Study on the Effect of Catalysts on CO_2 Conversion and Design of Novel Catalysts

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Abstract. The increase in CO_2 concentration in the atmosphere fosters the greenhouse effect, and yet the levels of energy demand in the world are rising. Electro-catalytic reduction of CO_2 ($ECRCO_2$) offers a dual solution, eliminating CO_2 and converting it into high-value chemical fuel, e.g., methane and methanol, and thus, addressing the shortage of energy. The technology supports a circular carbon economy though the selection of catalysts is a challenge as it determines the reaction efficiency and generates selectivity. Current catalysts including noble and transition metals are expensive, limited, unselective, and unstable, respectively, which reduces scalability. This paper is an analysis of $ECRCO_2$ focusing on catalyst development. It starts with the description of key variables that affect catalysts' performance which include material composition, surface, and electronic properties. Then it discusses the drawbacks of traditional catalysts, which consist of side reactions and deactivation. Finally, it proposes a different approach to the design of next-generation catalysts by using different materials like single-atom catalysts and metal-organic frameworks. The computational models together with the experimental validation will be viewed as one means of enhancing the activity, selectivity, and durability by this approach.

1 Introduction

Energy switch-over has become an urgent need due to the worldwide climate change. IEA notes that renewable energy represented over 30% of global electricity supply in 2022, with however intermittent sources such as wind and solar having to face 8% annual curtailment [1]. Meanwhile, energy-related CO_2 emissions hit a record 36.8 billion tons, underlining challenges to achieve carbon neutrality [1]. Electrocatalytic reduction of CO_2 ($ECRCO_2$) technology utilizing renewable energy and CO_2 to produce value-added fuels and chemicals is one such circular economy approach [2].

As the demand for global low-carbon development becomes more and more urgent, the direct utilization of carbon dioxide into chemicals has become a new direction in the field of catalysts. However, the current research is facing many challenges, on the one hand, the activity and efficiency of catalysts are not enough to realize the electrochemical reaction on

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an industrial scale; at the same time, the stability of the reaction also needs to be improved . Therefore, we need to dig deeper into the catalytic mechanism and find new material design ideas to improve the catalytic conversion performance.

Most of the catalysts that are commercially available for the CO_2 reduction reaction are traditional precious metal catalysts. A more economical energy technology solution will result from the production of high-value products like carbon monoxide, methane, methanol, and ethanol as well as a significant improvement in reduction efficiency if a novel kind of catalyst is employed in the CO_2 reduction reaction [2].

Transition metal catalysts for CO_2 reduction reaction (CO_2 RR) are studied via climatic-literature reviews and density functional theory (DFT) to elucidate structure-activity relationships. The important factors influencing conversion are the surface morphology (e.g., coral-like Ag nanostructures), electronic properties, composition, reaction environment and stability. Conventional catalysts are limited by low selectivity, large overpotentials, low active sites, poor stability and there is a lack of scalability. In order to mitigate these challenges, new designs of catalysts must emphasize nanostructuring to expand active sites, alloying/doping to tune electronic properties, hybrid function (e.g. MOFs), surface functionalization and optimization of electrolytes/reactors. The DFT can be used to direct choice of facets, stability predictions and even alloy composition, as well. Practical application is guaranteed through flexible production with materials that are available on earth. These measures provide a more selective, efficient and durable approach to sustainability of CO_2 RR development. To have performance visualization (e.g. Faradaic efficiency) confirm to a chart. With uploaded files or web searches, specific data can be analysed.

2 Key determinants catalyst conversion rate and activity

2.1 Structural and morphological characteristics

Two significant factors of the physicochemical properties, the structure, and the morphology predetermine the influence of catalysts on the chemical conversion processes. A well-defined pore structure is significant in mass transfer and in the accessibility of active sites in the NH_3 -SCR process. Studies have shown that the copper-based zeolite catalysts for SCR can be classified into micropores, mesopores and macropores based on pore size. Among them, microporous zeolites have better SCR performance than macroporous zeolites. [3]. In metal oxide catalysts,metal oxides that have oxygen vacancies foster surface redox kinetics, resulting in an increased C-O bond activation efficiency [4].

2.2 Chemical composition

It is also important that the chemical composition is considered. The interaction between the d-orbital electrons of the transition metal elements (iron, cobalt, and nickel) not only triggers a synergistic catalysis but also reduces the activation energy. In the study of FeN4-MN4/Gr (where M = Co, Ni, Cu, Zn), the d orbitals play a crucial role in the catalytic activity [5].

