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Enhancing Ammonia Synthesis and CO_2 Hydrogenation to Methanol via Nonthermal Plasma Catalysis: A Focus on Catalyst Pore Structure and Active Site Design

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Abstract: The increasing energy demand, climate change and sustainable development necessitate the transition from fossil fuels to renewable sources (such feedstock and energy). Green hydrogen is one of the key components in sustainable energies/fuels being crucial for reducing carbon emissions and achieving carbon neutrality. However, hydrogen storage and transportation are challenging, and chemical hydrogen storage reactions such as ammonia synthesis and CO_2 hydrogenation (to methanol) are considered promising solutions. Nonthermal plasmas (NTPs) are partially ionized gases with various energetic species, which are produced under ambient conditions being able to facilitate efficient chemical reactions under mild conditions. Importantly, NTP technologies can theoretically utilize green electricity produced by renewable energies (such as solar and wind) showing significant low-carbon potential. Previous studies have shown the catalysts design has an important impact on the performance of catalytic reactions under NTP conditions, and hence this aspect deserves attention. Here this mini review comments on the application of NTP catalytic technologies in ammonia synthesis and CO_2 hydrogenation to methanol, with a special focus on catalyst pore structure and active site design. The critical summary and perspective can serve as the most current snapshot of the relevant research fields in NTP technologies, helping their further development.

Keywords: Nonthermal plasma catalysis, Ammonia synthesis, CO_2 hydrogenation to methanol, Catalyst pore structure, Active metal sites.

1. Introduction

With the continuous development of human society and the advancement of technology, the demand for energy by us is ever increasing. Currently, the excessive use of fossil fuels (e.g., coal, natural gas), mainly for energy and chemicals synthesis, has led to a series of serious issues such as global climate change, the rise of sea levels, and increased environmental pollution. Each year, human activities emit about 36.7 billion metric tons of carbon dioxide (CO_2), with 80% from fossil fuel combustion [1-2]. Utilizing renewable energies (wind, solar, geothermal) is crucial for a sustainable society. Among these, green hydrogen is considered a key energy source for reducing carbon emissions and achieving carbon neutrality. Green hydrogen, produced through water electrolysis powered by renewable electricity, has the advantage of emitting only water upon combustion without other pollutants, such as CO_2, nitrogen oxides, volatile organic compounds, etc. [3]. Given the importance of green hydrogen in the utilization of renewable energy, the efficient and safe storage and transport of green hydrogen have become crucial aspects of its application. However, hydrogen storage faces multiple challenges, including safety and energy consumption issues with high-pressure storage, insulation and high energy demands for cryogenic liquid storage, capacity and cyclic stability issues for metal hydride storage, harsh reaction conditions for chemical storage, as well as insufficient hydrogen storage density and stability of nanomaterials and porous materials. Addressing these challenges is vital for the widespread application of hydrogen energy. Among these, hydrogenation reactions for chemical storage are considered a promising route. Such as ammonia synthesis ($N_2+3H_2 \rightleftharpoons 2NH_3$ ΔH=-92.4kJ/mol) and CO_2 hydrogenation to methanol ($CO_2+3H_2 \rightleftharpoons CH_3OH+H_2O$ ΔH=-49.5kJ/mol) have significant advantages in chemical hydrogen storage and utilization. In detail, ammonia synthesis via green hydrogen could reduce over 70% greenhouse gas emissions compared to traditional methods [4], and the use of green hydrogen in methanol synthesis can reduce CO_2 emissions by 50% [5]. However, these processes are typically constrained by thermodynamic equilibrium and kinetic limitations, requiring high temperatures and/or high pressures for stable molecule activation. Thus, new technologies operating under milder conditions are sought to enable sustainable energy storage.

