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CO₂ Reforming with CH₄ via Plasma Catalysis System

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Abstract

Reforming of CO₂ and CH₄ into syngas (mixture of H₂/CO) can be an economical way to reduce anthropogenic emission of CO₂ and CH₄ and to generate alternative fuel. Up to date, catalysis and nonthermal plasma are two feasible techniques for CO₂/CH₄ reforming. However, both techniques face some obstacles which limit their applications. For catalysis, high energy consumption and catalyst deactivation are the major disadvantages while nonthermal plasma has the drawbacks of low selectivity and unwanted byproduct formation. To overcome the above obstacles, combining catalyst and nonthermal plasma as a hybrid system can induce synergistic effects to enhance syngas production rate and stability of the operating system. For the purpose of enhancing CO₂ utilization efficiency, understanding the interactions between catalyst and nonthermal plasma is essential.

Keywords: reforming of CO₂, syngas, plasma catalysis, synergistic effects

1. Introduction

Utilization of carbon dioxide is imperative and there is urgent demand for effective carbon dioxide reducing techniques. Reforming of carbon with methane, which is also called dry reforming of methane (DRM, the term “dry” is to distinguish from steam reforming which is to reform methane with water vapor) can be a feasible process to convert CO₂ and CH₄ into syngas (mixture of H₂/CO). Currently, catalysis and nonthermal plasma are two essential techniques for DRM to generate syngas and to reduce the anthropogenic emissions of greenhouse gases (GHGs). Catalytic reforming of CH₄/CO₂ is a high-selectivity, high production rate and well developed technique to generate syngas. Up to date, several types of catalysts have been investigated for their catalytic activity toward DRM, including noble metal catalysts [1], nickel-based catalysts [2], cobalt-based catalysts [3], spinels [4] and perovskites [5].

However, high operating temperature is required for effective conversion. Moreover, coke deposition leads to subsequent catalyst deactivation. Thus, how to effectively reduce operating temperature and coke deposition remains the big challenge for catalytic reforming [6, 7]. On the other hand, nonthermal plasma stands for an energy-saving reforming for GHGs reduction and many kinds of nonthermal plasma reactor have been designed and developed to enhance CO_2/CH_4 conversion efficiency. Nonthermal plasma can generate syngas at a lower operating temperature since the driving force of nonthermal plasma is electric energy instead of thermal energy [8]. Even so, nonthermal plasma has some limitations including low GHGs conversions, low syngas selectivity and byproduct formation, e.g. carbon soot. The above disadvantages reduce the applicability of nonthermal plasma for DRM [9]. To overcome the shortcomings of catalytic reforming and nonthermal plasma reforming, combining catalyst and nonthermal plasma as a hybrid reactor can be a solution since various interactions can be induced between catalyst and nonthermal, including the change of physicochemical properties of catalyst, enhancement of electric field and activation of catalysis [10]. Based on the interactions between catalysis and nonthermal plasma, limitations of catalytic reforming and nonthermal plasma reforming including catalyst deactivation and byproduct formation can be resolved due to enhancement of reforming performance toward DRM [11–13].

In this chapter, application of three types of DRM system, i.e. catalysis, nonthermal plasma and hybrid plasma catalysis will be introduced and discussed for their fundamental concepts, including reaction mechanism, state-of-the-art development, opportunities and shortcomings. Some important features for various reactors will also be highlighted in this chapter as a reference.

2. Catalytic reforming

CO_2 and CH_4 are stable molecules under atmospheric pressure, thus the temperature required for inducing spontaneous dissociation of CO_2 and CH_4 is comparatively high. **Figure 1** shows thermodynamic equilibrium for CO_2/CH_4 reforming without catalyst achieved with Gibbs free energy minimization algorithm [14]. It indicates thermodynamic equilibrium of reactants (CO_2 and CH_4) and products (CO , H_2 , $\text{C}_{(s)}$ and $\text{H}_2\text{O}_{(g)}$) with the assumption that carbon formation is inhibited. Assuming that carbon formation is inhibited, the temperature required for effective conversion of CO_2/CH_4 is comparatively high ($> 550^\circ\text{C}$) while water vapor can be generated simultaneously. Actually, carbon stands for the major byproduct during reforming and influences thermodynamics as well. At a lower operating temperature, water vapor and carbon are the major products and their formation can be inhibited when operating temperature is increased to over 700°C . Generally speaking, to generate syngas efficiently, operating temperature should be higher than 700°C , which is energy-consuming.

Catalyst is required to reduce the operating temperature of DRM since both CO_2 and CH_4 are stable and a great amount of thermal energy is needed to induce reforming. Noble metal-based catalysts including Pt, Pd, Ir, Rh and Ru have been investigated for their activities. They possess great activities toward DRM and good resistivities for coke deposition. The

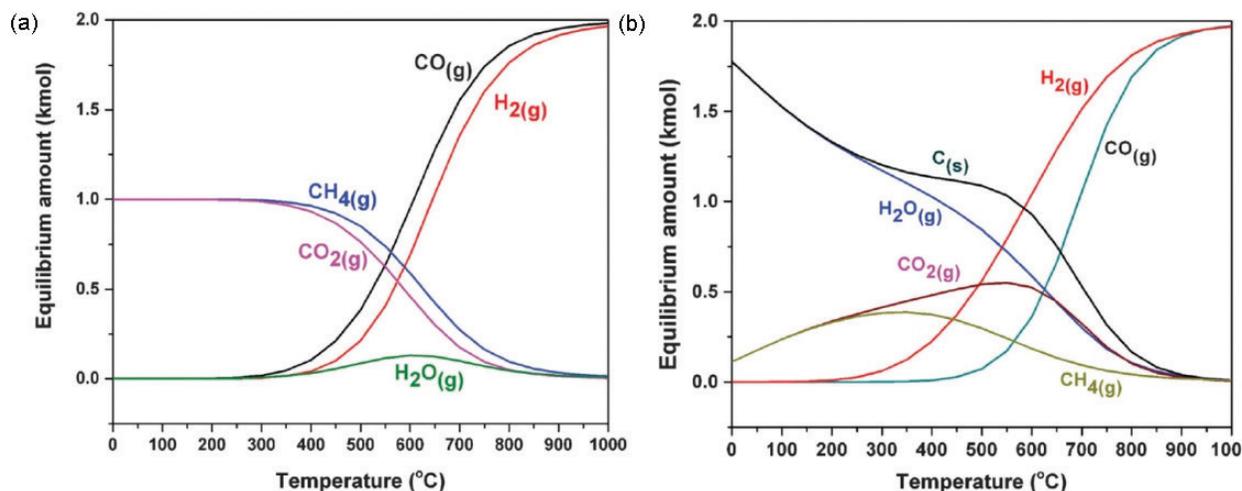


Figure 1. Thermodynamic equilibrium plots for DRM at 1 atm, from 0–1000°C and at inlet feed ratio of CO₂/CH₄ = 1 (a) Assuming no carbon formation occurs, (b) assuming carbon formation occurs. These plots were created by using Gibbs free energy minimization algorithm on HSC Chemistry 7.1 software [14].

activity order of the above metal catalysts also depends on support and preparation method. Generally, Rh and Ru catalysts are good candidates since they have better catalytic activities and durabilities than other noble metals [15, 16]. However, their costs are also high which limits their industrial applicability. Hence, transition metal-based catalysts such as nickel, cobalt-based catalysts are frequently developed and investigated. Ni-based catalysts are most applied for DRM since they have high adsorption capacities toward CO₂ and CH₄ and many researches have been conducted for the purpose of increasing selectivity of syngas and stability of catalyst in terms of resistivity of coke deposition [17,18].

