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Chapter

Plasma-Enabled Dry Methane Reforming

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Abstract

Plasma-enabled dry methane reforming is a promising technology for biogas upgrade and shows multiple benefits to provide additional energy and material conversion pathways. This chapter first presents the role of nonthermal plasma as a potential energy supply pathway in the low-temperature methane conversion: an appropriated combination of electrical energy provided by plasma ($\Delta G$) and the low-temperature thermal energy ($T\Delta S$) satisfies the overall reaction enthalpy ($\Delta H$) with higher energy conversion efficiency. Moreover, plasma-enabled dry methane reforming could be operated at much lower temperature than thermal catalysis with sufficient material conversion. Three kinds of typical packed-bed plasma reactor were introduced to give a better understanding of the application of plasma and catalyst hybrid system. Subsequently, plasma-enabled dry methane reforming was diagnosed by pulsed reaction spectrometry compared with thermal catalysis, presenting a clear overview of gas component changes and significant promotion in reactant conversion and product yield. The interaction between plasma and catalyst was summarized based on two aspects: catalyst affects plasma, and plasma affects catalyst. We discussed the coke formation behavior of Ni/Al$_2$O$_3$ catalyst in the plasma-enabled and thermal dry methane reforming, followed by the oxidation behavior. The interaction between plasma and catalyst pellets was discussed toward deeper insight into the mechanism.

Keywords: plasma catalysis, dry methane reforming, dielectric barrier discharge, biogas, methane conversion

1. Introduction

Dry methane reforming (DMR) has drawn keen attention as viable CO$_2$ utilization technology because it may have one of the greatest commercial potentials [1, 2].

$$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO} \ \Delta H = 247 \text{ kJ/mol} \quad (R1)$$

Moreover, products are the main components of syngas (H$_2$ and CO), which can be converted to the synthetic fuels as well as H$_2$ carrier via well-established C1 chemistry. Conventionally, the H$_2$/CO ratio from DMR is more suitable for Fischer-Tropsch synthesis than other methane reforming reactions [3–5]. Figure 1 shows the reaction enthalpy and Gibbs free energy of DMR (R1) with respect to temperature. According to the definition, reaction enthalpy (Eq. (1)) consists of two terms:

$$\Delta H = T\Delta S + \Delta G$$

(1)
DMR is categorized as uphill (endothermic) reaction where energy input ($\Delta H$) is indispensable in order to satisfy the conservation of energy. Moreover, the reaction does not occur spontaneously by the low-temperature thermal energy due to the large positive value of $\Delta G$ at low temperature. Figure 1 shows that at least 900 K is required to have a negative value of $\Delta G$, and all energy is supplied via high-temperature thermal energy. Such high-temperature heat is supplied by the combustion of initial feed that produces CO$_2$ as well as NO$_x$. Net CO$_2$ utilization is partly canceled unless combustion-generated CO$_2$ is utilized which is economically quite difficult. Moreover, heat transfer from the combustion gas flowing outside of the reactor to the catalyst bed governs the overall material throughput which is known as a heat transfer-limiting regime. Because the heat transport property of a fixed bed reactor is poor, excessively high-temperature operation beyond thermodynamic limitation (i.e., 900 K) is necessary.

To overcome the aforementioned problem, low-temperature DMR is demanded, pursuing a new technology, and potential use of nonthermal plasma is highlighted. Assume DMR is operated at a lower temperature than the thermodynamic limitation as schematically depicted in Figure 1. A part of the energy is supplied by a low-temperature thermal energy ($T\Delta S$), while the rest of energy is supplied by the electricity ($\Delta G$) under the nonthermal plasma environment so that $T\Delta S + \Delta G$ satisfies reaction enthalpy ($\Delta H$). Electrical energy is used to accelerate electrons; subsequently, the electron energy is transferred to the molecules to initiate DMR at much lower temperature than thermal catalysis. Electronic collision process is independent of reaction temperature if gas density does not change significantly. Meanwhile, a part of the electrical energy is converted to heat; electrical energy consumed by nonthermal plasma ($E$) is depicted in the dashed line in Figure 1: inevitably, $E$ is greater than $\Delta G$ at a fixed temperature. Although heat generated by nonthermal plasma is considered as energy loss (i.e., $E-\Delta G$), both excited species and heat are utilized via endothermic DMR, which enables efficient use of electrical energy without heat transfer limitation: electrification of reforming reaction, or chemical processes in general, has the greatest advantage that the energy transfer and the control are independent of temperature gradient.

