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Key Role of Catalyst Pore Structure in Nonthermal Plasma-assisted Heterogeneous Catalysis

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Abstract: This review systematically evaluates the critical role of catalyst pore architecture in nonthermal plasma (NTP)-assisted heterogeneous catalysis, focusing on its impact on reactive species diffusion, surface plasma micro-discharge behaviors, and reaction performances in typical NTP catalytic processes such as CO_2 hydrogenation and ammonia synthesis. Current research findings suggest porous catalyst structures can enhance local electric fields, with pore sizes approaching the Debye length promoting micro-discharges within the pores. Hierarchical porosity is beneficial to the NTP systems, improving not only catalyst dispersion but also the local mass transfer of plasma-induced reactive species (the improved accessibility of active sites), and thus the enhanced reaction performance. Case studies highlight that optimized pore structures (e.g., hierarchical mesoporous-microporous frameworks) significantly boost CO_2 conversion to methane and methanol under mild conditions. In ammonia synthesis, microporous materials like ZIF-8 and gyroid mesoporous silica achieve high ammonia yields. However, mechanistic insights into the complex role of catalyst pore structures in balancing species diffusion under plasma, tuning the interaction between active sites and plasma-induced species and optimizing energy efficiency are still lacking. Future research in this field should place greater emphasis on hierarchical mesoporous-microporous structures with large pore diameters, as well as the synergy between discharge and confined catalysis.

Keywords: Nonthermal plasma (NTP) catalysis, Pore architecture, Catalyst design, CO_2 hydrogenation, Ammonia synthesis.

1. Introduction

Plasma is the fourth-state of matter, which is of a partially or fully ionized gas consisting of high-energy free electrons, charged particles, neutral particles, and photons. Plasma is electrically quasi-neutral, but its components (charged and neutral species) exhibit unique collective behaviors under the influence of electric and magnetic fields. On Earth, plasma can be produced by discharge, heating, and other methods [1]. Plasmas can be categorized according to their states of thermal equilibrium. For a thermal plasma, all species (electrons, ions, and neutrals) within are in thermal equilibrium and have similar temperatures, such as arcs, sparks, and flames. Nonthermal plasmas (NTPs such as glow discharges and dielectric barrier discharges), on the other hand, have limited ionization with fewer free electrons (than thermal plasmas) [2-3]. Although the electrons are much hotter (typically in the range of 1-10 eV) than the ions and neutrals, the bulk gas temperature of non-thermal plasmas remains relatively low (usually ranges from near room temperature to a few hundred degrees Celsius) due to the lack of thermal equilibrium between electrons and other species [4]. However, the high reactivity of free electrons in NTPs can be used for many challenging chemical reactions, including volatile organic compounds (VOCs) degradation, CO_2 hydrogenation, CH_4 conversion, ammonia synthesis, due to its enriched high-energy free electrons for the rapid activation of stable molecules [5, 6].

NTPs themselves can drive many challenging chemical reactions, mainly decomposition reactions such as VOCs degradation and CO_2 decomposition to CO [7, 8]. The plasma-induced species could react in the gas discharge for chemical conversion but being non-selective. However, in the presence of a selective catalyst, the NTPs-induced species can interact with the catalyst surface to be selectively converted to the desired products, and this is exemplified by NTP-catalytic CO_2 hydrogenation over metallic nickel (Ni) catalysts to methane [9, 10]. Compared to the conventional thermal catalysis on metal surfaces (which commonly relies on energic metal surface for activation and conversion of substrates), NTP catalysis has a different activation mechanism employing the energic species in gas discharge to activate the reactant molecules then proceed to surface reactions [11]. The unique activation mechanism allows NTP catalysis promoting some challenging reactions under relatively mild conditions, such as nitrogen fixation and CO_2 valorization, in comparison with thermal catalysis. Taking ammonia synthesis as an example, the conventional thermal catalytic processes normally require 400–500 °C and 30–50 MPa, whilst NTP catalysis can enable ammonia synthesis under ambient conditions because that chemical bonds in N_2 molecule can be readily broke by plasma [12]. Another important note is that NTP catalytic processes are driven by electricity (electrified process), hence it can be theoretically powered by green electricity from the renewable energies (such as solar and wind), being sustainable and low-carbon [13]. Importantly, if NTP catalysis is applied to hydrogenation reactions (such as CO_2 hydrogenation to methane/methanol and N_2 hydrogenation to ammonia), it can utilize green hydrogen (produced by water electrolysis through using green electricity) as well, and such processes powered fully by green electricity can be promising technical solutions for future sustainable chemical/fuel production and energy storage [14-16].