Generally, pathways of catalytic reactions can be divided into three categories: Langmuir-Hinshelwood (L-H), Eley-Rideal (E-R) and Mars-van Krevelen (MVK), as described in **Table 1** [19]. Kinetic studies point out that DRM follows the reaction route of L-H mechanism. The reaction mechanism of DRM can be described as **Figure 2**, density functional theory (DFT) simulation results of DRM kinetics achieved with Pd/MgO catalyst indicate that CH₄ and CO₂ are firstly adsorbed on Pd and MgO surface and then dissociated into CO, O, C and H atoms [20]. It

Carbon structure	Designation	Temperature range (°C)
Surface carbide	C _α	200–400
Amorphous carbon films	C _β	250–500
Bulk Ni carbide	C _γ	150–250
Vermicular filaments/whiskers	C _v	300–1000
Graphite platelet films	C _c	500–550

Table 1. Details of different carbon species formed on the catalyst surface [21].

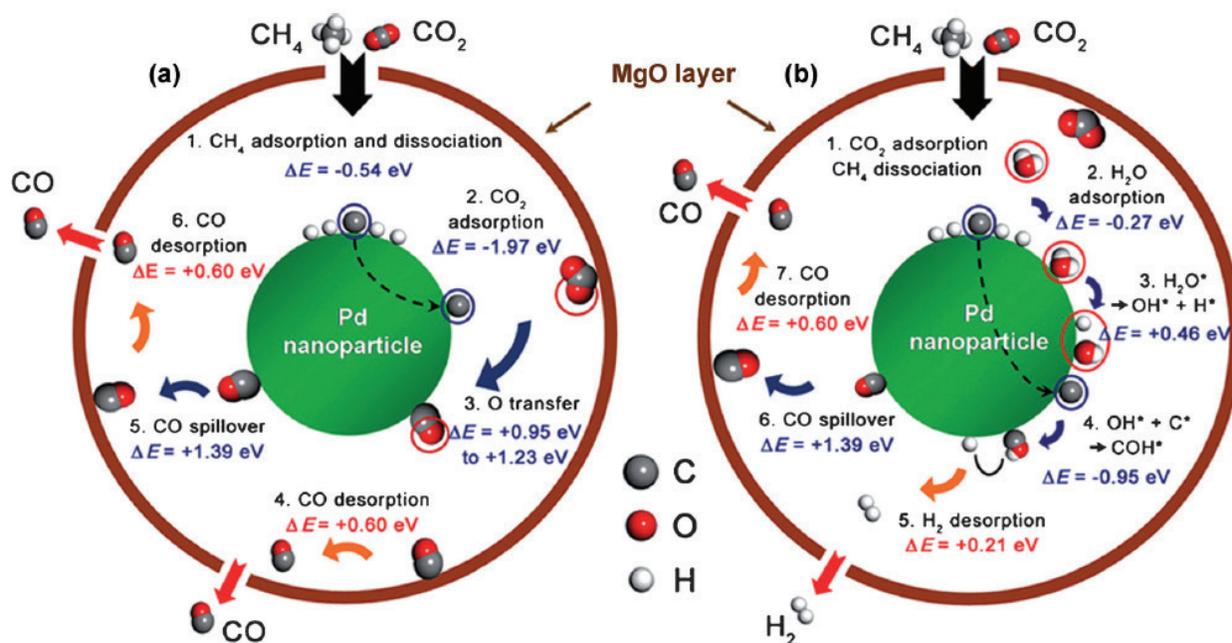


Figure 2. Results from DFT studies on the multifunctional CH_4 reforming mechanism under dry reforming conditions (a) and an H_2O atmosphere (b). The reaction proceeds in clockwise direction. Pd dissociates CH_4 and MgO binds and activates CO_2 . MgO opens a favorable CO production pathway. H_2O byproducts are attributed to H_2 production. Pd dissociates H_2O into PdOH and PdH, PdOH and PdC were combined into PdCOH. H_2 association from PdCOH and PdH is easier than direct H_2 association from two PdH. These CO and H_2 production pathways are accessible at low temperature and assure low-temperature activity of Pd-MgO/ SiO_2 (ME) [20].

is noted that CO desorption is an endothermic reaction, thus desorption of CO plays the role of rate-limiting reaction of DRM. Also, H atoms can further recombine to form H_2 and desorb onto effluent gas stream. Moreover, if water vapor is added into the gas stream, water molecules participate in catalysis and more active species can be generated such as OH^* , H^* and COH^* radicals, providing more formation routes of H_2 , resulting in higher generation rate of H_2 .

In terms of long-term operation of scaled-up catalytic reforming, coke deposition is the serious problem to shorten the duration of operation. Coke can be generated via several ways during reforming, as described in **Table 2**. Carbon formation can be classified into 5 categories, including the form of surface carbide, amorphous carbon films, metal carbide, whiskers and

Mechanism	Description
Langmuir-Hinshelwood	Both reactants are adsorbed on catalyst surface firstly. Next, adsorbed reactants can react with each other and form products. The final step is desorption of products and regeneration of active sites.
Eley-Rideal	One of reactants is firstly adsorbed on catalyst surface. Further reaction takes place between adsorbed specie and gas phase-specie.
Mars-van Krevelen	One of reactants is chemisorbed on catalyst, and then diffuses to lattice to react with the other adsorbed reactant.

Table 2. Categories of catalysis mechanisms.