Figure 1. Energy diagram of DMR.
Dielectric barrier discharge (DBD) is the most successful atmospheric pressure nonthermal plasma sources in industry applications [6] and is used exclusively for this purpose. DBD is combined with a catalyst bed reactor and generated at atmospheric pressure [7]. DBD is characterized as a number of transient discharge channels known as streamers with nanosecond duration. Because the streamer has a nature of propagation along the interface between two adjacent dielectric materials, namely, the catalyst pellet and the gas interface, excited species produced by DBD is transferred to the catalyst surface efficiently. Moreover, the heat generated by DBD is transferred directly to the catalysts; overall energy transfer from nonthermal plasma to the catalyst bed is efficient. If the electricity is supplied from the renewable energy such as photovoltaics and wind turbines, low-emission DMR is possible with free of combustion. Moreover, nonthermal plasma-assisted C1 chemistry enables renewable-to-chemical energy conversion, which provides an alternative and viable solution for the efficient renewable energy storage and transportation pathways.

The aforementioned thermodynamic analysis (Figure 1) implies that the temperature-benign and low-emission chemical processes are possible with the appropriate combination of nonthermal plasma and the heterogeneous catalysts. Meanwhile, such hybrid system does not work at room temperature simply because the overall reaction rate is kinetically controlled at much low temperature: Nevertheless, we would like to highlight that nonthermal plasma technology solves many technological obstacles such as the elimination of combustion as well as heat transfer limitation. Moreover, low-temperature operation suppresses coke formation which is one of the big issues in DMR. In this book chapter, we focus on low-temperature DMR and compare thermal and plasma catalysis. Plasma catalysis of DMR was diagnosed by pulsed reaction spectrometry [8], and results were compared with thermal catalysis to highlight the benefit of DBD and catalyst combination. Subsequently, the interaction between DBD and catalyst pellets was discussed toward deeper insight into the mechanism. Finally, future prospects of plasma catalysis of DMR are provided.

2. Packed-bed plasma reactor

Based on the location and number of plasma zone and catalyst bed, the combination of heterogeneous catalysts with plasma can be operated in three configurations: single-, two- and multistage, which are shown in Figure 2.

2.1 Single-stage reactor

In a single-stage reactor (Figure 2(a)), the catalyst is packed inside the plasma zone, where the interaction of plasma and catalysts occurs. Because thermal plasma (gas bulk temperature > 3000°C [9]) could damage catalyst, single-stage reactor is, therefore, suitable for nonthermal plasma sources. The single-stage reactor is widely applied in CH$_4$ reforming [10–14], direct conversion of CO$_2$ [15–19], VOCs abatement [20–22], exhaust matter removal [23], formaldehyde removal [24], NO$_x$ synthesis [25], and ozone synthesis [6]. There are two significant merits of single-state reactor: (I) great flexibility exists in terms of electrode and reactor configurations that the reactor can be constructed using inexpensive materials such as glass and polymers and (II) reactive species, ions, electrons, etc. generated by nonthermal plasma could modify the gas composition, which affects the surface reactions with catalyst synergistically. However, the interaction between plasma and catalyst is complex when the catalyst is placed directly in the plasma zone. The synergy of plasma and catalyst will be discussed further in Section 4 based on the single-state reactor.
Figure 3 depicts a single-stage DBD reactor for CH₄ reforming [26], mainly including a quartz tube reactor, high voltage (HV) electrode at the center, and ground electrode outside of the tube. Catalyst pellets are packed in the plasma zone between two electrodes, and both ends of the catalyst bed are fixed by metallic supports. The high voltage is applied between the HV centered electrode and ground electrode to generate dielectric barrier discharge over the pellet surface. Discharge power was measured by voltage-charge Lissajous analysis. The discharge gap, which is the distance between HV electrode and the ground electrode, is usually less than 10 mm [27]. Catalyst temperature is controlled by a furnace. The temperature distribution of the catalyst bed is measured by thermography through the observation window. **Figure 3(c)–(e)** shows an overview of the catalyst bed, DBD generated in the catalyst bed, and the temperature distribution during reforming reaction. The
catalyst bed temperature was clearly decreased because of the endothermic nature of DMR. In addition, gas temperature was estimated by optical emission spectroscopy (OES) of CO(B-A) transition [28], showing that catalyst temperature and gas temperature matched within a measurement error.