NTP is a plasma state wherein high-energy electrons coexist with a low-temperature background gas, resulting in an overall low temperature. Due to its high reactivity and low energy consumption, nonthermal plasma holds significant potential for applications in hydrogen storage reactions (e.g., ammonia synthesis, CO_2 hydrogenation) [6]. For example, the primary challenges in ammonia synthesis lie in the stringent reaction conditions and high energy consumption. The traditional Haber process requires high temperatures (450-600°C) and high pressures (150-300 atmospheres) to enable the reaction between nitrogen (N_2) and hydrogen (H_2) to produce ammonia [7]. Such conditions demand substantial energy input and entail complex equipment and high operational costs. Moreover, the triple bond in N_2 is notably stable, making N2 difficult to activate and thus limiting reaction efficiency [8]. In contrast to traditional methods, the NTP catalytic system enables efficient production under milder conditions. This is primarily because the high-energy electrons in NTP can directly activate nitrogen and hydrogen molecules, thereby facilitating reactions at lower temperatures and enhancing overall efficiency [9]. For CO_2 to methanol synthesis, industrial conditions typically range from 200-300°C and 50-100 bar, achieving CO_2 conversion selectivity over 90% and energy efficiency of 50-60% [10]. In contrast, the NTP catalytic system employing dielectric barrier discharge operates at ambient temperature and pressure, with CO_2 conversion rates exceeding 20% [11]. Due to the presence of reactive radicals and high-energy electrons, the NTP system effectively reduces the activation energy of the reactants and accelerates the activation of CO_2 and H_2, thereby promoting the reaction at lower temperatures and enhancing overall efficiency. This review primarily delves into the porous characteristics of catalysts and the design of active sites within NTP catalytic systems [12]. Firstly, the porosity of the support is pivotal for catalytic reactions in NTP systems; for instance, supports with high porosity can enhance the discharge effect of the NTP system, facilitating the activation of N_2 molecules and favoring the forward progression of ammonia synthesis reactions [13]. Secondly, active sites enhance the adsorption and activation of reactant molecules. By harnessing the density and distribution of active sites across different catalysts, catalytic activity under plasma conditions can be significantly influenced, thereby effectively increasing the selectivity for ammonia synthesis and carbon dioxide conversion to methanol, and improving hydrogen storage efficiency [14].

In summary, NTP exhibits numerous promising advantages in the development of novel catalytic systems for ammonia synthesis and CO_2 hydrogenation to methanol. This review provides a critical summary of relevant research cases from the past five years, focusing on the porous nature of catalyst supports and the design of active sites within the catalysts. This review serves as an important snapshot showcasing the latest advancements in NTP catalytic systems, fostering further technological progress.

2. Principles of Nonthermal plasma catalysis

2.1. Definition and characteristics of plasma

Plasma is the fourth state of matter consisting of free electrons and heavy particles, which can be generated by employing a high electric field. The free-moving charged particles in ionized gas possess unique properties, including high reactivity and the ability to initiate chemical reactions that are difficult to achieve under standard conditions. These attributes are particularly significant in energy and environmental catalysis, enhancing catalytic efficiency and facilitating green energy production. Plasma can be broadly categorized into Thermal Equilibrium Plasma (TEP) and NTP, each exhibiting unique characteristics, applications, and behaviors, making them suitable for different research and technological domains, especially in energy conversion. In plasma physics, classification is typically based on the temperature distribution of its constituent particles, particularly the relationship between electron temperature (T_e) and heavy particle temperature (T_h). In TEP, the electron temperature equals the heavy particle temperature ($T_e \approx T_h$), formed in high-energy density environments where all particles reach the same thermal equilibrium [15]. Conversely, in NTP, electron temperature and heavy particle temperature are unequal ($T_e \neq T_h$) [16]. Electrons gain energy from external electric fields, while heavy particles remain at lower temperatures due to mass differences, making electrons easier to accelerate [17]. NTP is widely applied in various technological fields, particularly in catalysis for energy-related reactions. NTP achieves efficient chemical reactions with lower energy input, which is crucial for developing energy-efficient and environmentally friendly catalytic technologies. By precisely controlling the plasma temperature distribution, catalytic reaction conditions can be optimized, enhancing energy conversion efficiency and reducing environmental pollution. For example, in CO_2 hydrogenation to methanol, combining catalysts with plasma (e.g., $Cu/\gamma\text{-}Al_2O_3$, $Pt/\gamma\text{-}Al_2O_3$, and MnO_x/ZrO_2) can improve CO_2 conversion rates and methanol yields. At ambient temperature, using $Cu/\gamma\text{-}Al_2O_3$ catalysts achieves a methanol yield of 11.3% and a CO_2 conversion rate of 21.2% [18]. Compared to traditional thermal catalytic systems requiring high pressure, NTP catalysis activates CO_2 with lower energy input, increasing energy efficiency and offering promising prospects for carbon capture and green hydrogen utilization.

