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A Comprehensive Review of Earth-Abundant Alternatives to Noble Metals

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ABSTRACT

Earth-abundant transition metals (EATMs), namely Ni, Fe, Co, Cu, and Mn, are exclusively low-priced and characterised by nonphaoticity and proneness in replacing precious or noble metals in the realm of advanced catalysis. Such wide chemical versatility gives them excellent activity and selectivity in a wide variety of green chemistry, renewed energy catalysis, and environmental remediation reactions. Advancements in the recent nanostructured design of catalysts, such as single-atom structures, heteroatom doping, heterostructure design, and amorphous materials, have significantly boosted the activity of EATM catalysts in reactions catalysed involving multi-metal water splitting, hydrogen evolution (HER), CO_2 reduction, and biomass valorisation, as well as numerous organic transformations. At the same time, biomimetic and molecular catalyst architectures have doubled efficiency and durability, and operando spectroscopy, coupled with computational catalyst screening, has increased the speed at which catalyst mechanisms are unravelled and materials optimised. Looking at comparative data against noble metal benchmarks, optimised EATM catalysts are capable of being competitive with or better than conventional ones in terms of activity, stability, and selectivity, making them critical towards scalable solar-to-fuel conversion and sustainable industry. An outline of recent developments, performance criteria and the evolving possibilities of application of the EATM catalysts in practical devices and processes is described, hence supporting its role in supporting a future of resources and environmentally friendly life.

Keywords: *Earth-abundant transition metals, sustainable catalysis, green chemistry, non-toxic catalysts, Fe Co Ni Mn Cu catalysts, water splitting, hydrogen evolution reaction, CO_2 reduction, biomass valorization, nanostructured catalysts, single-atom catalysts, heteroatom doping, heterostructures, bioinspired catalysis, operando spectroscopy*

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INTRODUCTION

The attention has shifted to pollution and climate change, and everyone is attempting to find ways to continue doing what they are doing without the situation getting any bad. Whereas other areas lie and are addressing the issue through a shift to a more environmentally friendly technology. Chemists are investing in what has been termed as green chemistry, which is quite simply a redesigning of chemical processes such that they cause less waste, consume less energy and avoid chemical processes that can be of harm to both the living things and the environment. A large portion of this mission entails catalysts. A catalyst, in simple words is a speed-enhancing material which aids in kicking off a reaction swiftly and simultaneously leaves itself unused [1].

It is basically out of the question to consider including noble metals in your long-term plans. Clean-tech alternatives have emerged in all directions, and they happen to be more desirable not only to society but to the planet as well. The noble metals, such as platinum, palladium and rhodium, have been a ready source for chemists due to their excellence at their jobs and can be found in fuel cells as well as certain luxury medicines. The issue is that they are expensive and limited, and their manipulation may even be poisonous [2, 3]. With clean-tech options coming on-line, there is no need to bet on these metals any longer. They are infrequent, environmentally destructive and simply are not sensible on a large scale.

This is the reason why scientists have resorted to metals found in abundance on earth, such as iron, nickel, cobalt, manganese and copper. They are ubiquitous in nature, much cheaper to make and way safer in general. In fact, big chemical industries such as ammonia production (the Haber-Bosch process) and synthetic-fuel production (the Fischer-Tropsch process) have already relied on these metals for decades [1].

Recent advances in nanotechnology allow scientists to reduce these metals to small particles or even a single atom, thereby rendering them way more effective. The new, nanoscopic variants of abundant metals on earth are more selective, active and stable. That creates opportunities in the area of clean energy (such as separating water to produce hydrogen), pollution remediation, and producing useful chemicals in a new manner [4].

Advances in catalytic science today suggest an especially promising pathway in the use of alloys, or, as they have come to be known, high-entropy alloys – compositions made of multiple species of metals that act in coordination within the same system [5]. When optimised, these systems can rival the performance of simple counterparts of a single metal. Their potential areas are the creation of clean-energy technologies, recycling technologies, and the construction of sustainable manufacturing processes [6, 7]. Despite these breakthroughs, there are a number of limitations that remain due to its catalytic nature; the catalytic components are often fast-wearing or even inert at an industrial scale. Researchers are therefore optimising design procedures, understanding the processes of functionalisation and coming up with strategies that will make these materials applicable to practical use in industries [8, 9].

Earth-Abundant Transition Metals: Overview and historical Context

This increasing demand for technologies that are catalytic, clean, cost-effective, and sustainable at the same time has led the scientific community to question metals with greater catalytic performance but that are also abundant, benign, and cost-effective. Other transition metals (i.e., iron (Fe), cobalt (Co), nickel (Ni), manganese (Mn), copper (Cu), titanium (Ti), vanadium (V), chromium (Cr), zirconium (Zr), niobium (Nb), and tungsten (W)) now are being pursued actively as meaningful substitutes to the traditional noble metals in catalysis. Together with the transition metals mainly found in the earth, they are generally referred to as earth-abundant transition metals (EATMs) that have the potential to transform chemical industries into green and affordable solutions.