2.2 Two-stage reactor

In the two-stage reactor, the catalyst is located at the downstream of plasma (Figure 2(b)). The gas is first addressed by the plasma and subsequently interacts with the catalyst [29]. Due to the separation of plasma and catalyst, both thermal and nonthermal plasma can be utilized. Because excited species generated in plasma have very short lifetimes, plasma mainly plays the role to preconvert the gas composition and then feed it into the catalyst reactor, e.g., in NOx removal process, due to the pretreatment of plasma, NO and NO2 were coexisted, which enhanced the following selective catalytic reduction in catalyst bed [30]; the other example is the benzene removal process where ozone (O3) was formed from background O2 by plasma, which promoted the decomposition of benzene in the next stage [31]. However, compared with the single-stage reactor, application of a two-stage reactor is limited in plasma catalysis and shows a lower performance for a given catalyst [32–37].

2.3 Multistage reactor

The multistage reactor can be described as a combination of more than one single-stage bed/reactor (Figure 2(c)). The multistage reactor gives a more flexible option in the industrialization of the plasma catalysis, attributing to the combination of catalysts with a different function for the expected reaction [38]. Chavade et al. [39] used a four-stage plasma and catalytic reactor system for oxidation of benzene. The results showed that the increase in stage number enhanced benzene conversion and CO2 selectivity. The same result can be found in biogas reforming process using a multistage gliding arc discharge system without catalyst [40]. Harling et al. [41] developed a three-stage reactor for VOCs removal. The combination of plasma and catalyst in series could significantly improve the efficiency of VOCs decomposition. At the same time, the formation of by-product such as NOx was suppressed.

3. DBD-enabled dry methane reforming

The pulsed reaction spectrometry using DBD with Ni/Al2O3 catalysts was investigated to develop a reforming diagnostic method [10]. Pulsed reforming enables the transient analyses of both CH4/CO2 consumption and H2 and CO generation. Furthermore, carbon formation was analyzed quantitatively without serious catalyst deactivation. The varied CH4/CO2 ratios between 0.5 and 1.5 were investigated at a fixed catalyst temperature near 600°C. The CH4/CO2 ratio was initially set to 0.5, and then the CH4/CO2 ratio was incremented stepwise until CH4/CO2 = 1.5, consecutively, while total flow rate was fixed at 1000 cm3/min. De-coking process (R2) was followed up after every pulsed reaction. System pressure was kept at 5 kPa during the reforming process. Discharge power was 85–93 W where specific energy input was ca. 1.2 eV/molecule. Commercially available catalyst pellets (11 wt% Ni-La/Al2O3, Raschig ring type: 3 mm) was packed for 40 mm length (total weight ca. 12 g; Ni 1.36 g; La 0.35 g). Figure 4 provides an overview of gas component changes in the entire hybrid reforming.
Reactant conversion and product yields are shown in Figure 5. The definition for conversion and yield were provided in Ref. [8]. CH$_4$ conversion and H$_2$ yield were monotonically increased with the CH$_4$/CO$_2$ ratio. There are two simultaneous routes for CH$_4$ conversion as shown in Figure 6. Route (I) is a reforming path: CH$_4$ is chemisorbed on metallic sites (adsorbed species are denoted by * in reaction). The adsorbed CH$_4$ fragments (CH$_x$*) is oxidized by CO$_2$* to form CH$_x$O* before complete dehydrogenations to C* occurs. In route (II), CH$_4$ almost irreversibly dehydrogenates toward carbon atom, and then C*-rich layer is oxidized slowly by CO$_2$* (R2), which can be evidenced in the de-coking process in Figure 4. When the CH$_4$/CO$_2$ ratio exceeded 1.0, CH$_4$ prefers to dehydrogenate to solid carbon through route (II) due to the low proportion of CO$_2$. Subsequently, a nonnegligible amount of solid carbon is produced, and CO$_2$ conversion and CO yield turned to proportionally decrease.
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$$\text{C} + \text{CO}_2 \rightarrow \text{CO} + \text{CO} \quad (\text{R2})$$

