Promising Utilization of CO₂ for Syngas Production over Mg²⁺- and Ce²⁺-Promoted Ni/γ-Al₂O₃ Assisted by Nonthermal Plasma

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ABSTRACT: Dry reforming of methane is conducted in a catalyst packed-bed dielectric barrier discharge (DBD) reactor aiming to improve the reaction efficiency. The MgO- and CeO₂-promoted Ni/γ-Al₂O₃ catalyst is tested to carry out the reaction. An interesting observation is that Ni/MgO_Al₂O₃ integration provides ~35 and 13% conversion of CH₄ and CO₂, respectively. The highest syngas ratio of 0.94 is obtained with Ni/MgO_Al₂O₃, whereas the ratio is only 0.57 with Ni/CeO₂_Al₂O₃ and 0.64 with bare DBD. In addition, Ni/CeO₂_Al₂O₃ offers the highest selectivity (68%) of CO due to the oxygen buffer property of CeO₂. Finally, the optimal acid/base property is highly desirable for the dry reforming reaction.

INTRODUCTION

Dangerous pathogens are becoming more widespread due to global warming, which leads to severe health issues such as dengue fever and West Nile virus. Global temperature dysregulation causes flooding, droughts, and storms, which contaminate drinking water. The frequency of viral dengue fever has also increased globally by 30-fold during the past 50 years in America. Healthy reforming of methane (DRM) offers the simultaneous conversion of two greenhouse gases (CH₄ and CO₂) into syngas (H₂ and CO), which are recognized as a primary feedstock in the petroleum industry for synthesizing valuable chemicals and synthetic fuels. Conventional, the existing technology for syngas synthesis is steam methane reforming (SMR), which demands huge thermal energy and also produces CO₂. When compared to SMR, the DRM reaction is environmentally benign and highly beneficial due to the production of the desired H₂/CO ratio for Fischer–Tropsch synthesis. Despite the advantages, DRM is limited due to a high operating temperature (>700 °C) to get a reasonable conversion of reactants. Moreover, catalyst deactivation due to CO disproportionation and CH₄ decomposition seems to be a drawback in this reaction.

In this context, nonthermal plasma (NTP) technology is gaining attention due to the initiation of reaction under ambient conditions and favoring no coke formation. Several NTP configurations such as glow discharge, corona discharge, and dielectric barrier discharge (DBD) were reported for various applications. NTP was widely tested for methanol production, syngas synthesis, wastewater treatment, and carbon dioxide decomposition. Among various NTP configurations, DBD has withdrawn special consideration due to advantages like (i) generation of high energetic electrons (1–10 eV), (ii) ability to initiate the chemical reaction at atmospheric pressure and temperature, (iii) offering high electron energy density, etc. However, DBD alone is not good enough to improve the selectivity of desired products, and hence catalyst integration is necessary. So far, researchers investigated the DRM reaction using novel metal-based (Ru, Pd, Pt, and Rh) and transition metal-based (Co, Ni, and Fe) catalysts. Several attempts also have been made by varying the support material (MgO, SiO₂, TiO₂, Al₂O₃, CeO₂, etc.) in thermocatalytic DRM. Despite the catalyst integration, thermocatalytic DRM shows more carbon deposition. A visible light-active material, such as TiO₂/ZnO, coupled with g-C₃N₄ was reported in our previous study. Mei et al. demonstrated DBD-assisted DRM with different support materials (γ-Al₂O₃, MgO, SiO₂, and TiO₂) and proved that γ-Al₂O₃ is the best support for this reaction. There are also several reports on a variety of different metals (Ni, Co, Cu, and Mn) while keeping the support as γ-Al₂O₃. Efforts have been made to improve the selectivity of products using Ni/γ-Al₂O₃-based catalysts because of economic viability. Different promoters also were added to the Ni/γ-Al₂O₃ support to reduce the carbon deposition. It is known that promoters improve the active sites and ensure the activity of the metal catalyst. Also, the promoter influences the acidic and/or basic property of the catalysts, which plays an important role in the reaction performance.

In this study, a systematic study has been reported to understand the role of the promoter in DRM. Ni/γ-Al₂O₃ modified with basic promoters is tested on the DRM reaction assisted by the DBD reactor. Variations in discharge characteristics due to catalyst integration into DBD and physicochemical
properties of catalysts have been thoroughly studied to understand the effect of the promoter-modified Ni/γ-Al₂O₃ catalyst on the DRM reaction.

■ RESULTS AND DISCUSSION

Characterization of Fresh Catalysts. Figure 1 presents the powder XRD pattern of the fresh catalyst. The significant peaks with \(d\)-spacing values of 0.2039, 0.1774, and 0.1253 nm represent the (111), (200), and (220) planes of Ni metal in both catalysts, respectively. Similarly, the characteristic peaks of cubic γ-Al₂O₃ at 0.2435 and 0.1409 nm represent the (400) and (440) planes, respectively.¹³ As the percentage loading of CeO₂ and MgO is very little, the signature peaks are not prominent. However, a small hump of the (200) plane at \(2\theta\) of 32.7° confirms CeO₂ in the case of Ni/CeO₂/Al₂O₃, whereas MgO is confirmed by the (222) plane at 63.1° in Ni/MgO/Al₂O₃.