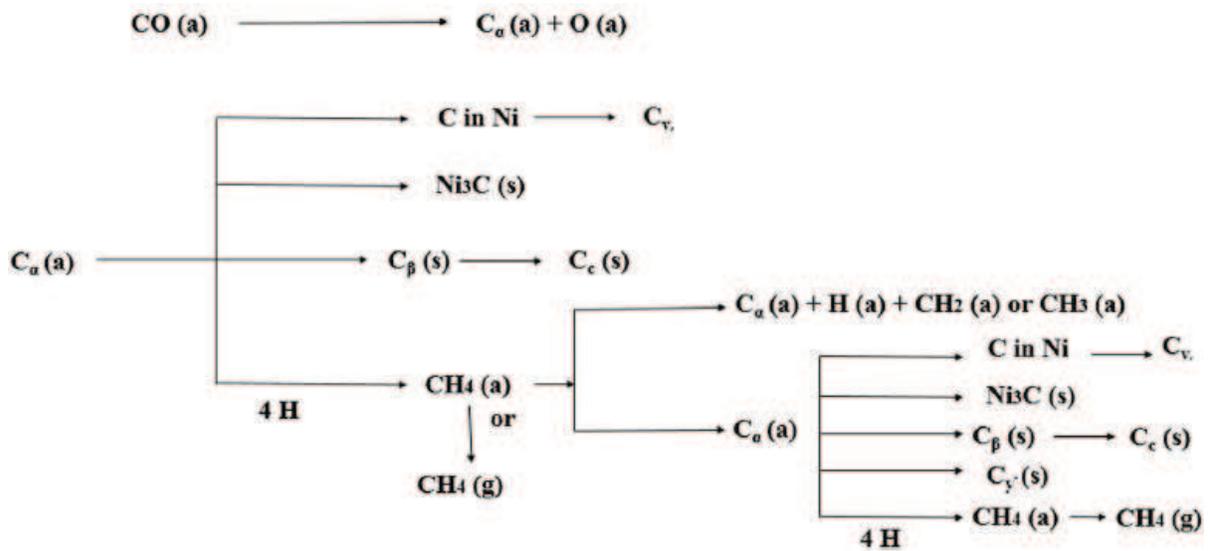


Figure 3. Mechanism of carbon formation at the catalyst surface [21].

platelet films, depending on the carbon source, temperature, structure and deposition site. Generally, C_α is firstly formed via dissociation of CO₂ and CH₄ and this reaction is feasible at a lower temperature. Other carbon species including C_β, C_γ, C_v and C_c can be further synthesized via several ways as listed in Figure 3 [21]. It is noted that carbon can be transferred from one form to another. For example, amorphous carbon film can be transformed into graphite platelet films when the temperature is increased. Another example is that carbon whiskers can be easily formed from many types of carbon at a high temperature. To effectively reduce the formation of C_α, operating temperature is suggested to be high. However, high operating temperature leads to formation of other carbon species. As a result, carbon deposition inevitably takes place since formation routes are various. Many works are conducted to reduce the problem of coke deposition, including catalyst modification via partial metal substitution, introduction of support and surface pre-treatment and reactor designing. Nevertheless, coke deposition still plays an important role in limiting performance and the increase of the cost of catalytic reforming.

3. Nonthermal plasma reforming

Nonthermal plasma stands for an alternative to treat GHGs since the driving force of non-thermal plasma is electronic energy instead of thermal energy. With the existence of external electric field, electrons can be accelerated and then collide with gas particles including CO₂, CH₄, intermediates, radicals and ions. When energy is transferred from electron to the above species, chemical reactions take place such as electron impact excitation, dissociation and ionization, Penney ionization and electron attachment. CH₄ and CO₂ can be directly dissociated into smaller fractions when the transferred energy exceeds 8.8 and 4.5 eV, respectively [22, 23]. The dissociated products including methyl radical, methylene,

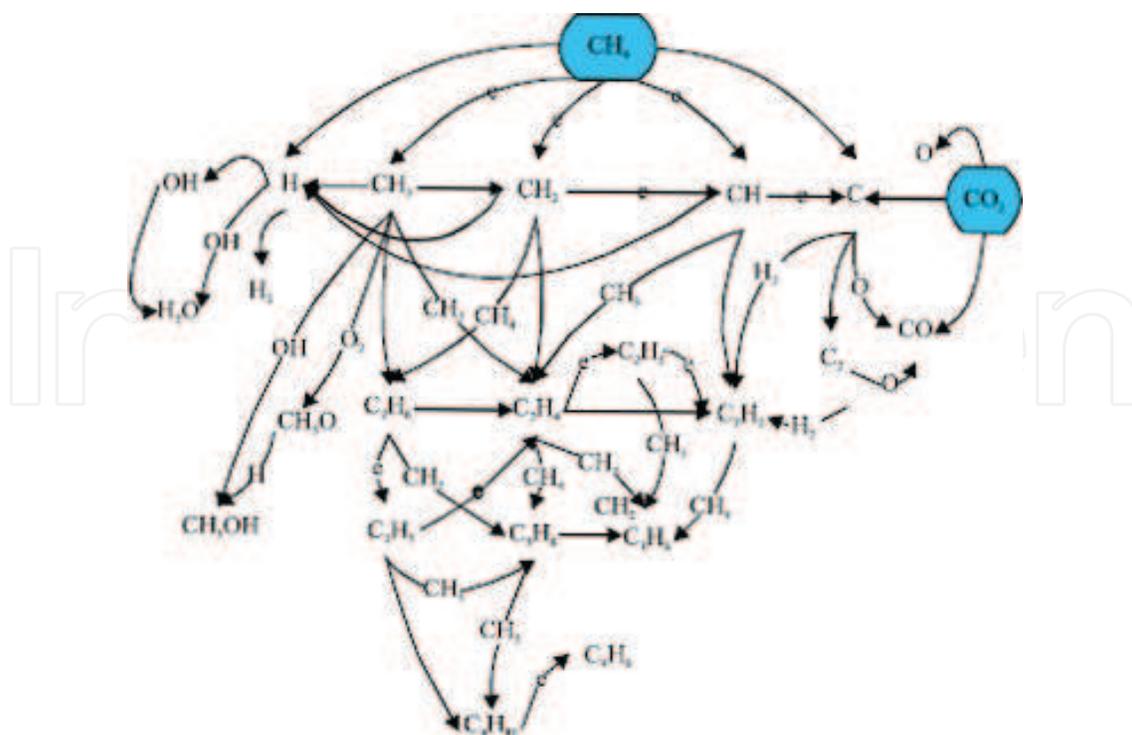


Figure 4. Possible reaction mechanisms in a nonthermal plasma reactor [24].

oxygen and hydrogen radical can further react with each other to form H_2 , CO and other byproducts, e.g. ethylene, water vapor and methanol. **Figure 4** depicts possible reaction routes for nonthermal plasma reforming [24]. CH_4 can be dissociated into various radicals, depending on how much energy is transferred from electron. On the other hand, CO_2 can also be dissociated into CO and O simultaneously. The above reactive species including radicals, H and O atoms can further react to form hydrocarbon radicals and molecules. Radicals mentioned beforehand can react with CH_4 and CO_2 to enhance their dissociation rates. It is noted that electrons can react with those particles to dissociate them into smaller fragments and the more important point is that radicals are unstable to have high activity toward other particles.