$$\text{CH}_4 \rightarrow \text{CH}_4^* \rightarrow \text{CH}_x^* + \frac{(4-x)}{2} \text{H}_2 (x = 0–3) \quad (\text{R3})$$

$$\text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad (\text{R4})$$

$$\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} \quad (\text{R5})$$

Compared with thermal reforming, both CH₄ conversion and H₂ yield were clearly promoted in hybrid reforming (Figure 5), and the main pathway of CH₄ conversion and H₂ yield could be simply described as CH₄ dehydrogenation (R3). It is proposed that CH₄ dehydrogenation was enhanced by the synergistic effect of DBD and catalyst. Molecular beam study revealed that dissociative chemisorption of CH₄ on the metal surface was enhanced by vibrational excitation [42]. The numerical simulation of one-dimensional streamer propagation demonstrated that the vibrationally excited CH₄ is the most abundant and long-lived species generated by low-energy electron impact [43]. The reaction mechanism of plasma-enabled catalysis could be explained by the Langmuir-Hinshelwood (LH) reaction scheme. The analysis of overall activation energy is expected to understand the contribution of plasma-generated reactive species.

The CO₂ conversion and CO yield were promoted in hybrid reforming compared to thermal reforming (Figure 5). H₂O was simultaneously produced as a by-product by reverse water gas shift (RWGS) reaction (R4). Reactivity of plasma-activated H₂O was confirmed by Arrhenius plot analysis where reaction order for H₂O was doubled by DBD [44]. Plasma-activated H₂O promotes reaction with adsorbed carbon; it creates additional pathways (R5) to syngas (H₂ and CO). The CO₂ conversion and CO yield were promoted in the hybrid reforming, illustrating that the reverse-Boudouard reaction (R2) was enhanced by DBD. The reaction between plasma-activated CO₂ and adsorbed carbon increases CO yield. The same result was obtained in the de-coking period [10]. Although excessive production of carbon is detrimental for catalyst activity and lifetime, the presence of adsorbed carbon creates key pathways for emerging plasma-induced synergistic effect. Consequently, plasma-activated CO₂ and H₂O would promote surface reaction and increase CO and H₂ yield. Figure 5 clearly shows that the slope of each line increased in hybrid reforming compared with thermal reforming, attributing to the nonthermal plasma-excited species. The increase of slope...
could be further explained by the promoted overall reaction order, which plays the key role in the estimation of the rate-determining step [44].

4. The synergy of plasma and catalyst

Synergism in plasma catalysis in the single-stage reactor is not fully understood due to the complex interaction between the various plasma-catalyst interaction processes [45–49]. Kim et al. [27] discussed the criteria for interaction between nonthermal plasma and the porous catalyst. The chemical species in nonthermal plasma are highly reactive; the lifetime is very short, e.g., O (^1D), 10 ns; O (3P), 50 μs; and OH, 100 μs: their one-dimensional diffusion length is limited from 0.7 to 65 μm. Plasma generated species within diffusion length from the external surface of pellets would contribute to the plasma-induced reaction pathways. The interdependence of plasma and catalyst can be discussed as two aspects: catalyst affects plasma, and plasma affects catalyst.

4.1 The effects of catalyst on plasma

With the packed catalyst in the plasma zone, gaseous species adsorbed on the catalyst surface increase the concentration of surface species. In addition, the electric field is enhanced near the catalyst surface due to catalyst nanofeatures [50, 51]. Moreover, the packed catalyst also enables the discharge type change, as well as microdischarge generation.

