Transactions on Environment, Energy and Earth Sciences
ISSN: 2960-1924, eISSN: 2960-2300 | Volume 5
EMCEME 2025

Research on Nanocatalysts and Their Application in the Catalytic Reduction of Carbon Dioxide

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Abstract. This article mainly elaborates on four aspects: the introduction and application of nanocatalysts, the performance advantages of nanoparticles, the catalytic reduction of carbon dioxide by nanoparticles, and prospects for the future. The first paragraph introduces why nanoparticles can act as catalysts, how nanoparticles are synthesized, and their applications. The second paragraph focuses on the favorable properties of nanoparticles, including their excellent stability, environmental friendliness, ability to reduce the required activation energy, high catalytic activity, and outstanding catalytic selectivity. The third paragraph describes in detail the process of carbon dioxide being catalytically reduced by nanoparticles to produce formic acid and methane. The prospect section summarizes the solved and unsolved challenges encountered in catalytic reduction reactions, as well as the specific directions for addressing the unsolved issues. The main problems include difficulties in the molecular activation of carbon dioxide, poor product selectivity, insufficient stability of nanocatalysts, and harsh reaction conditions for nanocatalysis.

Keywords: Nanoparticles; catalysis; methane; formic acid.

1. Introduction

Due to their characteristics such as large specific surface area and unsaturated coordination of surface atoms, nanoparticles exhibit high reaction activity and excellent performance in catalytic reactions. They can serve as high-efficiency catalysts and be applied in a variety of chemical reactions. For instance, in photocatalytic reactions, nanoparticles can leverage their optical and electronic properties to effectively facilitate the progress of reactions, enhance reaction rate and selectivity. This property enables them to play a crucial role in catalytic processes within fields like chemical engineering and environmental protection [1].

In small-sized nanocrystals, a high proportion of vertex and edge atoms possess the structural characteristic of coordination unsaturation. These sites have stronger adsorption capacity for reaction substrates and are more likely to serve as catalytically active sites, thereby enhancing reaction activity [2]. In contrast, large-sized nanocrystals mainly consist of low-activity face atoms on their surfaces, resulting in relatively lower catalytic activity. In the ethane hydrogenolysis reaction, when the size of Rh nanocrystals is approximately 2 nm, the turnover frequency (TOF) reaches a peak due to the high proportion of vertex/edge atoms; as the size increases, the proportion of face atoms rises, and the TOF decreases significantly [3].

The nucleation-growth mechanism is adopted to achieve size focusing by limiting nucleation time and controlling precursor concentration, such as in the synthesis of monodisperse metal nanoparticles. The use of dendrimer templates enables the preparation of ultra-small nanoparticles (1-2 nm) with an extremely narrow size distribution. Real-time monitoring of nanoparticle formation kinetics is conducted via "reporting reactions" to establish two-step nucleation (A→B), autocatalytic growth (A+B→2B), or four-step mechanisms (including an aggregation step), thereby precisely regulating the sizes of nanoparticles such as Rh, Ir, Pt, and Au [3].

Nanoparticles can be used to optimize catalytic performance. The performance of the catalytic performance can be enhanced by designing the surface coating or surrounding environment of nanoparticles. For example, core-shell structured nanocatalysts are constructed, where an oxide shell

is formed outside the metal nanoparticles. This not only prevents the sintering of metal particles but also ensures the porosity of the shell to allow molecular diffusion. Additionally, Atomic Layer Deposition (ALD) technology is also applied in the preparation of supported catalysts. Its self-limiting characteristic enables precise control over the size, composition of nanoparticles and the atomic deposition position [4].

2. Performance Advantages of Nanocatalysts

2.1. Stability

One of the advantages of catalysis is its excellent stability, as the support restricts the agglomeration of antiparticle. Carbon materials (such as biomass carbon, BC) and metal oxides (such as Al_2O_3) can act as supports. They prevent the interesting and agglomeration of antiparticles during reactions through the spatial confinement effect [5]. For example, when copper antiparticle (Cu Bps) is supported on IOS_2, the catalyst synthesized by the ammonia evaporation method can be recycled for a long time without significant attenuation in CO_2 hydrogenation activity. During the reaction, nickel-iron antiparticle (Ni_3Fe) and Meh_2 in-situ form a Mg_2Ni/Mg_2NEH_4 dual phase, which energetically catalyzes hydrogen storage. Moreover, Fe can accelerate the conversion between Mg_2Ni and Mg_2NEH_4, further improving the cycle stability.

2.2. Environmental Friendliness

The second advantage is its environmental friendliness combined with low cost. BC is derived from agricultural wastes such as pomelo peels, with a preparation cost of only 0.79-0.93 US dollars per kilogram, which is much lower than that of nano-supports like reduced graphene oxide (rGO). Additionally, Ni_3Fe/BC can be synthesized in one step via the solid-phase reduction method, which does not require high-temperature hydrogen reduction, thus reducing the preparation cost and energy consumption [6].