Unlike noble metals, EATMs are distributed around the world, significantly cheaper, and, overall, less toxic. Their extremely adaptable electronic structures and the ability to cycle through several oxidation states make them suitable for redox reactions—one of the most basic applications in the area of catalytic science. This is a change that has not been restricted to the problem of material availability, but where it is necessary to revisit the principles of a sustainable chemical design, in theory. The created environmental impact is significantly less, which testifies to their appropriateness in the future, where eco-efficiency is still prominent [10, 11].

Definition of EATMs and their Classification

Earth-abundant transition 'Metals' is a general term, including all metals in the first row of the d-block and some typical second and third-row elements whose abundance in the crust of the Earth allows commercial exploitation on a large scale. The metals listed in this group are Fe, Mn, Ni, Co, Cu and others exhibiting physicochemical properties complying with the needs of sustainable chemistry and with the goal of scalability and affordability, two main requirements of emerging green technologies. Their availability in large numbers is therefore also comparable to the need of economic feasibility and expansion to larger numbers.

Metallic components of this group are characterised by high-level structural deformability and a high ability to tolerate heterogeneous coordination environments. This enables them to be involved in a wide variety of catalytic reactions, at one extreme by the simple electronic transfer reaction and at the other more involved bond-forming and bond-breaking reactions. In contrast to the noble metals, the elements have been able to complete them without, or with minimal dependence on rare and uneconomical stabilising species or harsh reaction conditions, a characteristic that has cemented their use in sustainable chemistry [12].

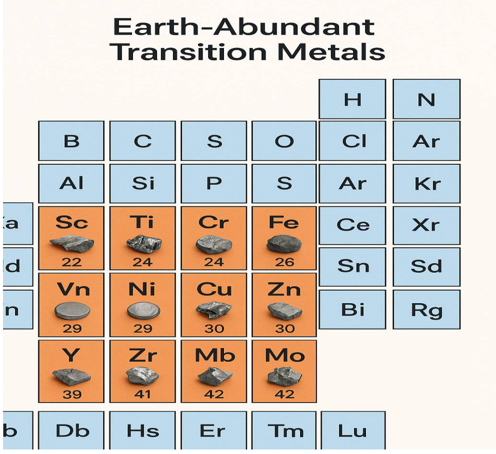

Fig.1: Earth-Abundant Transition Metals

The History of EATMs

Use of earth-abundant transition metals (EATMs) in catalysis started long before the twentieth century. An iconic application is the Haber-Bosch process of transforming atmospheric nitrogen and hydrogen gas into ammonia using iron-based catalysts, transforming agriculture by making it possible to produce fertiliser on a large scale and as such a foundation of contemporary chemistry. At the same time, the interest in the Fischer-Tropsch process arose, which uses iron or cobalt to turn gas mixtures of CO and H_2 (called syngas) into liquid hydrocarbons, resulting in synthetic fuels through coal or biomass [13].

Such a reaction was not only applied to colonial research severities but also upheld entire industries and subsidised hundreds of thousands of humans. Further, they showed that EATMs could meet the industrial catalytic requirements in case strategic design requirements were satisfied.

Later focus on the efficient and highly selective noble metals to produce smaller-scale syntheses put EATMs at the periphery of research and development over the next several decades. As the focus on ecological concern and the ecological and economic consequences of using noble metals has increased, the academic focus has also shifted to EATMs with their status as an environmental opportunity, as opposed to an industrial limitation [14].

Early Applications of EATMs and The Shift in Technology

In the current studies of catalysis, much research and literature have focused on the historic developments that formed the foundations of a defined field, and that research has been the subject of a nuanced discussion of research, development and commercialisation. The Haber-Bosch process and Fischer-Tropsch reaction belong to the most important landmark processes that took place. With improved nanotechnology, sophistication of computational modelling, less environmentally hazardous synthetic process and improved understanding of catalytic process, these discoveries can now be explained with more and heightened precision than in an era where this task was not possible.

The biggest developments in this regard include the scientific production of nanoparticles and nanocomposites using various types of metals. Migration to the nanoscale is to a large extent favourable in many aspects, such as surface activity, selectivity and electron-transfer performance. As a consequence, the materials are capable of competing with noble metals in reactions that comprise hydrogen evolution, oxygen reduction, conversion of carbon dioxide, and organic transformations, including reductive amination and hydroboration [15, 16].

A more recent turn away, bi- and trimetallic architectures, also called systematic or systematically addressed synergistic catalysis, have demonstrated that the selective collaborative variations of two or more ubiquitous metal components can induce a greater catalytic effect as compared to the discrete components [17]. Such multi-metallic assemblies can also be useful in electrocatalytic applications and, specifically (in this case), in environmental remediation where each step of the reaction leads to optimisation.