Transmission electron microscopy (TEM) images are presented in Figure 2. Ni/MgO/Al₂O₃ shows uniform distribution of Ni particles (Figure 2a), whereas agglomeration has been observed in Ni/CeO₂/Al₂O₃ (Figure 2b). Nanosized Ni has been found in both the catalysts. In the case of Ni/MgO/Al₂O₃, the observed average particle size is ~12 nm, which is lower than the average particle size (18 nm) of Ni/CeO₂/Al₂O₃. However, the TEM images confirm the metal distribution in a regular way, which may be due to the integration of promoters. The clear SAED (Figure 2c,g) pattern confirms the crystalline structure of the Ni particle. Besides, the fringes due to the Ni(111) plane are also found in TEM images, which is in good agreement with the XRD pattern.

Temperature-programmed reduction (TPR) of the prepared catalysts was performed to estimate the reducibility of various catalysts. Figure 3 shows the TPR profile of the fresh catalysts.
For NiO/γ-Al₂O₃, the reduction peak at around 400 °C is due to the loosely bound NiO on the γ-Al₂O₃ support, whereas the peaks observed at 400–650 °C are due to the reduction of NiO strongly interacting with the support. The mismatch in the TPR pattern for both catalysts is due to the presence of a promoter. In the case of the CeO₂-promoted catalyst, surface CeIV species are reduced at 520 °C, and the broad peak at 620 °C is due to the reduction of bulk NiO. The hump prominent in both the catalysts at higher temperatures is due to the reduction of surface MgO/CeO₂. The total H₂ consumption values during the TPR study for Ni/CeO₂-Al₂O₃ and Ni/MgO-Al₂O₃ are 2.075 and 1.901 mmol/g, respectively. This study proves that the promoters remain unreduced at 600 °C (reduction temperature for this study).

N₂ physisorption studies were conducted at −196 °C, and results are shown in Figure 4. The isotherms appear like type III with an H3 hysteresis loop. Table 1 summarizes the data from the physisorption studies. The surface area, total pore volume, and average pore diameter increased in the case of the MgO-promoted catalyst (Table 2). Similarly, the CO₂ adsorption study was conducted to determine the basic sites (Figure 5b), and it is worth noting that there are more basic sites for the Ni/MgO-Al₂O₃ catalyst.

Lewis and Brønsted acidic sites are determined by pyridine-FTIR spectra (Figure 6). One milliliter of dried pyridine was adsorbed on 50 mg of the catalyst for 12 h. Thereafter, the sample was dried at 120 °C for 1 h to remove the loosely adsorbed pyridine from the surface of catalysts. From that dried sample, 10 mg was taken and mixed thoroughly with 190 mg of dried KBr to maintain uniformity and palletized by hydraulic pressure. Finally, those plates were used to measure the FTIR spectra. As shown in Figure 6, the strong Lewis acidic site was recognized at 1446 cm⁻¹, and a weak interaction was observed at 1596 cm⁻¹. The presence of Brønsted acidic sites was identified from a peak at 1629 cm⁻¹, and a high intensity at around 1525 cm⁻¹ is due to the interaction of pyridine with both Lewis and Brønsted. On a closer look, the acidic nature (Lewis and Brønsted) decreased when MgO was used as the promoter. In a reverse way, one can say that there is more Lewis basicity in Ni/MgO-Al₂O₃ compared to Ni/CeO₂-Al₂O₃, which is most desirable for CO₂ adsorption. Interestingly, this study complements the CO₂ TPD results also.

**Physical Properties of Electrical Discharge.** A typical Lissajous figure looks like a perfect parallelogram (ABCD in Figure 7). Gas breakdown occurs in the discharge-on phase at the time of plasma ignition (lines BC and AD), whereas the discharge-off phase (lines AB and CD) appears when a displacement current is present in the circuit. The slope of the discharge-on phase represents the effective capacitance (Cₑffective) of the DBD reactor. Gas burning voltage (V₉₀) is defined as the minimum voltage required to decompose a gaseous molecule and can be calculated by measuring the distance between two lines BC and AD. Other electrical parameters like charge transfer per half cycle (dQ/sec) and peak-to-peak charge transfer (Qpeak-peak) are aligned in series. The total capacitance of the reactor Cₑffective is measured from Figure 8 and calculated from eq. 1.

\[
\frac{1}{C_{effective}} = \frac{1}{C_d} + \frac{1}{C_g}
\]

Figure 4. (a) N₂ adsorption—desorption isotherm. (b) Pore volume vs pore diameter.