Therefore, great efforts were made by academia to improve and advance NTP catalytic technologies regarding different aspects such as bespoke catalyst design, power source optimization and plasma reactor engineering. Bespoke catalyst design is paramount considering the different activation means from the thermal catalytic systems (as stated above), which is a key aspect to be investigated to improve the process efficiency of NTP catalytic systems. In designing a bespoke catalyst for NTP catalytic systems, the pore architecture of the catalysts constitutes a critical determinant of reaction performance, influencing not only on the diffusion and distribution of the plasma-induced reactive species but also on surface plasma microdischarge behaviors, hence affecting the activity and selectivity of the NTP catalytic system. Hence, considering the importance of the pore architecture of catalysts in NTP catalysis, here in this minireview, it will mainly discuss the recent studies conducted by several academic groups on how catalyst pore structure affects plasma catalysis. Finally, perspectives on future catalyst design for NTP catalysis such as CO_2 hydrogenation and ammonia synthesis are also presented in this review [17].

2. Effect of catalyst pore structure on NTP catalytic CO_2 hydrogenation

The global emphasis on carbon emission reduction and sustainable development has propelled significant interest in CO_2 capture and utilization, and CO_2 hydrogenation is one of key enabling technologies for CO_2 utilization. NTP-assisted catalysis has emerged as a prominent research focus due to its capability to readily break C=O bond and activate CO_2 under mild conditions. Some studies suggested that the discharge type primarily influences the catalytic efficiency of NTP, while recent research indicates that the catalyst pore structure also significantly affects efficiency. For example, the pore structure could affect the diffusion of plasma-generated reactive species and hence the reaction performance. In a study by Chen et. al. [18], the pore structure of silicalite-1 (S1) zeolite support was varied to prepare different Ni/S1 catalysts for NTP-catalytic CO_2 hydrogenation to methane, the Ni/D-S1 (desilicated silicalite-1) support with a hierarchical mesoporous-microporous structure demonstrated that mesopores substantially shortened the diffusion pathways for reactive intermediates, enabling their efficient migration and interaction with active Ni sites, thereby enhancing catalytic activity. At relatively lower voltages (6.0–7.0 kV), in dielectric barrier discharge (DBD) plasmas, the Ni/D-S1 catalyst exhibited lower activity compared to Ni/S1 and Ni/M-S1@Shell (mesoporous-microporous silicalite-1) catalysts due to the relatively low concentration of reactive species at such low input voltage. However, at 7.5 kV, the hierarchical pore structure facilitated the diffusion of abundant reactive species to the active Ni sites surface, achieving a peak CO_2 conversion rate of ~75%. The closed mesoporous structure of the M-S1 support hindered sufficient interaction between reactive species and Ni active sites, resulting in predominantly gas-phase reactions and poor CH_4 selectivity under NTP conditions. In contrast, the hierarchical pores of Ni/D-S1 promoted the dispersion of Ni sites and thus synergistic interactions between reactive species and Ni sites, enabling a CH_4 selectivity of ~98% at 7.5 kV. The same group later investigated plasma-assisted CO_2 hydrogenation to methanol over Cu-loaded mesocellular foam (MCF) catalysts [19], in which the large pore size (~8.5 nm) and high specific surface area (784 m^2 g^{-1}) of MCF provided expansive diffusion channels for reactive species, enhancing electric field intensity and surface microdischarges to promote methanol synthesis. Compared to control porous materials (e.g., S1, SiO_2, and SBA-15), the MCF-based system achieved a superior methanol space-time yield (STY) of ~130 μmol $gcat^{-1}$ h^{-1}, highlighting the critical role of mesopore structures in facilitating diffusion of reactive species. The “shielding protection” effect of MCF possibly enabled methanol diffusion into its internal cavities, preventing plasma-induced decomposition and improving methanol selectivity. Furthermore, Zn doping in the Cu_1Zn_1/MCF catalyst further optimized the interaction between active sites and CO-related intermediates, elevating the methanol STY to ~275 μmol g_{cat}^{-1} h^{-1} with a CH_3OH/CO STY ratio of ~0.009, significantly outperforming other control systems. This underscores the synergistic effect of pore architecture and active site engineering on reaction selectivity in plasma catalytic system.