Actually, direct dissociation of CO_2/CH_4 is difficult to take place in nonthermal plasma due to high energy demand. In terms of CO_2 , vibrational excited and electron excited CO_2 are more easily generated and participate in DRM since the energy required for excitation is lower than CO_2 dissociation. Those excited CO_2 possess higher energy, thus, energy required to generate CO, O, CO_2^+ and O_2^+ can be reduced as illustrated in **Figure 5**. In terms of CH_4 , CH_x ($x = 1-3$) radicals especially CH_3 (methyl radical) and CH_2 (methylene) are formed with different levels. These species are unstable and tend to react with other species [26]. When two or more radicals react with each other, higher hydrocarbons can be generated [25]. For example, when two CH_3^* radicals react with each other, ethane can be formed as illustrated in **Figure 6** [27]. From the perspective of DRM, hydrocarbons are byproducts since the purpose of DRM is to generate syngas. However, this process can be useful for generating hydrocarbons, such as plasma polymerization [28].

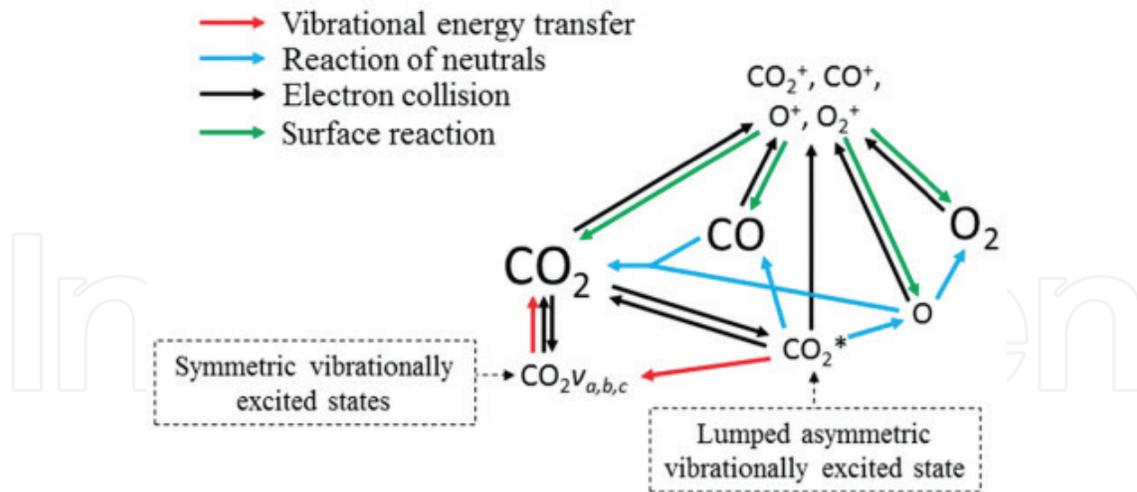


Figure 5. Reaction pathway of the CO₂ kinetic model [25].

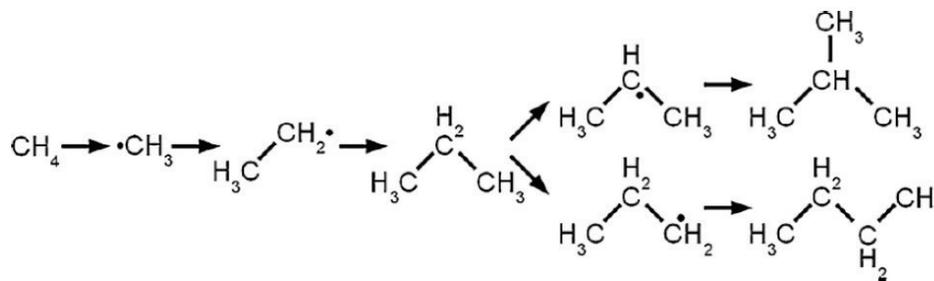


Figure 6. CH₄ branching mechanism [27].

4. Hybrid plasma catalysis

Combining nonthermal plasma with catalyst to form a hybrid system is expected to solve the obstacles of catalysis and nonthermal plasma due to the induction of various interactions. Figure 7 shows a conventional plasma catalysis reactor, catalyst is placed inside the discharge region of plasma reactor [29]. With this manner of reactor designing, various interactions can be induced to enhance the performance of reforming. Up to date, many interactions are discovered while some synergies are still vague. Many works are focusing on elucidation of synergies of plasma-catalysis interactions including experimental and simulation studies. Currently, those known interactions can be divided into two categories: plasma influencing catalyst and catalyst influencing plasma. Some interactions have positive effects on DRM, thus some researches are dedicated to modify those synergies. Those synergies will be briefly introduced below.

4.1. Plasma influencing catalyst

During discharge, a large amount of particles including electrons, ions, intermediates, excited species and radicals are generated. These particles may collide with catalyst and some energy

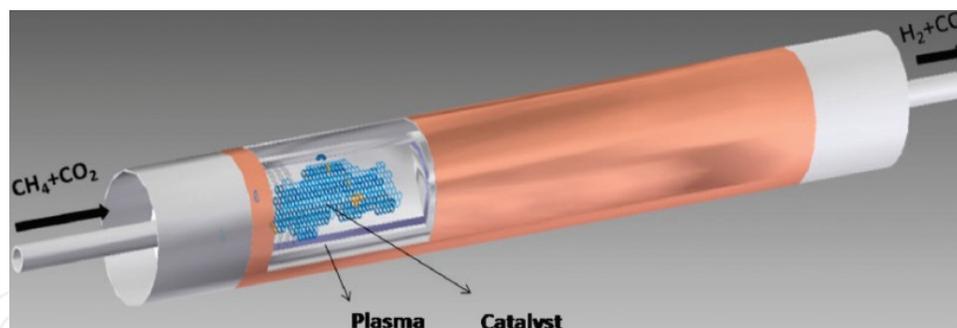


Figure 7. Schematic representation of the catalyst-packed dielectric barrier discharge reactor [29].

