



# Plasma-assisted catalytic dry reforming of methane: Highly catalytic performance of nickel ferrite nanoparticles embedded in silica



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## HIGHLIGHTS

- NiFe<sub>2</sub>O<sub>4</sub> nanoparticles (<10 nm) are embedded in porous silica.
- NiFe<sub>2</sub>O<sub>4</sub>#SiO<sub>2</sub> presents a high catalytic performance for plasma-assisted dry reforming.
- SiO<sub>2</sub> shells restrain the aggregation of Ni–Fe alloy particles.
- NiFe<sub>2</sub>O<sub>4</sub>#SiO<sub>2</sub> catalyst effectively suppresses carbon formation.

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## ABSTRACT

Spinel nickel ferrite nanoparticles (NiFe<sub>2</sub>O<sub>4</sub> NPs) embedded in silica (NiFe<sub>2</sub>O<sub>4</sub>#SiO<sub>2</sub>) was prepared to enhance the reaction performance of the dry reforming of methane in a coaxial dielectric barrier discharge reactor. NiFe<sub>2</sub>O<sub>4</sub> NPs of around 10 nm were effectively embedded in porous SiO<sub>2</sub> NPs (~100 nm in diameter). Compared to the supported Ni-based catalysts (Ni/γ-Al<sub>2</sub>O<sub>3</sub>, Ni–Fe/γ-Al<sub>2</sub>O<sub>3</sub>, Ni–Fe/SiO<sub>2</sub>, and NiFe<sub>2</sub>O<sub>4</sub>), the NiFe<sub>2</sub>O<sub>4</sub>#SiO<sub>2</sub> catalyst placed at the discharge zone exhibited excellent catalytic performance and high resistance to carbon formation during dry reforming under ambient conditions without the involvement of extra heat. The synergetic effect between the non-thermal plasma and the NiFe<sub>2</sub>O<sub>4</sub>#SiO<sub>2</sub> catalyst favored the conversion of CH<sub>4</sub> and CO<sub>2</sub> into syngas. The results indicated that the special structure of the as-synthesized NiFe<sub>2</sub>O<sub>4</sub>#SiO<sub>2</sub> catalyst was capable of restraining the aggregation of Ni–Fe alloy and suppressing the carbon formation in the reforming process.

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## 1. Introduction

The use of greenhouse gases (GHG), such as carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>), has attracted considerable attention because of its potential to relieve the existing greenhouse effect and produce relevant chemical products [1–3]. The dry reforming of CH<sub>4</sub> and CO<sub>2</sub> is a desirable way of producing syngas (CO and H<sub>2</sub>) with a low molar ratio of H<sub>2</sub> to CO, which is the primary chemical feedback for the gas-based petrochemical and liquid fuel processes, such as Fischer–Tropsch synthesis and methanol synthesis. Ni-based catalysts have been widely investigated for the dry reforming of methane because of the rich nickel content and the low cost compared to the noble metals [4–10]. Nevertheless, the dry reforming of CH<sub>4</sub>, a typical endothermic reaction operated above 973 K, suffers from high energy consumption, harsh operating conditions, catalytic deactivation because of coke formation, and

the sintering of supported metal catalysts [7–10]. To balance the drawbacks with the excellent catalytic performance, new catalysts with high resistance to carbon deposition are in urgent need for the dry reforming of CH<sub>4</sub> and CO<sub>2</sub>.

Dielectric barrier discharge (DBD) plasma may provide an alternative solution to the problem encountered during the conventional catalytic dry reforming of CH<sub>4</sub> since Siemens reported its first experimental investigation of simple barrier discharges in 1857 [11–19]. As typical non-thermal plasma, DBD plasma can initiate a series of ionization and chemical processes for the dry reforming of CH<sub>4</sub>, which are far from thermodynamic equilibrium under ambient operating conditions [11,15,16]. It is indicated that the chemical reactions in DBD are governed by electron temperature instead of the thermal processes or gas temperature. There are several drawbacks in dry reforming with the DBD plasma alone, including low conversion of reactants, poor selectivity of desired products, and low energy efficiency [20–24]. Numerous studies on the dry reforming of CH<sub>4</sub> suggested that the synergic effect of the combination between the plasma and the catalysts significantly

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enhance the reaction performance in conversion and selectivity [25–34]. Nevertheless, less attention has focused on the catalytic deactivation caused by coke formation during the dry reforming process. For plasma-assisted dry reforming, coke deposition arises from the decomposition of  $\text{CH}_4$  because the dissociation energy of  $\text{CH}_4$  (4.51 eV) is lower than that of  $\text{CO}$  (11.09 eV) [7,9,32].