2.2. Conventional thermal catalysis vs. NTP catalysis

Catalysis is a process that accelerates the rate of a chemical reaction through the use of a catalyst, which itself is not consumed in the reaction. As illustrated in the figure, traditional catalysis is characterized mainly by the following two aspects:

Firstly, traditional catalysis requires high temperatures and pressures, which raise the kinetic energy of reactant molecules, enhancing the likelihood of effective collisions. For instance, the Haber-Bosch process for ammonia synthesis operates at high temperatures (450-600°C) and pressures (150-300 bar) to overcome the reaction's high energy barrier [19]. Similarly, the conversion of CO_2 to methanol using traditional methods typically necessitates high temperatures (200-300°C) and high pressures (50-100 bar) along with a copper-based catalyst. While these methods are effective, they consume a substantial amount of fossil energy and produce significant CO_2 emissions [20]. Secondly, traditional catalysis requires providing sufficient energy to overcome the reaction energy barriers, thereby promoting chemical conversion. High temperatures and high pressures help increase the kinetic energy of the reactant molecules, thereby facilitating these barriers to achieve the chemical reaction [21]. In contrast, NTP catalysis is characterized mainly by the following two aspects: Firstly, NTP catalysis can achieve significant reaction rates and selectivity enhancements under milder reaction conditions. Under NTP conditions, the reaction temperature and pressure can be significantly reduced, thereby lowering energy consumption and environmental impact. NTP technology shows great potential in green chemistry and energy applications [22]. For example, combining NTP with fluidized catalysts (such as cobalt-nickel supported magnesium oxide) can significantly increase the ammonia production rate, with energy efficiency reaching 6.57 mg kW^{-1} H^{-1} [22]. Secondly, NTP utilizes the characteristics of plasma discharge to lower reaction energy barriers. During NTP conditions, the discharge phase contains numerous high-energy particles that collide with reactant molecules, activating and energizing them. These excited molecules then interact with the catalyst surface, initiating a series of surface chemical reactions that ultimately achieve the desired chemical conversion. For example, plasma catalysis using CoO/MgO catalysts can achieve up to a 35% CO_2 conversion rate and a maximum methanol yield of 10% under ambient conditions, outperforming thermal catalysis in terms of reaction conditions, thereby reducing energy consumption [20].

Overall, NTP catalysis achieves highly efficient chemical conversions by lowering reaction energy barriers under milder conditions, providing a new pathway for green and sustainable chemistry. As shown in Figure 1, NTP catalysis has significant advantages over conventional catalysis in reducing the strictness of reaction conditions and improving energy efficiency.

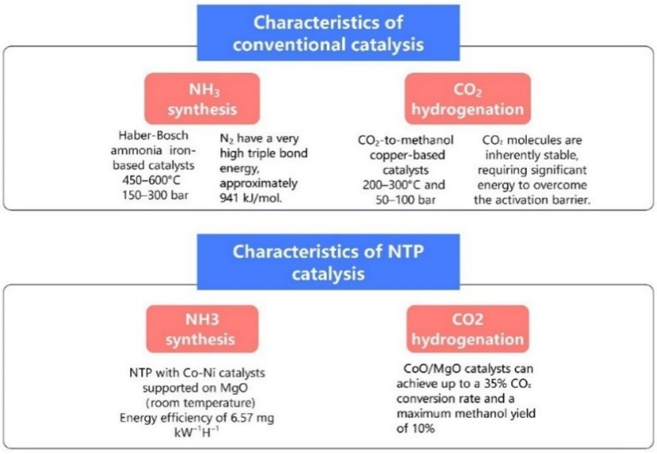

Figure 1: Comparison of traditional and NTP catalysis for chemical reactions.