2.3 Effect of reaction conditions

Reaction conditions (temperature, pressure, solvent polarity) have a great impact on catalytic performance.For the catalyst, calcination to a lower temperature is known to maintain its nanostructurality and avail against any loss of reactivity owing to sintering. According to the research, when the temperature rises, the diameter and size of the crystals will increase

compared to the original state, while the specific surface area decreases, resulting in a decline in the activity of the catalyst [6].

2.4 Effect of pH and impurity

PH and impurity are the other important factors. Acidic conditions enhance surface hydroxyl groups to facilitate proton-coupled electron transfer, however it may lead to catalyst corrosion. Therefore, we need to use neutral or weakly alkaline electrolyte solutions. Through a high reaction rate, a large number of hydrogen ions are consumed on the surface of the catalyst, thereby creating a liquid environment with a high pH level, which prevents the catalyst from being corroded. Consequently, the catalyst performance could be determined not only by intrinsic characteristics but also by reaction conditions which required well-resolved optimization.

3 Limitations of traditional catalysts

3.1 Inefficiency and poor Durability

Although conventional precious metal catalysts (e.g., Pt and Pd) are comercialized, they suffer from low catalytic efficiency, selectivity as well as sustainability. In the reaction for acetophenone, common catalysts (Co-Mn salt) have low atomic efficiency and produce toxic benzene and CO_2 as by-product [7]. At the same time, the catalyst particles will undergo agglomeration and sintering, causing the catalyst particles to become larger, the specific surface area to sharply decrease, and the number of active sites on the surface to significantly decline. As a result, the activity of the traditional catalyst is reduced, ultimately leading to poor efficiency and durability.

3.2 Environmental hazards and imperfect preparation technologies

However, the other significant challenge is environmental friendliness. The precious metal addiction implies mining and refining activities that are highly carbon-intensive and threatening to the environment. [8] The deposition of the catalyst as waste materials leads to heavy metal pollution that is inconsistent with the concept of green chemistry. Long-term operation is complex due to severe deactivation: thermal sintering causes the active phase particles to coarsen, and strong poison (such as CO) adsorbs on the reaction interface, blocking it. Continuous hydrogenation of the Pd/C catalysts significantly decreased their conversion of reaction [9]. Traditional preparations, such as impregnation, frequently lead to non-uniform active phase distribution, which leads in turn to local overdosing and uncontrolled reaction mass transfer. This bottleneck places a higher performance demand on the currently used catalysts—although there are chemically-available processes to bring the conversion toward completion or to meet competing product criteria, these processes have much poorer selectivity and/or sustainability [7]. Typical preparation techniques, such as impregnation frequently lead to uneven distribution of active species which results in local overloading and (or) non-adequacy of reaction mass transport. These constraints lead to an “efficiency bottleneck”—traditional catalysts can induce reactions, but they have difficulty doing so at high conversion rates with high selectivity and low environmental footprint.

4 Innovative design of novel catalysts

The research process of the catalysts is changing from empirical research to rational and intelligent design. Herein, recent advances are concentrated on the high-activity, selectivity and sustainability promote the improved efficiency of conversion as well as precision.

4.1 Nanomaterials based catalysts

Nanomaterials catalysts (such as MOFs and COFs) use ultra high specific surfaces (beyond 2000 m ⁋g) and tailorable pore environments to enhance the interaction of substrates with active sites, which become a promising candidate for the application of electrochemical devices. Covering layers of graphene over silicon nanowires is a feasible solution to maintain stability of the interface between silicon-based electrodes and the electrolyte. After 500 charge-discharge cycles, the resulting silicon nanowires show an exceptional coulombic efficiency of 99% and a huge reversible capacity of 1650 mA h g⁻ ¹ [10]. These are due to a confinement effect which stabilizes the reaction intermediate and inhibits side reactions.Meanwhile, this material can also reduce the overpotential of the reaction, significantly lowering the overpotential required for the reaction to start, thereby achieving the effect of saving electricity.However, the most crucial core advantage of nanomaterials is that they can precisely control the selectivity of reactions, allowing the generation of over a dozen products such as formic acid, methane, and ethylene.

