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# A Facile Fabrication of Supported Ni/SiO<sub>2</sub> Catalysts for Dry Reforming of Methane with Remarkably Enhanced Catalytic Performance

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**Abstract:** Ni catalysts supported on SiO<sub>2</sub> are prepared via a facile combustion method. Both glycine fuel and ammonium nitrate combustion improver facilitate the formation of much smaller Ni nanoparticles, which give excellent activity and stability, as well as a syngas with a molar ratio of  $H_2/CO$  of about 1:1 due to the minimal side reaction toward revserse water gas shift (RWGS) in CH<sub>4</sub> dry reforming.

**Keywords:** Ni catalysts; combustion method; dry reforming of methane; RWGS reaction; improved stability

### 1. Introduction

The availability of natural gas (or shale gas) in large reserves makes  $CH_4$  serve as a suitable feedstock used in C1 chemistry to produce desired fuels and chemicals [1]. Unfortunately, the chemical inertness of  $CH_4$  results in direct conversion, which constitutes a great challenge for highly efficient utilization [2]. Ideally, the best use of  $CH_4$  occurs when it is converted into syngas, which can facilitate further downstream conversion [3] by means of the methanol route [4] and Fischer–Tropsch synthesis (FTS) [5–12] due to good reactivity, unlike the  $CH_4$  which has a high dissociation energy C–H bond [1]. Among the most widely investigated technologies, there are comparable advantages associated with the dry reforming of  $CH_4$  (DRM) with  $CO_2$  for producing syngas [13]. On the one hand, compared to the other reforming processes, there is a 20% lower operating cost for DRM [14]; on the other hand, the reforming of  $CH_4$  using  $CO_2$  not only produces high purity syngas [15,16] but also reduces the emissions of two abundantly available greenhouse gases to alleviate global climate change [17–20].

In spite of the above-mentioned merits, DRM suffers from serious carbon deposits on the surface of Ni nanoparticles, which leads to a remarkable loss of active sites [21–25]. Recently, DRM research efforts have resulted in strategies to improve the stability of the catalyst [26]. Based on the fact that smaller Ni nanoparticles efficiently improve catalytic performance by avoiding carbon accumulation [27–32], the general concept is to develop the catalyst preparation protocol to obtain small Ni nanoparticles encapsulated in the support or confined by the stable porous oxide layer to prevent sintering [33,34]. For example, Tomishige et al. reported that the solid solution catalyst of nickel–magnesia, which was prepared by the co-precipitation method, showed high and stable activity without carbon deposits for 100 days [35,36]. Kawi et al. synthesized a Ni-yolk@Ni@SiO<sub>2</sub> nanocomposite with a yolk-satellite shell structure to efficiently inhibit the sintering of Ni, which resulted in negligible carbon deposition, and the CH<sub>4</sub> conversion was 10% after the first 2 hours of reaction under the conditions of 800 °C, a gas hourly



space velocity (GHSV) of 1440  $L \cdot g^{-1} cat \cdot h^{-1}$ , a Wcat of 0.01 g, and a CO<sub>2</sub>:CH<sub>4</sub>:N<sub>2</sub> ratio of 1:1:1 [37]. Similarly, Wang et al. pointed out that the Ni nanoparticle cores encapsulated by the mesoporous Al<sub>2</sub>O<sub>3</sub> shells show superior coke resistance because of the confinement effects which prevent the Ni nanoparticles from agglomeration at high temperatures, and the CH<sub>4</sub> and CO<sub>2</sub> conversions under the reaction conditions of 800 °C, CO<sub>2</sub>/CH<sub>4</sub> of 1/1, and a weight hourly space velocity (WHSV) of 36 L·h<sup>-1</sup>·gcat<sup>-1</sup> were about 88% and 92%, respectively [38].

Herein, different from the above-mentioned encapsulated Ni catalysts with relatively complicated preparation procedures, we propose a facile one-step strategy to prepare the SiO<sub>2</sub> supported Ni catalysts toward the controlled formation of nanoparticle size and Ni-support interaction, which could lead to high activity and stability. Following the conventional impregnation method, glycine  $(C_2H_5NO_2)$  and ammonium nitrate  $(NH_4NO_3)$  were introduced into the impregnated solution of nickel precursor  $(Ni(NO_3)_2 \cdot 6H_2O)$ , as shown in Scheme 1. It was expected that the mixed materials with  $C_2H_5NO_2$  as fuel and  $NH_4NO_3$  as combustion improver reacted exothermically after ignition which finished within a short time-frame with a very high temperature and release of a large quantity of gases, such as  $CO_2$ , water, and  $N_2$ . We thought this process might facilitate the formation of smaller crystalline materials and regulate the metal-support interaction, resulting in improved catalytic performance in the DRM reaction. To demonstrate the effects of the above combustion process on the catalytic performance, several characterizations, such as Brunauer-Emmett-Teller (BET), transmission electron microscopy (TEM), X-ray diffraction (XRD), H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) and thermogravimetric (TG), were employed to characterize the catalyst.

