Article

Plasma Promotes Dry Reforming Reaction of CH₄ and CO₂ at Room Temperature with Highly Dispersed NiO/ γ -Al₂O₃ Catalyst

Shan-Shan Lin ^{1,2}, Peng-Rui Li ^{1,2}, Hui-Bo Jiang ^{1,2}, Jian-Feng Diao ^{2,*}, Zhong-Ning Xu ^{2,*} and Guo-Cong Guo ²

¹ College of Chemical Engineering, Fuzhou University, Fuzhou 350116, China; linshanshan@fjirsm.ac.cn (S.-S.L.); lipengrui@fjirsm.ac.cn (P.-R.L.); jianghuiibo@fjirsm.ac.cn (H.-B.J.)

² State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China; gcguo@fjirsm.ac.cn

* Correspondence: diaojianfeng@fjirsm.ac.cn (J.-F.D.); znxu@fjirsm.ac.cn (Z.-N.X.)

Abstract: Plasma is an efficient method that can activate inert molecules such as methane and carbon dioxide in a mild environment to make them reactive. In this work, we have prepared an AE-NiO/ γ -Al₂O₃ catalyst using an ammonia-evaporation method for plasma promoted dry reforming reaction of CO₂ and CH₄ at room temperature. According to the characterization data of XRD, H₂-TPR, TEM, XPS, etc., the AE-NiO/ γ -Al₂O₃ catalyst has higher dispersion, smaller particle size and stronger metal-support interaction than the catalyst prepared by the traditional impregnation method. In addition, the AE-NiO/ γ -Al₂O₃ catalyst also exhibits higher activity in dry reforming reaction. This work provides a feasible reference experience for the research of plasma promoted dry reforming reaction catalysts at room temperature.

Keywords: DBD plasma; DRM; NiO/ γ -Al₂O₃ catalyst; ammonia-evaporation method

Citation: Lin, S.-S.; Li, P.-R.; Jiang, H.-B.; Diao, J.-F.; Xu, Z.-N.; Guo, G.-C. Plasma Promotes Dry Reforming Reaction of CH₄ and CO₂ at Room Temperature with Highly Dispersed NiO/ γ -Al₂O₃ Catalyst. *Catalysts* **2021**, *11*, 1433. <https://doi.org/10.3390/catal11121433>

Academic Editors: Maria Chiara Spadaro, Antonio Vita, PengYi Tang and Jerome Vernieres

Received: 30 September 2021
Accepted: 15 November 2021
Published: 25 November 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Increasing global energy demand and fossil fuel consumption have brought a lot of carbon dioxide (CO₂) emissions and environmental pollution problems [1]. According to the latest data, the concentration of CO₂ in the atmosphere has reached 410 ppm [2]. The excessively high CO₂ concentration in the atmosphere has caused significant environmental problems such as the greenhouse effect and brings hidden dangers to the progress and development of human society [3,4].

Therefore, considerable efforts have been made to limit CO₂ emissions and reduce the concentration of CO₂ in the atmosphere, such as carbon capture, utilization and storage [5,6], catalytic conversion of CO₂ and eliminate and utilize carbon dioxide [7]. However, to optimize the structure of energy consumption and satisfy the demand of economic feasibility, the strategies of CCUS is not suitable for large-scale promotion. However, the catalytic conversion of CO₂ into value-added chemicals has attracted more and more attentions, especially the reaction of Dry Reforming of Methane (DRM) [8].

The DRM (Equation (1)) is use two main greenhouse gases (CO₂ and CH₄) as reaction materials, which can not only use the CO₂ in the atmosphere as a raw material, but it can also bring economic benefits. Moreover, the H₂ and CO were generated from the dry reforming process with a low H₂/CO molar ratio about to 1, which is an ideal raw material for carbonylation and Fischer-Tropsch synthesis [9–11].

In the conventional dry reforming reaction research, since CO₂ and CH₄ are very stable inert molecules ($E_{(C=O)} = 803$ kJ/mol, $E_{(C-H)} = 413$ kJ/mol), the dry reforming reaction usually needs a high temperature (>700 °C) to overcome the thermodynamic limitations [12]. The high temperature reaction conditions are bound to cause high energy consumption and catalyst deactivation [13]. Han et al. reported that the conversion of CO₂

and CH₄ decreased to 51% and 42% from 81% and 64% using the Ni/ γ -Al₂O₃ as catalyst under the condition of 800 °C, and the flow of 20 mL/min after maintaining 5 h [14]. Traditional Ni-based catalysts are very prone to decrease in activity or even inactivation due to high temperature during the dry reforming reaction. Son et al. studied the coke formation over Ni/ γ -Al₂O₃ in the DRM reaction. In addition, they found the coking rate is 3.38 mg_c/g_{cat}·h while the conversion of CO₂ and CH₄ decreased to 84.6% and 81.2% from 97.3% and 96.5% with 850 °C [15]. The carbon deposition of catalyst is an important factor hindering the stability of the catalyst, especially the carbon deposition on the active components caused by methane cracking reaction (Equation (2)) and Boudouard reaction (Equation (3)).

Despite the traditional thermal dry reforming reaction research is relatively extensive and there has been a small-scale industrial production, but they still suffer from problems such as carbon deposition and catalyst deactivation due to high temperature reaction conditions [16].