**Table 1. Surface Properties of Prepared Catalysts**

| catalyst | surface area (m²/g) | total pore volume (cc/g) | average pore diameter (nm) |
|----------|---------------------|-------------------------|---------------------------|
| Ni/γ-Al₂O₃ | 116                 | 0.19                    | 5.28                      |
| Ni/ CeO₂-Al₂O₃ | 182                 | 0.3                     | 6.54                      |
| Ni/ MgO-Al₂O₃ | 201                 | 0.4                     | 8.04                      |

*BET method. **At P/P₀ 0.95 mmHg. BJH method (from desorption isotherm).
In general, the effective capacitance \( (C_{\text{eff}}) \), which is equal to the dielectric capacitance \( (C_d) \) in a fully packed system,\(^4^3\) plays a crucial role in the reaction mechanism, and it can be measured from Figure 7. As can be seen from Figure 8b, the effective capacitance increases with an increase in discharge power, and the catalyst packed DBD reactor exhibits the highest effective capacitance. The charge transfer per half cycle and peak-to-peak charge transfer also increase for the catalyst packed reactor. As shown in Figure 8c, bare DBD shows an increase in \( dQ \) value from 3.26 to 10.89 \( \mu \text{C} \), whereas, for the catalyst packed reactor, it increases from 8.02 to 14.20 \( \mu \text{C} \). Table 3 presents the electrical characteristics under different packing conditions.

**Effect of Catalysts on the DRM Reaction.** Plasma electric field, as well as power density, enhance with an increase in SIE (specific input energy), which affects directly the conversion of reactants.\(^4^7\) Figure 9 shows the inclined curve of conversion with respect to SIE regardless of the packing condition. The \( \text{CH}_4 \) and \( \text{CO}_2 \) conversion enhances due to the catalyst packing compared to the no packing DBD. This can be explained by an electrical parameter like the peak-to-peak charge transfer and charge transfer per half cycle increase with the integration of catalyst packing, which enhances the effective capacitance. The gas-burning voltage also decreases with the packed-bed reactor, which is responsible for more and more reactant cracking. As shown in the earlier discussion, the Ni/MgO/\( \gamma \)-Al\(_2\)O\(_3\) catalyst offers more surface area and small particle size, which remarkably affect the conversion of \( \text{CH}_4 \) and \( \text{CO}_2 \). Additionally, the basic nature also enhances with the incorporation of MgO. Therefore, the \( \text{CO}_2 \) conversion also improves compared to that for Ni/CeO\(_2\)/Al\(_2\)O\(_3\) packing. However, the highest \( \text{CH}_4 \) and \( \text{CO}_2 \) conversion values are observed to be 34.7 and 13\%, which reduced to 30 and 12.1\%, respectively, with Ni/CeO\(_2\)/Al\(_2\)O\(_3\) at an SIE of 5.4 J/mL. Compared to Ni/\( \gamma \)-Al\(_2\)O\(_3\), Mg- and Ce-promoted Ni/\( \gamma \)-Al\(_2\)O\(_3\) exhibits more conversion of reactants (Table S1).

Figure 10 presents the selectivity of the major products \( \text{H}_2 \) and CO in the DRM reaction, while our previous study reported...
some small amounts of light hydrocarbon formation in the DRM reaction. The selectivity of H\textsubscript{2} reached 35\% with Ni/ MgO\textsubscript{2}Al\textsubscript{2}O\textsubscript{3}, while the selectivity of CO was found to be 68\% with Ni/CeO\textsubscript{2}Al\textsubscript{2}O\textsubscript{3} at an SIE of 5.4 J/mL. A reasonable increase in product selectivity was observed with the catalyst packing reactor, possibly due to an increase in electric field and/
or power density, which improves the conversion of reactants. It is worth noting that CO selectivity is always high irrespective of the SIE with Ni/CeO$_2$-Al$_2$O$_3$. Here, CeO$_2$ plays an important role by initiating the secondary reaction in-between deposited carbon and active oxygen species because CeO$_2$ can release loosely bound oxygen$^{45}$ when electric discharge arises. Hence, CO selectivity enhances compared to that for the Ni/MgO-Al$_2$O$_3$ packed reactor.

Figure 11 depicts the selectivity of higher hydrocarbons with the variation of SIE. Mainly, there is a possibility to form C$_2$, C$_3$, and C$_4$ hydrocarbons in the DBD plasma reactor. Interestingly, the percentage of hydrocarbon selectivity shows irregularity in nature with increasing SIE. The addition of different catalysts to plasma influences the higher hydrocarbon formation. The C$_2$H$_6$ selectivity increases with an increase in SIE, whereas C$_3$ and C$_4$ selectivity slightly decreases. It signifies that the CH radical is formed from a higher hydrocarbon chain at a higher SIE, forming C$_2$H$_6$. Because of that, the selectivity of long-chain hydrocarbons is lower than the selectivity of C$_2$H$_6$, irrespective of catalyst packing. The order of C$_2$H$_6$ formation is Ni/
MgO_{Al_2O_3} > Ni/CeO_{2-Al_2O_3} > only DBD, whereas the maximum C_4H_{10} selectivity is observed with Ni/CeO_{2-Al_2O_3}. A comparison study is presented in Table S1 where Mg- and Ce-induced Ni/γ-Al_2O_3 shows more amount of hydrocarbons compared to only Ni/γ-Al_2O_3.

