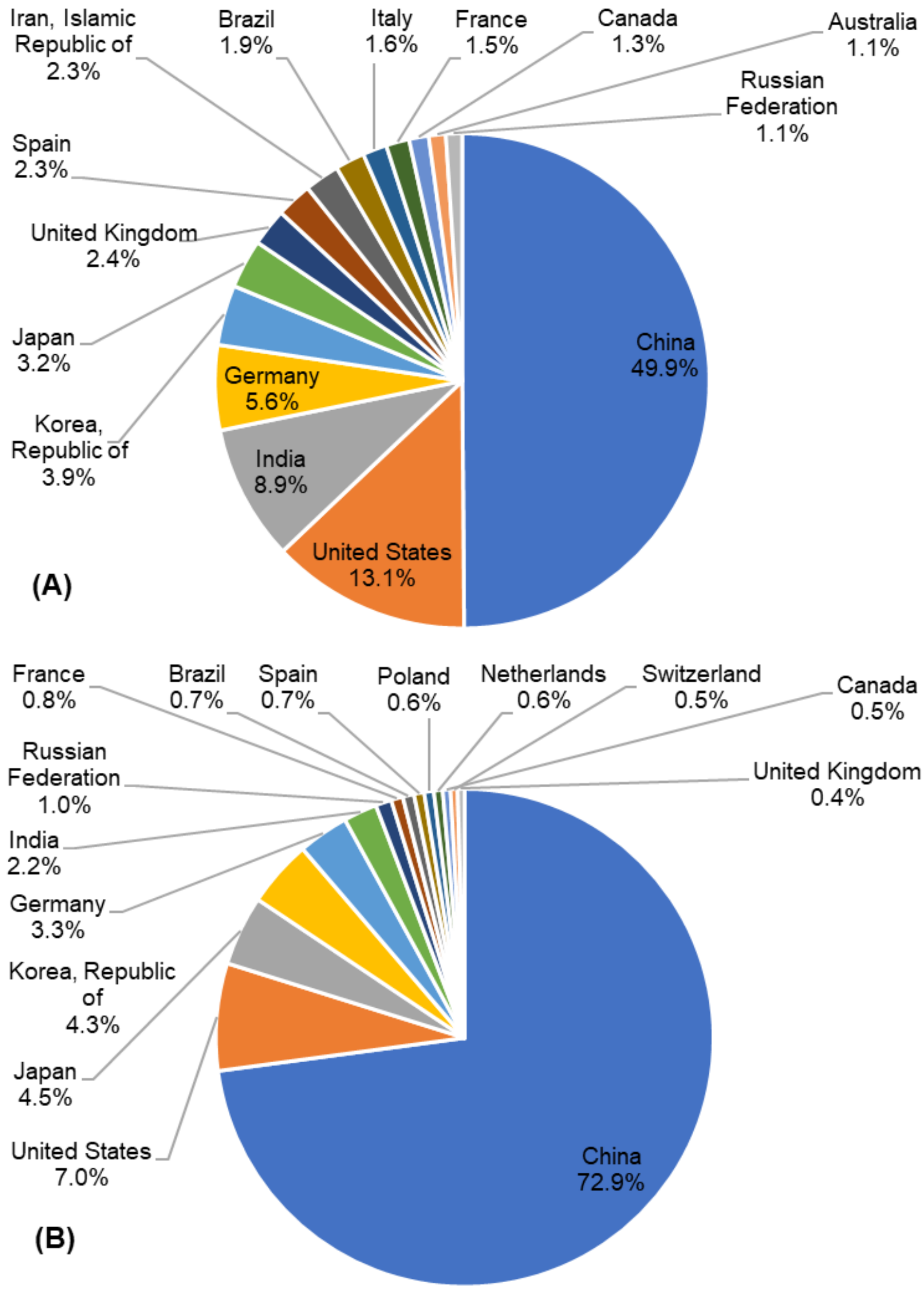


Figure 2. Top countries or regions in terms of journal (left) and patent (right) publications related to non-noble metal catalysts / catalysis.

The CAS content curation team evaluates scientific publications and indexes the various concepts that are being discussed in them. The top concepts that appeared in journals and patents are shown in Figure 3. Among the top concepts in journals, electrochemical reaction catalysts, water splitting, and hydrogen evolution reaction represent the electrocatalyst-related reactions/applications, whereas enzymes are related to biocatalysts. In patents, the top 15 concepts are mostly bio-related, followed by concepts related electrochemical reaction catalysts. This trend in patents shows that biocatalysts and electrocatalysts have high possibility of commercialization. In addition to these top concepts, photocatalysts and homogeneous catalysts are also important concepts of sustainable catalysts.

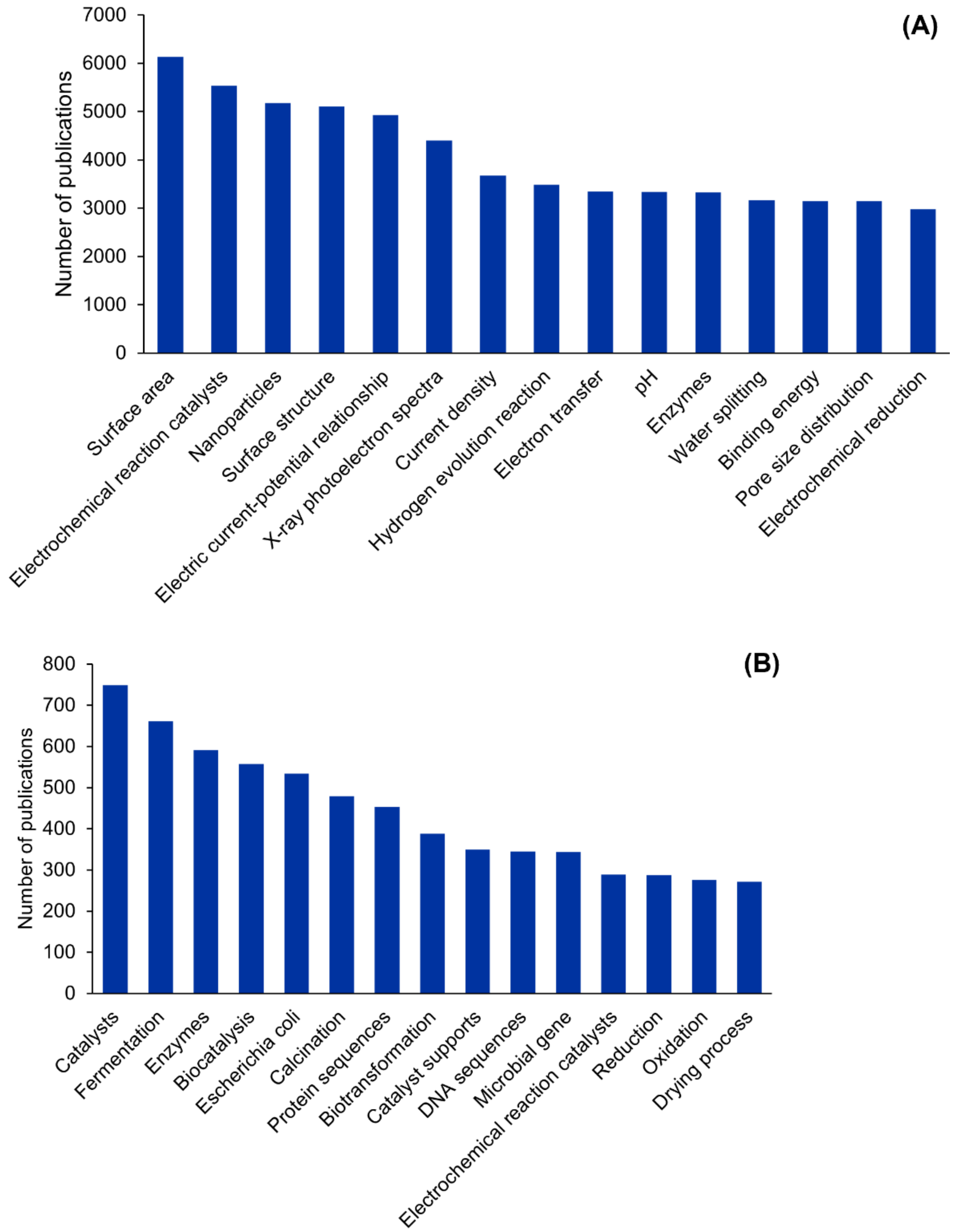


Figure 3. Top 15 concepts reported in non-noble metal catalysts / catalysis-related publications in (A) journals and (B) patents during 2012–2022.