In recent years, researchers have taken many measures to reduce the temperature of the dry reforming reaction, such as nonthermal plasma technology (NTP). NTP can activate gas molecules at bulk gas temperature without additional heating to generate highly reactive electrons, ions, and various charged groups [17]. Currently, NTP mainly includes dielectric barrier discharges (DBD), gliding arcs discharge, glow discharge and corona discharges [18]. Among them, the ease of operation and easy upgradability of DBD plasma has attracted a lot of attention. DBD plasma can generate high-energy electrons at room temperature and atmospheric pressure due to its non-equilibrium character. The energy of high-energy electrons is usually between 1 to 10 eV, which is sufficient to activate some inert molecules such as CH₄ (4.5 eV) and CO₂ (5.5 eV) [19,20]. Accordingly, DBD plasma can activate some thermodynamically restricted reactions at a low temperature [21].

Generally, DBD plasma achieves the reaction enthalpy (ΔH) required for DRM through the combination of low temperature and Gibbs energy [22], and can cooperate with the catalyst to promote the progress of CO₂ and CH₄ reforming reactions [23]. Song et al. combined 7 wt.% Ni/ γ -Al₂O₃ catalyst with DBD plasma into the DRM without any heating, the conversion of CO₂ and CH₄ were 32.6% and 55.5% at the discharge power of 130 W, total flow rate of 30 mL/min and the CH₄/CO₂ ratio of 1 [24]. Tu et al. applied 10 wt.% Ni/ γ -Al₂O₃ into the reaction of methane reforming at the discharge power of 60 W, resulting the conversion of CO₂ and CH₄ were 26.2% and 44.1% [25]. In addition, many studies have shown that the reforming reaction of CO₂ and CH₄ combined with plasma at room temperature can also generate hydrocarbons, oxides and liquid hydrocarbons in addition to syngas [26–29]. Although the problems such as low conversion rate and complicated products still exist, the addition of plasma provides novel sights to lower the temperature of the methane reforming reaction, which deserves further research.

In this work, all catalysts were packed around the high-voltage electrode in the middle part of the discharge zone of the reactor in order to obtain the coupling effect of catalyst and plasma [30].

2. Results and Discussion

2.1. Effect of Preparation Methods on Catalyst Performance

TI-NiO/ γ -Al₂O₃ and AE-NiO/ γ -Al₂O₃ were all synthesized and evaluated under the same condition. As shown in Figure 1a,b, when there was only plasma with no catalyst filled, the conversion of CO₂ and CH₄ are very low. However, with the addition of catalyst, the coupling effect of catalyst and plasma can promote the conversion of CO₂ and CH₄ significantly. Many studies have proved that the combination of catalyst and

plasma can significantly promote the dry reforming reaction of CO₂ and CH₄ at room temperature [25,31,32]. In this work, compared to the TI-NiO/ γ -Al₂O₃, the AE-NiO/ γ -Al₂O₃ catalyst combined with plasma can better promote the conversion of CO₂ and CH₄. It was worth noting that when the input power was controlled to 140 W, the plasma combined AE-NiO/ γ -Al₂O₃ can convert 80.3% and 86.4% of CO₂ and CH₄ while the plasma combined with TI-NiO/ γ -Al₂O₃ only were 23.4% and 34%. Whether the AE-NiO/ γ -Al₂O₃ catalyst or the TI-NiO/ γ -Al₂O₃ catalyst was used, the conversion of CO₂ and CH₄ under the effect of the plasma was significantly higher than that when only the plasma was used. It also showed that in the plasma-catalyzed dry reforming reaction, the catalyst is still the key to determining the reaction efficiency.

In addition to the conversion of CO₂ and CH₄, the selectivity of AE-NiO/ γ -Al₂O₃ to the CO and H₂ was also slightly higher than that of TI-NiO/ γ -Al₂O₃. As shown in Figure 1c,d, when the input power was 140 W, the selectivity of AE-NiO/ γ -Al₂O₃ to CO and H₂ reached at 44.3% and 43.6%, while the TI-NiO/ γ -Al₂O₃ 38.1% and 38.6%, respectively. There are also individual exceptions, such as the selectivity of H₂ without catalyst was higher than that with catalyst, when the input power was 80 W. That may be caused by the cleavage of CH₄ to generate the H₂ and other free radicals (Equations (4)–(6)) in the absence of a catalyst. As shown in Figure S1a,b, when the input power was 140 W, the yield of CO and H₂ were reached at 37% and 37.7%, respectively. There was a H₂/CO ratio of 1.11, which is suitable for F-T synthesis [33].

The symbols (*) and (+) correspond to the excited and ionic states, respectively.

It can be seen from the Figure S1a, during the dry reforming reaction with plasma promoted, with the input power increasing, the decomposition of CO₂ (Equations (11)–(13)) leads to an increase in CO in the product. The yield of CO was 32.2% rising to 37%, when AE-NiO/ γ -Al₂O₃ catalyst combined plasma with 80 W input rising to 140 W input.