3. Catalyst support design for NTP-catalytic ammonia synthesis and CO_2 hydrogenation

3.1. Effect of pore structure of catalyst supports

The pore structure of catalysts plays a critical role in plasma catalysis, influencing plasma discharge and providing protection for products. The interaction between plasma and the catalyst enhances plasma discharge, lowering the reaction energy barrier and improving catalytic efficiency. This interaction further lowers the reaction energy barrier and enhances the catalytic efficiency of the catalyst. For instance, in the study by Maria et al., Zeolite 5A was used as a support in a NTP system for ammonia synthesis. Zeolite 5A has a uniform pore size (~0.5 nm), ensuring efficient diffusion of reactants and products without mass transfer limitations. Due to these structural characteristics, the integration of NTP with Zeolite 5A demonstrated significant synergistic effects. Emission spectroscopy results in the study showed a significant enhancement in peak intensity within the 300-400 nm wavelength range, indicating an elevated catalytic effect of micro-discharges generated by the plasma. This effect is mainly attributed to the interaction between low-temperature plasma and the zeolite's porous structure, significantly enhancing the energy yield in the ammonia synthesis catalytic system. When Zeolite 5A was used in the reactor, the observed energy yield was 15.5 g-NH_3/kWh, which is at least 50 times higher than the yield obtained using plasma alone under the same equivalent molar flow conditions (0.16 g-NH_3/kWh) [23].

Moreover, most studies use various porous supports to load metal catalysts for ammonia synthesis or CO_2-to-methanol systems, enhancing plasma discharge effects. In another study by Maria et al., Zeolite Imidazolate Frameworks (ZIFs) were used. Unlike Zeolite 5A, ZIFs are supports for metal catalysts. ZIF-8 contained zinc ions, while ZIF-67 contained cobalt ions. These metal centers themselves possess high catalytic activity as they can influence the electronic environment, thereby promoting NTP discharge effects and enhancing the activation of nitrogen and hydrogen molecules. Additionally, both ZIF-8 and ZIF-67 have uniform window pore sizes of 3.4 Å, facilitating the diffusion of reactant gases (N_2 and H_2) and products (NH_3) through the framework, thereby exhibiting high catalytic performance. For instance, in the study, with a 1:3 nitrogen-to-hydrogen ratio, the ammonia synthesis rate for ZIF-8 was 19.35 μmol NH_3/min g_cat, and for ZIF-67, it was 21.55 μmol NH_3/min g_cat. However, in the absence of any catalyst within the plasma, the ammonia synthesis rate dropped significantly to about 0.386 μmol NH_3/min, which is approximately 70 times lower compared to when ZIF catalysts were used [24]. Due to these characteristics, ZIF-8 and ZIF-67 are used as catalysts for plasma-induced ammonia synthesis. In other studies, there are numerous cases of using porous supports to load metal catalysts. γ-Al_2O_3 is well-known for its high specific surface area, typically ranging between 100 and 300 m^2/g. This high surface area is beneficial for dispersing copper aggregates, enhancing catalytic activity by providing more active sites for the reaction. Its pore volume usually ranges from 0.3 to 0.8 cm^3/g, with pore sizes typically in the mesoporous range, approximately 2 to 50 nm. These characteristics allow it to accommodate reactant molecules and facilitate their diffusion to the active sites, balancing the accessibility of reactants and the stability of the catalyst structure, which is advantageous for both CO_2-to-methanol synthesis and ammonia synthesis reactions. The porous nature of γ-Al_2O_3 allows for efficient adsorption and diffusion of reactant molecules and enhances plasma discharge effects. This is particularly beneficial in plasma catalysis. For example, when plasma alone is used without a catalyst, the CO_2 conversion rate is 6.1%, and methanol selectivity is 3.7%. However, the combination of Cu/γ-Al_2O_3 catalyst and plasma significantly improves the conversion rate. At a 4 wt% copper load, the CO_2 conversion rate increased to 9.8%, with methanol selectivity reaching 47.5%. The energy consumption for producing CH_3OH significantly decreased from 855.9 kJ/mol in a pure plasma system to 41.6 kJ/mol in the plasma-Cu/γ-Al_2O_3 system [25]. Additionally, with γ-Al_2O_3 as the support, Rh/γ-Al_2O_3 with a 2 wt% Rh load produced 1.43 vol% ammonia with an energy efficiency of 0.94 g NH_3/kWh, demonstrating the best catalytic performance among various metal-loaded γ-Al_2O_3 catalysts [26]. The ammonia concentration significantly increased by 95% compared to the bare plasma reactor. In the study by Li et al., mesoporous silica (SBA-15) was used as a support, exhibiting a highly ordered mesoporous structure. In the study, a Ni-Mg 0.02/SBA-15-IWI catalyst developed using the incipient wetness impregnation (IWI) method exhibited the highest ammonia synthesis rate of 4.4 mmol h^{-1} g_cat^{-1} at 9.5 kV energy input, outperforming the in-situ-doped Ni-Mg 0.02/SBA-15 in-situ catalyst (3.7 mmol h^{-1} g_cat^{-1}). The IWI method involves adding magnesium oxide to the SBA-15 material, better maintaining the mesoporous structure of SBA-15. However, when developing the Ni-Mg 0.02/SBA-15 in-situ catalyst using the in-situ doping method, residual magnesium within the SBA-15 reduced the average pore diameter of the catalyst. Consequently, the Ni-Mg 0.02/SBA-15-IWI catalyst had a larger average pore size of 5.41 nm, significantly higher than the 4.19 nm average pore size of the Ni-Mg 0.02/SBA-15 in-situ catalyst [27]. The larger pore size facilitated the diffusion of plasma-active species into the pores, promoting micro-discharges on the catalyst surface and enhancing catalytic efficiency, thereby increasing the ammonia synthesis rate.