In this perspective, 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/enzymes. Data regarding these subfields was obtained by further narrowing the original search query (See **Methods**). Figure 4 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 during 2012-2022 period were similar for biocatalysts, electrocatalysis and homogeneous catalysts, whereas relatively lesser patents were published using photocatalysts (Homogeneous catalyst: 675; electrocatalyst: 694; photocatalyst: 338; biocatalyst: 745). We provide analysis of the developments and publications in these subfields in the sections that follow.

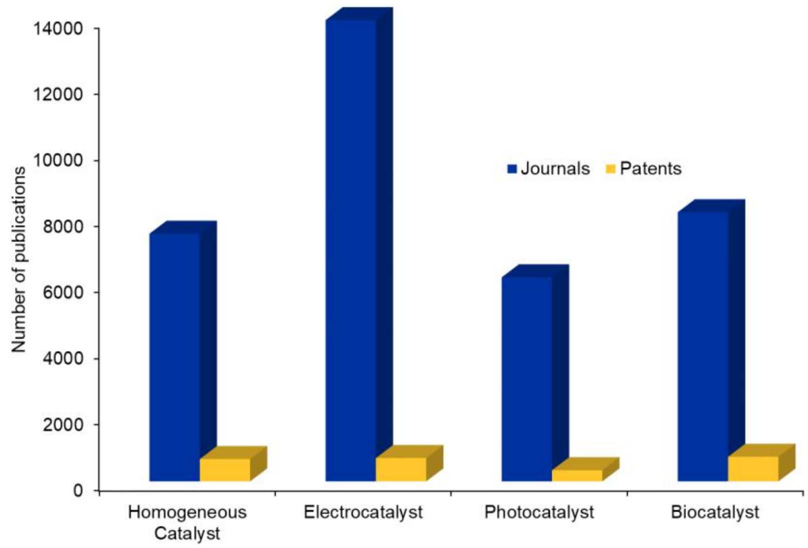


Figure 4. Publication volumes for the four subfields: Homogeneous Catalyst, Electrocatalyst, Photocatalyst, and Biocatalyst in journals and patents.

Electrocatalysts

Electrocatalysts participate in electrochemical reactions as the electrodes, or the catalytic materials coated on the surface of electrodes. Platinum is the most used electrode material in electrochemical devices because of its catalytic activity. However, its limited abundance and high costs are hurdles that impede 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 main search query data using a narrow electrocatalyst specific search query (See **Methods)**. In general, electrocatalyst-related publications show steady growth in journals and a slower growth in patents (Figure 5). Publication volume of journals is considerably higher than patents in the past decade, which demonstrates that there is much research interest in this topic yet a lag in commercialization of materials, development and application of electrocatalysts. We anticipate that there will be more innovative ideas to be commercialized in the future, resulting in a higher growth in patents.

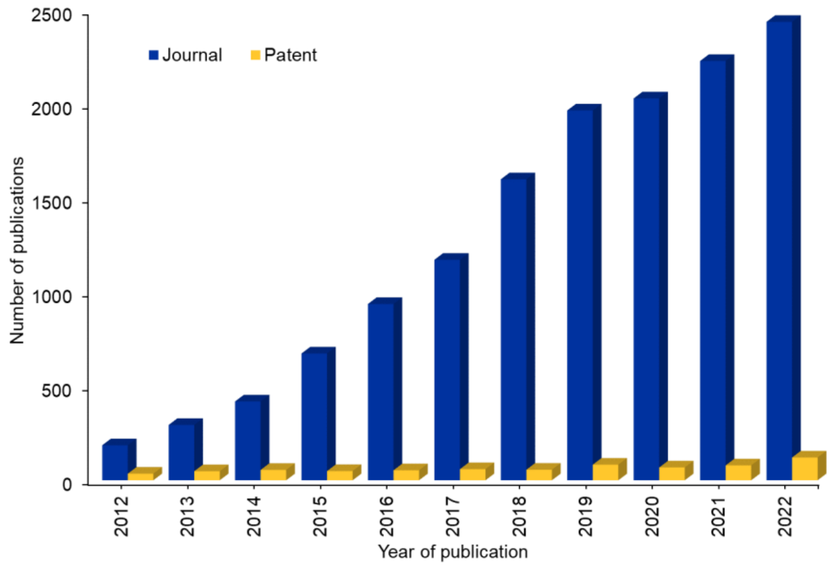
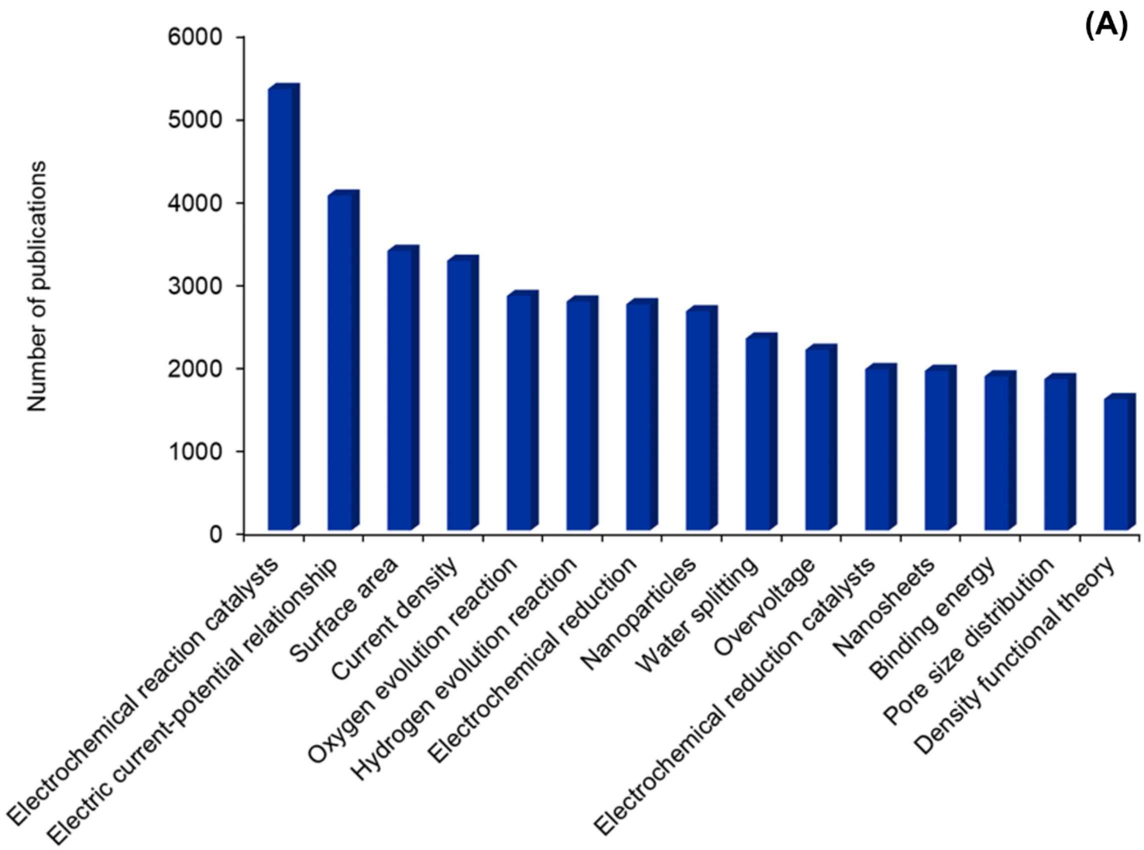


Figure 5. Annual publication trends of electrocatalysts in journals and patents.