In addition, the free radicals produced by methane cracking combined to produce low-carbon compounds, mainly C₂H₆ and C₂H₄, and no obvious liquid products were detected in this work. As shown in Figure 1e,f, there is almost no generation of hydrocarbons when the input power was less than 120 W with the absence of a catalyst. However, in the presence of the catalyst, with the input power increasing, the selectivity to C₂H₆ and C₂H₄ increase significantly. Similar results were reported by Tu et al. [28]. They compared the use of a single plasma and a packed catalyst combined with plasma in the dry reforming reaction of CO₂ and CH₄, the addition of the catalyst increased the hydrocarbon content in the product. The catalyst still plays a vital role in the dry reforming of CO₂ and CH₄ by plasma promoted. It is not difficult to find by comparing Figure 1e,f, C₂H₆ is the main hydrocarbon products with the maximum selectivity was 17.3% when used the TI-NiO/ γ -Al₂O₃ catalyst combined with plasma 140 W input. However, when the catalyst was changed to AE-NiO/ γ -Al₂O₃, the selectivity to C₂H₆ decreased while the selectivity

to C_2H_4 increased, especially when the input power was 80 W, the selectivity to C_2H_4 reached 11.3%. The generation of C_2H_4 is an attractive phenomenon, which provides a very significant reference for plasma-assisted the reforming reaction of CO_2 and CH_4 to produce high value-added products at room temperature and ambient pressure.

Comprehensive analysis of the conversion, selectivity, and products in the dry reforming reaction by plasma promoted, the AE-NiO/ γ - Al_2O_3 catalyst is more active rather than the TI-NiO/ γ - Al_2O_3 catalyst.

Figure 1. Effect of different reaction modes on the performance of the dry reforming reaction by plasma promoted: (a) conversion of CO_2 , (b) conversion of CH_4 , (c) selectivity to CO, (d) selectivity to H_2 , (e) selectivity to C_2H_4 , (f) selectivity to C_2H_6 ($CO_2/CH_4 = 1:1$, total feed flow rate 20 mL/min, 600 mg catalyst, room temperature and ambient pressure).

2.2. Catalyst Characterization

Table 1 lists the physical parameters of γ -Al₂O₃ and catalysts prepared by the traditional impregnation method and the ammonia-evaporation method. The physical properties of the catalysts prepared by the two methods are not much different. It is worth noting that due to the difference in the preparation methods, the actual Ni loading of the catalyst prepared by the ammonia-evaporation method is lower than that prepared by the impregnation method. About the BET results, the occupation of the active metal leads to the decrease of the Specific surface area. Similar results are also mentioned in the report of Dieuzeide [34]. However, it is puzzling that the activity exhibited by the catalyst shows an opposite trend to the change of the BET area.

Table 1. The physical parameters of γ -Al₂O₃ and catalysts prepared by different methods.

Sample	^a Ni Loading	^b S _{BET} (m ² g ^{−1})	^c Average Pore Diameter (nm)	^d Pore Volume (cm ³ g ^{−1})
γ -Al ₂ O ₃	—	234.1	7.6	0.56
TI-Ni/ γ -Al ₂ O ₃	7.9%	222.2	8.3	0.60
AE-Ni/ γ -Al ₂ O ₃	6.8%	219.4	8.3	0.59

^a measured by ICP; ^b Brunauer-Emmett-Teller surface area; ^c The BJH desorption average pore width; ^d Single point adsorption total pore volume at P/P₀ = 0.97.

Figure 2 shows the PXRD patterns of the fresh samples. The PXRD pattern of the γ -Al₂O₃ support shows four major diffraction peaks located at $2\theta = 36.3^\circ$, $2\theta = 38.8^\circ$, $2\theta = 44.9^\circ$ and $2\theta = 66.8^\circ$ (PDF # 46–1131). The PXRD pattern of AE-NiO/ γ -Al₂O₃ and TI-AE-NiO/ γ -Al₂O₃ have no obvious diffraction peaks of NiO at $2\theta = 37.3^\circ$, $2\theta = 43.3^\circ$, $2\theta = 62.9^\circ$ and $2\theta = 75.4^\circ$ (PDF # 47-1049), this could be attributed to the very small amount of NiO supported on bulk γ -Al₂O₃ and could also be correlated to the small crystal size of NiO. In addition, we found that the XRD peaks of the AE-NiO/ γ -Al₂O₃ catalyst and TI-NiO/ γ -Al₂O₃ catalyst are slightly larger compared to the support γ -Al₂O₃. That may be caused by impregnation and calcination during the preparation of the catalyst.

Figure 2. PXRD patterns of γ -Al₂O₃, TI-Ni/ γ -Al₂O₃, AE-Ni/ γ -Al₂O₃ (☆NiO, ★ γ -Al₂O₃).

To confirm the size of the diameter crystallite, Scherrer calculation (Equation (14)) was performed (D is the diameter crystallite, κ is a dimensionless shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM), and θ is the Bragg angle). According to the calculation of Scherrer calculation, the crystallite sizes of support Al_2O_3 in the $\text{AE-NiO}/\gamma\text{-Al}_2\text{O}_3$ and $\text{TI-NiO}/\gamma\text{-Al}_2\text{O}_3$ catalysts are 10.5 nm and 11.4 nm, respectively.