In parallel, the availability of green-chemistry-based strategies toward synthesis has enabled new methods of preparing such catalytic materials under easily reproducible, mild, environmentally non-hazardous conditions, most often at room temperature and in non-polar solvent-free conditions. Such a development of methodology widens the carbon footprint of the catalyst generation and makes processes less sensitive to delicate substrates, e.g., biomass feedstocks and pharmaceutical intermediates [18].

In short, transition metals of earth-abundant (EM) character have now grown to become more than a default answer but a modern-day catalytic standard. A marriage of contemporary technological innovation and emerging industrial demands, combined with the feasibility of high-throughput synthesis, aligns such systems with the heart of next-generation chemistry, a field that needs always to balance performance with economic and environmental responsibility.

Catalytic approach of EATMs and the Advancements

The area of earth-abundant transition metal-based catalysis has been an area of research since its inception, but like research in other catalytic fields, it has moved over the last two decades to become more of a mechanism-based discipline. This is possible through the highly convergent nature of nanoscience, surface chemistry and computational modelling that present a comprehensive control over the structure and compositions of catalysts and distribution of their active sites. The ultimate goal is to eliminate economically untenable noble metal dependence and find functionally equivalent but more sustainable alternatives based on abundant elements (such as Fe, Co, Ni, Mn, Cu, Ti, V, Cr, Mo, and W) and maintain activity, selectivity, and long-term stability under realistic conditions at the same time [19, 20].

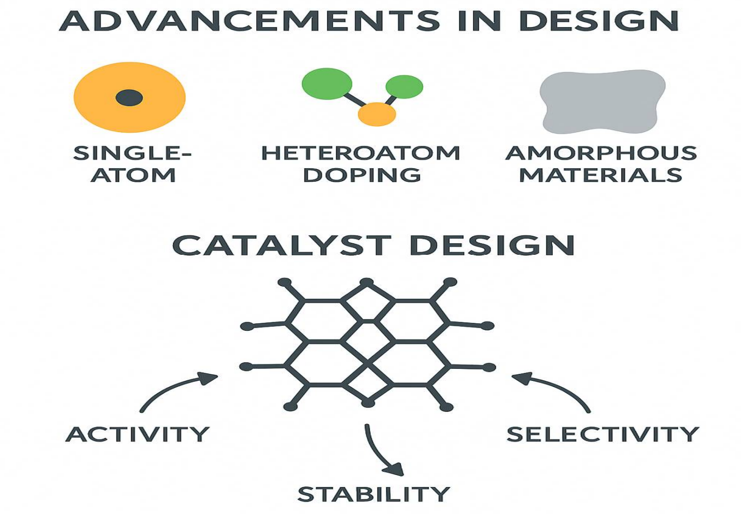

Fig.2: Advancements in Catalyst Design

Synthesis, Properties, and Mechanistic Relevance of Nanocatalysts

Nano-catalysts made of earth-abundant metals form the basis of a fundamental type of material in modern green chemistry. Greater surface-to-volume ratios make it more convenient to expose catalytically active sites, thereby leading to the increases in reaction rates at lower quantities of metals than those associated with bulk materials. In addition to having a smaller particle size, the dimensional nature of the nanoscale also develops quantum and surface effects that can, in principle, tune adsorption energy and reaction pathways [21, 22].

Classical synthetic procedures allow the positioning of highly defined sizes, shapes, and crystal orientations of nanoparticle surfaces, all of which have a direct effect on the catalytic activity. As an example, the exposed high-index facets of nanoparticles of nickel and cobalt have been shown to increase the reaction rates of the hydrogen evolution reactions and those of oxygen evolutions because optimum intermediate binding energies are optimised [14]. At the same time, the reactivity in oxidative and hydrogenative processes of iron and manganese nanorods, nanoplates, and hollow spheres depends on available facets [18].

The development of green synthetic approaches is also becoming central to the research as more emphasis is paid to extracts of vegetative tissue, renewable solvents, and electrochemical manufacture at ambient temperatures in order to reduce the impact on the environment without loss of exquisite control over the nanoscale structure and form [23]. These methods prove very beneficial when making large-volume catalysts, where sustainability is of utmost consideration.

Mechanistically, nanocatalysts tend to act in heterogeneous mechanisms whereby substrate molecules are adsorbed on a metal surface, where they are transferred electrons or atoms and finally desorbed as products. Another factor that allows lower activation barriers and facilitates the presence of alternative mechanistic pathways that are not, in reality, available in macroscopic materials is the large number of low-coordination sites (i.e., edges, steps, and vacancies) per unit volume at the nanoscale in comparison to bulk.

Single-Atom Catalysts (SACs) and Supported Catalysts

The rise of single-atom catalysts (SACs) made of earth-abundant metals in the field of catalytic science can be considered as one of the most significant breakthroughs in the design of effective catalytic systems. SACs consist of single metal atoms anchored to suitable substrates that are preferably nitrogen-doped carbon, metal oxides or layered. SACs have outstanding activity at very low loadings due to optimal utilisation of metal atom resources. This is of particular importance to the scarcer but abundant transition metals, like molybdenum and tungsten.