Without packed materials, discharge mode is the “free-standing” filamentary discharge propagating across the gas gap (Figure 7(a)). With a packed catalyst,

![Image](https://example.com/figure7.png)

**Figure 7.** (a) Filamentary discharge without catalyst pellet, (b) time-resolved images of surface streamers propagating on the surface of γ-Al₂O₃ (reproduced with permission from ref 54. Copyright 2016 IOP Publishing), and (c) distributions of the electron density and total ion density with a 100 μm pore (reproduced with permission from ref 56. Copyright 2016 Elsevier).
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the surface streamer is propagated with the close contact with the catalyst surface, and intensive partial discharges occur between the contact area of catalysts [52, 53]. The time-resolved visualization of surface streamer propagation and partial discharge were detected by Kim et al. [54] with an intensified charge-coupled device (ICCD) camera. Figure 7(b) shows time-resolved images of surface streamers (i.e., primary surface streamer and secondary surface streamer) propagating on the surface. Enhanced catalytic performance in the presence of a catalyst is closely linked with the propagation of surface streamers [55]. Moreover, with packed catalyst, microdischarge is generated inside catalyst pores (when the pore sizes >10 μm) [56, 57]. Zhang et al. [56] investigated microdischarge formation inside catalyst pores by a two-dimensional fluid model in the μm range (Figure 7(c)), indicating that the plasma species can be formed inside pores of structured catalysts in the μm range and affect the plasma catalytic process.

4.2 The effects of plasma on catalyst

The plasma also affects the catalyst properties, which are summarized as the following aspects:

(I) Modification of physicochemical properties of the catalyst by plasma, which is widely used in catalyst preparation processes [58]. With plasma preparation, the catalyst obtains a higher adsorption capacity [59], higher surface area, and higher dispersion of the catalyst material [60–62], leading to a plasma-enhanced reactivity.

(II) It is possible that plasma makes changes in the surface process with the catalyst. As for the CH₄ reforming process, the deposited carbon from Ni catalysts can be removed effectively by plasma-excited CO₂ and H₂O [8]. The other example of the synergism is NH₃ decomposition for the application of fuel cell, where NH₂ conversion reached 99.9% when combining plasma and catalyst, although the conversion was less than 10% in the case of either plasma or catalyst only reaction [63].

(III) Based on Arrhenius plot analysis, plasma can decrease the activation barriers (overall activation energy), attributed to the vibrational excitation, which is schematically depicted in Figure 8. The net activation barrier will be \( E_{a,v}^{\text{ad}} - E_{\text{vib}} \) in an adiabatic barrier crossing case and \( E_{a,v}^{\text{nonad}} - E_{\text{vib}} - E^* \) in a nonadiabatic barrier crossing case, respectively [64]. The activation barrier decrease was reported in toluene destruction process [65]. In steam methane reforming, the preexponential factor was increased clearly by plasma, attributing to plasma-activated H₂O removes adsorbed carbon species, which regenerate active sites for subsequent CH₄ adsorption [11].

(IV) The excited species or dissociated species might create other pathways with the presence of catalyst, e.g., during the CO₂ plasma oxidation process, plasma-enhanced CO₂ oxidized NiAl₂O₃ catalyst to form a NiO layer, which could drive an oxidation-reduction cycle in dry methane reforming reaction. The same NiO layer was found when specific energy input (SEI) was sufficiently high: the O₂ that dissociated from CO₂ plays the key role in the oxidation process. The details will be interpreted in Section 5.2.
5. Discussion

5.1 Coke formation behavior

Coke formation behavior was studied as a reaction footprint to track reaction pathways induced by DBD [26]. Coke morphology and their distribution over the 3 mm spherical Ni/Al₂O₃ catalyst pellets were obtained after 60 min DMR. Figure 9 shows cross-sectional carbon distribution, where (a)–(c) and (d)–(f) correspond to plasma catalysis and thermal catalysis in low, middle, and high temperatures. For the thermal catalysis with the temperature at 465°C, carbon deposition over the entire cross-section was obvious. With the temperature increased, coke was decreased and finally became nondetectable at ca. 620°C. At low temperature, plasma catalysis suppressed the coke formation significantly over the entire cross-section.