As seen in Figure 12, the catalyst packed reactor provides the best yield of major products at any SIE. The maximum H_2 and CO yields are found to be 12 and 12.8%, respectively, with Ni/MgO_{Al_2O_3} at the highest SIE of 5.4 J/mL, whereas Ni/CeO_{2-Al_2O_3} shows a maximum yield of CO, highlighting that CeO_2 facilitates the adsorption of CO_2.

The ideal H_2/CO ratio of 1 is expected from the stoichiometry of DRM. However, in general, the observed ratio deviates from unity due to the formation of some light hydrocarbons. Figure 13a presents the H_2/CO ratio with increasing SIE at different packed-bed DBD reactors. In this work, the highest H_2/CO ratio obtained is 0.64 with bare DBD, which improves to 0.94 with Ni/MgO_{Al_2O_3}. It is worth mentioning that Ni/CeO_{2-Al_2O_3} packed DBD shows the lowest H_2/CO ratio, which is in agreement with the observed highest CO selectivity. Furthermore, a less probable reverse water-gas shift reaction (eq 2) and reverse Boudouard reaction (eq 3) may also contribute marginally to the decreasing syngas ratio:

\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad (2) \]

\[ \text{CO}_2 + \text{C}_x \rightarrow 2\text{CO} \quad (3) \]

The carbon balance as a function of SIE is presented in Figure 13b. In general, the catalyst facilitates the adsorption of intermediate products, leading to the formation of higher hydrocarbons. However, the lowest carbon balance is observed around 89% with the MgO-promoted catalyst at the highest SIE, whereas the without packing condition is slightly higher (92%) at the same applied SIE.

**Post-analysis of Used Catalysts by TGA.** One of the major drawbacks in the DRM reaction is the short deactivation of catalysts due to carbon deposition. To investigate the carbon deposition, the TGA experiment was done with post-reacted catalysts (Figure 14). The weight loss of both catalysts below 400 °C was assigned to the desorption of CO/CO_2 due to the burning of the binder existing in catalysts. To confirm this observation, the TGA was conducted with a freshly prepared catalyst (before reaction), and the weight gain was observed after 250 °C, which continued up to 400 °C. However, the weight loss observed after 400 °C for the used catalysts was due to the oxidation of deposited carbon under an oxygen atmosphere. It is found that Ni/CeO_{2-Al_2O_3} shows the lower weight loss compared to Ni/MgO_{Al_2O_3}. Significantly, it can be concluded that the CeO_2-promoted catalyst is more carbon-resistant compared to the MgO-promoted catalyst.

**Energy Efficiency of DRM.** The energy efficiency has been calculated at the highest discharge power in bare plasma and with catalyst packing condition (Figure 15a). It was observed that the Ni/MgO_{Al_2O_3} packed system offered 1.9709 mmol/kJ, which is almost 52.6% greater than the bare plasma.
15b depicts the energy efficiency with respect to the total conversion of reactants from the reported literature. This work demands almost the highest energy efficiency compared to a previous study. A comparative result with the previous publications is presented in Table 4.

Plausible Plasma Catalytic Reaction Mechanism. Figure 16 describes the plasma catalytic interaction, where the support of the catalyst facilitates adsorption of CO2, whereas CH4 may be adsorbed by metal particles. Usually, the DBD catalytic reaction follows multiple heterogeneous reaction pathways (Langmuir−Hinshelwood and Eley−Rideal mechanisms).16 Although Ni metal favors the adsorption of CH4, the majority of CH4 decomposition is initiated by DBD as the electron density of this experiment is 3.6048 × 10^{16} \text{ cm}^{-3} (Figure S1). It was also reported that excited methyl radicals might be adsorbed and lead to the deposition of reactive carbon and the formation of H radicals. As a result, carbon deposition is quite common in this reaction. To sweep out the deposited carbon, highly reactive oxygen species are preferable, and in that point, CO2 decomposition offers the required excited oxygen (Figure 16, third and fourth steps). In this situation, basic supports are more appropriate in the DBD-based DRM reaction as they have the ability to adsorb more CO2 and decompose readily, which is beneficial to reduce carbon deposition.42

CONCLUSIONS

This paper demonstrates the easiest method to utilize the atmospheric CO2 for the synthesis of value-added chemicals. In that regard, catalyst-assisted plasma DRM is studied, and typical results indicate that Ni/MgO-Al2O3 integration with DBD plasma provides better performance compared to Ni/CeO2-Al2O3. The detailed mechanism of the DRM reaction is explained schematically. Acidic and basic sites present in the catalyst play a crucial role in delivering a good syngas ratio. NH3 and CO2 TPD, respectively, confirmed that Ni/MgO-Al2O3 offered more basic sites compared to Ni/CeO2-Al2O3. TEM confirms the nanosize Ni metal present in both of the catalysts. The MgO-promoted catalyst shows the smallest particle size and the highest surface area with a uniform distribution of Ni metal on the surface of the catalyst. As Ni metal is responsible for CH4 cracking and a basic support is highly demandable for reasonable CO2 conversion, Ni/MgO-Al2O3 performs better than Ni/CeO2-Al2O3 in the DRM reaction. Finally, the highest syngas ratio was obtained by the MgO-promoted catalyst, whereas less carbon deposition was achieved with the CeO2-promoted catalyst. The loosely bound oxygen in CeO2 can participate in the reaction, influencing the recombination reaction with deposited active carbon, which is responsible for obtaining the maximum selectivity of CO.