It is possible to systematically optimise the local coordination environment (planar, tetrahedral or octahedral) to reproduce active sites similar to enzymes. Take one example of the Fe-N_4 motifs incorporated in carbon matrices as a high-performance oxygen reduction reaction, as they stabilise key intermediates and multi-electronic paths [24]. At the same time, cobalt single atoms on the surface of carbon that contains defects were also used in selective hydrogenation of nitriles, where the active sites are uniform and reduce the occurrence of side reactions [25].

Another important type is catalysts based on nanoparticles, of which earth-abundant metal nanoparticle catalysts typically have conductive, porous or chemically active supports. Such substrates prevent particle agglomeration whilst also being involved in catalytic cycles via electronic interactions, sometimes forming metal-support interfacial sites of unusual reactivity. Nickel nanoparticle auxiliaries coated with titanium oxide (TiO_2) have been found to completely increase the catalytic conversion of CO_2 and hydrogen. The mechanism of this augmentation is in having an optimised rate of electron transfer on the surface, as was shown by a recent experimental result presented by Porter et al. [26].

Design of Ligand, Role of Doping and Synergistic effects of EATMs

Systematic addition of exogenous crystal atoms into the crystalline lattice or surface, often called doping, is an area of high potential interest in allowing control of the electronic structure of earth-abundant catalysts. It should be mentioned that a change in adsorption energies of intermediates in oxygen evolutions can be tuned by the d-band centre shifts that occur in cobalt-based catalysts by replacing iron [27]. In parallel, it is shown that nitrogen- or phosphorus-doping of carbon-outfitted iron catalysts enhances conductivity and electron density at active sites, respectively accelerating turnover frequencies in the field of hydrogenation and oxidation of compounds [28].

The introduction of different metals since both metals within bimetallic or polymetallic alloys has particularly strong synergistic doping effects, either because the different metals' conjoint presence formed new active centres or because they altered the electronic and geometric characteristics of individual metals. Another carefully thought-out model is the NiFe alloy system of water splitting, wherein water splitting is catalysed by iron sites that activate oxygen evolution and nickel sites that activate hydrogen evolution; the interface can act synergistically to both reactions [29, 30].

Homogeneous - Ligand design: A design of ligands is usually linked to homogeneous catalysis but has been extended to heterogeneous catalysis as well. Organic or inorganic ligands custom-ligated to supports allow specific design of the steric and electronic surroundings of active sites, and selectivity and stability can thus be improved [31]. As an example, easily synthesised pincer-type ligands immobilised on porous supports can stabilise earth-abundant metal centres against aggregation or oxidation to allow their long-term continuous catalytic use under otherwise demanding conditions.

Electronic Structure and Mechanistic Principles of EATMs

State-of-the-art spectroscopic techniques, combined with density functional theory (DFT), are of critical importance to extend the basis of a rational approach to catalyst design. Variable oxidation states and the ability to undergo redox reactions are highly correlated with the reactivity of earth-abundant transition metals and occur under relatively mild conditions. At the same time, numerous mechanistic catalytic processes relying on molecular hosting rely on the multi-electron, multi-proton transfer pathways that are highly dependent on the surrounding coordination structures and electronics [3, 6].

As an illustration, one can compare the two opposite paradigms of Mn-, Fe-, Ni- and Co-based oxidation and hydrogenation systems whereby the catalytic process involves high-valent metal oxo species and involves the use of tightly bound and stabilised hydride species at the metal sites or at the metal-support interfaces [6-6]. A better understanding of these mechanistic pathways allows selective catalyst tuning; such tuning may consist of the replacement of ligands, the specific engineering of supports, and the production of targeted defects to maximise catalytic turnover.

Descriptors of the electronic structure (charge-density distribution, d-band centre and projected density of states (PDOS)) have been shown to be useful in explaining trends in catalysis. The high-throughput screening with these parameters, therefore, can be used, alongside machine-learning algorithms, to allow the swift identification of promising materials before they are even synthesised [19].