The aforementioned catalysts and supports leverage plasma discharge effects on porous support surfaces to enhance catalytic efficiency. However, in other studies, the pore structure serves more as a protective measure for the plasma. In plasma catalysis, the protection of plasma, especially in ammonia synthesis, is crucial. According to Tu et al., using mesoporous catalysts like MCM-41 can effectively achieve this. MCM-41 has a uniform hexagonal arrangement of mesopores with a typical diameter of 2.5 nm, providing large pore volume and diameter. The short lifespan of plasma-induced active species prevents their diffusion into the mesopores of MCM-41, thus shielding ammonia molecules within the pores from these reactive species. This pore size (~2.5 nm) being smaller than the plasma discharge's Debye length (αD) prevents plasma formation inside the mesopores, offering a "shielding protection" effect that enhances ammonia synthesis yield. Using MCM-41, the ammonia synthesis rate (RNH_3) significantly increased compared to plasma alone. The rate with plasma alone was 575 μmol/g/h, which increased to 1131 μmol/g/h with silica, and further to 1452 μmol/g/h with MCM-41. The Ni/MCM-OUT catalyst achieved the highest energy yield of 1.2 g NH_3/kWh, significantly higher than the yield with plasma alone [28].

3.2. Active sites engineering for improving the NTP catalysis

In NTP catalysis, designing active sites is crucial for enhancing reaction efficiency, such as ammonia synthesis and CO_2 hydrogenation to methanol. The effectiveness of catalysts depends on the nature and density of these active sites, which can be metal nanoparticles, oxides, or other materials. Generally, higher density of active sites increases interactions with reactants, enhancing the reaction rate [29].

Bimetallic catalysts often outperform monometallic ones. In CO_2-to-methanol conversion, the $7Ni_3Co$ catalyst shows the highest alcohol yield at 4.7 mmol g_cat^{-1} h^{-1}, 2.6 times higher than 10Ni or 10Co catalysts. This is mainly due to the lower energy barrier (0.63 eV) in the rate-limiting step of methanol synthesis, indicating that the surface of the $7Ni_3Co$ catalyst provides a more favorable reaction pathway and faster conversion rate. This catalyst achieves 46% methanol selectivity and 24% CO_2 conversion at room temperature (35°C) and atmospheric pressure (0.1 MPa) [30].

For ammonia synthesis, studies have shown that the introduction of promoters such as magnesium and potassium can enhance the electronic density of active sites, thereby improving the activation of nitrogen. In the study by Rouwenhorst et al., the $5Mg\text{-}2Ru/\gamma\text{-}Al_2O_3$ catalyst exhibited the highest ammonia yield of 0.17 mol% under plasma enhancement, significantly higher than the control catalyst without Mg. Specifically, these catalysts showed a significant reduction in apparent activation energy under plasma enhancement: $2Ru/\gamma\text{-}Al_2O_3$: 20 kJ/mol, $5Mg\text{-}2Ru/\gamma\text{-}Al_2O_3$: 36 kJ/mol, $10K\text{-}2Ru/\gamma\text{-}Al_2O_3$: 41 kJ/mol, and $5Cs\text{-}2Ru/\gamma\text{-}Al_2O_3$: 27 kJ/mol. Additionally, the $10K\text{-}2Ru/\gamma\text{-}Al_2O_3$ catalyst achieved an ammonia yield of 0.09 mol% at 330°C, indicating that the addition of potassium also effectively increased the density of active metal sites on the catalyst, thus enhancing ammonia yield [31].