By the analysis of scanning electron micrographs (SEM) and Raman spectrum, fine carbon filaments were detected on the external pellet surface in plasma catalysis [26]. In contrast, thick fibrous carbon deposition was observed on the external surface in thermal catalysis, as well as in the internal pores in both thermal and plasma catalysis.
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catalyses. The CH$_4$ dehydrogenation on catalyst is enhanced by nonthermal plasma, contributing to the generation of highly filamentous and amorphous carbon. Such nonthermal plasma-enhanced reaction has been demonstrated by carbon nanotube growth [66] and plasma-enabled steam methane reforming [67]. The fine amorphous carbon filaments, deposited in the external surface of catalyst, prove that the interaction of DBD occurs mainly in the external surface. Consequently, DBD generation and plasma-excited species diffusion are inhibited in the internal pores of catalyst.

5.2 Oxidation behavior of Ni/Al$_2$O$_3$ catalyst

The nickel (Ni) of Ni/Al$_2$O$_3$ catalyst was oxidized slightly by CO$_2$ in the thermal catalysis [68, 69]. However, the significant Ni oxidation by CO$_2$ (R6) was demonstrated when the catalyst were packed in nonthermal plasma zone. In this case, Ni uptakes surface oxygen beyond the adsorption/desorption equilibrium (i.e., Langmuir isotherm) to form NiO, which further promotes CH$_4$ dehydrogenation without solid carbon deposition (R7):

$$\text{Ni} + \text{CO}_2 \rightarrow \text{NiO} + \text{CO} \quad \text{(R6)}$$

$$\text{NiO} + \text{CH}_4 \rightarrow \text{Ni} + \text{OH} + \text{CH}_3 \quad \text{(R7)}$$

The specific energy input (SEI) is a critical operational parameter in plasma-enabled CO$_2$ treatment process due to the fact that dominant reaction pathway shifts dramatically with SEI:

$$\text{SEI} = C \times \frac{\text{Discharge power (W)}}{\text{Total flow rate (cm}^3/\text{min)}} \quad \text{(eV/molecule)} \quad (2)$$

SEI expresses energy consumption by discharging per unit volume of the feed gas, which could be further interpreted as average electrical energy (eV) per molecule. In Eq. (2), C is the conversion factor of the unit [10]. Two contrasting conditions are demonstrated in plasma-enabled CO$_2$ oxidation: one is designated as the direct oxidation route; with a small SEI, CO$_2$ dissociation to CO and 0.5 O$_2$ (R9) is negligible, and then the plasma-excited CO$_2$ dominates the oxidation process (R8). The other is the indirect oxidation route where O$_2$ provides an additional oxidation pathway; with a large SEI, CO$_2$ is dissociated into CO and O$_2$ (R9) without heterogeneous catalysts by electron impact [70, 71], followed by Ni oxidation by O$_2$ (R10).

Direct oxidation route: Ni + CO$_2$ → NiO + CO

Indirect oxidation route: CO$_2$ + e → 1/2 O$_2$ + CO + e

$$\text{Ni} + 1/2 \text{O}_2 \rightarrow \text{NiO} \quad \text{(R10)}$$

The plasma-enhanced direct oxidation route (R8) is further investigated because the plasma-enabled synergistic effect was demonstrated distinctly without O$_2$ [8, 10, 26]. Ni oxidation behavior without O$_2$ was studied with SEI = 0.46 eV/molecule. The CO$_2$ conversion is far below 1% when the SEI was smaller than 0.5 eV/molecule [72, 73]; in the plasma and thermal oxidation, the CO$_2$ flow rate, catalyst temperature, and the oxidation time were controlled as 1000 cm$^3$/min, 600°C, and 70 min, respectively.
After DBD-enhanced oxidation and thermal oxidation, the formation of NiO and its distribution over the cross-section of 3 mm spherical pellet were investigated by Raman spectroscopy and optical microscope. Results showed that the NiO layer was recognized clearly with the thickness of ca. 20 μm. In contrast, the NiO layer was not identified after thermal oxidation. We should point out that the plasma-excited CO$_2$ has a strong oxidation capability of Ni catalyst. In addition, the effect of DBD is inhibited in the internal pores beyond 20 μm from the pellet surface.