4.2 Metal-rich catalysts

Metal-rich catalysts based on transition metals such as Fe, Co, Ni and Mn exhibit best performance and are cost-effective. Nitrogen-doped carbon-based Ni single-atom catalysts (Ni-N-C) exhibit >99% conversion in H2-ethylene hydrogenation, outperforming palladium counterparts and avoiding heavy metal pollution [11]. These materials tailor the electronic property of metal active sites through tuning the coordination environment and promoting reactant adsorption and activation.At the same time, it also has the advantage of being able to reduce the reaction overpotential. Moreover, it has good stability and corrosion resistance, which is of crucial importance for the practical application of the carbon dioxide electro-catalytic reduction technology.

4.3 Novel composite catalyst system for thermal catalysis

New composite catalyst systems for thermal catalysis have been developed to push the boundaries of efficiency and precision. For instance, chiral microenvironments prepared from palladium nanoparticles and DNA hybrids have been developed to achieve over 98% conversion in enantioselective additions [11]. In another approach, the synergistic effect between cobalt and manganese ions in Co-Mn spinel oxides significantly promotes the mobility of lattice oxygen; specifically, the introduction of a secondary metal into the spinel lattice has been shown to lower the apparent activation energy by approximately 20 kJ/mol, thereby facilitating efficient catalytic oxidation under mild conditions [12].

5 Current challenges

Despite their promise, novel catalysts still face significant challenges. Scale-up synthesis remains a bottleneck: nanoscale products synthesized in the laboratory often exhibit structural inhomogeneity when production scale is expanded, leading to significant

fluctuations in conversion rates [13]. The underlying mechanisms of many high-performance catalytic systems (e.g., bimetallic sites, synergistic catalysis) also require further investigation. Although in-situ characterization and DFT calculations provide useful information, their weakness is high computational cost and resolution limits in complex systems [14].

6 Future directions

The integration of advanced computational tools, particularly artificial intelligence (AI) and machine learning (ML), is set to revolutionize the paradigm of catalyst development. By leveraging high-throughput screening and sophisticated data mining, these methodologies enable the precise prediction of composition-structure-property relationships, potentially accelerating the discovery timeline for novel materials by more than twofold [15]. Furthermore, the development of biomimetic catalysts that emulate the active sites of metalloenzymes holds immense promise for achieving exceptional selectivity under ambient conditions, offering a transformative pathway toward the decarbonization of the global chemical industry.

7 Conclusion

Overall, the literature analysis and experimental data presented in the review help to outline the main factors that affect the activity of transition metal catalysts in ECR-CO_2. As illustrated in this article, the catalytic efficiency (encompassing activity, selectivity, and stability) is dominated by structural-morphological characteristics, chemical composition, and local interface architecture. Meanwhile, several published studies and literature have outlined three novel catalysts capable of substituting conventional catalysts during the electrochemical reduction of carbon dioxide. They are nanomaterial catalysts, metal-rich catalysts, and a novel composite catalyst system of thermal catalysis. They have also been introduced with their advantages, characteristics and the prospects of their usage in the future.

The results indicate that the rational design of non-noble metal catalysts is essential and achievable to reach high-performance and sustainability at the scale of industrial peculiarities effectively overcoming the performance of classic noble metal catalysts. This underlines the significance of basic catalytic systems in the fabrication of effective catalytic systems.

This study concludes with the recognition of the need to bridge the gap existing between theoretical prediction and experimental validation which has significant implications for further research. These identified structure-activity correlations form the basis of the rational design of the next generation catalysts, expediency in finding materials with higher performance capability and lower environmental footprints. In general, an active and selective synthesis of catalysts could be controlled and guided by the application of modern computational tools (e.g., DFT) and by the analysis of reaction mechanisms and prediction of catalyst behaviour.

Next-generation ECR-CO_2 catalysts in the future will integrate different areas including AI, ML, and high-throughput experimentation to screen properties of materials faster and shorten the time scales of development, creating a new generation of smart catalyst design. Additionally, these design concepts can be implemented on catalysts not only in a broader range of chemical reactions, but also in reactions with highly inert substrates. Lastly, the maximum potential of the ECR-CO_2 technology can be reached through coordinated activities that are geared towards enhancing the stability of catalysts in non-laboratory environments, and reliable scalability of the procedures of producing the products. As long as the innovative process continues, electrocatalytic conversion of CO_2 might become a

game-changer in the context of a sustainable circular economy and a primary element of the global community in mitigating CO_2 emissions.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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