Applications of EATM Catalysts in Green Chemistry

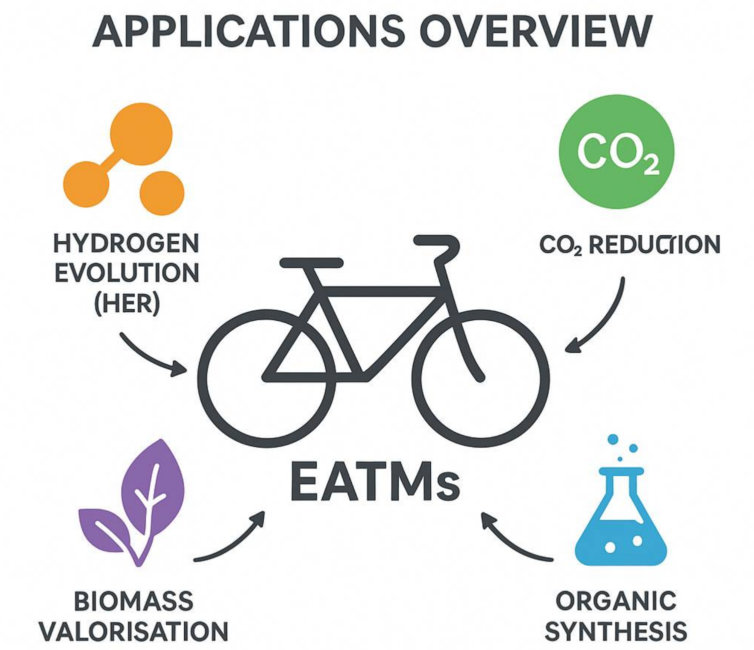

Fig.3: Overview of Applications of EATM Catalysts

Earth-abundant transition-metal catalysts (EATM catalysts) have taken the central stage in current green-chemistry applications, underpinning such processes as sustainable energy conversion, eco-friendly production of chemicals, and modern recycling technology. These catalytic platforms reduce the economic cum environmental burdens significantly by replacing the limited and expensive noble-metal-based systems with first-row transition metals, Fe, Co, Ni, Mn and Cu, and their compounds, in particular. Their coordination environments are easily tuned, and the oxidation states are extensive and variable, and their structural flexibility also allows the catalytic performance of a wide variety of transformations germane to energy, industrial and environmental remediation processes.

Transformations Related to Energy

Hydrogen Evolution Reaction (HER) & Splitting of Water

Under the context of renewable hydrogen production, catalytic materials based on the abundant earth-based metals, i.e., Fe, Co, Ni, Mn, and Cu, have also been reportedly demonstrated to rule the roost in terms of their performance in the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Such forms of catalytic systems are mostly synthesized in the form of either chalcogenide, phosphide, nitride, carbides, or layered double hydroxides, which imparts some of them with a special catalytic stability, efficiency, rate of transferring electrons, and resistance under acidic and alkaline solutions [23, 29]. These materials are a realistic possibility regarding the green hydrogen production, because they enable efficient and scalable mechanisms of split water and directly contribute to decarbonisation efforts.

Oxygen Evolution Reactions and Oxygen Reduction Reactions (OER/ORR)

Fuel cells and metal-air batteries continue to have the generation of stable and active catalysts as one of their main challenges. High-entropy alloys and metal X-ides (borides, carbides, pnictides, and chalcogenides), based on transition metals, have desirable characteristics regarding conductivity, chemical stability, and deactivation resistance, which therefore bypasses the use of platinum-group-metal-based catalysts. The usage of dopants or taking advantage of synergetic activity of numerous active places additionally increases the OER and ORR tasks; in certain cases, these strategies reach the same or even improved performance as compared to the noble-metal standards [36, 37].

Electrocatalysis for Ammonia and Production of Fuel

At ambient conditions, electrocatalytic ammonia production is a clean alternative not only to the energy- and carbon-intensive Haber-Bosch scheme but also to hydrogen-based ammonia synthesis. Experimental studies published in recent years show that addressable single-atom catalysts, and nanostructured catalysts, in particular, with Fe, Co, and Mo implanted in them, purport to exhibit promising nitrogen-reduction activities and selectivity [32]. At the same time, development is underway of carbon-neutral synthesis of fuels via an electrochemical process using CO_2 or biomass-based starting materials.

Organic Synthesis and Industrial Process of EATMs

Reductive Amination

The carbonyl compound reduction amination is part of the foundation of the pharmaceutical and fine-chemical synthesis. Fe, Co, Ni, Ti and Zr catalytic processes have proved to be more efficient in carrying out this transformation than the conventional processes, therefore limiting waste production and annulling the use of toxic stoichiometric reductants [22].

Hydrosilylation and Hydroboration Reactions

Hydroboration and hydrosilylation are additive reactions in that they give the organosilicon and organoboron products, respectively. Traditional catalytic systems use precious metals but first-row transition metals Fe, Co, and Ni can all enable the activation of silane and borane without the noble-metal analogues of such [16]. These reactions are atom-efficient methods to highly functionalised derivatives with utility in materials chemistry, agrochemicals and medicinal chemistry.

C–H Activation

Direct functionalisation of C-H bonds forms part of the cornerstones of modern synthetic chemistry, which allows the intricate synthesis of complex molecules without the required modification of reagents. This development is towards greener electrophilic reagents that arduously employ iron, cobalt, and nickel catalysts that make regioselective and chemoselective transformations possible within relatively mild conditions [14, 24].