$$D = \frac{\kappa\lambda}{\beta \cos \theta} \quad (14)$$

H_2 -TPR profiles of the $\text{AE-NiO}/\gamma\text{-Al}_2\text{O}_3$ and $\text{AE-NiO}/\gamma\text{-Al}_2\text{O}_3$ catalysts are displayed in Figure 3. For all catalysts, one shoulder peak was observed between 400–550 °C and the other discrimination peak was located between 600–950 °C. The Shoulder peak at moderate temperature is attributed to the reduction of NiO particles that weakly interact with the support. The second significant peak at high temperature is related to NiO, which has a stronger interaction with the support. As can be seen from the TPR curve, the second H_2 consumption peak on $\text{AE-NiO}/\gamma\text{-Al}_2\text{O}_3$ was higher than $\text{TI-NiO}/\gamma\text{-Al}_2\text{O}_3$, which are located at 810 °C and 700 °C, respectively. That may be due to the stronger interaction of NiO on the $\text{AE-NiO}/\gamma\text{-Al}_2\text{O}_3$ than on the $\text{TI-NiO}/\gamma\text{-Al}_2\text{O}_3$. It can also be seen from the curves of $\text{AE-NiO}/\gamma\text{-Al}_2\text{O}_3$ and $\text{TE-NiO}/\gamma\text{-Al}_2\text{O}_3$, the curve of $\text{AE-NiO}/\gamma\text{-Al}_2\text{O}_3$ is smoother than $\text{TI-NiO}/\gamma\text{-Al}_2\text{O}_3$, that may be caused by the distribution of NiO on $\text{AE-NiO}/\gamma\text{-Al}_2\text{O}_3$ is more uniform than that on $\text{TI-NiO}/\gamma\text{-Al}_2\text{O}_3$.

Figure 3. H_2 -TPR profiles of the calcined $\text{AE-NiO}/\gamma\text{-Al}_2\text{O}_3$ and $\text{AE-NiO}/\gamma\text{-Al}_2\text{O}_3$ samples.

Figure 4 shows the TG results of $\text{AE-Ni}/\gamma\text{-Al}_2\text{O}_3$ and $\text{TI-Ni}/\gamma\text{-Al}_2\text{O}_3$. It's clear that the catalysts prepared by the ammonia evaporation method and the traditional impregnation method have approximately the same weight loss temperature, the weight loss temperature in the first stage was about 140 °C while the second stage was 520 °C. In this experiment, according to the TG results, the calcination temperature of all the catalysts was set to 600 °C, and the catalysts prepared by the two methods have good thermal stability.

Figure 4. TG results of AE-NiO/ γ -Al₂O₃ and TI-NiO/ γ -Al₂O₃.

The TEM, HRTEM images and size distribution of AE-NiO/ γ -Al₂O₃ catalyst are shown in Figure 5. The catalyst particles are highly dispersed in Figure 5b,c. As can be seen from the size distribution chart, the average particle diameter of NiO was 2.5 nm. When analyzing the exposed crystal plane, it was found that the crystal plane spacing of the exposed particles was 0.203 nm, which was consistent with the NiO (200) crystal plane, indicating that the active component is NiO. Compared with Figure 6 (TEM images of TI-NiO/ γ -Al₂O₃), it is obvious that the distribution of NiO on AE-NiO/ γ -Al₂O₃ is more uniform and the particle diameter of NiO (2.5 nm) is smaller than that of TI-NiO/ γ -Al₂O₃ (4.5 nm). Compared with the TEM and HRTEM images of AE-NiO/ γ -Al₂O₃, TI-NiO/ γ -Al₂O₃ are relatively unevenly distributed, with an average particle size of 4.5 nm. The lattice fringes are not clear, and the exposed crystal plane of NiO cannot be confirmed.

X-ray Photoelectron Spectroscopy (XPS) measurements were performed to determine the existing form of the Ni on the surface of the γ -Al₂O₃. The binding energy of Ni 2p are shown in Figure 7. It's observed that the binding energy of Ni in the AE-NiO/ γ -Al₂O₃ or TI-NiO/ γ -Al₂O₃ does not change before and after the reaction. The binding energy around 856.0 eV and 862.0 eV can be attributed to Ni 2p_{3/2} and its satellite peak Ni 2p_{3/2}sat, respectively [35]. It has been proposed that the Ni 2p_{3/2} peak with a binding energy of 856 eV and the corresponding shake-up satellite peak at 862 eV were characteristics of NiAl₂O₄ [36]. The same conclusion was also reported by Huang et al. [37]. The energy band at 873 eV can be attributed to Ni 2p_{1/2} of NiO. Furthermore, satellite peak Ni 2p_{1/2}sat can be observed at binding energy of 880 eV, which is due to the presence of Ni ions in NiO coming from the nickel configuration 2p⁵3d⁹4s [38]. Therefore, based on the XPS results, it can be concluded that nickel mainly exists in the form of active phase NiO and a very small amount of inactive NiAl₂O₄ on the surfaces of all prepared samples.

Figure 5. TEM and HRTEM images of AE-NiO/γ-Al₂O₃ catalyst, (a–d) are images under the different scales.

Figure 6. TEM and HRTEM images of TI-NiO/γ-Al₂O₃ catalyst, (a–d) are images under the different scales.

Figure 7. Ni 2p XPS spectra of TI-NiO/ γ -Al₂O₃, TI-NiO/ γ -Al₂O₃-used and AE-NiO/ γ -Al₂O₃, AE-NiO/ γ -Al₂O₃-used.