can be transferred onto catalyst surface. The most important part of transferred energy is thermal energy. Thermal energy can be transferred from electrons to particles on catalyst surface to heat up the particle, forming a hot spot, as shown in **Figure 8**. It is observed that with the packing of catalyst on the electrode, the surface temperature of electrode is increased since catalyst can absorb thermal energy transferred from particles [30]. As a result, catalytic reforming may take place on catalyst surface if local temperature (hot spot) exceeds the temperature required for catalysis. Next, local high temperature may induce restructuring of metal oxide clusters since their internal energy is increased. The result is that physicochemical properties of catalyst can be altered during reforming, such as particle size, pore structure, valence of metal, metal-support interactions, surface area, surface free energy, surface acidity/basicity and oxygen vacancy. In terms of catalysis, the above characteristics influence its catalytic activity well: firstly, particle size influences adsorption heat and thus adsorption and desorption rate are further changed. Electron bombardments can result in smaller average metal cluster size (**Figure 9**) and adsorption heat between CO_2/CH_4 and catalyst and further enhance CO_2/CH_4 adsorption and H_2/CO desorption rate [31]. Secondly, pore structure also affects CO_2/CH_4 adsorption on surface and inside pores. Larger pore size may be feasible for reforming since the resistance of diffusion can be lower and leads to better desorption. However, the relationship between pore size and operating parameter of nonthermal plasma is still unclear, thus, how to control the pore size remains a challenging task [32]. Thirdly, larger surface area and density of oxygen

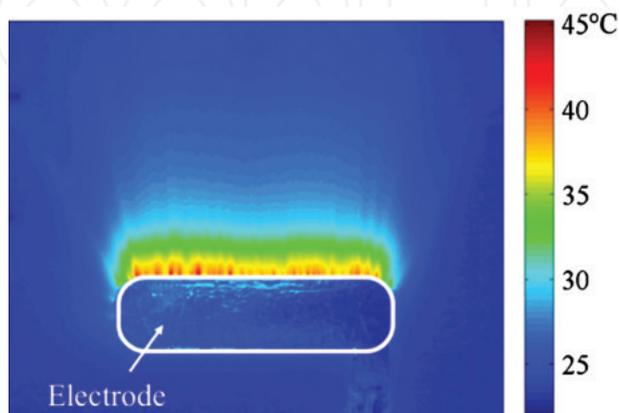


Figure 8. Absolute temperature distribution in a DBD, showing the occurrence of surface hot spots [30].

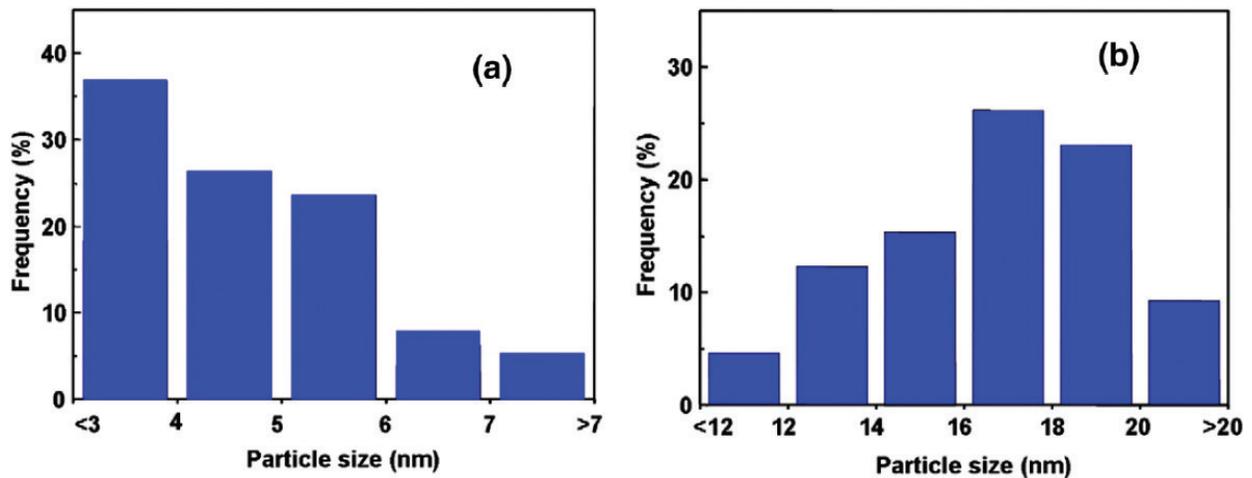


Figure 9. Particle size distribution achieved with TEM of (a) Plasma treated Ni/MgO and (b) conventional Ni/MgO catalysts [31].

vacancy are beneficial toward DRM since the former provides more adsorption sites and the latter provides more oxidizing agent [33]. Moreover, electron and ion bombardments can alter the chemical bonding between metal and oxygen, hence, density of oxygen in catalyst lattice can be increased. Fourthly, nonthermal plasma can affect the surface acidity/basicity since acidic and basic active species can be generated and then collide with catalyst. For catalytic reforming, surface acidity plays an important role since adsorbed CO₂ is acidic. In other words, catalyst possesses surface basicity are favorable for CO₂ adsorption and further dissociation [34]. Lastly, nonthermal plasma generates various stable and active species. Those active species can react with other species or can be adsorbed on catalyst surface, as presented in **Figure 10**. In plasma catalysis system, alternate reaction routes are provided since various active species are generated. Active species such as ions, radicals and electrons can be adsorbed to react

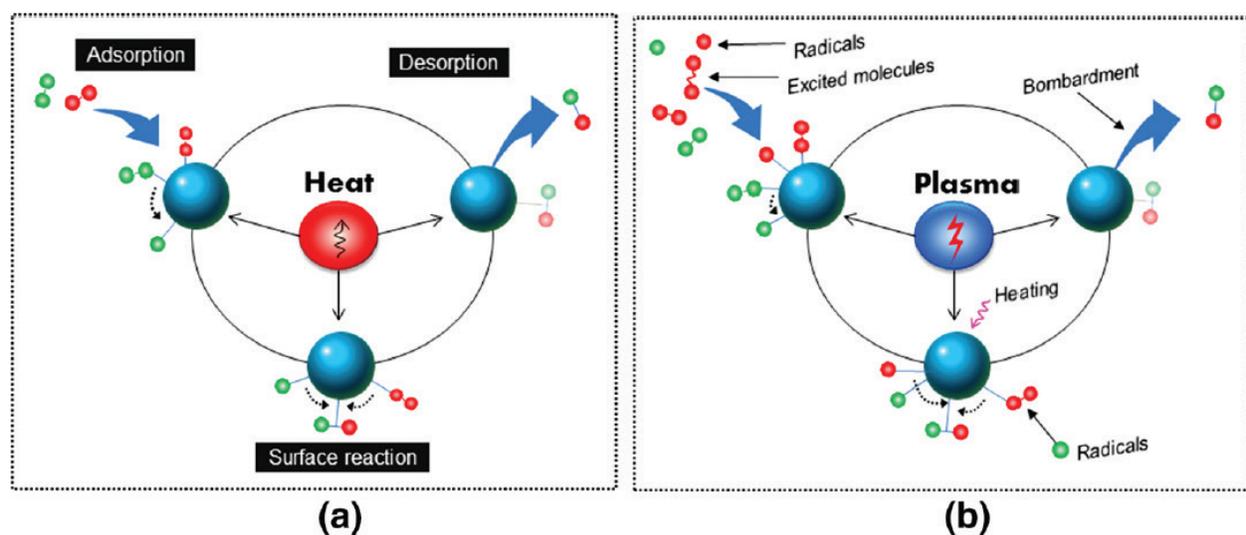


Figure 10. Three key steps in (a) thermal catalysis and (b) plasma-catalysis [10].

with other active species or can react with adsorbed species directly without prior adsorption. Hence, DRM does not necessarily follow L-H mechanism, which requires both two reactants are adsorbed on catalyst surface. In summary, nonthermal plasma can be applied for catalyst modification due to its capability to improve the physicochemical properties of catalyst. Also, non-thermal plasma can be combined with catalyst and the dissipated energy during discharge can possibly induce catalytic reforming. The most important advantage is that nonthermal plasma provides more reaction routes and more active species participating in DRM.