Monometallic catalysts also perform well in these reactions. For example, in the CO_2-to-methanol reaction, the CuO-MgO/β catalyst under plasma conditions achieves 72.0% methanol selectivity and 8.5% CO_2 conversion at room temperature and atmospheric pressure (30°C and 0.1 MPa). In contrast, the traditional bimetallic Cu-Ni catalyst achieves 98.7% methanol selectivity and 7.9% CO_2 conversion at 225°C and 4 MPa, indicating that the CuO-MgO/β catalyst can operate efficiently at ambient conditions, offering significant advantages over traditional catalysts that require higher temperatures and pressures. Similarly, the Cu-ZnO/MgO catalyst achieves 91% methanol selectivity and 7.6% CO_2 conversion at 200°C and 5 MPa, further demonstrating the superiority of high-density active sites at ambient conditions [29].

For ammonia synthesis, the Ni/Al_2O_3 catalyst exhibits the highest ammonia synthesis rate of 471 μmol g^{-1} h^{-1}, which is a 100% increase compared to using plasma alone, proving the critical interaction between plasma and metal active sites on the catalyst surface [33]. Additionally, Wang et al.'s study using NH_3-TPD (ammonia temperature-programmed desorption) showed that the presence of weak acid sites facilitated ammonia desorption, accelerating the ammonia synthesis reaction and thereby increasing catalytic efficiency. Specific data showed ammonia desorption from weak acid sites between 120-300°C, medium acid sites between 320-530°C, and strong acid sites between 550-730°C. In this study, adding different metals such as Ni, Cu, and Fe to the Al_2O_3 support significantly reduced the density of acid sites on the catalyst surface, thereby accelerating the ammonia synthesis reaction: Al_2O_3: 0.97 mmol NH_3 per gram, Ni/Al_2O_3: 0.46 mmol per gram, Cu/Al_2O_3: 0.45 mmol per gram, Fe/Al_2O_3: 0.33 mmol per gram [19].

Overall, through the careful design of active sites and interfaces in bimetallic and monometallic catalysts, the catalytic performance of NTP systems can be significantly enhanced, making them more feasible for sustainable chemical production such as green ammonia and CO_2 utilization. These innovations are crucial for improving reaction efficiency and reducing energy consumption, especially in the context of green ammonia production and CO_2 utilization.

4. Conclusion

Here we provide a critical review on the application of NTP catalysis in ammonia synthesis and CO_2 hydrogenation to methanol, with a special focus on two important aspects affecting the performance, that is, the pore structure of catalyst carriers and active metal sites. Firstly, the review of the literature highlights the critical role of catalyst support pore structure in enhancing the performance of NTP catalysis systems for ammonia synthesis and CO_2 hydrogenation to methanol. High porosity in supports like Zeolite 5A, ZIFs, γ-Al_2O_3, and SBA-15 enhances plasma discharge effects, facilitates the diffusion of reactants and products, and provides a protective environment for the generated products, thereby improving overall catalytic efficiency. Secondly, the unique porous structures also support the stabilization and dispersion of active metal sites, ensuring their optimal interaction with reactant molecules and plasma-generated species. The design and engineering of active sites in catalysts, whether monometallic or bimetallic, significantly impact the reactivity and efficiency of NTP catalysis. Active sites composed of metals like Co, Ni, Cu, and Ru, often enhanced with promoters such as Mg and K, show increased electronic density and improved reactant activation, thus achieving higher reaction rates and selectivity under ambient conditions.