In the thermal oxidation, CO$_2$ is most likely adsorbed at the perimeter between Ni nanocrystals and Al$_2$O$_3$ interfaces [74–76] (Figure 10(a)). Subsequently, the adsorbed CO$_2$ oxidize Ni to NiO near the perimeter. It is clear that the reaction sites for thermal oxidation are limited in the perimeter. The Ni oxidation reaction terminates after the reaction sites are fully oxidized by adsorbed CO$_2$. In plasma-enhanced oxidation reaction, CO$_2$ is firstly excited by electron impact. The vibrationally excited CO$_2$ plays the key role to enhance adsorption process and subsequent oxidation reaction of Ni catalyst, leading to an extensive Ni nanoparticle oxidation, which occurs not only in the perimeter but also in the terrace, step, and kink (Figure 10(b)). Figure 10(c) and (d) show hemispherical catalyst pellets after thermal and plasma oxidation. After thermal oxidation, the external surface and cross-section of catalyst pellets remained black. In contrast, after plasma oxidation, the external surface was oxidized and has showed whitish color change (oxidized stage); in the meantime, the cross-section of the hemispherical pellet has been kept black (unoxidized stage).

The vibrationally excited CO$_2$ by DBD would induce Ni oxidation to form the oxygen-containing active species (i.e., NiO) rather than simple adsorption, leading to oxygen-rich surface beyond Langmuir isotherm. Incoming plasma-excited CO$_2$ would carry a few eV internal energy due to the gas phase vibration-to-vibration energy transfer [77, 78], which is the main source of energy for NiO formation. Plasma-excited CO$_2$ could promote the adsorption flux; however, the adsorbed CO$_2$ is finally desorbed by the equilibrium limitation unless it forms NiO. In addition, the plasma-induced nonthermal heating mechanism plays another key role in the

Figure 10.
Ni oxidation pathways: (a) thermal oxidation including CO$_2$ adsorption near the perimeter of Ni catalysts and (b) plasma-enhanced oxidation. Hemispherical catalyst pellets: (c) thermal oxidation and (d) plasma oxidation.
enhancement of Ni oxidation. Charge recombination and association of radicals can release energy corresponding to 1–10 eV/molecule on catalyst surface. When this excess energy is directly transferred to the adsorbed CO$_2$, Ni oxidation may be enhanced without increasing macroscopic catalyst temperature. This reaction scheme is explained by nonthermal plasma-mediated Eley-Rideal mechanism, rather than precursor-type adsorption enhancement.

In the DMR process, the oxygen-rich surface (NiO layer) has a capability of oxidizing a large flux of ground-state CH$_4$ efficiently. Consequently, CH$_4$ is not necessarily preexcited. CH$_4$ is almost fully reacted in the NiO layer (20 μm thickness) to inhibit the coke deposition toward the internal pores [26]. However, in the thermal catalysis, NiO is generated in a negligible amount. The ground-state CH$_4$ can diffuse into internal pores and deposit coke as previously confirmed [26]. Formation of NiO shell (Figure 10(d)) and the coke formation behavior (Figure 9) are well correlated in plasma catalysis as further discussed in the next section.

5.3 Interaction between DBD and catalyst pores

Although the synergies of plasma and catalyst have been summarized in Section 4, the interaction between DBD and catalyst pores will be further discussed in this section based on the carbon formation and oxidation behavior, as well as DBD-enhanced DMR. For the plasma catalysis, carbon deposition in the internal pores could be remarkably prevented, and fine amorphous carbon filaments were deposited only on the external surface of pellets. A similar trend was observed when NiO was formed in the limited region over the external surface (20 μm depth) only when DBD was superimposed. The results of coke formation behavior and oxidation behavior of Ni-based catalyst in plasma catalysis evidence that the interaction of DBD and catalyst occurs at the external surface of the pellets and the effect thickness is ca. 20 μm. Neither generation of DBD nor diffusion of plasma-generated reactive species in the internal pores is possible. Although DBD and pellet interaction is limited in the external surface, conversion of CH$_4$ and CO$_2$ was promoted clearly compared with thermal catalysis: this is the clear evidence of reaction enhancement by DBD.