4.2. Catalyst influencing plasma

Packing catalyst into discharge region can affect plasma properties including electric field, electron density and energy distribution. Most of catalysts are dielectrics, which can be polarized to form electric dipole, i.e. surface electric potential. Electric potential can further interact with external electric field, electron and other charged particles. Thus, discharge behavior of plasma is influenced by the existence of catalyst and its dielectric constant. **Figure 11** shows the dependence of deposited power, current density and electron temperature on the dielectric constant (ϵ_p) of packing catalyst [35]. Since the catalyst with a higher dielectric constant

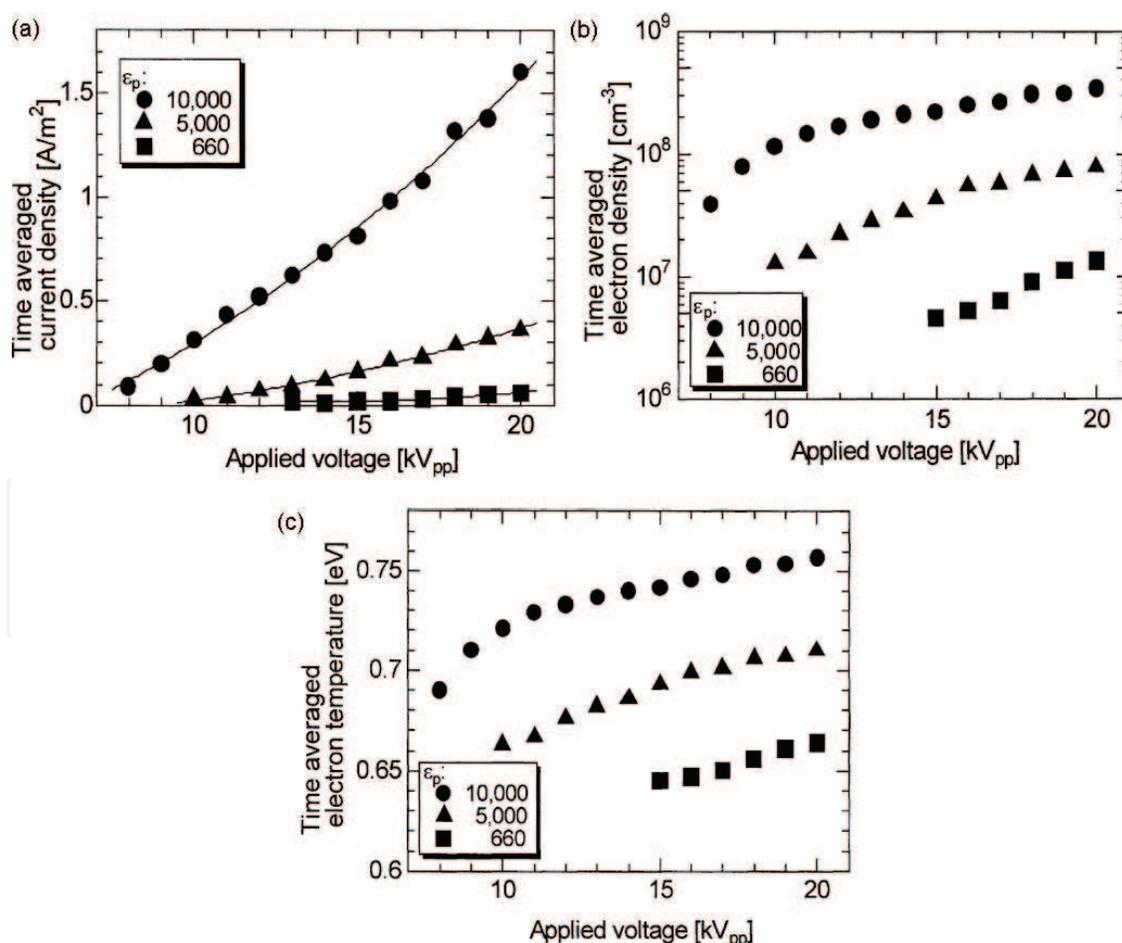


Figure 11. Simulation results of (a) time averaged input power, (b) time averaged discharge current and (c) time- and space-averaged electron temperature as a function of applied voltage for various pellet dielectric constant [35].

leads to higher polarization, plasma catalysis reactor with the catalyst possessing a higher dielectric constant has higher deposited energy, current density and electron temperature.

Catalysts generally possess various types of pores, e.g. micropore or macropore, the geometry and distribution of pores can also influence discharge properties. Local discharge may take place inside the pore if the size of pore is appropriate (larger than Debye's length), which is called microdischarge. Once discharge takes place inside the pore, species adsorbed inside the pore can be dissociated or excited into smaller fragments or active species to further provide alternative routes for CO₂/CH₄ reforming.

During discharge, photons can be generated via excitation-relaxation. Photons may be absorbed by catalyst if the catalyst possesses a band structure similar to photocatalyst, i.e. a valence band (VB) and a conduction band (CB). The photons with kinetic energy higher or equal to the gap between VB and CV can transfer its energy to catalyst to activate electron near VB edge to CB and leave a hole in VB. Hence, electron-hole pair is formed at CB and VB, respectively. Electron at CB can induce reduction of CO₂ into CO, and electron hole at VB can oxidize CH₄ into CO and H₂, as indicated in **Figure 12** [36]. As a result, syngas generation can be enhanced if photocatalytic conversion of CO₂/CH₄ can be activated. Unfortunately, photocatalysis has an important obstacle: recombination of electron-hole pair. Excited electron at CB is very stable and tends to return to VB, which is recombination of electron-hole pair. Recombination leads to lower energy utilization rate, as a result, how to reduce recombination rate is essential.