EXPERIMENTAL SECTION

DBD Setup. The detailed discussion of the experimental setup was described elsewhere.14,16 Briefly, a coaxial DBD reactor was designed by using a quartz tube whose inner diameter was 20 mm and the outer diameter was 23 mm. A stainless steel mesh (12 cm in length) was wrapped around the outside of the tube, which acts as the outer electrode, whereas the inner electrode was designed using a stainless steel rod (8 mm outer diameter). The effective discharge volume and discharge gaps are 24 mL and 6 mm, respectively. Plasma was generated using a high-voltage transformer (Jayanthi Transformer, Chennai) and measured using an HV probe. The outer electrode was connected to the ground while keeping a 400 nF capacitor in series (Figure 17). All electrical parameters were recorded using a digital oscilloscope (Tektronix TDS2014B), and the discharged power was calculated by the Lissajous method.

Experimental Method. Pure CH4 and CO2 were mixed at a 1:1 ratio and introduced into the DBD plasma while keeping a
constant total gas flow rate of 30 mL/min. The product analysis was done with a microgas chromatograph (Agilent 490) equipped with two TCDs. One TCD was connected to 10 m Porapak U (channel 1), and another one was connected to 10 m MS5A (channel 2). Channel 1 detected CO2 quantitatively, whereas H2, CH4, and CO were analyzed in channel 2.

The conversion of reactants, selectivity and/or yield of the products, H2/CO ratio, the balance of carbon, energy efficiency (Eeff), and specific input energy (SIE) were calculated from the following equations:

conversion of CH4 (%) = \left( 1 - \frac{CH_4_{out} \text{ (mmol/min)}}{CH_4_{in} \text{ (mmol/min)}} \right) \times 100 \tag{4}

conversion of CO2 (%) = \left( 1 - \frac{CO_2_{out} \text{ (mmol/min)}}{CO_2_{in} \text{ (mmol/min)}} \right) \times 100 \tag{5}

selectivity of H2 (%) = \frac{H_2 \text{ produced (mmol/min)}}{2 \times CH_4 \text{ converted (mmol/min)}} \times 100 \tag{6}

selectivity of CO (%) = \frac{CO \text{ produced (mmol/min)}}{(CO_2 \text{ converted + CH4 converted}) \text{ (mmol/min)}} \times 100 \tag{7}

yield of H2 (%) = \frac{H_2 \text{ produced (mmol/min)}}{2 \times CH_4_{in} \text{ (mmol/min)}} \times 100 \tag{8}

yield of CO (%) = \frac{CO \text{ produced (mmol/min)}}{(CO_2_{in} + CH_4_{in}) \text{ (mmol/min)}} \times 100 \tag{9}

H2 = \frac{H_2 \text{ produced (mmol/min)}}{CO \text{ produced (mmol/min)}} \tag{10}

carbon balance (%) = \frac{(CO_2_{out} + CH_4_{out} + CO_2_{out}) \text{ (mmol/min)}}{(CO_2_{in} + CH_4_{in}) \text{ (mmol/min)}} \times 100 \tag{11}

SIE (J/mL) = \frac{\text{power (W)}}{\text{total feed flow rate (mL/min)}} \times 60 \tag{12}

E_{eff} \text{ (mmol/kJ)} = \frac{1000 \times (H_2 \text{ converted + CO_2 converted}) \text{ (mmol/min)}}{60 \times \text{discharge power (W)}} \tag{13}

Catalyst Preparation. MgO- and CeO2-modified 15% Ni/γ-Al2O3 catalysts were synthesized by a two-step impregnation method. Commercially available γ-Al2O3 (cylindrical with 3 mm O.D., Alfa Aesar) was calcined at 400 °C for 4 h to remove the adsorbed moisture and other impurities. An aqueous solution of Mg(NO3)2·6H2O (Merck) was used as the precursor of the 2%
MgO promoter, whereas Ce(NO₃)ₓ·₆H₂O (Sigma-Aldrich) was used as the source of 2% CeO₂. The support was impregnated into the previously prepared aqueous solution with constant stirring at 80 °C for 4 h. Therefore, the beads were kept in a hot air oven overnight at 120 °C for complete drying. After that, the required amount of Ni(NO₃)ₓ·₆H₂O (Sigma-Aldrich) solution was added dropwise to the dried beads with constant stirring for 4 h. Then, the catalysts were dried at 110 °C for 12 h followed by calcination at 500 °C under an atmospheric airflow for 4 h. Finally, the catalysts were reduced by a 30 ml/min H₂ flow at 600 °C with a time span of 4 h and named as Ni/MgO·Al₂O₃ and Ni/CeO₂·Al₂O₃.