Small particle size and uniform dispersion of metallic particles seem to be capable of reducing carbon deposition and improving the stability of the catalysts [32,33]. In this context, the method for the preparation of small particles of nickel (Ni, <20 nm) by the reduction of spinel oxide ( $\text{NiM}_2\text{O}_4$ ) has attracted special attention [35–37]. Ni and its bimetallic alloy (such as Ni–Fe, Ni–Co, Ni–Cu) are homogeneously dispersed on a stable oxidic matrix, which exhibits excellent catalytic performance and high resistance to coking. Previous papers suggested that the catalytic activity of spinel nickel ferrite ( $\text{NiFe}_2\text{O}_4$ ) prepared using traditional method is unsatisfactory for the dry reforming of  $\text{CH}_4$  [10,35]. Large particles of the  $\gamma$ -NiFe alloy and the instability of iron oxides formed by the reduction of  $\text{NiFe}_2\text{O}_4$  could account for the poor activity and the unsatisfied molar ratio of  $\text{H}_2/\text{CO}$  [10]. Ni-based catalysts with superior structures are being developed to control the aggregation of Ni-based alloy particles and suppress the carbon deposition.

Recent literature reported that metal nanoparticles (NPs) embedded in porous material present high catalytic activity and good durability for the dry reforming of  $\text{CH}_4$  [38–40]. The mono-dispersed and ultrafine active metal particles in an embedded structure can effectively hinder coke formation and suppress the sintering of the active metal [32,39]. Therefore it is possible to encapsulate ultrafine spinel NPs such as  $\text{NiFe}_2\text{O}_4$  within porous silicon ( $\text{SiO}_2$ ). This method can ensure a higher dispersion of  $\text{NiFe}_2\text{O}_4$  NPs, leading to improvement in sintering of  $\text{NiFe}_2\text{O}_4$  NPs and their resistance to coke formation. In this paper,  $\text{NiFe}_2\text{O}_4\#\text{SiO}_2$  was prepared by the modified Stöber approach and used to investigate the dry reforming of  $\text{CH}_4$  and  $\text{CO}_2$  in a DBD reactor under ambient conditions without the involvement of extra heat.

## 2. Experimental

### 2.1. Materials

All of the chemicals were of analytical grade and used as commercially obtained without any further purification. Ferric nitrate hexahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , >98%), aluminum oxide ( $\gamma\text{-Al}_2\text{O}_3$ , >99.5%), Oleic acid ( $\text{C}_{18}\text{H}_{34}\text{O}_2$ , >98.5%), sodium oleate ( $\text{C}_{18}\text{H}_{33}\text{NaO}_2$ , >98%), and nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , >98%) were purchased from Chengdu Kelong Chemical Reagent company. Absolute ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , >99.7%), ammonia solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ , >25%), and tetraethyl orthosilicate (TEOS,  $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$ , >99%) were purchased from Chongqing Chuandong Chemical (Group) Co., Ltd. Polyethylene glycol (PEG-20000,  $\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{H}$ , >99.8%) and poly-(vinylpyrrolidone) (PVP-K30,  $(\text{C}_6\text{H}_9\text{NO})_n$ , >99.5%) were purchased from Aladdin Industrial Corporation.

### 2.2. Preparation of catalysts

$\text{NiFe}_2\text{O}_4$  NPs were prepared by the modified hydrothermal method. 3 mmol  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 6 mmol  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were dissolved in 200 mL ethanol solution (50 wt%) by vigorously stirring at room temperature for 1.5 h. 10.0 g sodium oleate and 10.0 g PEG-20000 were added into the above solution and continuously agitated for 3 h at room temperature. The as-prepared solution was transferred to a 500 mL Teflon-lined stainless autoclave and subjected to a hydrothermal treatment at 467 K for 12 h. After cooling the solution to room temperature, hexane and ethanol solutions were added to the synthesized solution to form  $\text{NiFe}_2\text{O}_4$  NPs. Then

the powder was obtained by centrifugation and dried at 353 K for 12 h in an oven.