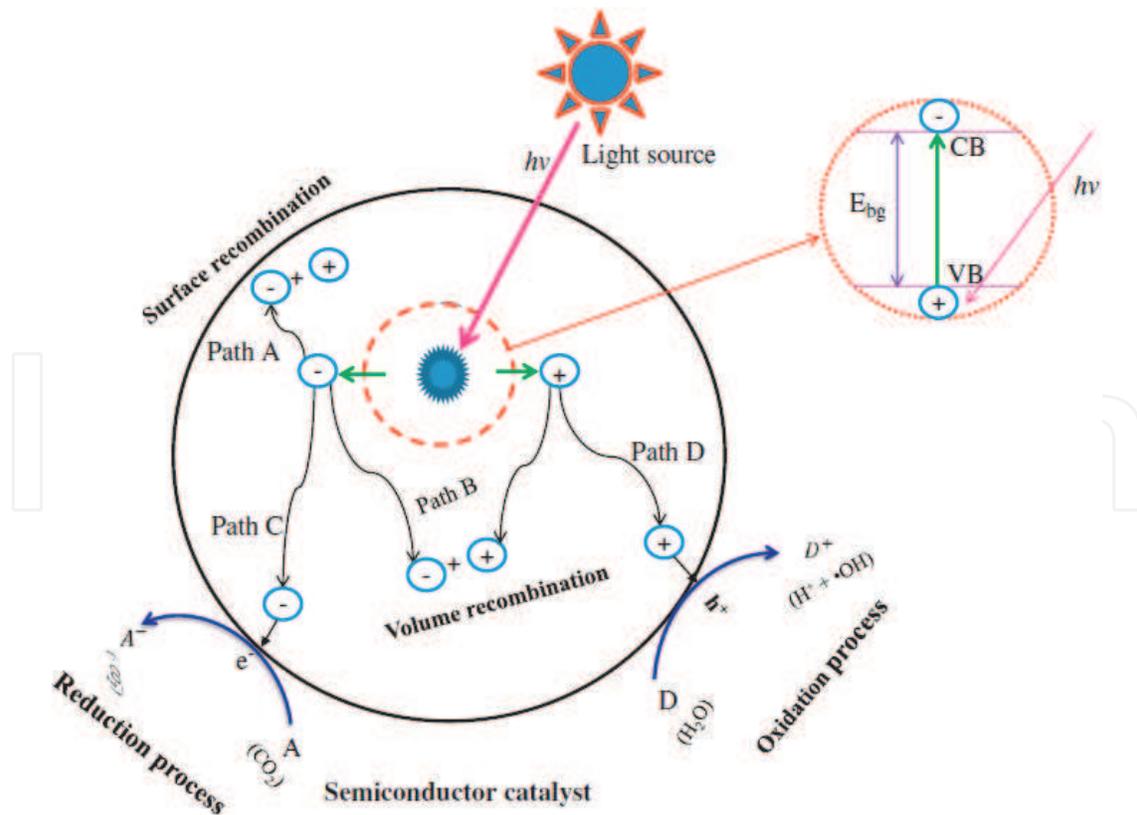


Figure 12. Mechanism and pathways for photocatalytic oxidation and reduction processes on the surface of heterogeneous photocatalyst [36].

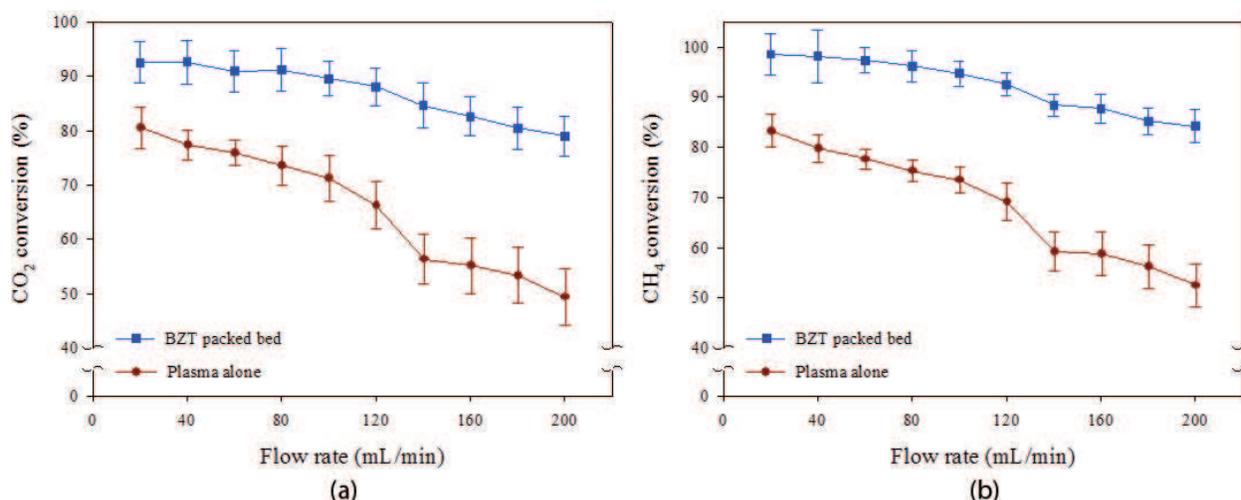


Figure 13. (a) CO₂ and (b) CH₄ conversions achieved with various reactors [37].

Chung and Chang (2016) combined BaZr_{0.05}Ti_{0.05}O₃ (BZT) catalyst (particle size ranging from 210 to 420 μm) and spark plasma reactor to form a hybrid system [37]. Results show that packing catalyst BZT into discharge region can increase electric field and current density, indicating that more kinetic electrons are generated in hybrid reactor. CO₂ and CH₄ conversions can be enhanced since the energy and amount of free electrons are increased, as shown in **Figure 13** [37]. Next, the selectivities of H₂ and CO are also increased after packing BZT, and this can be attributed to the fact that catalyst provides formation site for H₂ and CO. Last, in terms of energy efficiency (moles of syngas generated per kilowatt-hour input), packing BZT into plasma reactor leads to higher energy consumption, thus, the energy efficiency achieved