Findings of the two studies above demonstrate the interplay between pore structures and plasma-catalyzed CO_2 hydrogenation. The first systematically investigated Ni/silicalite-1 catalysts with varying pore architectures under both thermal and NTP conditions, employing comprehensive characterization to establish structure-performance relationships. The results unequivocally demonstrated the necessity of hierarchical porosity and high metal dispersion for enhanced NTP catalytic performance. The second study focused on Cu/MCF catalysts for NTP-driven CO_2-to-methanol conversion, innovatively exploring Zn doping effects. It comparably evaluated diverse porous materials for supporting Cu-based catalyst, corresponding catalyst stability, and energy consumption, providing critical data for guiding the rational design of catalysts for this system.

Regarding catalyst design, current studies predominantly address singular factors (e.g., pore structure or metal doping), lacking systematic exploration of multifactorial synergies. Future efforts should adopt holistic approaches integrating pore geometry, metal dispersion, and active site properties, complemented by high-throughput experimentation and computational modeling for precision catalyst design. Additionally, the complex synthesis protocols reported in these studies pose scalability challenges. Subsequent research should prioritize simplified, cost-effective fabrication methods to accelerate industrial adoption of this technology.

3. Effect of catalyst pore structure on NTP catalytic ammonia synthesis

The Carreon team from the United States focused on the catalytic efficiency of ammonia synthesis. They investigated how the pore size and morphology of catalysts influence the catalytic rate, concluding that the pore morphology of the catalyst plays a crucial role in catalytic efficiency.

Carreon et al. [20] introduced Ni-MOF-74 as a plasma catalyst, where its 1.03×0.55 nm^2 one-dimensional pores and open Ni sites significantly enhanced ammonia yield (21.17 μmol min^{-1} $g_{cat}{}^{-1}$), a 35% improvement over pure Ni catalyst. The porous structure of MOFs not only promotes reactant diffusion but also enhances the residence time of active species through confinement effects. However, structural disordering (When the energy of plasma species is transferred to chemical bonds or atoms via collision under high-power conditions, this leads to slight distortions in molecular structures and the formation of defects.) at high power (300 W) led to yield decline, indicating the stability issues of MOFs in plasma environments. In this study, the Carreon team embarked on a journey of exploring catalysts for ammonia synthesis driven by NTP. Under plasmas produced by radio frequency, microporous Ni-MOF-74 demonstrated the promoting effect on ammonia synthesis, marking the preliminary feasibility verification stage of the research. However, the organic/inorganic hybrid MOF materials are instable under plasma conditions, and the occurrence of structural disorder under high input power can be observed, and hence, the exploration of catalytic materials with high stability in a high input power environment is highly desired.