The  $\text{NiFe}_2\text{O}_4\#\text{SiO}_2$  sample was prepared by the modified Stöber method. 0.1 g  $\text{NiFe}_2\text{O}_4$  NPs and 1.5 g PVP-K30 were added to 200 mL ethanol solution (80 wt %) with ultrasonic dispersion at 323 K for 0.5 h, and the suspension was vigorously stirred at room temperature for 4 h. 5 mL of TEOS and 5 mL of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  were injected into the above solution system. After stirring at 323 K for 10 h, the suspension was separated by centrifuge at 4500 rpm for 10 min, washed with ethanol and water, and dried at 373 K for 6 h. The sample was eventually calcined at 873 K for 3 h in air to obtain  $\text{NiFe}_2\text{O}_4\#\text{SiO}_2$ .

Supported Ni catalysts (including  $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ ,  $\text{Ni-Fe}/\gamma\text{-Al}_2\text{O}_3$ , and  $\text{Ni-Fe}/\text{SiO}_2$ ) were prepared by the conventional impregnation method.  $\gamma\text{-Al}_2\text{O}_3$  bulks were commercially obtained, while  $\text{SiO}_2$  particles were synthesized by hydrolysis and polycondensation of TEOS.  $\gamma\text{-Al}_2\text{O}_3$  or  $\text{SiO}_2$  was added to the  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution or the mixed solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  at 343 K and then dried at 363 K. The dried samples were calcined at 873 K in air for 3 h.

### 2.3. Plasma system

Fig. 1 shows a schematic diagram of the setup for the experiment of dry reforming assisted by plasma and catalysts, which is similar to the previous work [32]. The mixed gases of  $\text{CH}_4$  and  $\text{CO}_2$ , controlled by mass flow controllers, were injected into the annular gap between the inner ceramic-tube ( $\phi 16 \times 2$ ) and the outer glass-tube ( $\phi 25 \times 2.5$ ). The discharge gap and the discharge length are 2 mm and 150 mm, respectively. The glass-tube, covered with wire entanglements, was connected to a high voltage supply while the ceramic-tube, filled with metal aluminum powder, served as the grounded electrode. A 30 KV AC voltage power was employed to operate the discharge of the plasma generator and the frequency range was 5–20 KHz. The voltage amplitude caused corresponding changes in the output power when it was adjusted.

### 2.4. Characterization of catalysts

The X-ray powder diffraction (XRD) of catalysts was recorded with the Bruker D8 Advance X-ray Powder Diffractometer.

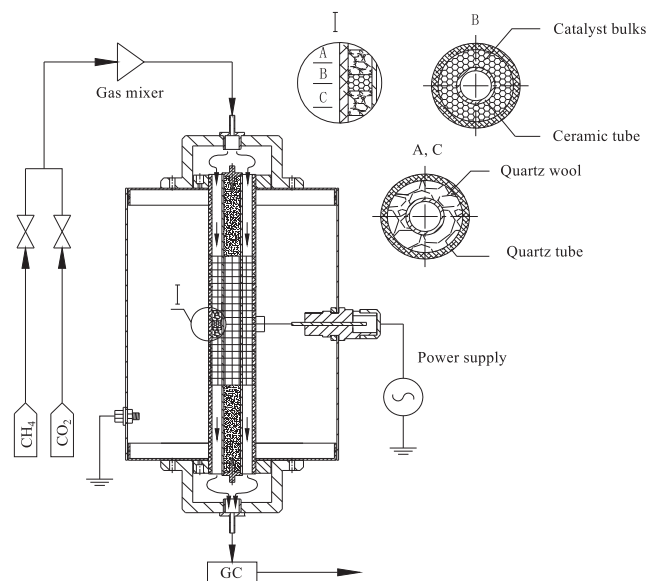


Fig. 1. Schematic diagram of the DBD plasma.

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