Selected Electrocatalysts Concepts

Original top 15 concepts in electrocatalysts include some non-directly relevant terms (ex. X-ray photoelectron spectra, cyclic voltammetry, electric impedance, and electron transfer) that could disguise the trend of electrocatalysts development by making other concepts in lower ranking. Thus, we further looked into the selected concepts in electrocatalysts in journals and patents (Figure 6). Except the electrochemical reaction, the top three reaction concepts that appeared in journals are oxygen evolution reaction, hydrogen evolution reaction, and water splitting. Nanomaterials, for instance, nanoparticles and nanosheets are often studied in journals. In patents, the top concepts are fuel cells, fuel cell related terms (fuel cell electrode/cathode/anode, etc.), doping, nanomaterials, and composites, which demonstrates that these applications are primarily commercialized.



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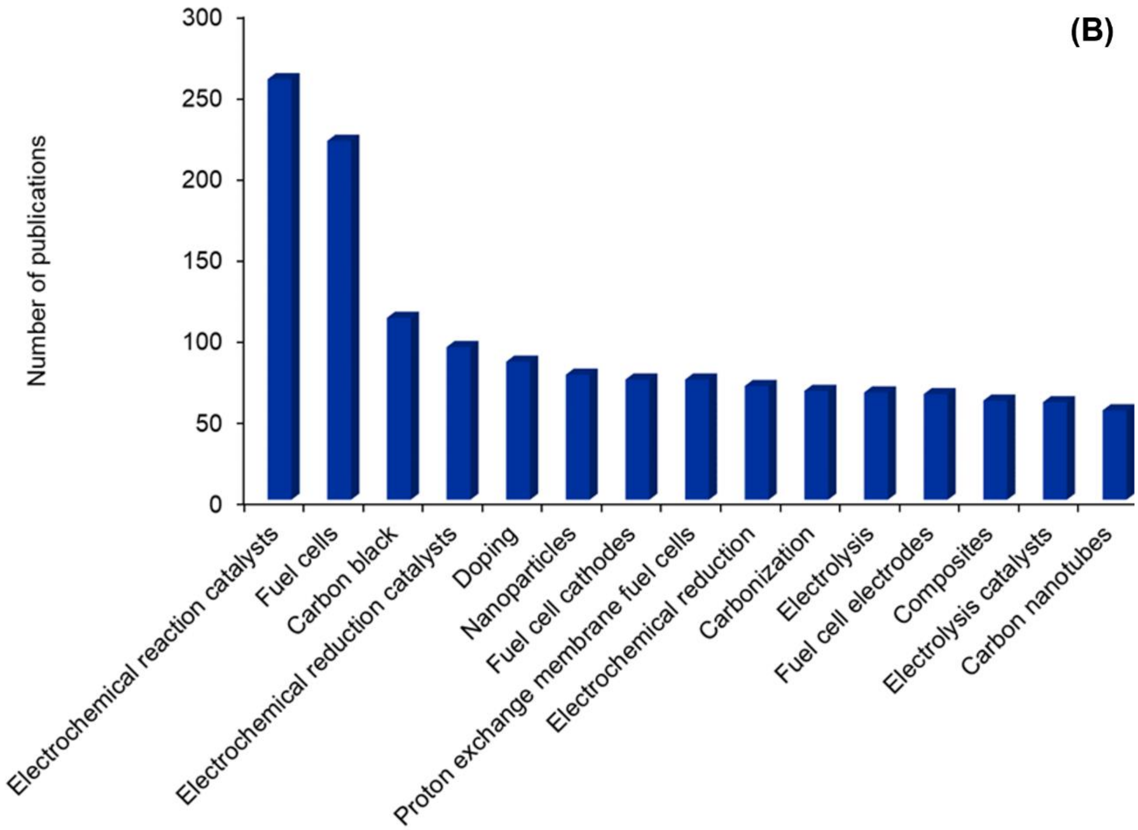


Figure 6. Selected electrocatalyst-related concepts in journals (A) and patents (B).

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 volumes of top 15 RXN-classified concepts (Figure 7, 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 7, Right), electrochemical reaction / reduction catalysts and nanoparticles / sheets are predominantly present in the electrocatalyst related publications, followed by electrolysis, OER, HER, and water splitting catalysts. Carbon based nanomaterials are usually used as conducting supports, while nanostructured electrocatalysts exhibit high activity due to higher surface area.[76]

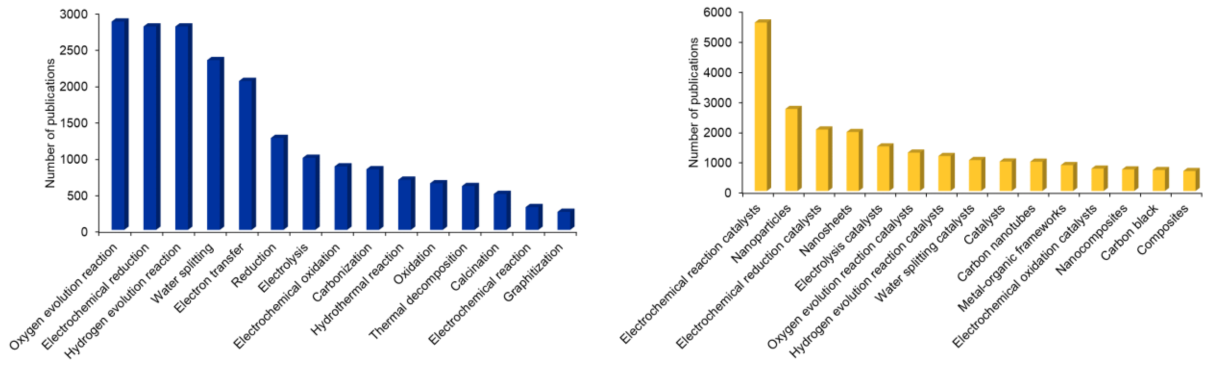


Figure 7. Left: top 15 reaction-related concepts of electrocatalysts frequently appeared in publications; right: top 15 usage-related concepts of electrocatalysts frequently appeared in publications.

The Mostly Used Substances

To further reveal the trend of substances used as electrocatalysts, herein we 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 the electrode with non-noble metal electrocatalysts, while platinum based electrodes are used for the comparison with the alternative electrodes.[18] Nickel, graphene, cobalt, nitrogen, and iron are also frequently used for electrocatalyst research. 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] Cobalt and nickel complexed as CoNi carbonate hydroxides (CoNiCH) and formed a core-shell structure [$Cu(OH)_2$@CoNiCH] with $Cu(OH)_2$ to perform 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]