2.3. Reduction of Activation Energy

Meanwhile, nanocatalysis lowers the energy barrier of hydrogen storage reactions. Nanocatalysts reduce the dehydrogenation/hydrogenation activation energy of Meh_2: the initial dehydrogenation temperature of pure Meh_2 is as high as 350℃, while after adding 10wt% Ni_3Fe/BC nanocatalyst, the initial dehydrogenation temperature decreases to 184.5℃. Furthermore, the dehydrogenation activation energy decreases from 154.90 $kJ \cdot mol^{-1}$ to 102.01 $kJ \cdot mol^{-1}$, and the hydrogenation activation energy decreases from 70.75 $kJ \cdot mol^{-1}$ to 47.47 $kJ \cdot mol^{-1}$[7].

2.4. High Catalytic Activation Energy

Another advantage of nanocatalysis is the high catalytic activity of gold antiparticle (Au Bps). Generally, the smaller the size of antiparticle (Bps), the higher their catalytic activity [8]. For example, when metal antiparticle such as Cu, Au, and Ni is supported on carriers like Al_2O_3, ZrO_2, and CeO_2, their specific surface area increases significantly, exposing more active sites and accelerating the adsorption and activation of CO_2. Taking the RWGS reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) as an example, the NiO/CeO_2 nanocatalyst achieves a CO_2 conversion rate of approximately 40% and a selectivity close to 100% under the conditions of 700℃ and 0.1MPa, which is far superior to non-nano metal catalysts. Strong interactions form between metal antiparticle and carriers, such as CeO_2 and TiC, regulating the electronic structure of metals and reducing the energy barrier for CO_2 dissociation. For instance, when Cu Bps are supported on the TiC (001) surface, the CO_2 adsorption energy increases from -0.62 eV (pure TiC) to -1.12 eV (Cu_4/TiC), significantly promoting the activation of CO_2, and the efficiency of generating CO and methanol is 5-12 times that of commercial Cu/ZnO catalysts [9].

2.5. Excellent Catalytic Selectivity

Last but not least, nanocatalysis can precisely regulate product selectivity and reduce by-products. The composition of antiparticle and carriers collaboratively regulate products, and by selecting different metal antiparticle and carriers, target products such as CO, methanol (MeOH), or methane (CH_4) can be generated. For example, Cu Bps tend to catalyze the hydrogenation of CO_2 to produce MeOH and CO; Ni Bps prefer CO_2 methanation (for example, the Ni/CeO_2 nanocatalyst has a methane selectivity of 99%); and when Au Bps are supported on ZrO_2, the CO selectivity for the RWGS reaction exceeds 90%. Meanwhile, by designing the structure of nanocatalysts (such as supporting, doping, and assembling), target products like N_2 or NH_3 can be generated. For example, when Fe-Cu alloy antiparticle are supported on N-doped carbon nanofibers, Cu accelerates the conversion of NO_3^- to NO_2^-, and Fe improves the N_2 selectivity (reaching 98%); while the Co-Fe@Fe_2O_3 nanocatalyst inhibits the hydrogen evolution reaction by regulating the d-band center of Fe, achieving an NH_4^+ selectivity of 99%. On the other hand, assembled nanocatalysts (such as CC/Fe_3O_4@C) reduce the generation of harmful by-products like NO and N_2O through the synergistic effect of the Fe-C interface, with an N_2 selectivity exceeding 82% [10].

3. Carbon Dioxide Catalytic Reaction

3.1. The Redox Conversion of Carbon Dioxide to Formic Acid

Using formate dehydrogenase (FDH), a biological catalyst that relies on the cofactor nicotinamide adenine dinucleotide (NAD^+/NADH), to enzymatically catalyze the reduction of carbon dioxide (CO_2) to formic acid; and copper nanoparticles (CuNPs) as the chemical catalyst, which are loaded onto the surface of a carbon felt (CF) electrode via electrodeposition. The CuNPs serve the dual function of immobilizing FDH and regenerating the cofactor NADH.In a 0.1 M phosphate-buffered saline (PBS) system, with CO_2 gas bubbled through and a reductive potential of -1.0 V (vs Ag/AgCl) applied, the CuNPs catalyze the electrochemical reduction of NAD^+ to regenerate NADH. The regenerated NADH then provides electrons for the FDH-catalyzed reduction of CO_2. Throughout the process, efficient NADH regeneration is achieved without the need for adding electron mediators, with the yield of 1,4-NADH reaching 82.3%. This yield outperforms the previously reported 67% yield of Cu nanorods and 80% yield of Cu foam electrodes. This characteristic eliminates the toxicity interference and cost issues associated with mediators. Meanwhile, the porous structure and high electrical conductivity of CuNPs facilitate electron transfer from the electrode to NAD^+, enhancing the sustainability of the reaction. Additionally, an FDH-NAD^+ complex constructed using a polyethylene glycol (PEG) flexible linker shortens the distance between the cofactor and the enzyme's active site to the nanoscale, addressing the key issue of slow cofactor diffusion in traditional systems. Experiments show that the formic acid production of this complex system is 8.5 mM, which is 5.7 times higher than the 1.5 mM production of the "free FDH + CuNPs" system. The molar productivity reaches 11.8 $\mu M \cdot mU^{-1} \cdot h^{-1}$, a relatively high level among similar FDH-mediated CO_2 reduction systems [11].