#### 2. Results and Discussion

#### 2.1. Characterization of the Catalyst Sample

As shown in Figure S1, all the fresh Ni/SiO<sub>2</sub> catalysts exhibit apparent diffraction peaks at 20 values of 37.3°, 43.2°, 63.0°, 75.4°, and 79.4° assigned to the NiO (JCPDS 22-1189). For the reduced catalysts (Figure 1a), Ni/SiO<sub>2</sub>-0/0 prepared by the conventional wetness impregnation method displayed the most intensive diffraction peaks at 20 values of 44.5°, 52.2°, and 77.0°, which are the characteristic peaks of metallic Ni (JCPDS 1-1206). According to Figure S1, the peak at 37.3° should be assigned to NiO. As the NH<sub>4</sub>NO<sub>3</sub> was introduced into the impregnated solution with nickel nitrate, the resulting catalyst (Ni/SiO<sub>2</sub>-0/1) exhibited almost the same diffraction peak intensity at 44.5°. However, for the case of  $C_2H_5NO_2$ , Ni/SiO<sub>2</sub>-2/0 displays a much weaker diffraction peaks. Interestingly, the addition of both  $C_2H_5NO_2$  and NH<sub>4</sub>NO<sub>3</sub> results in almost no detectable diffraction peaks for Ni nanoparticles (Ni/SiO<sub>2</sub>-2/1), suggesting that smaller Ni nanoparticles can be obtained by synergistic effects of fuel and combustion improver in the combustion process, as presented in Scheme 1.



**Scheme 1.** One-step facile synthesis of Ni catalysts supported on silica (SiO<sub>2</sub>) prepared by the combustion of Ni(NO<sub>3</sub>)<sub>2</sub>–C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>–NH<sub>4</sub>NO<sub>3</sub> impregnated in the porous SiO<sub>2</sub>.

TEM images of the reduced catalysts are depicted in Figure 1b,c. The Ni/SiO<sub>2</sub>-2/1 displays an average Ni nanoparticle size of only  $6.1 \pm 2.7$  nm which is significantly smaller than that for Ni/SiO<sub>2</sub>-0/0 ( $31.3 \pm 13.5$  nm). The significant difference in the Ni nanoparticle size further confirms the synergistic effects of C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> and NH<sub>4</sub>NO<sub>3</sub> in reducing the Ni nanoparticle size. The combustion process between N<sub>2</sub>O and NH<sub>3</sub> is highly exothermic. The decomposition of nickel nitrate produces N<sub>2</sub>O gas at 250 °C, while the decomposition of C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> gives NH<sub>3</sub> along with CO<sub>2</sub> and H<sub>2</sub>O. The combustion process is triggered by the reaction between N<sub>2</sub>O and NH<sub>3</sub> to form N<sub>2</sub> and H<sub>2</sub>O [39]. When NH<sub>4</sub>NO<sub>3</sub> is further added, NH<sub>3</sub> and N<sub>2</sub>O can be formed via its decomposition at a low temperature of about 200 °C, thereby promoting combustion. The high-temperature stage in a short-duration favors the formation of ultra-small nanoparticles in a short time which may be in the order of seconds [40].



**Figure 1.** (a) XRD patterns of reduced Ni/SiO<sub>2</sub> catalysts prepared with the combustion method by using different ratios of  $C_2H_5NO_2$  to  $NH_4NO_3$ . (b,c) TEM images and Ni size distribution of the reduced Ni/SiO<sub>2</sub>-0/0 and Ni/SiO<sub>2</sub>-2/1 catalysts, respectively. (d) H<sub>2</sub>-TPR profiles of the fresh Ni/SiO<sub>2</sub> catalysts prepared with the combustion method.

Figure 1d exhibits the reduction behavior of fresh Ni/SiO<sub>2</sub> catalysts with different molar ratios of  $C_2H_5NO_2$  to NH<sub>4</sub>NO<sub>3</sub>. As expected, NH<sub>4</sub>NO<sub>3</sub> does not obviously change the H<sub>2</sub>-TPR profile compared to the case of Ni/SiO<sub>2</sub>-0/0, as both catalysts show a strong reduction peak at 300–450 °C with a small right shoulder peak at 450–510 °C. However,  $C_2H_5NO_2$  only (Ni/SiO<sub>2</sub>-2/0) notably weakens the peak at lower temperatures, accompanied by a shift in the right shoulder peak to the higher reduction temperature with enhanced intensity. For Ni/SiO<sub>2</sub>-2/1, the high temperature reduction peak is further intensified and shifts to a higher reduction temperature range. This result suggests that the smaller Ni nanoparticle size results in a more difficult reduction owing to a stronger metal-support interaction [41]. The reduction profiles correspond to the XRD and TEM results.