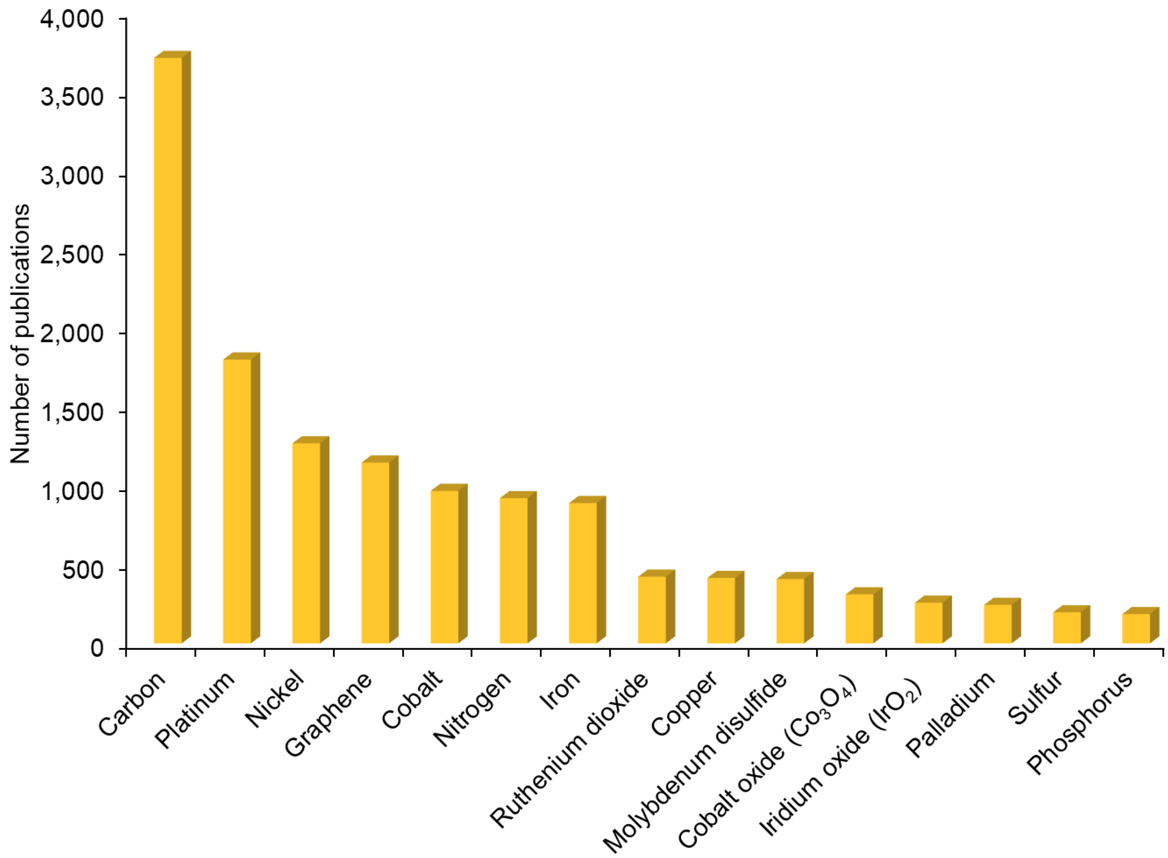
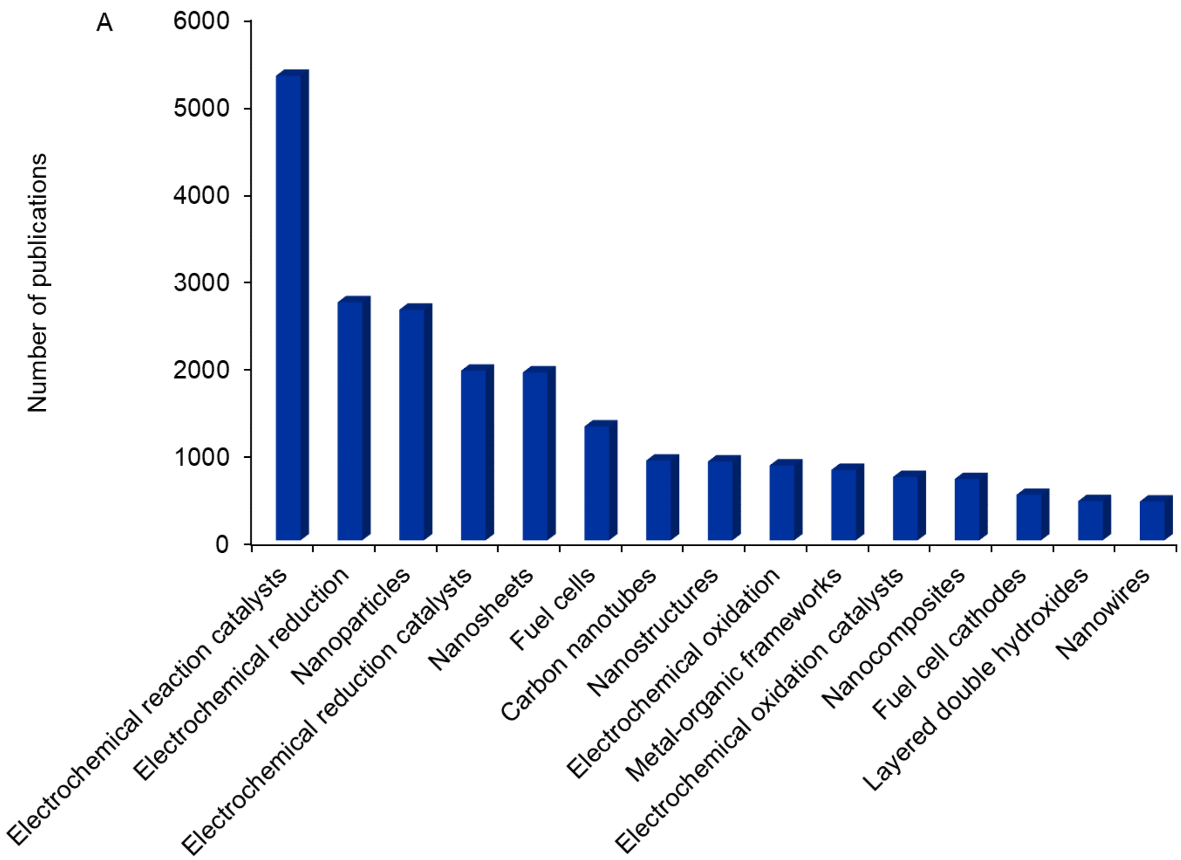


Figure 8. Top 15 mostly used substances in electrocatalysts-related publications.

Fuel Cell Related Concepts

We further reveal the fuel cell-related analysis by manually selecting fuel cell-related concepts from the electrocatalysts dataset, followed by data analysis. Figure 9 displays that nanomaterials are widely 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]


A
Number of publications
6000
5000
4000
3000
2000
1000
0
Electrochemical reaction catalysts
Electrochemical reduction
Nanoparticles
Electrochemical reduction catalysts
Nanosheets
Fuel cells
Carbon nanotubes
Nanostructures
Electrochemical oxidation
Metal-organic frameworks
Electrochemical oxidation catalysts
Nanocomposites
Fuel cell cathodes
Layered double hydroxides
Nanowires