3. Experiment Section

3.1. Preparation of Catalysts

AE-NiO/ γ -Al₂O₃ catalyst was prepared by an ammonia-evaporation method (AE), in which Nickel nitrate hexahydrate (Damas-beta, 99%) was adopted as the metal precursor with the γ -Al₂O₃ balls (Diameter 1.5 mm) as the support. Synthetic method described as follows: 2.2 g Ni(NO₃)₂·6H₂O was dissolved in 100 mL deionized water, stirring for 5 min until the nickel salt dissolving completely. Then added the appreciate volume of 28% ammonia aqueous solution to ensure that the pH value of mixed solution is between 10–11 and stirring for 30 min. After that, taking 5.0 g γ -Al₂O₃ into the nickel ammonia solution and stirring overnight, all the above steps were performed at room temperature (RT). Then suspension was heated at 70 °C to evaporate ammonia and deposited the nickel species on γ -Al₂O₃. The step of evaporation was stopped when the pH value of the suspension is decreased to 6–7. Next, washing the precipitate by filtration with deionized water for 3–5 times and drying the solid ball under the vacuum condition at 80 °C for 12 h. Finally, calcined at 600 °C for 4 h in air atmosphere to obtain the AE-NiO/ γ -Al₂O₃ catalyst.

TI-NiO/ γ -Al₂O₃ catalyst was prepared by the traditional impregnation method (TI) which was described as follows: 2.2 g Ni(NO₃)₂·6H₂O was dissolved in 100 mL deionized water, stirring for 5 min until the nickel salt dissolved completely, then added 5.0 g γ -Al₂O₃ balls (Diameter 1.5 mm) to stirring overnight. In addition, after washing the precipitate with deionized water for 3–5 times, drying the solid balls at 80 °C for 12 h in a vacuum condition. Finally, calcined at 600 °C for 4 h in air atmosphere to obtain the TI-NiO/ γ -Al₂O₃ catalyst.

3.2. Characterization of Catalysts

ICP: The content of loaded Ni was analyzed by Inductively Coupled Plasma (ICP), which was carried out on Ultima2 plasma emission spectrometer from Jobin Yvon (Paris, France).

PXRD: Powder X-ray diffraction (PXRD) patterns of the catalysts powder was collected by a Rigaku (Tokyo, Japan) Miniflex II diffractometer using a Cu-K α radiation ($\lambda = 1.5406$ Å) with a scan speed of 0.5 °/min in the range of 5–80°.

TEM: Transmission electron microscopy (TEM) was performed on JEOL JEM 2100F (Beijing, China) field-emission transmission electron microscopy operated at 120 kV.

XPS: X-ray photoelectron spectroscopy (XPS) was performed on an Escalab 250 (Waltham, MA, USA) spectrometer (VG Systems) equipped with an Al-K α (1486.6 eV) anode as X-ray source. The binding energies were corrected by C1s peak at 284.6 eV, providing experimental error is within ± 0.1 eV.

BET: The surface area of samples was determined by N₂ adsorption-desorption isotherms which performed on Micromeritics ASAP 2020 (Shanghai, China) with the liquid nitrogen temperature (77 K).

TG: Thermogravimetric (TG) analysis was performed on a METTLER TOLEDO (Shanghai, China) thermogravimetric analyzer with a heating rate of 5 K/min from 298 to 1273 K in nitrogen (N₂).

TPR: H₂ temperature-programmed reduction experiments (H₂-TPR) was carried on Autochem II 2920 (Shanghai, China). The sample was pretreated under a 30 mL/min argon purge at 160 °C for 60 min, then cooled to 50 °C, and then heated to 950 °C at 10 °C/min. The reducing gas was 10% H₂/Ar.

3.3. Evaluation of Activity

As shown in Figure 8, the experiments were performed in a coaxial dielectric barrier plasma reactor. Catalytic activity was evaluated by a continuous flow fixed-bed plasma reactor with a power supply (CTP-2000K, Nanjing Suman Plasma Technology Co, Ltd., Nanjing, China) which the applied AC voltage varied from 0~30 kV with an adjustable frequency of 5~20 kHz and a Tektronix TBS-2102 two-channel digital oscilloscope to observe and record the electrical signals such as the applied voltage, the current and so on. The plasma was generated inside a coaxial alundum tube which is 656 mm long and has an outer diameter and an inner diameter of 16 mm and 10 mm, respectively. The discharge gap of plasma reactor is 3 mm. In addition, the diameter of the inner electrode is 4 mm. In the preparation stage of the dry reforming reaction, 600 mg catalyst were directly placed in the discharge region in contact with the plasma electrode.

Figure 8. Experimental system diagram.

The reactant and product gases were analyzed by an online Gas Chromatograph (GC) (Shimadzu GC-2014) equipped with flame ionization detector (FID) and thermal conductivity detector (TCD). TCD is equipped with TDX-01 column for detecting hydrogen, carbon monoxide, methane, and carbon dioxide while FID is equipped with PLOT-Q column to detect low-carbon alkanes such as methane, ethane, and ethylene. The raw material gas is a 1:1 mixture of methane and carbon dioxide without dilution gas, and the mass flow meter is set to 20 mL/min.