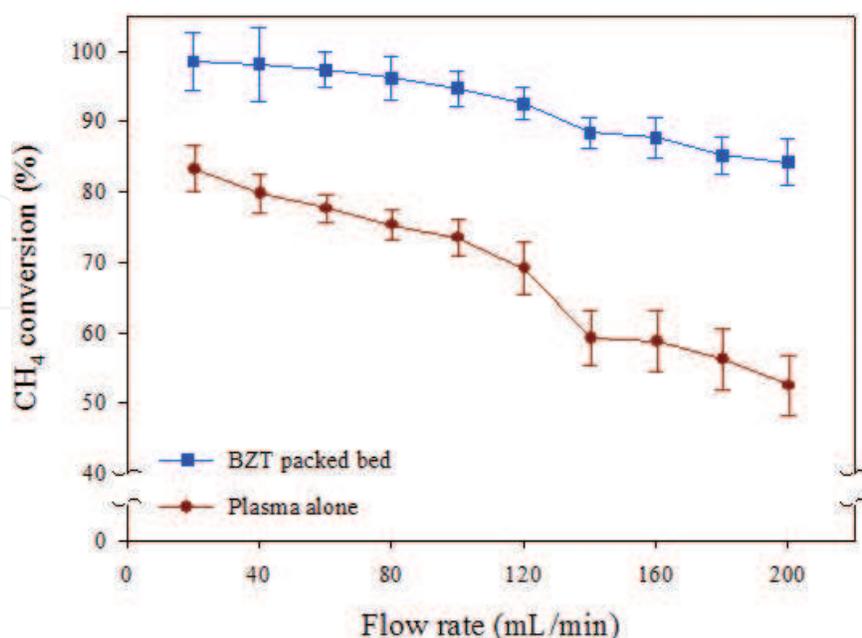


Figure 14. Energy efficiencies achieved with various reactors [37].

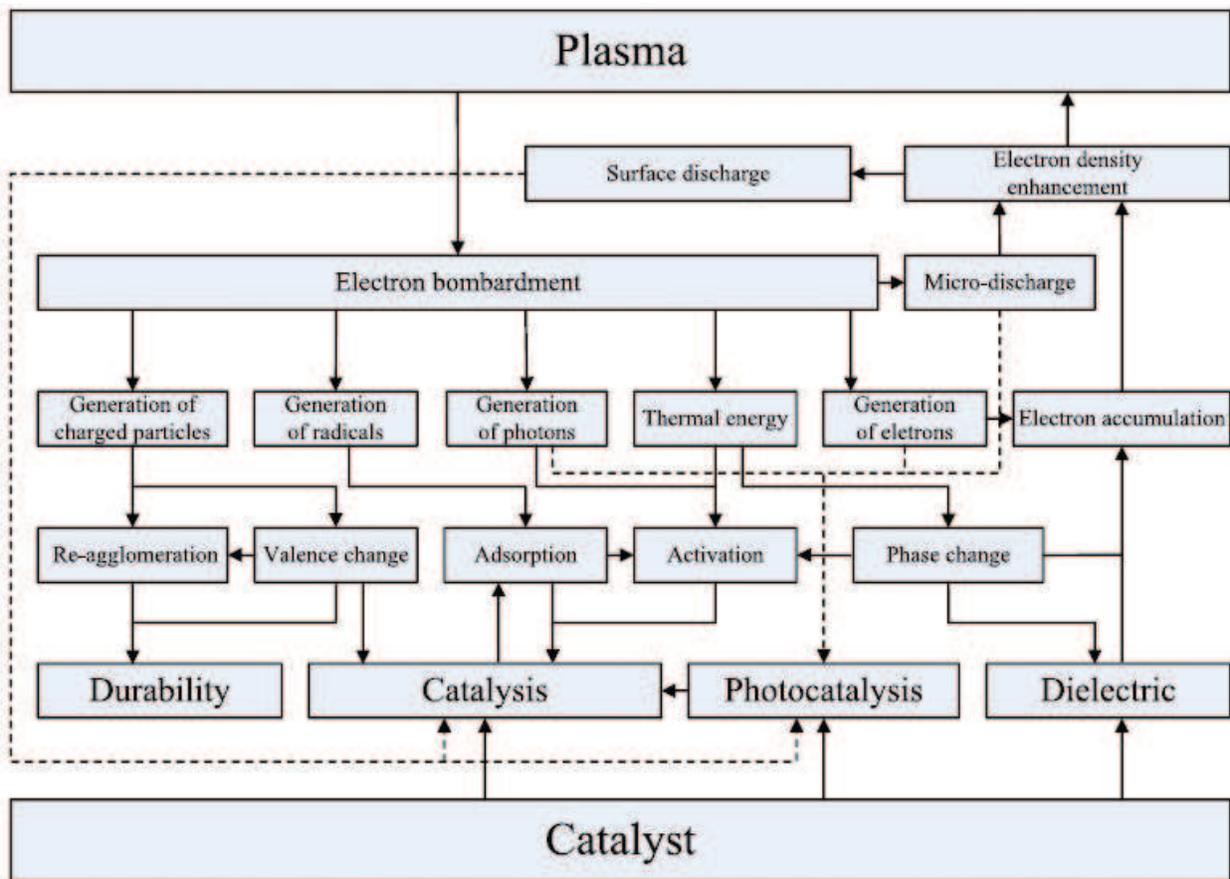


Figure 15. Interactions between nonthermal plasma and catalysis [33].

with the hybrid reactor is not necessarily higher than plasma reactor at a low reactant feeding rate. Increasing feeding rate can result in higher energy utilization rate to generate syngas and further enhance synergies between plasma and catalyst as shown in Figure 14 [37].

Overall, interactions between nonthermal plasma and catalysis are presented in Figure 15. Since electrons can be generated via nonthermal plasma to attain high kinetic energy. Energetic electrons can hit on catalyst surface to transfer energy and further influence the physicochemical properties of catalyst including particle size, surface area and pore structure. On the other hand, packing catalyst into plasma reactor can alter discharge behavior of plasma, depending on electrical and geometrical properties of catalyst. However, there remains unclear synergies and requires more works to discover and elucidate detailed interactions.

5. Conclusions

Catalysis and nonthermal plasma are two efficient approaches to generate syngas from CO₂ and CH₄. Catalytic conversion of CO₂ and CH₄ follows the mechanism of L-H mechanism and CO desorption is the rate-determining step. Coke formation via multiple routes is the most important obstacle to limit the application of catalytic reforming. On the other

hand, nonthermal plasma provides an alternative reaction mechanism to convert CO_2 and CH_4 . During discharge, various active species can be generated to dissociate CO_2 and CH_4 , including free electron, radicals and vibrational excited species. However, the above phenomenon leads to byproducts formation that reduces syngas production rate. Combining catalyst and nonthermal plasma to form a hybrid system is a promising way to enhance converting efficiency of CO_2 and CH_4 into syngas, since various interactions can be induced in the hybrid system. The form and the degree of interactions depend on properties of catalyst, nonthermal plasma and the way of combination. Hence, properties of catalyst and nonthermal plasma should be taken into account when designing a hybrid system. For catalyst, surface structure, band structure, thermal stability, catalytic activity and dielectric constant are important. In other words, temperature, electron density and energy are key factors to be considered. Even though detailed synergistic effects are unknown, the development of plasma catalysis system is optimistic for the future application on DRM.

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