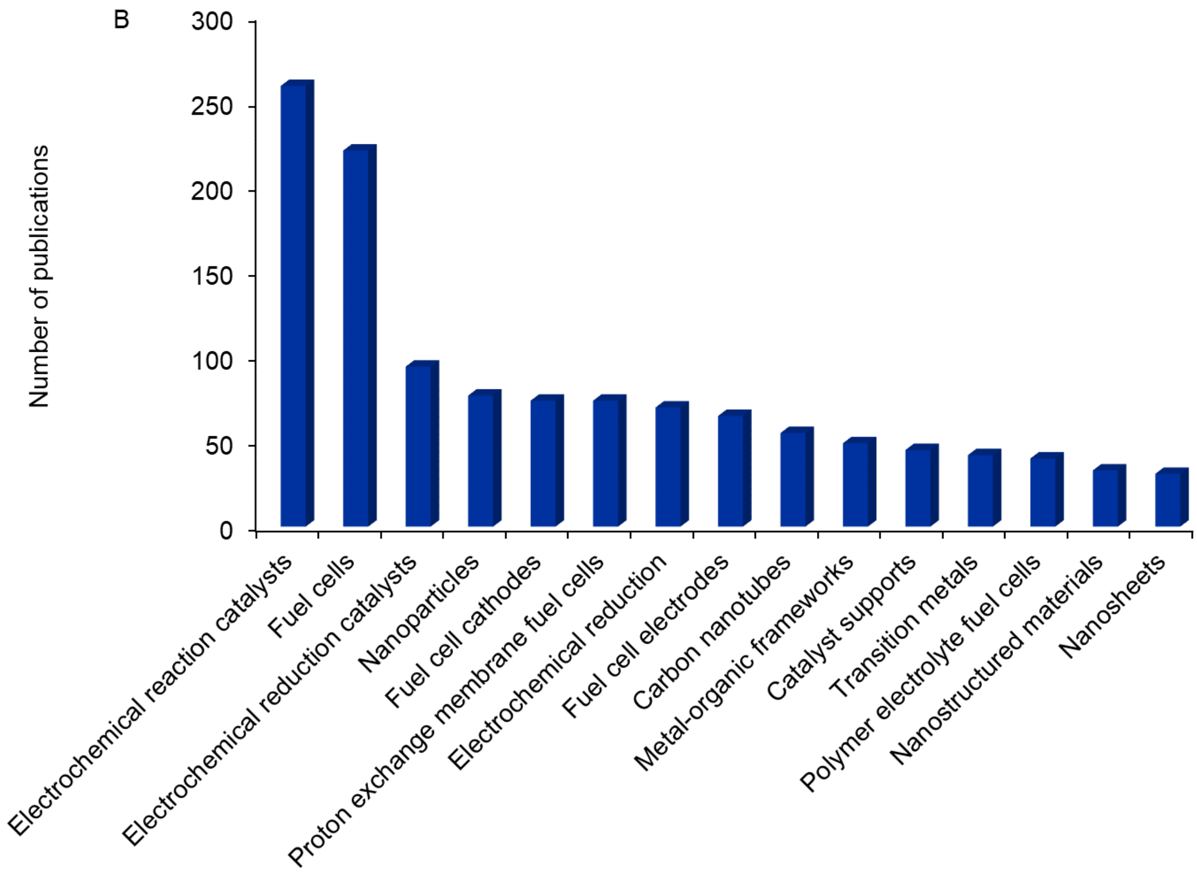


Figure 9. Human intelligence-selected fuel cell-related concepts in journals (A) and patents (B).

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 the energy and environmental problems. Most of the photocatalysts known till date either function under UV light irradiation or do 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 documents related to both photocatalysis and photo electrochemistry.

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. 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.

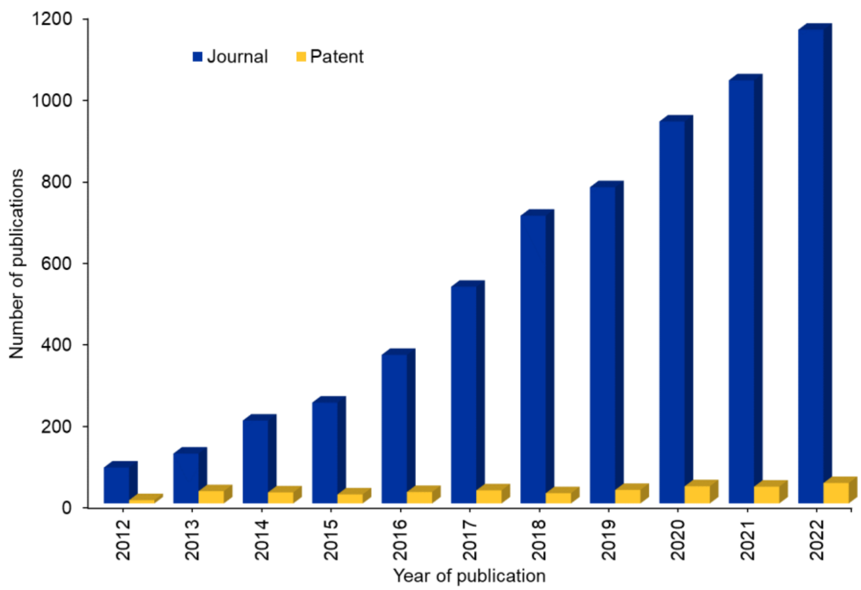


Figure 10. Year-wise number of publications related to photocatalysts

Figure 10 shows the number of publications 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.

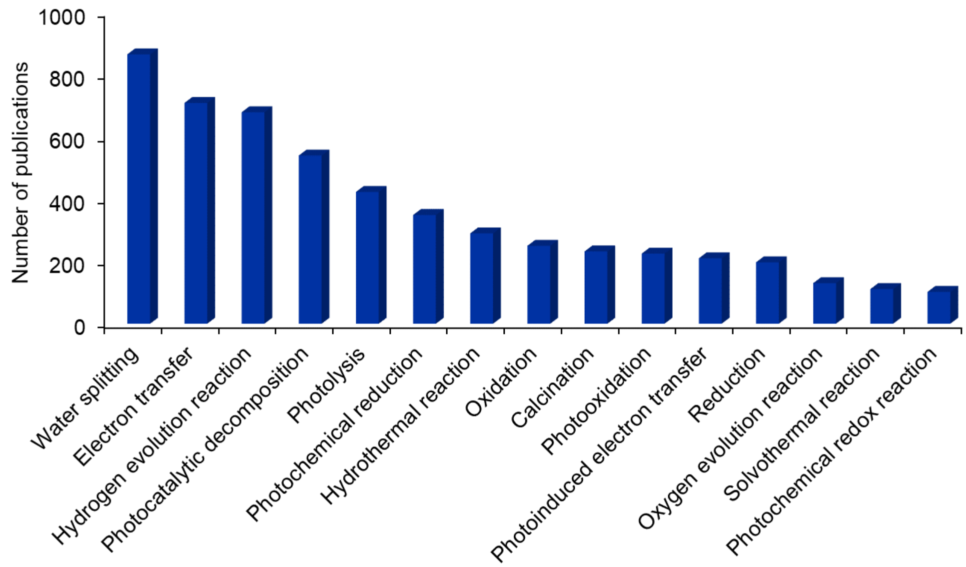


Figure 11. Top 15 reaction concepts to which photocatalysts are applied

The CAS Content Collection™ 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, photocatalysts are widely used in 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™ a list of the topmost used devices or parts of devices was generated and are listed in Figure 12. Photocatalysts are extensively fabricated as photocathodes, photoanodes, photoelectrochemical cells, followed by solar cells.

