Supporting Information

Manuscript title: Plasma-catalytic Conversion of CO₂ and H₂O into H₂, CO and Trace of CH₄ over NiO/Cordierite Catalysts

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This supporting information includes the following contents:

- (1) Detailed description of the DBD reactor;
- (2) Catalyst preparation methods;
- (3) Catalyst characterization methods;
- (4) The pretreatment conditions of H₂-TPR and CO₂-TPD;
- (5) Hydrogen and oxygen evolution versus RH in CO₂-H₂O conversion by plasma only;
- (6) The influence of support;
- (7) CO and CH₄ selectivity over NiO/cordierite catalysts;
- (8) The rate expression of the reactions involved in this study.

(1) Detailed description of the DBD reactor:

The DBD reactor setup is shown in Figure S1 as below. Plasma was generated in a cylindrical reactor made of corundum as dielectric barrier with the outer diameter of 24.5 mm and 2.1 mm wall thickness, wrapped by stainless mesh which was 200 mm long and 0.02 mm thick as the outer electrode. It was connected to an AC high voltage through an insulated wire at a frequency of 8.95 kHz. The inner electrode was a stainless steel rod of 14.0 mm diameter, which was electrical grounded, placed on the axis of the reactor. The total length of the reactor was 317.0 mm, while the discharge length was 200.0 mm and the discharge gap was fixed at 3.15 mm. The electric parameters were determined by a high-frequency AC power supply (0-50 kV) coupled with a modem (CTP-2000K/P, Suman, China). The products were experimentally determined as a function of input power (W), which can be calculated from the area of the Lissajous curves.



Figure S1. Schematic overview of DBD reactor

(2) Catalyst preparation methods:

All chemical reagents (analytical purity) were purchased from Sinopharm Chemical Reagent Co., Ltd, China and employed without further purification. Deionized water was used as solvent in all experiments. The NiO samples were prepared by hydrothermal method, the precursor of each sample were dried at 80 °C for 12 h and calcinated at 400 °C for 3 h. In addition, the muffle furnace was in an air atmosphere and set with a heating rate

- of 10 °C min⁻¹.
- (a) The sphere NiO was synthesized via a simple hydrothermal method. Typically, 9.508 g of Ni(NO₃)₂·6H₂O was dissolved in 80 mL of deionized water. Then 40 mL of solution containing 2.4 g urea (1 mol/L) was added dropwise to the above aqueous solution under vigorous stirring for 30 min. After that, the mixture was transferred into a 150 mL teflon-lined stainless autoclave and heated at 110 °C for 6 h. After cooling to room temperature, the resulting precipitate was collected and washed with deionized water and ethanol for several times. Finally, the powder was dried at 80 °C for 12 h and then calcined at 400 °C for 3 h.
- (b) The grain NiO was also prepared by a hydrothermal method. In a typical synthesis, 50 mL of 0.5 mol/L Ni(NO₃)₂·6H₂O and 50 mL of 1 mol/L NaOH were prepared respectively, and the ion diffusion reaction was carried out under the water bath condition and kept at 70 °C for 12 h. The obtained product was repeatedly washed with deionized water and ethanol, and then dried at 80 °C for 12 h. The precursor were obtained and followed by calcination at 400 °C for 3 h.
- (c) The sheet NiO was prepared by a facile hydrothermal process. In a typical process, 12 mmol Ni(NO₃)₂·6H₂O and 48 mmol CO (NH₂)₂ were dissolved in a 120 mL deionized water under vigorous stirring for 10 min to form a homogeneous solution. Then 8 mL ammonia was dropwise added into the mixed solution and stirred continuously for 30 min. After that, the mixed solution was transferred into a 150 mL Teflon-lined stainless-steel autoclave and kept at 120 °C for 15 h. After completing the reaction, the autoclave was cooled down to room temperature naturally, and the obtained product was finally washed with deionized water and ethanol for several times. Subsequently, the assynthesized NiO product was dried at 80 °C for 12 h. Finally, the obtained product was calcined in a muffle furnace at 400 °C for 3 h.



Figure S2. Diagram of preparation methods

(3) Catalyst characterization:

X-ray diffraction (XRD) patterns from 10° to 80° were collected on a D8 Advance (Bruker Ltd., Germany) automated powder X-ray diffraction meter using Cu-K (λ = 0.1541 nm) radiation with a scan rate of 6°/min at 40 kV and 40 mA. The average crystalline size was determined from multiple characteristic diffraction peaks through the Scherrer equation. Scanning electron microscopy (SEM) images were obtained on an S-4800 microscope (Hitachi Ltd., Japan) operating at an accelerating voltage of 5 kV. The BET specific surface areas were measured by nitrogen adsorption-desorption at -196 °C on an automatic volumetric apparatus (ASAP 3020, Micromeritics Ltd., United States). The redox behavior was evaluated by hydrogen temperature programmed reduction (H₂-TPR) experiments on a chemisorption analyzer (Chemisorb 2720, Micromeritics Ltd., United States). On the same instrument, CO₂ temperature programmed desorption (CO₂-TPD) experiments were carried out. The detailed degassing conditions for BET-BJH, H₂-TPR and CO₂-TPD are shown in the next paragraph. The surface chemical states of the catalysts were examined by X-ray photoelectron spectroscopy (XPS, 5400 ESCA, Physical Electronics, Inc., United States). The Raman spectra were recorded using a Raman spectrometer (Bruker) under ambient conditions using a 532 nm argon ion laser as the excitation source. The spectra resolution was 0.1 cm⁻¹ and laser power was 2 mW.