In the aforementioned studies, metal-organic framework (MOF) catalysts were found to facilitate plasma catalytic reactions and enhance ammonia synthesis rates. The Ni-MOF-74 catalyst featured a pore size of 1.03×0.55 nm^2 and achieved an ammonia synthesis rate of 21.17 μmol min^{-1} $g_{cat}{}^{-1}$ in experiments. However, the underlying mechanisms are still unclear. In subsequent research, the authors shifted their focus to zeolitic imidazolate frameworks (ZIFs), specifically ZIF-8 and ZIF-67, which exhibit a uniform pore aperture of 3.4 Å (0.34 nm). This further reduction in pore size led to a significantly higher ammonia synthesis rate of 42.16 μmol min−1 gcat−1, demonstrating that smaller pore dimensions are advantageous for promoting catalytic reactions. Carreon et al. [21] systematically compared the ammonia synthesis performance of two zeolitic imidazolate frameworks (ZIFs), i.e., ZIF-8 and ZIF-67, in atmospheric-pressure DBD plasma. The ZIFs with microporous structure (0.34 nm) significantly outperformed traditional zeolites (e.g., 5A zeolite with a 0.5 nm pore size) and oxides (e.g., Al_2O_3), and the rates are respectively two times and five times higher. Experimental data showed that ZIF-8 achieved an ammonia synthesis rate as high as 42.16 μmol min^{-1} $g_{cat}{}^{-1}$, 70 times higher than that of plasma alone. This advantage stems from the confinement effect of micropores, which enhances the activation efficiency of N_2 and H_2. Additionally, the weak dipole-dipole interactions between the polar pore walls of ZIFs and ammonia molecules reduce product adsorption-induced catalyst deactivation, sustaining high reaction rates. Building upon the research on material stability issues in 2018, this study focuses on the performance of materials with different pore structures in a specific plasma environment. The research on ZIF-8 and ZIF-67 reveals that ZIF-8 exhibits advantages in terms of stability and ammonia synthesis rate, attributed to its polar micropores with a diameter of 0.34 nm. This represents a significant discovery regarding the catalytic stability conferred by the pore - size structure of the catalyst.

Building on the results of the previous two experiments, the following experiments further investigate the effects of pore morphology and pore size on the reaction rate of inorganic catalysis to enhance ammonia synthesis. This study demonstrates that the gyroid mesoporous catalyst exhibits the highest yield. Compared with the pore sizes in the previous two experiments, the mesoporous size here ranges from 3.26 to 3.92 nm, which is larger than those in the earlier trials. These findings are similar to the conclusions drawn by the Bogaerts research group regarding the pore structural dimensions of catalysts. Carreon et al. [22] expanded the use of porous materials such as mesoporous silica (3.26–3.92 nm) and macroporous silica (98 nm) with different morphologies (spherical vs. gyroid) in the plasma catalytic system. The gyroid mesoporous silica exhibited the highest ammonia yield (160.7 μmol min^{-1} $g_{cat}{}^{-1}$), far surpassing spherical mesoporous (61.2 μmol min^{-1} $g_{cat}{}^{-1}$) and macroporous materials (low yield due to the low surface area of 19.8 m^2 g^{-1}). This disparity arises from the high surface area (723 m^2 g^{-1}) and three-dimensional interconnected pore channels of the gyroid structure, which promote the diffusion of plasma-active species and surface reactions. Additionally, the "protective effect" of mesopores effectively inhibits in-situ ammonia decomposition, whereas macroporous materials lack sufficient surface area to provide adequate reaction sites. Building upon the aforementioned research, the studies in 2025 advanced to the investigation of hierarchical structure design. Through research on different types of porous materials and their morphologies, it was discovered that the unique structure of gyroid mesoporous silica can enhance the local electric field and suppress ammonia decomposition, achieving a higher ammonia yield. This achievement further clarifies the synergistic mechanism between the pore size and pore morphology of the catalyst and the plasma. By combining the geometric field effect with confined catalysis, it provides more in-depth theoretical and practical guidance for the design of novel catalyst structures, which is conducive to improving the catalytic reaction efficiency.