Carbonylative Transformations and Asymmetric Hydrogenation

Carbonylative coupling conditions, as well as asymmetric hydrogenation, find wider application with non-precious metals that are abundant in earth, thus extending the applications of non-precious metals into asymmetric synthesis and maintaining high enantioselectivity in pharmaceutical manufacturing [22-27].

Plastic Depolymerization and Recycling

Effective plastic recycling is gaining more and more prominence in the present-day environmental sustainability debate. The existing research studies are targeting catalytic mixtures that include Fe, Co, and Ni to favour an exclusive separation of polyesters and polyolefins under comparatively lower temperatures and pressures [9]. These processes are in line with circular economy models and can, therefore, recycle waste plastics to monomers or higher-value intermediates.

Environmental catalysis and photocatalytic uses

Elimination of contaminants and decarbonization of CO_2

The opportunities available with earth-abundant transition metal catalysts currently span a broad arena of well-established synthetic and energy-related applications, also including environmental remediation. Some of the representative benefits entail purification of water, breaking down of pollutants, and photocatalytic reduction of CO_2. One of the most interesting examples has to do with bifunctional catalysts that can harbour reductive and oxidative pathways [38, 22]). As an example, one piece of evidence involves the use of photocatalysts built of Fe or Co on a semiconductor to concurrently solve the astronomical pollution of the environment by destroying organic pollutants and providing solar fuels by splitting water.

Comparative Performance of Earth-Abundant Transition Metals to Noble Metals

Replacing noble-metal catalysts with so-called earth-abundant catalysts can be viewed as a critical paradigm in modern catalysis driven by the need and desire to be environmentally benign, cost-effective, and resource-efficient. A formal case study of activity, selectivity, cost-effectiveness, durability and scalability illustrate situations when earth-abundant catalysts match, or surpass, the performance of noble metals, and also where considerable challenges remain. The current discussion takes into consideration exemplary case studies in an attempt to explain these differences.

Catalytic Activity and Selectivity

Activity and selectivity are interconnected elements that are usually highlighted when considering a catalytic system by scholars. In the literature of today, there are many summaries of architectures which have been encountered that perform similarly to (and even outclass) their noble metal analogues – especially in discrete processes.

In a recent survey, Ghoshal and Sarkar [11] characterised a single atom via a bimetallic catalyst (VRu(g-CN)) in which the second-row transition metal vanadium replaces ruthenium in the reduction of carbon dioxide. Supportive DFT studies reveal that VRu(g-CN) has a high value of Faradaic efficiency of over 99 per cent, improved stability and decreased hydrogen production as compared with Ru 2 g-CN. The results present the ability of both earth-enhanced and noble metal synergy to perform better than the noble metal.

Basing their study on high-throughput computational screening, Wang et al. [37] found the new active catalyst Ni_3Mo, and this active material shows a reasonable activity in catalytic dehydrogenation of alkanes to substitute the active portion, i.e., platinum, of a certain petrochemical process. The Ni_3Mo possessed a higher ethylene selectivity and stability as compared to the industrially relevant conditions and was better than Pt in the catalytic efficiency and operational stability.

In water oxidation catalysis, amorphous mixed-metal oxides made of Fe, Ni and Co have been demonstrated by Smith et al. [32] to have oxygen evolution reaction (OER) activity rivalling that of IrO_2 and RuO_2, often used as standards. Tunability in the composition and structure of these amorphous materials can allow these materials to be optimised to have catalytic properties independent of rare, expensive noble metals.

Cost Analysis

The commonly used metals found on earth (Fe, Ni, Co and Mn) tend to be less costly than Pt, Pd, Rh and Ru. However, the short-term economic benefit heavily relies on the situation of application as well as the level of production. In their article on catalytic efficiency in organic synthesis, Komarova and Perekalin [17] emphasised that catalyst consumption by weight features a negligible part of overall reaction expenditure, as the costs involved in substrate, reagent and purification expenses prevail. As a result, significant savings are realised mainly on large-scale processes or precious-metal-intensive processes.

The middle-ground strategy is a call on the so-called hybrid noble-earth catalysis systems. Xing et al. [41] synthesised nanosheet arrays of OH_2 Co Co-grafted 2-3 nano-Pt ultrafine nanoparticles, which showed the same hydrogen evolution reaction (HER) activity as the pure Pt with a significant reduction in the consumption of noble metals. Li et al. [19] reported similar results, as they synthesised hydrated nano-Ru-decorated cobalt carbonate hydroxide (CoCH) nanowires that displayed improved kinetics of the HER in alkaline conditions owing to synergistic metal support interaction. These studies reveal the possibility of keeping the high catalytic activity and reducing expenses on materials by adding minor levels of noble metal.

Operational Stability and Durability

High stability in the face of thermally intensive, chemically challenging and electrochemically stressful environments is a primary requirement of industrial catalytic systems because the catalytic materials are subjected to such conditions. There is a substantial literature that has already recognised that, under these conditions, the many earth-abundant catalysts, especially those used in acid water oxidation, will suffer significant decreases in activity due to dissolution or structural degradation. Contrastingly, Li et al. (2020) conclude that composites of Ni, Mn and Sb oxides have high OER activity even in the presence of acidic conditions, thus closing the gap between the stability that traditionally exists between these solutions and noble-metal catalysts.