(4) The pretreatment conditions of H₂-TPR and CO₂-TPD:

H₂-TPR measurements for fresh catalysts were performed on a chemisorption analyzer (Chemisorb 2720, Micromeritics Ltd., USA) equipped with a thermal conductivity detector (TCD). Prior to the TPR measurement, 0.02 g of catalyst was outgassed in Helium at 300°C for 30 min and then cooled down to room temperature. Subsequently, 5% H₂/N₂ gas was introduced at a flow rate of 30 mL/min while the temperature of the furnace was increased at a heating rate of 10°C /min to 750°C.

 CO_2 -TPD measurements were performed on the same apparatus as the H₂-TPR. Prior to TPD experiments, 0.1 g of catalyst was first degassed at 300°C in Helium for 30 min then cooled down to room temperature. Thereafter, the sample was exposed to 5% of CO_2/N_2 gas mixture at a flow rate of 30 mL/min for 60 min, followed by Helium purge for another 60 min. Then the TPD profiles were obtained by heating the sample from ambient temperature to 700°C at a heating rate of 10°C /min.

(5) Hydrogen and oxygen evolution versus RH in CO₂-H₂O conversion by plasma only:

Figure S3 shows the H_2 and O_2 evolution versus RH (%) in the case of CO_2 - H_2O conversion by plasma only. The H_2 concentration increases with the rise of RH, probably mainly due to the water vapor splitting process. However, the O_2 concentration shows an unpredictable change with the increase of RH, and there is obvious fluctuation in the RH range of 0-10%. With further increase the RH over 10%, the O_2 concentration gradually increases. Due to the limitation of the experimental conditions, it's quite difficult to distinguish the source of the observed oxygen since both CO_2 and H_2O contain oxygen atoms.



Figure S3. Hydrogen and oxygen evolution versus RH (%) in CO₂-H₂O conversion by plasma only

(6) The influence of support:

The as prepared NiO catalysts need to be loaded on the support to form an in-plasma catalysis system. As a result, the selection of support is an important issue. We have compared two kinds of supports including nickel foam and cordierite. As shown in Figure S4 (a) and (b), the two kinds of supports all showed higher CO_2 conversion than the blank. One possible reason is the partial packed reactor shows higher performance than plasma only. This positive effect is probably due to the filamentary micro discharges that might enhance the interactions between plasma and catalysis. Another reason is the active components such as nickel that played a private role. As shown in Figure S4 (c) and (d), the cordierite support shows higher H_2 and CH_4 formation. It was probably due to the Mg, Al, Si components that promoted the water vapor splitting process. Moreover, the NiO catalysts can be loaded more uniformly on the surface of cordierite. Finally, we chose cordierite as the support in this study.



Figure S4. The influence of support: Nickel foam and Cordierite (a) CO₂ conversion (%); (b) CO yield (%); (c) H₂ production (ppm); (d) trend of CH₄ yield (%)

(7) CO and CH₄ selectivity over NiO/cordierite catalysts

As seen from Figure S5, NiO-sphere shows higher CO and CH_4 selectivity among the catalysts. Moreover, the plasma-catalysis system shows higher CO and CH_4 selectivity than the cordierite support, indicating the addition of catalysts promoted the converted CO_2 towards desired products.



Figure S5. (a) CO and (b) CH₄ selectivity over NiO/cordierite catalysts.

(8) The rate expression of the reactions involved in this research:

Reactions:	Rate expression:
$e^- + H_2O \rightarrow H^{\bullet} + \bullet OH + e^-$	5.8×10^{-9} [cm ³ /molecule s]
	(2000-6000 K)
$e^- + CO_2 \rightarrow CO + O^* + e^-$	$1.81 \times 10^{-10} $ [cm ³ /molecule s]
	(2620-4470 K)
$\mathrm{CO}+\bullet\mathrm{OH}\to\mathrm{CO}_2+\mathrm{H}\bullet$	5.4×10^{-14} [cm ³ /molecule s]
$\bullet OH + \bullet OH + M \longrightarrow H_2O_2 + M$	$6.89 \times 10^{-31} \text{ [cm}^6/\text{molecule}^2 \text{ s]}$
$\mathrm{H}\bullet + \mathrm{O}^{\ast} \to \bullet \mathrm{OH}$	$4.36 \times 10^{-32} [\text{cm}^6/\text{molecule}^2 \text{ s}]$
$\mathrm{H} \bullet + \mathrm{H} \bullet \longrightarrow \mathrm{H}_2$	$9.1 \times 10^{-33} $ [cm ⁶ /molecule ² s]
$O^* + O^* + M {\rightarrow} O_2 + M$	$5.21 \times 10^{-35} [\text{cm}^6/\text{molecule}^2 \text{ s}]$
$\bullet OH + H_2O_2 \rightarrow H_2O + HO_2$	$1.7 \times 10^{-12} $ [cm ³ /molecule s]
$\mathrm{HO}_2 + \mathrm{O}^* \to \bullet\mathrm{OH} + \mathrm{O}_2$	5.8×10^{-11} [cm ³ /molecule s]
$H\bullet + \bullet OH + M \longrightarrow H_2O + M$	$6.87 \times 10^{-31} [\text{cm}^6/\text{molecule}^2 \text{ s}]$