Collectively, these studies not only demonstrated the evolutionary trajectory from catalyst exploration to the elucidation of structure-performance relationships but also established a multiscale framework linking plasma-catalyst interfacial dynamics to macroscopic reactor performance. However, several challenges remain to be addressed, including further optimizing the matching between pore structures and plasma parameters, enhancing material structural stability and longevity, and improving energy efficiency and scalability. Addressing these issues will be crucial for the practical implementation of NTP-driven ammonia synthesis.

4. Effect of catalyst pore structure on plasma microdischarge behaviors

In addition to the studies on catalyst pore effect during plasma catalytic research, designated effort on researching the fundamentals of pore effect on plasma discharges was made both numerically and experimentally by the Bogaerts group in Belgium.

Bogaerts et al. [23] developed a two-dimensional fluid model to investigate the formation of microdischarges in catalyst pores, revealing that pore size and applied voltage are critical parameters governing discharge characteristics. At an applied voltage of 20 kV, distinct size-dependent behaviors were observed: for pores larger than 200 μm, ionization predominantly occurred within the pore interior, accompanied by a significant enhancement of electron density in the vicinity and inside the pores. Remarkably, even for a 10 μm pore, substantial influence on the total ion density was detected. When examining a fixed pore size of 30 μm under varying voltages, the study found negligible impact on plasma properties at 2 kV. However, as the voltage exceeded 10 kV, a pronounced enhancement of the ionization process occurred, leading to a substantial increase in ion density both near and within the pores. These findings demonstrate that plasma species can indeed form inside catalyst pores and potentially interact with the catalyst surface, thereby influencing plasma-catalytic processes. As the foundational study in this series of pore structure investigations, this work established a fundamental two-parameter model (pore size and voltage) and obtained preliminary insights into the relationship between Debye length and pore dimensions. While this research provides important groundwork for subsequent studies on pore structure ionization, it should be noted that the work was conducted under idealized conditions: the use of helium as the working gas (which exhibits substantially different properties from actual reactive gases) and the omission of surface diffusion effects limit the direct applicability of the results to practical catalytic systems. These limitations position the current study primarily as a mechanistic exploration, highlighting the need for further research under more realistic conditions.

Following earlier studies that employed a two-dimensional fluid model to investigate the dual parameters of voltage and pore diameter, subsequent research narrowed the focus of simulations to examine pore diameter specifically, exploring its size and morphology. Bogaerts utilized a two-dimensional fluid model with fixed pore depth to study pore morphology and a Particle-In-Cell with Monte Carlo Collision (PIC-MCC) model to analyze pore diameter size, drawing the preliminary conclusion that larger pore diameters approaching the Debye length facilitate discharge. Bogaerts et al. [24, 25] used a two-dimensional fluid model to study the influence of different pore shapes (conical small pores, cylindrical pores, conical large pores) on electric field enhancement and plasma generation. The results showed that conical small pores had significant electric field enhancement at the pore opening and bottom corners, with a high ionization rate; cylindrical pores only had electric field enhancement at the bottom corners, with a limited increase in ionization rate; conical large pores had the strongest electric field at the bottom, and the ionization rate peaked at the bottom. By integrating the ionization rate, it was found that the conical small pores had the highest integrated ionization rate of 8.68×10^{11} s^{-1}, indicating that they may perform better in plasma catalysis. Compared with the 2016 two-parameter analysis of “pore size–voltage”, this study introduced pore parameters in greater detail, clarified the conditions under which pore shape and size exert their influences, and constructed a theoretical model incorporating dimensions (10–200 μm) and geometric configurations (conical, cylindrical). By employing the PIC/MCC (particle-in-cell/Monte Carlo collision) model to enhance microkinetic resolution, it was demonstrated that electric field enhancement induced by pore shapes promotes plasma generation, and pore sizes approaching the Debye length also exhibit discharge enhancement effects. However, the study remained limited to idealized pore geometries (differing from the complex pore networks of actual catalysts) and lacked experimental validation, thereby providing theoretical targets for optimizing pore structures in subsequent experimental investigations.