For DBD, due to the enhanced physical interaction between propagating streamers and catalysts, plasma and catalyst contact area, as well as the streamer propagation from one pellet to the other, are promoted significantly. Nevertheless, electron density in a narrow filamentary channel is of the order of $10^{14}$ cm$^{-3}$ [6, 79, 80]; in contrast, molecule density at standard condition is approximately $10^{19}$ cm$^{-3}$, indicating that a major part of the gas stream is neither ionized nor excited. Consequently, the extremely low proportion of ionized and excited species is inadequate to explain the net increase of CH$_4$ and CO$_2$ conversion and selectivity change by DBD. However, if reactive species are fixed and accumulated on the surface of the catalyst, the gross conversion of materials will be promoted. For this reason, the hetero-phase interface between DBD and the external pellet surface provides the most important reaction sites. In Section 5.2, nonthermal plasma oxidation of Ni to NiO creates a critically important step for plasma-enabled synergistic effect.

As Section 4.1 mentioned, gas breakdown is hard to occur in a pore smaller than 10 μm. For the pores catalyst with a pore size less than 2 nm, standard Paschen-type gas breakdown is impossible. To sum up, the external surface of pellet plays the key role for the DBD and catalyst interaction; however, the internal pores play a minor role.
6. Conclusion and outlook

The synergistic effect induced by DBD was clearly observed both in the CH$_4$ and CO$_2$ conversion and in the syngas yield. CH$_4$ dehydrogenation was enhanced by the synergistic effect of DBD and catalyst. Plasma-activated CO$_2$ and H$_2$O would promote surface reaction and increase CO and H$_2$ yield. The analysis of overall activation energy is expected to understand the contribution of plasma-generated reactive species.

In plasma catalysis, the fine amorphous carbon filaments, deposited in the external surface of catalyst, prove that the interaction of DBD occurs mainly in the external surface. The DBD generation and plasma-excited species diffusion are inhibited in the internal pores of the catalyst. Moreover, although the interaction between plasma and catalyst is limited in the external surface, the coke deposition was inhibited significantly in the internal pores by DBD, which is the clear evidence of reaction enhancement by DBD.

Oxidation behavior of Ni-based catalyst in nonthermal plasma-enabled catalysis showed that the NiO layer was generated in the external surface with the thickness of ca. 20 μm during plasma oxidation. In the internal pores, Ni oxidation is inhibited due to the negligible interaction with DBD. Contributing to the NiO layer, the surface of catalyst uptakes more oxygen beyond thermal equilibrium, which is known as Langmuir isotherm, creating a new reaction pathway via NiO. In the plasma catalysis of DMR, NiO drives the oxidation-reduction cycle, which promotes CH$_4$ dehydrogenation on the surface. Consequently, carbon deposition is suppressed effectively.

For further improvement of plasma-enhanced DMR, the following issues should be investigated:

(1) The effect of radical injection on reaction enhancement should be kinetically analyzed by the Arrhenius plot method, and the analysis of the overall activation energy is expected to understand the contribution of plasma-generated reactive species.

(2) Exploring new types of catalysts, dedicated to plasma catalysis, is an important subject of research. We have demonstrated that the interaction of DBD and catalyst occurs only at the external surface of the pellets, and the effected thickness is ca. 20 μm, which means a majority of the active sites in pores of catalyst do not interact with any excited species. New catalyst preparation method such as catalytic functionalization of reactor wall and catalyst coating for the reactor may be beneficial to strengthen the synergistic effect of nonthermal plasma and catalytically functionalized surface.

(3) The catalyst activity of partially oxidized catalyst and the nonthermal plasma heating mechanism have not been demonstrated experimentally yet; moreover, diagnosis of intermediate species on the surface, created by plasma-derived species, as well as their reaction dynamics are expected to be investigated for deep insight in plasma catalysis.

(4) Although the plasma-induced energy transfer mechanism is commonly accepted in particle growth, it has yet to be investigated within the scope of plasma catalysis. Deep understanding of highly transient and nonequilibrium energy transfer via excited molecules, without macroscopic temperature change, need to be studied.

(5) The individual contribution of radical injection and heat generation, as well as combination of those, must be understood. The gap between macroscopic and microscopic understanding, including various time scales covering nanoseconds to the millisecond, should be bridged by consistent manner.
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