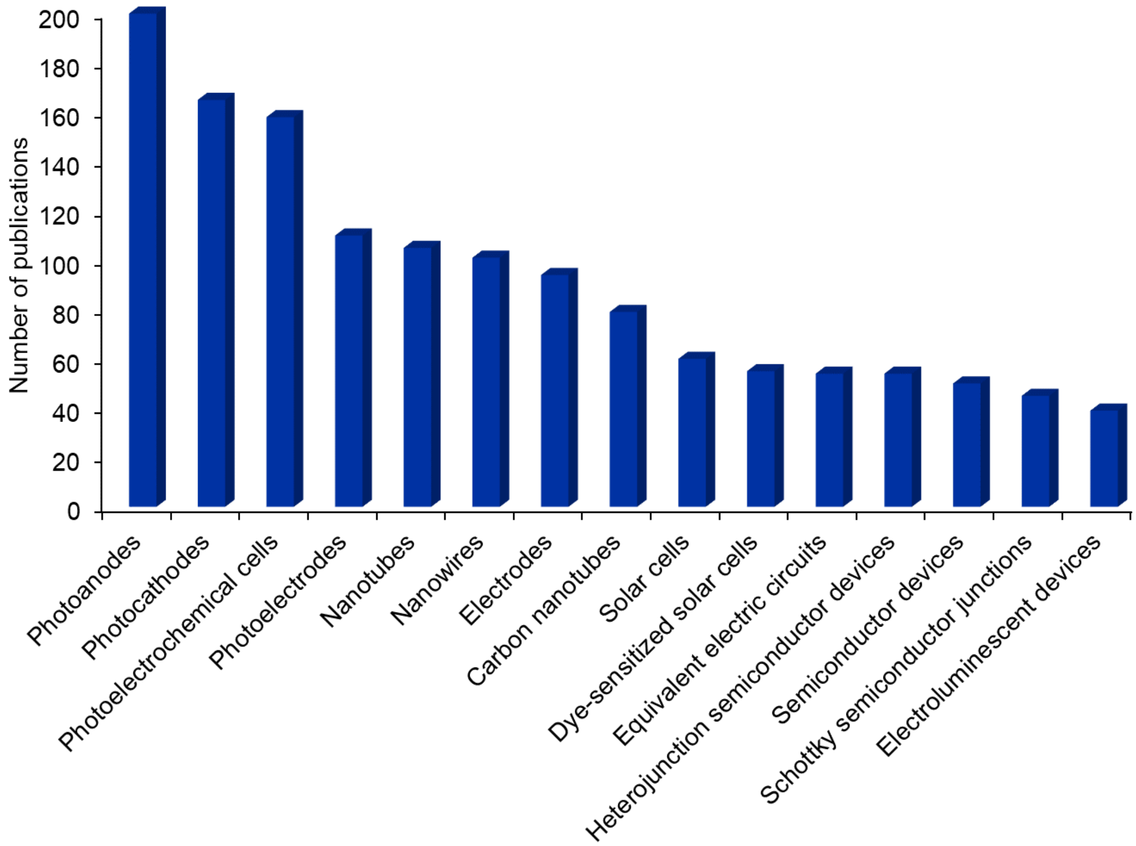


Figure 12. Top 15 device-based concepts using photocatalysts

Frequently Used Substances and their Growth Trend

The substances present in the documents were indexed in the CAS Content Collection™ according to their role. An analysis of the top substances with the catalyst role showed that 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.

The 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 it. 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 reporting 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.

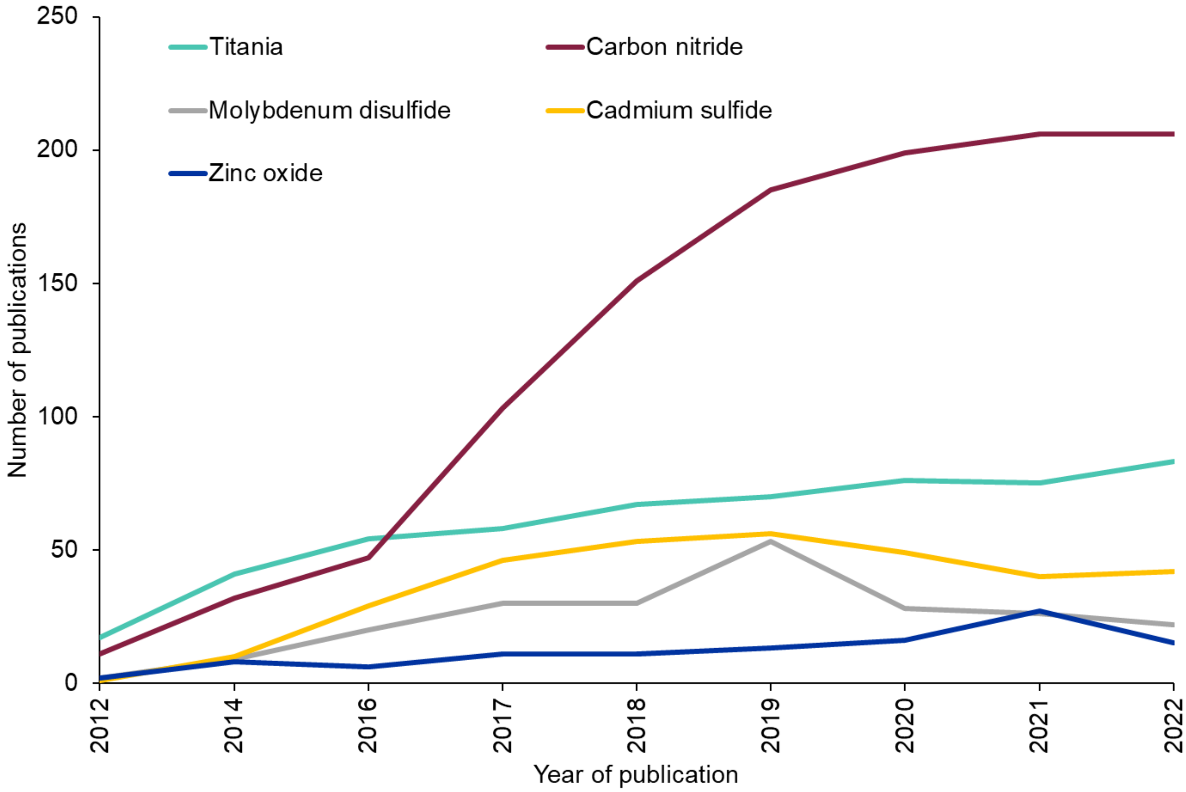


Figure 13. Number of publications using different photocatalysts in the last 11 years

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 2 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

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gas emissions, water pollution and human rights violations. Therefore, there is ongoing research to find alternatives to PGMs for greater overall sustainability.

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 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.

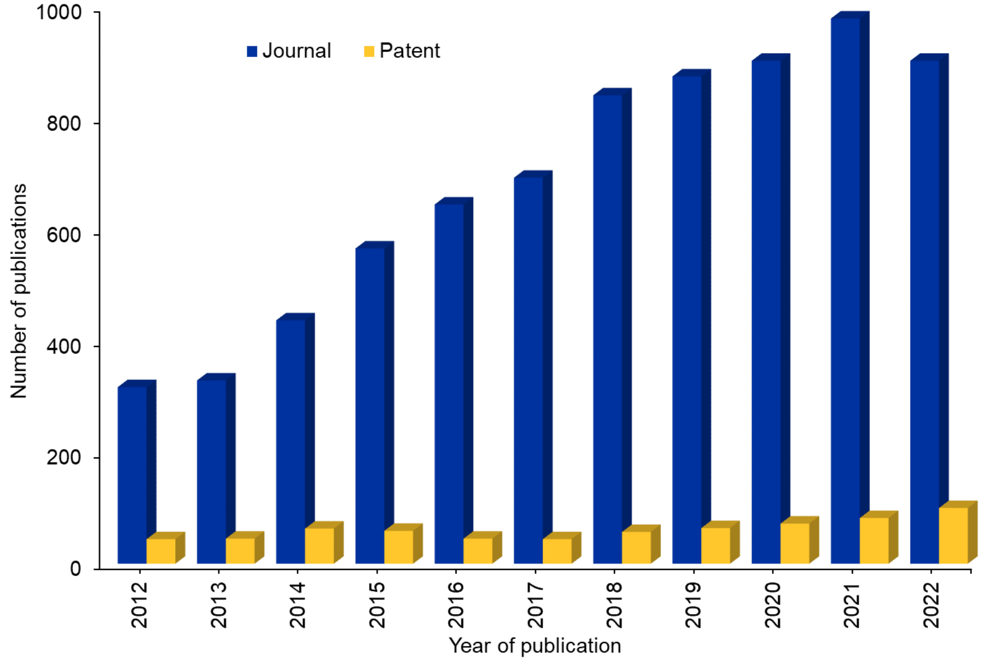

Figure 14. Annual number of publications in homogeneous catalysts among journals and patents.

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.[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.

The Mostly Used Substances

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 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] 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.