Future research should optimize catalyst support pore size and distribution, enhancing plasma-active interactions and reactant diffusion. Advanced techniques to monitor plasma-catalyst interactions will also be crucial. Exploring bimetallic and alloy catalysts with novel promoters could unveil new pathways for enhanced performance. Emphasis on the development of scalable and economically viable NTP catalytic systems will be necessary to transition from laboratory-scale studies to industrial applications. Investigating the long-term stability and reusability of NTP catalysts in continuous operation settings will also be essential to ensure sustainable and practical deployment in green energy and chemical production processes. Finally, interdisciplinary collaboration combining plasma physics, materials science, and chemical engineering will be instrumental in advancing the field of NTP catalysis, aiming for breakthroughs in energy-efficient and environmentally friendly catalytic technologies.

References

[1] *Global Carbon Project. (2021). Carbon Budget and Trends 2021. https://www.globalcarbonproject.org/carbonbudget/.*

[2] *International Energy Agency. (2020). Global Energy Review: CO_2 Emissions in 2019. https://www.iea.org/articles/global-co2-emissions-in-2019.*

[3] International Energy Agency. (2019). The Future of Hydrogen. https://www.iea.org/reports/the-future-of-hydrogen#.

[4] International Renewable Energy Agency. (2021). Renewable Energy Statistics 2021. https://www.irena.org/publications/2021/Aug/Renewable-energy-statistics-2021.

[5] International Renewable Energy Agency. (2021). Innovation Outlook: Renewable Methanol.

[6] Fridman, A. (2008). Plasma Chemistry. Cambridge University Press. https://doi.org/10.1017/CBO9780511546075.

[7] Ertl, G. (2008). Heterogeneous catalysis on atomic scale. Chem. Rec., 8(3), pp. 123-133. https://doi.org/10.1016/S1381-1169(01)00460-5.

[8] Zhang, X., Liu, Y., & Chen, H. (2020). Low-temperature plasma-catalytic synthesis of ammonia at ambient conditions. J. Energy Chem., 30(1), pp. 20-26.

[9] Palma, V., Cortese, M., Renda, S., Ruocco, C., Martino, M., & and Meloni, E. (2020). A Review about the Recent Advances in Selected NonThermal Plasma Assisted Solid–Gas Phase Chemical Processes. Nanomaterials, 10(8). https://doi.org/10.3390/nano10081596.

[10] Gao, Y., Wang, H., & Zhang, L. (2020). Plasma-assisted CO_2 conversion to methanol: A review. Chem. Eng. J., 396, 125179.

[11] Zhang, X., Chen, J., & Li, W. (2021). Application of dielectric barrier discharge plasma in CO_2 conversion: A review. J. CO_2 Util., 44, 101398.

[12] Li, Y., Zhang, H., Wang, X., Liu, J., & Chen, Z. (2021). Synergistic Effect of Plasma and Oxygen Vacancies on Ammonia Synthesis over TiO_2-based Catalysts. Catal. Sci. Technol., 11(5), pp. 1234-1245. 10.1039/CST2021X12345.

[13] Xie, Q., Zhuge, S., Song, X., Lu, M., Yu, F., Ruan, R. and Nie, Y. (2019). Non-thermal atmospheric plasma synthesis of ammonia in a DBD reactor packed with various catalysts. J. Phys. D: Appl. Phys., 53, 064002.

[14] Chen Z, Koel, B. E., & Sundaresan, S. (2021). Plasma-assisted catalysis for ammonia synthesis in a dielectric barrier discharge reactor: key surface reaction steps and potential causes of low energy yield. J. Phys. D: Appl. Phys., 55, 055202.

[15] Chattopadhyay, S. (2024). Existence of Small-Amplitude Double Layers in Two-Temperature Non-Isothermal Plasma. Ukr. J. Phys., 68(12). 10.15407/ujpe68.12.795.

[16] Karthik, C., Sarngadharan, S. C., & Thomas, V. (2023). Low-Temperature Plasma Techniques in Biomedical Applications and Therapeutics: An Overview. Int. J. Mol. Sci., 25(1). 10.3390/ijms25010524.

[17] Korn, G. (2014). Power to the Electrons. Physics, 7, 125. https://physics.aps.org/articles/v7/125.

[18] Zhang, X. M. et al. (2023). Boosting methanol production via plasma catalytic CO_2 hydrogenation over a MnO_x/ZrO_2 catalyst. Catal. Sci. Technol., 13(8), pp. 2529-2539. https://doi.org/10.1039/d2cy02015g.