Meanwhile, single-atom catalysts (SACs) are developments of particular interest in parallel. SACs based on Fe, Co, and Ni were investigated, and their superiority was emphasised as compared to the increased atom economy, uniform active site and coordination environment [22]. This will increase activity and stability and allow earth-abundant catalysts to overcome deactivation under challenging reaction conditions.

The scale and our industry relevance

On an industrial scale, cost-effectiveness requires an overlap in evaluating inherent reactivity and designing the catalytic system that exploits both earth-common metals as well as noble ones. Others involve scalability in catalyst synthesis, cost of synthesis, reproducibility and compatibility with integration. It has been interesting in this regard that the N3Mo and the Fe-Ni-Co oxide structural groups have been synthesised using reliable and cost-effective processes that can be deployed in large-scale chemical production and in the electrolysis procedures. However, compared to the other systems, such systems may perform poorly in terms of catalyst recovery and the ability to maintain their stability of operations without the need for frequent regeneration and replacement of the catalyst.

Hybrid catalysts are therefore an intermediate solution towards commercialisation in that they couple a relatively small proportion of noble metal species into an earth-abundant scaffold. This design permits the concurrent utilisation of high catalytic performance, stability, and low price, which is especially suitable in electrochemical fuel cells, water electrolysers, and large-scale carbon dioxide conversion processes.

Challenges and Limitations of Earth-Abundant Transition Metal Catalysts

EAMs in transition-metal catalysis Have EAM-based transition-metal catalysts become an appealing paradigm towards substituting comparable noble-metal analogues in energy conversion, organic synthesis, and environmental remediation? They are cost-effective by virtue of low material costs and their prevalence, and they may overcome the performance constraints that are inherent in classic noble-metal catalysts. Despite major advancements in synthesis and catalyst design, however, there remain major obstacles to overcome, both material- and mechanism-related and, more globally, in terms of workability and scalability.

Stability and Durability

One key drawback of EAM catalysts, especially of first-row transition metals like Fe, Co, Ni and Mn, is that they are not as stable at an operating condition when compared to noble-metal analogues. Whereas noble metals like Pt, Ru and Ir can stay without substantive changes in activity and resistance to corrosion over long times, oxidation, leaching or reconstruction of the reaction surface often occurs with many EAMs. In particular, the effect is relevant to oxidising environments, like the oxygen evolution reaction (OER) in water splitting and high-temperature oxidative dehydrogenation.

As an example, the initial active Fe- and Co-based oxides can be dissolved or passivated to less active phases in acidic or alkaline conditions and hence turnover frequency and long-term efficiency [37]. Sintering, phase changes or the development of inert layers of catalytically inactive surface deposits are often considered to be the cause of the loss of catalytically active sites. Surface passivation strategies, heteroatom doping, and encapsulation in stable matrices have all been found to reduce such problems [7], but in general add further complexity and can even sacrifice intrinsic catalytic activity.

Activity and Selectivity

Although the performance of earth-abundant metal (EAM) catalysts has been shown to exploit many noble metal advantages, there remains the major shortcoming of high selectivity and turnover rates associated with the noble metals. Fe- and Ni-based materials used to convert CO_2 result in the formation of mixed products in CO_2 reduction, including CO, H_2, and formate, instead of a product with high Faradaic efficiency. Similar trends can be found in cross-coupling transformations, where it is common to find that EAMs require higher loading levels, extended reaction conditions, or higher reaction temperatures to perform comparably to Pd- or Rh-based catalysts; this may result in undesirable side reactions, inefficiency with atom economy, and more involved purification [14].

Also, functional group tolerance is less broad, restricting their application in the production of advanced molecules. A catalytic cycle with many steps may include thermodynamically competing intermediate steps and thus low selectivity of the products. Hydrogen evolution reactions (HER), Co- and Ni-based catalysts may show hydrogen adsorption of energies that adversely affect the trade-off between turnover rates and prolonged lifetime. Considerable flexibility in the approach to improving selectivity exists, with many methods being available, including ligand design, support tuning, and modification of the coordination environment, although in the latter case, it may be necessary to optimise a large number of variables [44].

Mechanistic Complexity

Earth-abundant metals (EAMs) show an extraordinary tolerance to enter into several redox states in cycles, thus catalysing a wide range of redox transformations. This naturally broad reactivity of these regimes of reactivity makes rational catalyst design problematic since it is challenging to control where oxidation-reduction will take place prior to synthesis. This leads to the case where the EAM-based catalysts often work through one-electron radical processes that give rise to very reactive intermediates which may be attacked by side reactions or irreversibly poison the catalytic surface.