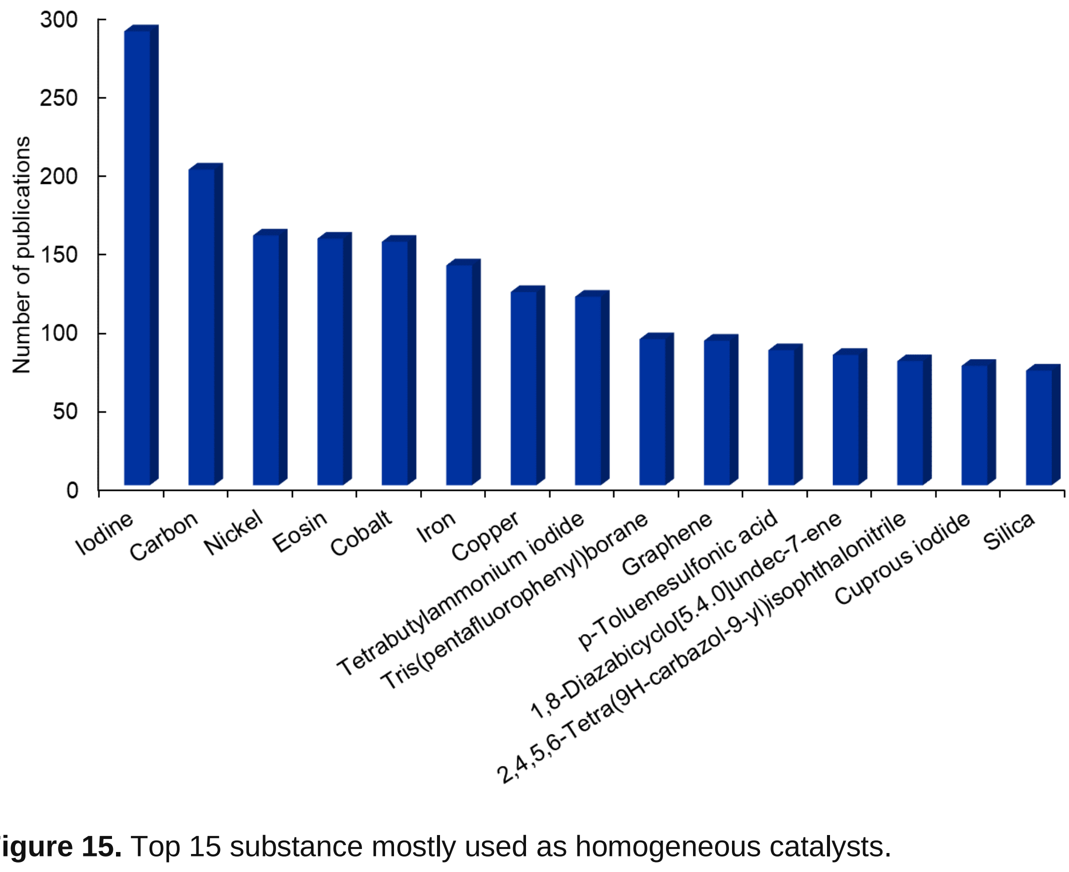

Figure 15. Top 15 substance mostly used as homogeneous catalysts.

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, and fungi), they are organic, biodegradable, non-toxic 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]

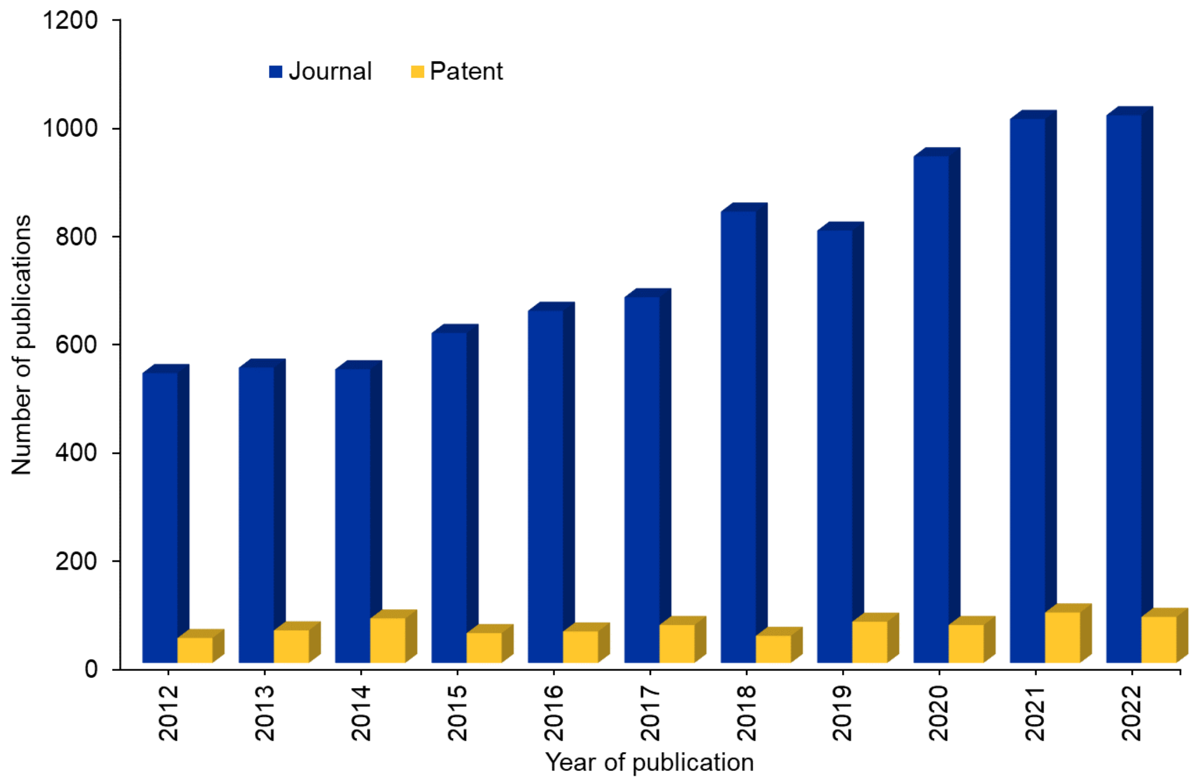

Figure 16. Annual publication trend of biocatalysts from 2012 to 2022.

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.

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 4.

Table 4. 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]

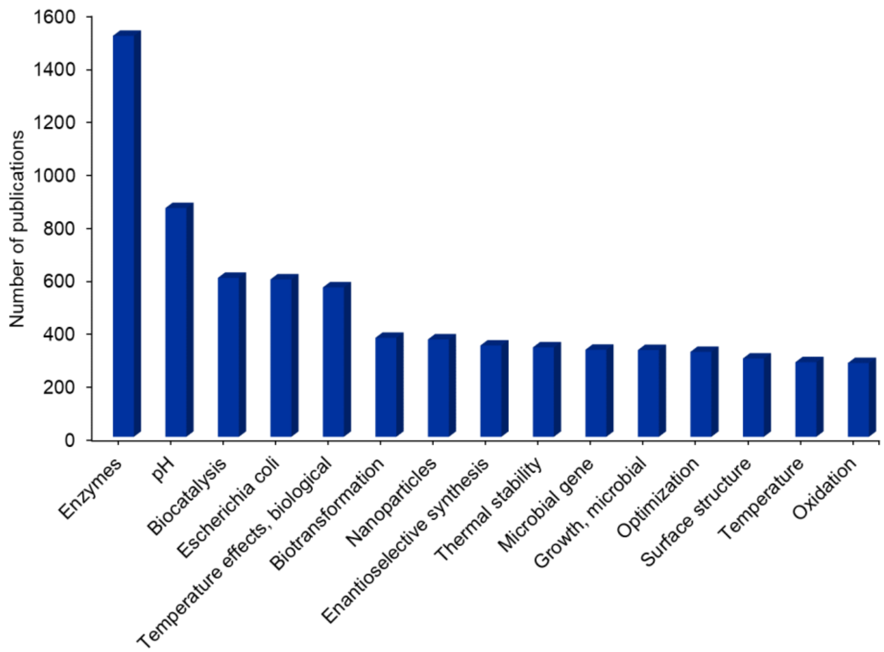

Figure 17. Top 15 concepts of biocatalysts in journals from 2012 to 2022.