#### 2.2. Activity Evaluation

Figure 2 shows the catalytic performance in the  $CH_4$  dry reforming reaction with  $CO_2$  over the as-prepared catalysts. In the case of catalytic activity, the  $CH_4$  conversion over  $Ni/SiO_2$ -0/0 exhibits a rapid drop from 78.3% to 53.0% in the early ten hours and then gradually becomes stable. In contrast,  $Ni/SiO_2$ -0/1 gives a milder and continuous decrease in  $CH_4$  conversion until the end of the reaction. Surprisingly,  $Ni/SiO_2$ -2/0 exhibits a stable and higher  $CH_4$  conversion over the whole reaction period of 50 hours. Furthermore,  $Ni/SiO_2$ -2/1 displays a more stable and even higher  $CH_4$  conversion. The  $CO_2$  and  $CH_4$  conversions are similar for all  $Ni/SiO_2$  catalysts. However, in the corresponding

reaction period, the CO<sub>2</sub> conversion is always slightly higher compared to the CH<sub>4</sub> conversion. When the DRM reaction over Ni/SiO<sub>2</sub>-2/1 is stable, the conversion rates of CH<sub>4</sub> and CO<sub>2</sub> are 83.6% and 90.6%, respectively, which are slightly lower than their equilibrium conversion rates at 91% and 95% calculated by HSC chemistry 6.0 (Table S1). Also, in the case of the H<sub>2</sub>/CO molar ratio, it follows the same trend as that for CH<sub>4</sub> conversion over all the Ni/SiO<sub>2</sub> catalysts. Specifically, for the Ni/SiO<sub>2</sub>-2/1 catalyst, the desired H<sub>2</sub>/CO molar ratio at the value of 1/1 is obtained, which results from the efficiently suppressed reverse water gas shift (RWGS) reaction. How the Ni/SiO<sub>2</sub> morphology affects the catalytic performance is discussed briefly in the following part.



**Figure 2.** CH<sub>4</sub> conversion (**a**), CO<sub>2</sub> conversion (**b**), and H<sub>2</sub>/CO molar ratio (**c**) as a function of time on stream for Ni/SiO<sub>2</sub> catalysts prepared with the combustion method at different molar ratios of C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> to NH<sub>4</sub>NO<sub>3</sub> (black line: conventional wetness impregnation method; purple line: NH<sub>4</sub>NO<sub>3</sub> only; blue line: C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> only; red line: 2/1 ratio of C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> to NH<sub>4</sub>NO<sub>3</sub>). The reaction was carried at 800 °C with 200 mg of catalyst and a molar ratio of CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> = 9/9/2 with 160 mL/min.

The DRM reaction is extremely endothermic. Equation (1) shows that the DRM process can produce a syngas with an  $H_2/CO$  ratio of 1:1. During the DRM process, several reactions simultaneously occur, like CH<sub>4</sub> dissociation (Equation (2)), reduction of CO<sub>2</sub> to CO (Equation (3)), and the RWGS reaction (Equation (4)).

$$CH_4 + CO_2 = 2CO + 2H_2 (\Delta H_{298K} = +247 \text{ kJ mol}^{-1})$$
(1)

$$CH_4 = C(s) + 2H_2 (\Delta H_{298K} = +75 \text{ kJ mol}^{-1})$$
(2)

$$C(s) + CO_2 = 2CO (\Delta H_{298K} = +171 \text{ kJ mol}^{-1})$$
(3)

$$CO_2 + H_2 = CO + H_2O (\Delta H_{298K} = +41.2 \text{ kJ mol}^{-1})$$
(4)

The driving force for Equations (2)–(4) strongly depends on the temperature, reactant partial pressure and catalyst structures. In the investigated Ni/SiO<sub>2</sub> catalysts, both activation of CH<sub>4</sub> and CO<sub>2</sub> can occur on the active Ni surface since SiO<sub>2</sub> support is inert material. It is believed that CH<sub>4</sub> activation tends to form an intermediate, like  $CH_x$  or a formyl group, but dissociates directly to C species and  $H_2$ at high temperature. Essentially, the DRM reaction of Ni catalysts might follow a dynamic redox type mechanism as the CO<sub>2</sub> oxidizes  $Ni^0$  to  $Ni^{+\delta}$  to give CO, and the oxidative state  $Ni^{+\delta}$  is reduced to  $Ni^0$ by C species as a result of CH<sub>4</sub> dissociation. As seen from the above reaction cycle, it is clear that the presence of O from CO<sub>2</sub> helps the dissociation of CH<sub>4</sub>. To avoid the catalyst deactivation resulting from carbon accumulation, the C species from  $CH_4$  dissociation must react timely with  $CO_2$  to give CO. The reaction rate of this step is closely related to the Ni nanoparticle size, as the larger Ni surface favors the formation of multicarbon C<sub>n</sub> species, which are potential precursors of carbon deposits such as coke. The smaller Ni nanoparticles allow a smaller amount of carbon species on the Ni nanoparticle surface. Thus, it is easier to keep the monoatomic C species isolated, and in time, they are oxidized by CO<sub>2</sub> to CO. By minimizing the rate of C species combination, the carbon accumulation could be effectively suppressed. Indeed, as shown in Figure 3, Ni/SiO<sub>2</sub>-0/0, with an average nanoparticle size of 31.3  $\pm$  13.5 nm, gives the highest amount of carbon deposits with 2.7 mg carbon deposits gCH $_4^{-1}$ 