Instrumentation Technique. The prepared catalysts were confirmed by powder XRD (PANalyticalXpert pro) using Cu Kα (λ = 1.541 Å) in a 2θ range of 10°–90°. Transmission electron microscopy (TEM) images were captured using a JOEL JEM-2100 emission microscope at an accelerating voltage of 200 kV. N₂ adsorption–desorption studies were performed at −196 °C to measure the surface area and pore size distribution of the catalysts (Quantachrome, NOVA2200e). To estimate the reduction temperature of the fresh catalysts, the TPR experiment was performed up to 900 °C under a constant H₂ flow at a heating rate of 10 °C/min by MicrotracBEL Corp., Japan. Acidic and basic sites of the catalysts were measured by NH₃ and CO₂ TPD (MicrotracBEL Corp.) at a 10 °C/min heating rate up to a maximum of 600 °C (NH₃ TPD) and 800 °C (CO₂ TPD) after the pretreatment of all samples at 500 °C under a helium flow for 1 h to remove the surface impurity. In addition, Lewis and Bronsted acid sites were also estimated by Py-FTIR using a BRUKER (TENSOR II). TGA of post-reacted catalysts was performed by powder XRD (PANalyticalXpert pro) using Cu Kα (λ = 1.541 Å) in a 2θ range of 10°–90°. Transmission electron microscopy (TEM) images were captured using a JOEL JEM-2100 emission microscope at an accelerating voltage of 200 kV.

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REFERENCES

(1) Arora, S.; Prasad, R. An Overview on Dry Reforming of Methane: Strategies to Reduce Carbonaceous Deactivation of Catalysts. RSC Adv. 2016, 6, 108668–108688.
(2) Perego, C.; Bortolo, R.; Zennaro, R. Gas to Liquids Technologies for Natural Gas Reserves Valorization: The Eni Experience. Catal. Today 2009, 142, 9–16.
(3) Zeng, Y. X.; Wang, L.; Wu, C. F.; Wang, J. Q.; Shen, B. X.; Tu, X. Low Temperature Reforming of Biogas over K-, Mg- and Ce-Promoted Ni/Al₂O₃ Catalysts for the Production of Hydrogen Rich Syngas: Understanding the Plasma-Catalytic Synergy. Appl. Catal., B 2018, 224, 469–478.
(4) Theofanidis, S. A.; Galvita, V. V.; Poelman, H.; Marin, G. B. Enhanced Carbon-Resistant Dry Reforming Fe-Ni Catalyst: Role of Fe. ACS Catal. 2015, 5, 3028–3039.
(5) Egawa, C. Methane Dry Reforming Reaction on Ru(001) Surfaces. J. Catal. 2018, 358, 35–42.
(6) Li, D.; Li, X.; Bai, M.; Tao, X.; Shang, S.; Dai, X.; Yin, Y. CO₂ Reforming of CH₄ by Atmospheric Pressure Glow Discharge Plasma: A High Conversion Ability. Int. J. Hydrogen Energy 2009, 34, 308–313.
(7) Rueangjitt, N.; Seethawong, T.; Chavadej, S.; Sekiguchi, H. Plasma-Catalytic Reforming of Methane in AC Microsized Gilding Arc Discharge: Effects of Input Power, Reactor Thickness, and Catalyst Existence. Chem. Eng. J. 2009, 155, 874–880.
(8) Li, M.-W.; Tian, Y.-L.; Xu, G.-H. Characteristics of Carbon Dioxide Reforming of Methane via Alternating Current (AC) Corona Plasma Reactions. Energy Fuels 2007, 21, 2335–2339.
(9) Snoeckx, R.; Zeng, Y. X.; Tu, X.; Bogaerts, A. Plasma-based Dry Reforming: Improving The Conversion and Energy Efficiency in a Dielectric Barrier Discharge. RSC Adv. 2015, 5, 29799–29808.
(10) Chawdhury, P.; Ray, D.; Subrahmanyam, C. Single Step Conversion of Methane to Methanol Assisted by Nonthermal Plasma. Fuel Process. Technol. 2018, 179, 32–41.
(11) Chawdhury, P.; Kumar, D.; Subrahmanyam, C. NTP Reactor for a Single Stage Methane Conversion to Methanol: Influence of Catalyst Addition and Effect of Promoters. Chem. Eng. J. 2019, 372, 638–647.
(12) Chawdhury, P.; Ray, D.; Nepak, D.; Subrahmanyam, C. NTP-Assisted Partial Oxidation of Methane to Methanol: Effect of Plasma Parameters on Glass-Packed DBD. J. Phys. D: Appl. Phys. 2019, 52, No. 015204.
(13) Chawdhury, P.; Ray, D.; Vinodkumar, T.; Subrahmanyam, C. Catalytic DBD Plasma Approach for Methanol Partial Oxidation to Methanol Under Ambient Conditions. Catal. Today 2019, 337, 117–125.
(14) Ray, D.; Nepak, D.; Janampelli, S.; Goshal, P.; Subrahmanyam, C. Dry Reforming of Methane in DBD Plasma over Ni-Based Catalysts: Influence of Process Conditions and Support on Performance and Durability. Energy Technol. 2019, 7, 1801008.
(15) Ray, D.; Reddy, P. M. K.; Challapalli, S. Glass beads packed DBD-plasma assisted dry reforming of methane. Top. Catal. 2017, 60, 869–878.
(16) Ray, D.; Reddy, P. M. K.; Subrahmanyam, C. Ni/Mn/γ-Al₂O₃ Assisted Plasma Dry Reforming of Methane. Catal. Today 2018, 309, 212–218.
(17) Chandana, L.; Subrahmanyam, C. Non-thermal discharge plasma promoted redox transformation of arsenic(III) and chromium(VI) in an aqueous medium. Chem. Eng. J. 2017, 329, 211–219.
(18) Chandana, L.; Reddy, P. M. K.; Subrahmanyam, C. Atmospheric Pressure Non-Thermal Plasma Jet for The Degradation of Methylene Blue in Aqueous Medium. Chem. Eng. J. 2015, 282, 116–122.

ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01442.

Fitting peak of HX and comparative study of different packing conditions on the dry reforming reaction (PDF)

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Notes
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(19) Ray, D.; Subrahmanyam, C. CO₂ Decomposition in a Packed DBD Plasma Reactor: Influence of Packing Materials. RSC Adv. 2016, 6, 39492–39499.

(20) Ray, D.; Saha, R.; Subrahmanyam, C. DBD Plasma Assisted CO₂ Decomposition: Influence of Diluent Gases. Catalysts 2017, 7, 244.

(21) Ray, D.; Chawdhury, P.; Subrahmanyam, C. A Facile Method to Decompose CO₂ Using a g-C₃N₄-Assisted DBD Plasma Reactor. Environ. Res. 2020, 183, 109286.

(22) Kameshima, S.; Mizukami, R.; Yamazaki, T.; Prananto, L. A.; Nozaki, T. Interfacial Reactions Between DBD and Porous Catalyst in Dry Methane Reforming. J. Phys. D: Appl. Phys. 2018, 51, 114006.

(23) Mahammadunissa, S.; Reddy, P. M. K.; Ramaraju, B.; Subrahmanyam, C. Catalytic Nonthermal Plasma Reactor for Dry Reforming of Methane. Energy Fuels 2013, 27, 4441–4447.

(24) Foppa, L.; Silaghi, M.-C.; Larmier, K.; Comas-Vives, A. Intrinsic Reactivity of Ni, Pd and Pt Surfaces in Dry Reforming and Competitive Reactions: Insights from First Principles Calculations and Microkinetic Modeling Simulations. J. Catal. 2016, 343, 196–207.

(25) Mancino, G.; Gimino, S.; Lisi, L. Sulphur Poisoning of Alumina Supported Rh Catalyst during Dry Reforming of Methane. Catal. Today 2016, 277, 126–132.

(26) Zhang, J.; Wang, H.; Dalai, A. K. Effects of Metal Content on Activity and Stability of Ni-Co Bimetallic Catalysts for CO₂ Reforming of CH₄. Appl. Catal., A 2008, 339, 121–129.

(27) Usman, M.; Wan Daud, W. M. A.; Abbas, H. F. Dry Reforming of Methane: Influence of Process Parameters—A Review. Renewable Sustainable Energy Rev. 2015, 45, 710–744.

(28) Laosiripojana, N.; Assabumrungrat, S. Catalytic Dry Reforming of Methane over High Surface Area Ceria. Appl. Catal., B 2005, 60, 107–116.

(29) Pawar, V.; Ray, D.; Subrahmanyam, C.; Janardhanan, V. M. Study of Short-Term Catalyst Deactivation Due to Carbon Deposition During Biogas Dry Reforming on Supported Ni Catalyst. Energy Fuels 2015, 29, 8047–8052.

(30) Ray, D.; Nepak, D.; Vinodkumar, T.; Subrahmanyam, C. g-C₃N₄ Promoted DBD Plasma Assisted Dry Reforming of Methane. Energy 2019, 183, 630–638.

(31) Mei, D.; Ashford, B.; He, Y.-L.; Tu, X. Plasma-Catalytic Reforming of Biogas over Supported Ni Catalysts in a Dielectric Barrier Discharge Reactor: Effect of Catalyst Supports. Plasma Processes Polym. 2017, 14, 1600076.