[19] Wang, Y. L. et al. (2019). Plasma-enhanced catalytic synthesis of ammonia over a Ni/Al_2O_3 catalyst at near-room temperature: insights into the importance of the catalyst surface on the reaction mechanism. ACS Catal., 9(12), pp. 10780-10793. https://pubs.acs.org/doi/10.1021/acscatal.9b02538.

[20] Ronda-Lloret, M., Wang, Y. L., Oulego, P., Rothenberg, G., Tu, X., & Shiju, N. R. (2020). CO_2 hydrogenation at atmospheric pressure and low temperature using plasma-enhanced catalysis over supported cobalt oxide catalysts. ACS Sustain. Chem. Eng., 8(47), pp. 17397-17407. https://pubs.acs.org/doi/10.1021/acssuschemeng.0c05565.

[21] Li, X. M. et al. (2021). Synergistic Catalysis of the Synthesis of Ammonia with Co-Based Catalysts and Plasma: From Nanoparticles to a Single Atom. ACS Appl. Mater. Interfaces., 13(44), pp. 52498-52507. https://pubs.acs.org/doi/10.1021/acsami.1c12695.

[22] Zhang, B. Q. et al. (2024). Reinforcement of fluidized catalysts with DBD plasma assisted for green ammonia synthesis. Int. J. Hydrogen Energy., 60, pp. 521-531. https://doi.org/10.1016/j.ijhydene.2024.04.079.

[23] Shah, J. R., Gorky, F., Lucero, J., Carreon, M. A., & Carreon, M. L. (2020). Ammonia Synthesis via Atmospheric Plasma Catalysis: Zeolite 5A, a Case of Study. Ind. Eng. Chem. Res., 59(11), pp. 5167-5176. https://pubs.acs.org/doi/10.1021/acs.iecr.9b05220.

[24] Zhang, J. et al. (2020). Synthesis of ammonia using mesoporous ZIF-8 and ZIF-67 catalysts in plasma. J. Catal., 389, pp. 123-134.

[25] Cui, Z. L. et al. (2022). Plasma-Catalytic Methanol Synthesis from CO_2 Hydrogenation over a Supported Cu Cluster Catalyst: Insights into the Reaction Mechanism. ACS Catal., 12(2), pp. 1326-1337. https://pubs.acs.org/doi/abs/10.1021/acscatal.1c04678.

[26] Patil, B. S. et al. (2021). The role of heterogeneous catalysts in the plasma-catalytic ammonia synthesis. Catal. Today., 362, pp. 2-10. https://doi.org/10.1016/j.cattod.2020.06.074.

[27] Li, S. C., Shao, Y., Chen, H. H., & Fan, X. L. (2022). Nonthermal plasma catalytic ammonia synthesis over a Ni catalyst supported on MgO/SBA-15. Ind. Eng. Chem. Res., 61(9), pp. 3292-3302. 10.1021/acs.iecr.1c04968.

[28] Wang, Y. L. et al. (2022). Shielding Protection by Mesoporous Catalysts for Improving Plasma-Catalytic Ambient Ammonia Synthesis. J. Am. Chem. Soc., 144(27), pp. 12020-12031. https://pubs.acs.org/doi/10.1021/jacs.2c01950.

[29] Chen, Q. et al. (2024). Plasma-catalytic CO_2 *hydrogenation to methanol over CuO-MgO/Beta catalyst with high selectivity. Appl. Catal. B Environ., 342, 123422. https://doi.org/10.1016/j.apcatb.2023.123422.*

[30] Wang, Y. L. et al. (2024). Engineering Ni-Co bimetallic interfaces for ambient plasma-catalytic CO_2 *hydrogenation to methanol. Chem., 10(8), pp. 2590-2606. https://doi.org/10.1016/j.chempr.2024.06.022.*

[31] Rouwenhorst, K. H. R., Kim, H., & Lefferts, L. (2019). Vibrationally Excited Activation of N2 in Plasma-Enhanced Catalytic Ammonia Synthesis: A Kinetic Analysis. ACS Sustain. Chem. Eng., 7(20), pp. 17515-17522. https://pubs.acs.org/doi/full/10.1021/acssuschemeng.9b04997.