3.4. Calculation of Parameters

The activity of DRM catalyst was calculated using Equations (15)–(23) as follows:

$$C_{CH_4}(\%) = \frac{CH_4 \text{ converted}}{CH_4 \text{ input}} \times 100 \quad (15)$$

$$C_{CO_2}(\%) = \frac{CO_2 \text{ converted}}{CO_2 \text{ input}} \times 100 \quad (16)$$

$$S_{H_2}(\%) = \frac{H_2 \text{ produced}}{CH_4 \text{ converted} \times 2} \times 100 \quad (17)$$

$$S_{CO}(\%) = \frac{CO \text{ produced}}{CO_2 \text{ converted} + CH_4 \text{ converted}} \times 100 \quad (18)$$

$$S_{C_2H_4}(\%) = \frac{C_2H_4 \text{ produced} \times 2}{CH_4 \text{ converted} + CO_2 \text{ converted}} \times 100 \quad (19)$$

$$S_{C_2H_6}(\%) = \frac{C_2H_6 \text{ produced} \times 2}{CH_4 \text{ converted} + CO_2 \text{ converted}} \times 100 \quad (20)$$

$$Y_{H_2}(\%) = \frac{H_2 \text{ produced}}{CH_4 \text{ input} \times 2} \times 100 \quad (21)$$

$$Y_{CO}(\%) = \frac{CO \text{ produced}}{CO_2 \text{ input} + CH_4 \text{ input}} \times 100 \quad (22)$$

The ratio of H_2/CO molar in the product and carbon balance (based on major gas products) have been calculated as:

$$\frac{H_2}{CO} = \frac{H_2 \text{ produced}}{CO \text{ produced}} \quad (23)$$

The energy efficiency with respect to the conversion of CH_4 and CO_2 has been calculated as:

$$P_{\text{discharge}} = \int_{t_0}^{t_1} V(t)I(t)dt \quad (24)$$

where C_i , S_i , Y_i represents conversions, selectivity and yield, respectively. 'i' is a variable which changes according to reactants and products whereas ' B_{carbon} ' stands for carbon balance.

In this work, all discharge power calculations used the Q-V Lissajous graph. As shown in Figure 9, the input power of plasma was 120 W, the Y coordinate value of the CH1 output signal was taken as X Axis data, Y coordinate value of CH2 output signal was used as Y axis data, the discharge power was proportional to the area of the closed curve. Calculation formula such as Equation (24) [39].

Figure 9. (a) Q-V Lissajous Graphics; (b) Power output voltage data saved by oscilloscope. (Filled with 600 mg catalysts and the input power of 120 W).

4. Conclusions

All of the above illustrate that the AE-NiO/ γ -Al₂O₃ catalyst exhibits high catalytic activity due to its small particle size, high active metal dispersion and strong metal-support interaction. Compared with the catalyst prepared by the traditional impregnation method, the catalyst prepared by the ammonia-evaporation method is more suitable for plasma-promoted dry reforming reaction. Especially when the input power of DBD plasma is 140 W and without any additional heating, the conversion of CO₂ and CH₄ can reach 80.3% and 86.4%, respectively. What's more, the AE-NiO/ γ -Al₂O₃ catalyst is beneficial to generate higher value-added products of C₂H₄ under the promotion of plasma, which has important reference significance for the plasma-promoted dry reforming reaction to generate high value-added products. Herein, this study provides a feasible catalyst synthesis method for the research of plasma catalytic dry reforming reaction catalyst.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11121433/s1>, Figure S1: Effect of different reaction modes on the performance of the plasma dry reforming reaction: (a) yield of CO, (b) yield of H₂, (c) selectivity to C₂H₆, (d) selectivity to C₂H₄. Figure S2: PXRD patterns of AE-Ni/ γ -Al₂O₃-used, TI-Ni/ γ -Al₂O₃-used. Figure S3: TG results of AE-Ni/ γ -Al₂O₃-used and TI-Ni/ γ -Al₂O₃-used. Figure S4: EDX results of AE-NiO/ γ -Al₂O₃-used and TI-NiO/ γ -Al₂O₃-used. Figure S5: (a) Nitrogen adsorption isotherms of γ -Al₂O₃, (b) BJH desorption average pore size distribution of γ -Al₂O₃, (c) Nitrogen adsorption isotherms of AE-NiO/ γ -Al₂O₃, (d) BJH desorption average pore size distribution of AE-NiO/ γ -Al₂O₃, (e) Nitrogen adsorption isotherms of TI-NiO/ γ -Al₂O₃, (f) BJH desorption average pore size distribution of TI-NiO/ γ -Al₂O₃. Table S1: Input Power, Output Power (Discharge Power) and Efficiency.

Author Contributions: Data curation, writing—original draft preparation S.-S.L.; catalytic test, data curation, discussion P.-R.L.; data curation, investigation, discussion H.-B.J.; supervision, conceptualization, writing—reviewing and editing J.-F.D. and Z.-N.X.; supervision and discussion G.-C.G. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Key R&D Program of China (2017YFA0206802, 2017YFA0700103, 2018YFA0704500), the National Natural Science Foundation of China (22172171).