3.2. The Redox Conversion of Carbon Dioxide to Methane

Pt NPs/HTSO composite catalysts with different particle sizes were prepared by acid-base mediated alcohol reduction (ABAR) method, such as xPHTSO, where x represents the Pt particle size: 1.8, 3.4, 4.3, 7.0 nm. The nucleation rate of Pt precursor ($H_2PtCl_6 \cdot 6H_2O$) was changed by adjusting the amount of acid (HCl) or base (NaOH) added in the reaction system: in an alkaline environment, $PtCl_6^{2-}$ was easily converted to $PtCl_{6-x}(OH)_x^{2-}$ which was more reducible, resulting in fast nucleation, a large number of nuclei and small-sized Pt NPs; the acidic environment inhibited the dissociation of H_2PtCl_6, leading to slow nucleation, a small number of nuclei and large-sized Pt NPs. Meanwhile, inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to ensure that the Pt loading of all samples was about 1.8 wt%, so as to eliminate the interference of loading on catalytic performance; transmission electron microscopy and X-ray diffraction were used to verify that the Pt NPs had

uniform particle size, good dispersion and no agglomeration. The Pt NPs prepared by ABAR method did not require stabilizers such as polyvinylpyrrolidone, and the precise control of particle size was achieved by adjusting the acid-base environment, with clean catalyst surface free of carbon impurities: CO pulse chemisorption showed that the Pt particle size calculated based on adsorption capacity was consistent with the TEM results, and only 7.0PHTSO had a slight deviation due to pore limitation. However, for PVP-modified Pt NPs, namely 1.7Pt@PVP/HTSO, the residual PVP on the surface blocked the active sites, so that the yields of CH_4 and H_2 decreased to 2.5 $\mu mol \cdot g^{-1} \cdot h^{-1}$ and 39.0 $\mu mol \cdot g^{-1} \cdot h^{-1}$ respectively, which were only 25.8% and 66.4% of those of 1.8PHTSO, highlighting the importance of clean surface for catalytic performance. At the same time, this method can be extended to supports such as C_3N_4 and commercial TiO_2 and has universality [12].

4. Outlook

At present, the challenges include difficulty in CO_2 molecular activation: as an inert gas, CO_2 has high stability which restricts the progress of reactions; poor product selectivity, as the complex pathways of catalytic reduction lead to a low proportion of target products; insufficient stability of nanocatalysts, as nanocatalysts are prone to deactivation due to sintering, oxidation, carbon deposition, or excessive enhancement of metal-support interaction (SMSI); and harsh reaction conditions for nanocatalysis, as most CO_2 nanocatalysis systems require high temperatures, high pressures, or strong electrolyte environments, resulting in high energy consumption and strict equipment requirements that make it difficult to meet the application demands of "green and low-carbon" development.

The main logic of nanocatalysis in solving CO_2 catalytic challenges is the precise matching of "structure-performance-mechanism": by regulating the size, composition, and support properties of nanoparticles, collaborative active sites are constructed to overcome the activation energy barrier of CO_2; combined with process optimization and theoretical calculations, high-selectivity and high-stability conversion of CO_2 under mild conditions is achieved.

Currently, the strategy of precisely designing nanocatalyst structures to enhance CO_2 activation and selective regulation has been proposed to address the first two challenges mentioned above. Specifically, by adjusting the size, composition, crystal plane, and support properties of nanoparticles, a "multi-active-site collaboration" system is built to realize efficient activation of CO_2 and directional generation of target products. Meanwhile, the support and interface interactions can be optimized to improve stability and catalytic synergy; this specifically includes the selection of supports with special electronic and structural properties (such as metal oxides), and the regulation of metal-support interaction to enhance catalyst stability and construct collaborative active sites, so as to address the third challenge mentioned above.

However, further efforts are still needed: the expansion of photo-electro-thermal multi-field coupled catalysis should be carried out to further reduce reaction energy consumption; in addition, the integration of in-situ characterization and machine learning needs to be promoted to accelerate the efficiency of catalyst screening and optimization, and ultimately the industrial application of CO_2 catalysis should be achieved.

5. Conclusion

This paper aims to summarize the catalytic properties of nanoparticles and their advantages as well as areas for improvement in the experimental research on catalytic reduction of carbon dioxide. Nanoparticles have achieved environmental friendliness while enhancing product selectivity. Currently, the only remaining tasks are to optimize reaction efficiency and reduce reaction energy, so as to achieve industrial application.

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