Two of the most utilised in situ and operando methods of probing oxidation-state changes during the dynamic processes of catalytic reactants in the fast-growing realm of modern research are suggested by the acronyms XAS and EISD, namely, x-ray absorption spectroscopy and electrochemical impedance spectroscopy [42]. An example of such modes of investigation being useful is the recent report of a fast structural rearrangement observed in the course of NiFe layered double hydroxides catalysing the OER. However, mechanistic understandings brought about by such observations tend to be system-specific; thus, they do not usually allow the development of universally applicable principles of design. In this case, the process of optimisation should be carried out individually.

Industrial and Practical Barriers

Industrially, there are some non-intrinsic limitations on the scalability of electrochemically active machinon (EAM)-based catalysis. A significant percentage of the homogeneous EAM complexes are very air sensitive and are affected by moisture, and inert-atmosphere work procedures must be used, which increases the cost of operational expenses. Catalyst separation and recycling efficiencies are also weak in these systems, especially against those that are water-soluble [1].

In addition, integration with existing industrial infrastructure would form a huge impediment. Years of process optimisation have given noble metals advantages over methods often necessitating changes in reactor design or changes to operating parameters based upon an EAM. Also, commercial availability of the optimised ligand and pre-catalyst libraries is scant [5].

As much as EAMs offer lower costs per unit of mass compared to the noble metals, the fact that they have low turnover figures, shorter lifetimes of catalysts and mandatory replacements may eat into their cost benefit. By extension, Docherty et al. (2017) asserts that economic feasibility needs to be determined using the entire holistic model that combines the cost of the catalyst and the catalytic performance of the operational operation.

7.0 Future Perspectives and Opportunities

Recent research on earth-abundant transition-metal (EATM) catalysts holds enormous potential to expand the generation of green energy, clean, environmentally friendly chemical synthesis, and environmental remediation. To a specific degree, the focus was placed on manganese-, iron-, cobalt-, nickel-, and copper-based water oxidation and general water splitting systems, reactions which, in the case of the achievement of both economical and efficient performance, would enable large-scale solar-to-fuel conversion and renewable hydrogen production [12, 132, 38, 44].

One notable opportunity facing modern catalytic chemistry is the methodical synthesis of biomimetic and molecularly constructed catalytic platforms that have the same catalytic proficiency that accompanies natural catalytic assemblages, like the photosynthetic water-oxidising complex [20]. The most recent developments in the area capitalize on the multifaceted approach, i.e., the next-generation nanostructuring methods, heteroatom doping, heterostructured designs, among others, to increase catalytic performance, stability, and selectivity [8, 17].

There is also parallel development in the direction of amorphous and single-atom catalytic moieties, which offer access to very high active-site densities with tunable electronic properties, which could deliver even better performance than crystalline analogues in terms of both activity and stability [10, 21].

In addition to their usefulness in energy conversion, increased attention is now being focused on the use of EATM catalytic systems as a platform technology to carry out biomass valorisation and production of green chemicals due to their intrinsically low cost, high efficiency and multifield flexibility [41]. The current literature would hence be focused on improving the selectivity of the reactions and increasing the stability of the catalysts at thermally relevant temperatures.

In the nearest future, it is expected that EATM catalytic entities coupled with more versatile and bifunctional architectures, which can carry out multi-reactions in parallel or otherwise work in a complementary fashion, will give rise to next-generation energy storage and conversion technologies [35, 36]. It is anticipated that by using the latest synthesis methodologies and operando spectroscopic diagnostics, combined with high-throughput screening and the use of machine learning, even more complex catalytic systems can be discovered, optimised and brought to commercial uses much faster [39, 40].

CONCLUSION

The development of earth-abundant transition metal (EATM) catalysts represents a significant advancement in sustainable catalysis and modern Green Chemistry. Catalysts based on metals such as iron, cobalt, nickel, manganese, and copper provide cost-effective and environmentally friendly alternatives to traditional noble-metal catalysts. Their wide availability, lower toxicity, and strong catalytic efficiency make them highly suitable for key technologies including water splitting, hydrogen generation, biomass conversion, and activation of inert chemical bonds.

Recent progress in nanostructured, amorphous, and bifunctional catalytic systems has further enhanced the activity, selectivity, and operational versatility of EATM catalysts. These advancements have expanded their applicability across green energy and sustainable chemical manufacturing processes. Despite these achievements, challenges remain in improving long-term catalyst stability, scalability for industrial applications, and deeper mechanistic understanding under realistic reaction conditions.

Future research integrating advanced materials engineering, computational modelling, and operando characterization techniques will be crucial for optimizing the design and performance of these catalysts. As global efforts continue toward cleaner and more resource-efficient technologies, EATM catalysts are expected to play a central role in shaping sustainable catalytic systems. Rather than simply replacing noble metals, they represent a transformative approach that can redefine the paradigm of high-performance, environmentally responsible catalysis in both energy and chemical industries.

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