Data Availability Statement: The authors confirm that the data supporting the findings of this study are available within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Gao, X.; Lin, Z.; Li, T.; Huang, L.; Zhang, J.; Askari, S.; Dewangan, N.; Jangam, A.; Kawi, S. Recent Developments in Dielectric Barrier Discharge Plasma-Assisted Catalytic Dry Reforming of Methane over Ni-Based Catalysts. *Catalysts* **2021**, *11*, 455. [CrossRef]
- Zhang, Z.; Pan, S.-Y.; Li, H.; Cai, J.; Olabi, A.G.; Anthony, E.J.; Manovic, V. Recent advances in carbon dioxide utilization. *Renew. Sustain. Energy Rev.* **2020**, *125*, 109799. [CrossRef]

3. Armaroli, N.; Balzani, V. The future of energy supply: Challenges and opportunities. *Angew. Chem. Int. Ed. Engl.* **2007**, *46*, 52–66. [\[CrossRef\]](#)
4. Karnauskas, K.B.; Miller, S.L.; Schapiro, A.C. Fossil Fuel Combustion Is Driving Indoor CO₂ Toward Levels Harmful to Human Cognition. *Geohealth* **2020**, *4*, e2019GH000237. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Shukla, R.; Ranjith, P.; Haque, A.; Choi, X. A review of studies on CO₂ sequestration and caprock integrity. *Fuel* **2010**, *89*, 2651–2664. [\[CrossRef\]](#)
6. Zhang, Z. Energy and environment issues in carbon capture, utilization and storage. *Energy Sources Part A Recovery Util. Environ. Eff.* **2020**, 1–4. [\[CrossRef\]](#)
7. Song, C. Global challenges and strategies for control, conversion and utilization of CO₂ for sustainable development involving energy, catalysis, adsorption and chemical processing. *Catal. Today* **2006**, *115*, 2–32. [\[CrossRef\]](#)
8. Chung, W.-C.; Chang, M.-B. Review of catalysis and plasma performance on dry reforming of CH₄ and possible synergistic effects. *Renew. Sustain. Energy Rev.* **2016**, *62*, 13–31. [\[CrossRef\]](#)
9. Delikonstantis, E.; Scapinello, M.; Stefanidis, G. Investigating the Plasma-Assisted and Thermal Catalytic Dry Methane Reforming for Syngas Production: Process Design, Simulation and Evaluation. *Energies* **2017**, *10*, 1429. [\[CrossRef\]](#)
10. Dybkjaer, I.; Aasberg-Petersen, K. Synthesis gas technology large-scale applications. *Can. J. Chem. Eng.* **2016**, *94*, 607–612. [\[CrossRef\]](#)
11. Owgi, A.H.K.; Jalil, A.A.; Hussain, I.; Hassan, N.S.; Hambali, H.U.; Siang, T.J.; Vo, D.V.N. Catalytic systems for enhanced carbon dioxide reforming of methane: A review. *Environ. Chem. Lett.* **2021**, *19*, 2157–2183. [\[CrossRef\]](#)
12. Luisetto, I.; Sarno, C.; De Felicis, D.; Basoli, F.; Battocchio, C.; Tuti, S. Ni supported on γ -Al₂O₃ promoted by Ru for the dry reforming of methane in packed and monolithic reactors. *Fuel Process. Technol.* **2017**, *158*, 130–140. [\[CrossRef\]](#)
13. Carrillo, A.J.; Serra, J.M. Exploring the Stability of Fe–Ni Alloy Nanoparticles Exsolved from Double-Layered Perovskites for Dry Reforming of Methane. *Catalysts* **2021**, *11*, 741. [\[CrossRef\]](#)
14. Han, J.W.; Park, J.S.; Choi, M.S.; Lee, H. Uncoupling the size and support effects of Ni catalysts for dry reforming of methane. *Appl. Catal. B Environ.* **2017**, *203*, 625–632. [\[CrossRef\]](#)
15. Son, I.H.; Lee, S.J.; Song, I.Y.; Jeon, W.S.; Jung, I.; Yun, D.J.; Jeong, D.-W.; Shim, J.-O.; Jang, W.-J.; Roh, H.-S. Study on coke formation over Ni/ γ -Al₂O₃, Co-Ni/ γ -Al₂O₃, and Mg-Co-Ni/ γ -Al₂O₃ catalysts for carbon dioxide reforming of methane. *Fuel* **2014**, *136*, 194–200. [\[CrossRef\]](#)
16. Nikoo, M.K.; Amin, N.A.S. Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation. *Fuel Process. Technol.* **2011**, *92*, 678–691. [\[CrossRef\]](#)
17. Bogaerts, A.; Tu, X.; Whitehead, J.C.; Centi, G.; Lefferts, L.; Guaitella, O.; Azzolina-Jury, F.; Kim, H.-H.; Murphy, A.B.; Schneider, W.F.; et al. The 2020 plasma catalysis roadmap. *J. Phys. D Appl. Phys.* **2020**, *53*, 443001. [\[CrossRef\]](#)
18. Khoja, A.H.; Tahir, M.; Amin, N.A.S. Recent developments in non-thermal catalytic DBD plasma reactor for dry reforming of methane. *Energy Convers. Manag.* **2019**, *183*, 529–560. [\[CrossRef\]](#)
19. Ashford, B.; Tu, X. Non-thermal plasma technology for the conversion of CO₂. *Curr. Opin. Green Sustain. Chem.* **2017**, *3*, 45–49. [\[CrossRef\]](#)
20. Mehta, P.; Barboun, P.; Go, D.B.; Hicks, J.C.; Schneider, W.F. Catalysis Enabled by Plasma Activation of Strong Chemical Bonds: A Review. *ACS Energy Lett.* **2019**, *4*, 1115–1133. [\[CrossRef\]](#)
21. Snoeckx, R.; Rabinovich, A.; Dobrynin, D.; Bogaerts, A.; Fridman, A. Plasma-based liquefaction of methane: The road from hydrogen production to direct methane liquefaction. *Plasma Process. Polym.* **2017**, *14*, e1600115. [\[CrossRef\]](#)
22. Neyts, E.C.; Ostrikov, K.K.; Sunkara, M.K.; Bogaerts, A. Plasma Catalysis: Synergistic Effects at the Nanoscale. *Chem. Rev.* **2015**, *115*, 13408–13446. [\[CrossRef\]](#)
23. 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 Environ.* **2012**, *125*, 439–448. [\[CrossRef\]](#)
24. Song, H.K.; Choi, J.-W.; Yue, S.H.; Lee, H.; Na, B.-K. Synthesis gas production via dielectric barrier discharge over Ni/ γ -Al₂O₃ catalyst. *Catal. Today* **2004**, *89*, 27–33. [\[CrossRef\]](#)
25. 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 Process. Polym.* **2017**, *14*, e1600076. [\[CrossRef\]](#)
26. Goujard, V.; Tatibouët, J.-M.; Batiot-Dupeyrat, C. Use of a non-thermal plasma for the production of synthesis gas from biogas. *Appl. Catal. A Gen.* **2009**, *353*, 228–235. [\[CrossRef\]](#)
27. Wang, A.; Harrhy, J.H.; Meng, S.; He, P.; Liu, L.; Song, H. Nonthermal plasma-catalytic conversion of biogas to liquid chemicals with low coke formation. *Energy Convers. Manag.* **2019**, *191*, 93–101. [\[CrossRef\]](#)
28. Wang, L.; Yi, Y.; Wu, C.; Guo, H.; Tu, X. One-Step Reforming of CO₂ and CH₄ into High-Value Liquid Chemicals and Fuels at Room Temperature by Plasma-Driven Catalysis. *Angew. Chem. Int. Ed. Engl.* **2017**, *56*, 13679–13683. [\[CrossRef\]](#)
29. Liu, S.; Winter, L.R.; Chen, J.G. Review of Plasma-Assisted Catalysis for Selective Generation of Oxygenates from CO₂ and CH₄. *ACS Catal.* **2020**, *10*, 2855–2871. [\[CrossRef\]](#)
30. Wang, Q.; Yan, B.-H.; Jin, Y.; Cheng, Y. Dry Reforming of Methane in a Dielectric Barrier Discharge Reactor with Ni/Al₂O₃ Catalyst: Interaction of Catalyst and Plasma. *Energy Fuels* **2009**, *23*, 4196–4201. [\[CrossRef\]](#)