(32) Zeng, Y.; Zhu, X.; Mei, D.; Ashford, B.; Tu, X. Plasma-Catalytic Dry Reforming of Methane over γ-Al₂O₃ Supported Metal Catalysts. Catal. Today 2015, 256, 80–87.

(33) Kameshima, S.; Tamura, K.; Ishibashi, Y.; Nozaki, T. Pulsed Dry Methane Reforming in Plasma-Enhanced Catalytic Reaction. Catal. Today 2015, 256, 67–75.

(34) Mei, D.; Liu, S. Y.; Tu, X. CO₂ Reforming with Methane for Syngas Production Using a Dielectric Barrier Discharge Plasma Coupled with Ni/γ-Al₂O₃ Catalysts: Process Optimization through Response Surface Methodology. J. CO₂ Util. 2017, 21, 314–326.

(35) Le, T. A.; Kim, T. W.; Lee, S. H.; Park, E. D. CO and CO₂ Methanation over Ni Catalysts Supported on Alumina with Different Crystalline Phases. Korean J. Chem. Eng. 2017, 34, 3085–3091.

(36) Gao, J.; Jia, C.; Li, J.; Zhang, M.; Gu, F.; Xu, G.; Zhong, Z.; Su, F. Ni/Al₂O₃ Catalysts for CO Methanation: Effect of Al₂O₃ Supports Calcined at Different Temperatures. J. Energy Chem. 2013, 22, 919–927.

(37) Laguna, O. H.; Centeno, M. A.; Romero-Sarria, F.; Odriozola, J. A. Oxidation of CO over Gold Supported on Zn-Modified Ceria Catalysts. Catal. Today 2011, 172, 118–123.

(38) Wu, M.; Fu, Y.; Zhan, W.; Guo, Y.; Guo, Y.; Wang, Y.; Lu, G. Catalytic Performance of MgO-Supported Co Catalyst for the Liquid Phase Oxidation of Cyclohexane with Molecular Oxygen. Catalysts 2017, 7, 155.

(39) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure Appl. Chem. 2015, 87, 1051–1069.

(40) Romero Toledo, R.; Bravo Sánchez, M.; Rangel Porrás, G.; Fuentes Ramírez, R.; Pérez Larios, A.; Medina Ramírez, A.; Martínez Rosas, M. Effect of Mg as Impurity on the Structure of Mesoporous γ-Al₂O₃: Efficiency as Catalytic Support in HDS of DBT. Int. J. Chem. React. Eng. 2018, 16, 2017041.

(41) Popova, M.; Dimitrov, M.; Dal Santo, V.; Ravasio, N.; Scotti, N. Dehydrogenation of Cyclohexanol on Copper Containing Catalysts: The Role of the Support and The Preparation Method. Catal. Commun. 2012, 17, 150–153.

(42) Khoja, A. H.; Tahir, M.; Amin, N. A. S. Cold Plasma Dielectric Barrier Discharge Reactor for Dry Reforming of Methane over Ni/γ-Al₂O₃-MgO Nanocomposite. Fuel Process. Technol. 2018, 178, 166–179.

(43) Mei, D.; Zhu, X.; He, Y.-L.; Yan, J. D.; Tu, X. Plasma-Assisted Conversion of CO₂ in a Dielectric Barrier Discharge Reactor: Understanding the Effect of Packing Materials. Plasma Sources Sci. Technol. 2015, 24, No. 015011.

(44) Brandenburg, R. Corrigendum: Dielectric Barrier Discharges: Progress on Plasma Sources and on the Understanding of Regimes and Single Filaments. Plasma Sources Sci. Technol. 2018, 27, No. 079501.

(45) Mahammadunissa, S.; Reddy, P. M. K.; Lingaiah, N.; Subrahmanyam, C. NiO/Ce₁₋ₓNiₓO₂−x as an Alternative to Noble Metal Catalysts for CO Oxidation. Catal. Sci. Technol. 2013, 3, 730–736.

(46) Tu, X.; Whitehead, J. C. Plasma Dry Reforming of Methane in an Atmospheric Pressure AC Gliding Arc Discharge: Co-Generation of Syngas and Carbon Nanomaterials. Int. J. Hydrogen Energy 2014, 39, 9658–9669.

(47) Tu, X.; Gallon, H. J.; Twigg, M. V.; Gorry, P. A.; Whitehead, J. C. Dry Reforming of Methane over a Ni/Al₂O₃ Catalyst in a Coaxial Dielectric Barrier Discharge Reactor. J. Phys. D: Appl. Phys. 2011, 44, 274007.

(48) Zhang, A.-J.; Zhu, A.-M.; Guo, J.; Xu, Y.; Shi, C. Conversion of Greenhouse Gases into Syngas via Combined Effects of Discharge Activation and Catalysis. Chem. Eng. J. 2010, 156, 601–606.

(49) Tu, X.; Whitehead, J. C. Plasma-Catalytic Dry Reforming of Methane in an Atmospheric Dielectric Barrier Discharge: Understanding the Synergistic Effect at Low Temperature. Appl. Catal., B 2012, 125, 439–448.