Following three previous simulation studies, Bogaerts conducted experiments based on the dry reforming of methane to further investigate the effects of pore structure and pore size on catalytic reaction efficiency. Compared with the earlier conclusion that simply larger pore sizes promote reactions, this experiment reached a further conclusion: the combination of macropores and micropores is conducive to plasma discharge. Bogaerts et al. experimentally studied the performance of 3D porous Cu and CuO catalysts with different pore sizes in plasma catalytic dry reforming [26]. The experimental results showed that in most cases, the smaller the pore size, the higher the conversion rates of CH_4 and CO_2. For example, among CuO catalysts, CuO-1000 (synthesized using 1 μm silica templates) had higher conversion rates than other samples due to the pore size being close to the Debye length and electric field enhancement; among Cu catalysts, Cu-10 showed the highest conversion rate. In addition, the study also found that reaction selectivity was related to conversion rate, with higher conversion rates generally corresponding to higher syngas selectivity and lower unsaturated hydrocarbon and oxygenate selectivity. As the latest achievement in this series of studies, this work represents a transition from theoretical modeling to experimental validation, expanding the research scope from single pore geometries to multicomponent catalysts (such as Cu/CuO) and incorporating material surface properties as new parameters. It demonstrated that the combination of macroporous supports with specific pore sizes (close to the Debye length) and microporous metallic active components can effectively enhance catalytic reaction efficiency. Although the catalyst systems remained relatively simple, this study for the first time observed an electric field enhancement-dominated catalytic mechanism within Debye-scale pores, providing experimental evidence for the design of nanoporous catalysts and marking a critical transition from mechanistic exploration to application-oriented research.

Collectively, the research group has demonstrated a progressive trajectory from parameter screening to mechanistic refinement and experimental validation, elucidating how catalyst pore structures influence plasma-catalyst interactions. Current findings highlight that designing microporous architecture at Debye-length scales favors plasma catalytic reactions by enhancing electric field confinement and reactive species transport. While these insights provide a foundational framework, challenges remain in addressing complex real-world catalyst architectures, multicomponent reaction systems, and surface diffusion kinetics. Further experimental investigations are therefore needed to unravel the underlying mechanisms governing pore structure–plasma interactions under practical conditions, bridging fundamental understanding with scalable catalyst design.

5. Conclusion and perspective

This review highlights the pivotal role of catalyst pore structure in enhancing the efficiency of NTP-assisted heterogeneous catalysis for key chemical processes such as CO_2 hydrogenation and ammonia synthesis. The findings reported in open literature underscore that an optimized pore architecture, especially hierarchical porous structures, facilitates the diffusion of plasma-generated reactive species, improves local electric fields, and enhances the interactions at active sites, leading to improved reaction performance under mild plasma conditions. The case studies by three research groups reveal that specific pore characteristics significantly influence both discharge properties and the selectivity to desired products. For instance, catalysts such as Ni-MOF-74 and gyroid mesoporous silica demonstrate the promising effects of finely tuned pore sizes and morphologies on ammonia yield and CO_2-to-methanol conversion rates. However, challenges such as the mechanistic complexities of species diffusion, catalyst stability under plasma conditions, and scaling fabrication methods remain pressing issues for future research. Going forward, a systematic exploration of the synergistic interactions among pore architecture, active site distributions (in a pore network), and plasma conditions is essential. Emphasis on advanced computational modeling and high-throughput experimental methodologies can aid in achieving more effective and rational catalyst designs for getting insights into the unknown aspects above. This will facilitate the full realization of NTP catalysis as a transformative technology for green chemical production, aligning with global efforts towards sustainable development and carbon neutral manufacturing processes.

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