-
31. 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. [\[CrossRef\]](#)
 32. Ray, D.; Reddy, P.M.K.; Subrahmanyam, C. Ni-Mn/ γ -Al₂O₃ assisted plasma dry reforming of methane. *Catal. Today* **2018**, *309*, 212–218. [\[CrossRef\]](#)
 33. Cao, Y.; Gao, Z.; Jin, J.; Zhou, H.; Cohron, M.; Zhao, H.; Liu, H.; Pan, W. Synthesis Gas Production with an Adjustable H₂/CO Ratio through the Coal Gasification Process: Effects of Coal Ranks and Methane Addition. *Energy Fuels* **2008**, *22*, 1720–1730. [\[CrossRef\]](#)
 34. Dieuzeide, M.L.; Iannibelli, V.; Jobbagy, M.; Amadeoa, N. Steam reforming of glycerol over Ni/Mg/ γ -Al₂O₃ catalysts. Effect of calcination temperatures. *Int. J. Hydrog. Energy* **2012**, *37*, 14926–14930. [\[CrossRef\]](#)
 35. Peck, M.A.; Langell, M.A. Comparison of Nanoscaled and Bulk NiO Structural and Environmental Characteristics by XRD, XAFS, and XPS. *Chem. Mater.* **2012**, *24*, 4483–4490. [\[CrossRef\]](#)
 36. Xu, Z.; Zhen, M.; Bi, Y.; Zhen, K. Catalytic properties of Ni modified hexaaluminates LaNi_yAl_{12-y}O_{19-δ} for CO₂ reforming of methane to synthesis gas. *Appl. Catal. A Gen.* **2000**, *198*, 267–273. [\[CrossRef\]](#)
 37. Huang, X.; Sun, N.; Xue, G.; Wang, C.; Zhan, H.; Zhao, N.; Xiao, F.; Wei, W.; Sun, Y. Effect of pore geometries on the catalytic properties of NiO–Al₂O₃ catalysts in CO₂ reforming of methane. *RSC Adv.* **2015**, *5*, 21090–21098. [\[CrossRef\]](#)
 38. Olszewska, D. Application of XPS method in the research into Ni ion-modified montmorillonite as a SO₂ sorbent. *Fuel Process. Technol.* **2012**, *95*, 90–95. [\[CrossRef\]](#)
 39. Snoeckx, R.; Aerts, R.; Tu, X.; Bogaerts, A. Plasma-Based Dry Reforming: A Computational Study Ranging from the Nanoseconds to Seconds Time Scale. *J. Phys. Chem. C* **2013**, *117*, 4957–4970. [\[CrossRef\]](#)