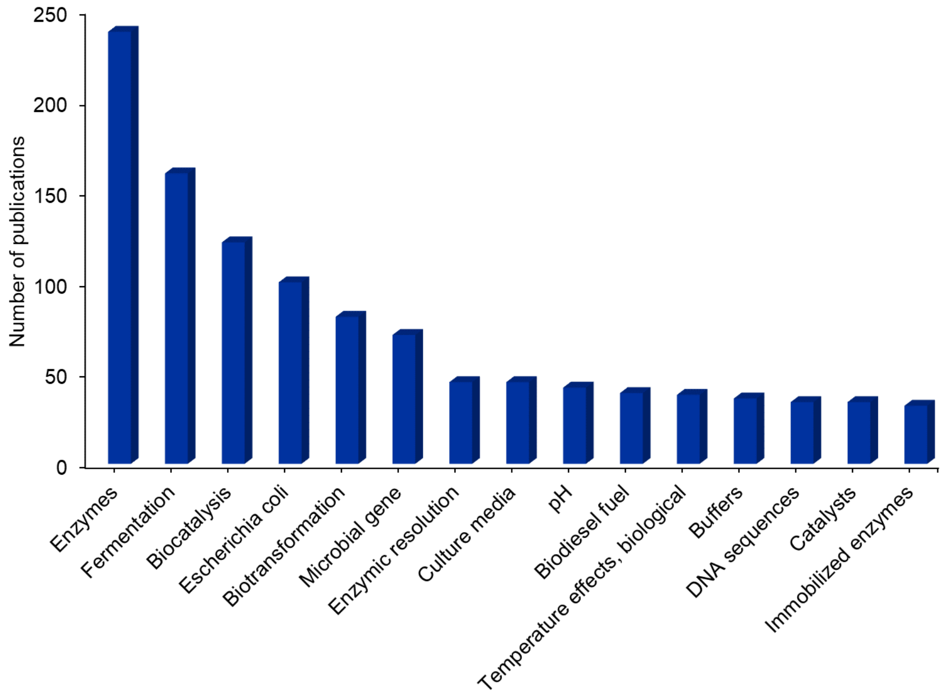

Figure 18. Top 15 concepts of biocatalysts in patents from 2012 to 2022.

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 are related to enzyme production, such as fermentation, microbial gene, Escherichia coli, Pseudomonos, mutation, encapsulation. Concepts such 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 catalyze various reaction (especially stereoselective/regioselective reactions), and polymerizations.

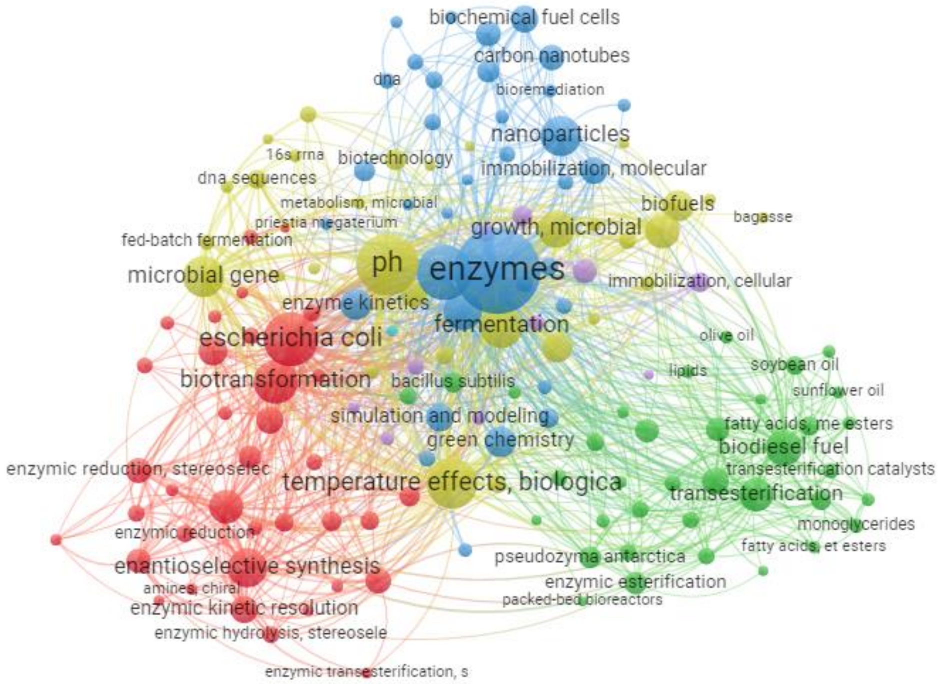

Figure 19. Biocatalyst 150 co-occurring concepts

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]

In Figure 20, triacylglycerol lipase and lipase 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.

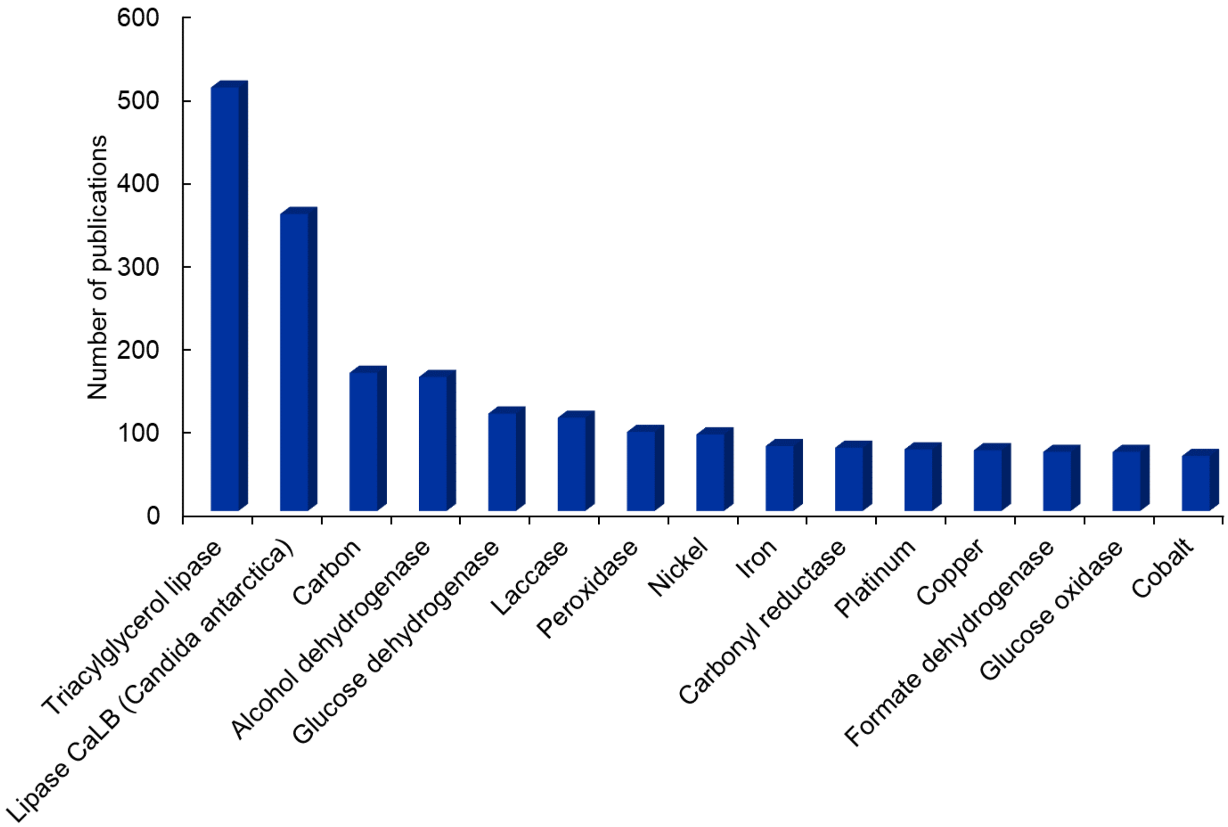

Figure 20. Top 15 substances mostly appeared in the field of biocatalysts.

Conclusions

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 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 materials continue 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.

Methods

This report used data from the CAS Content Collection™, 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).

To capture more specific data, four search queries of (1) Homogeneous catalysts; (2) Electrocatalysts; (3) Photocatalysts; (4) Biocatalysts are used to retrieve 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?)

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.

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