as the BET surface area is decreased to the largest extent (Table S2). In contrast, the Ni/SiO<sub>2</sub>-2/1 with a smaller nanoparticle size of  $6.1 \pm 2.7$  nm is significantly coke-resistant, as the amount of carbon deposits decreases to 0.9 mg carbon deposits gCH<sub>4</sub><sup>-1</sup>. The above experimental results reflect that the smaller Ni nanoparticle size is favorable to lower carbon deposits and thereby improve the catalyst stability, as shown in Figure S2. It should be noted that, in spite of the significant decrease in carbon deposits over Ni/SiO<sub>2</sub>-2/1 catalyst, a considerable amount of coke is still formed during the DRM reaction of 50 hours. It can be deduced that most of the carbon deposits might not locate on the Ni nanoparticle surface but are located on the SiO<sub>2</sub> support since the catalytic activity is quite stable. It is reasonable for us to imagine that the Ni nanoparticles are lying on the SiO<sub>2</sub> support and not confined by porous layer material, which provides a chance for the carbon species to grow continuously along the SiO<sub>2</sub> support surface initiated by the Ni nanoparticle and finally form strips of nanofiber.



**Figure 3.** TG patterns of spent Ni/SiO<sub>2</sub> catalysts after the dry reforming (DRM) reaction of 50 hours. The catalytic results are shown in Figure 2.

As seen from Figure 2, the H<sub>2</sub>/CO molar ratio is highly dependent on the CO<sub>2</sub> conversion. A lower CO<sub>2</sub> conversion can cause a decrease in the molar ratio of H<sub>2</sub>/CO to a large extent as a result of the RWGS reaction, as the higher concentration of CO<sub>2</sub> drives the reaction to the right side (Equation 4). At 800 °C, the standard free energy for the RWGS reaction ( $\Delta G^0 = -8545 + 7.84T$ ) and the reduction of CO<sub>2</sub> to CO ( $\Delta G^0 = 39810 - 40.87T$ ) [13] is -132.68 kJ mol<sup>-1</sup> and -4043.51 kJ mol<sup>-1</sup>, respectively. It can be speculated that the reduction of CO<sub>2</sub> to CO, C(s) + CO<sub>2</sub> = 2CO, occurs more easily as a result of the lower  $\Delta G$ . Comparing the value of  $\Delta G$  in the RWGS reaction, the CO<sub>2</sub> that oxidizes the C species to CO is more thermodynamically favored than its RWGS reaction. As the lower CO<sub>2</sub> conversion corresponds to lower CH<sub>4</sub> conversion, the C(s) species dissociated from CH<sub>4</sub> is not sufficient for its reaction with CO<sub>2</sub>. Therefore, the CO<sub>2</sub> reacting with H<sub>2</sub> toward the RWGS reaction is promoted. In order to minimize the side reaction toward the RWGS, it is necessary to operate the DRM reaction with a high CO<sub>2</sub> conversion rate.

#### 3. Materials and Methods

#### 3.1. Catalyst Preparation

The supported Ni catalysts were prepared with SiO<sub>2</sub> support (Tosoh Kabushiki-gaisha, Tokyo, Japan) by the combustion method, and the combustible materials contained hydrate glycine (C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>), ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) with different C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>/Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and NH<sub>4</sub>NO<sub>3</sub>/Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O molar ratios. Briefly, the aqueous solution of the desired amounts of C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>, NH<sub>4</sub>NO<sub>3</sub> and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was added into the SiO<sub>2</sub> support at room temperature by incipient wetness impregnation, followed by drying with a rotary evaporator for 2 hours at 80 °C, and then overnight at 120 °C. Afterwards, the dried solid materials were calcined

in air for 1 hour at 300 °C with a heating rate of 1 °C/min and another 3 hours at 550 °C with a heating rate of 2 °C/min. The calcined samples were denoted as Ni/SiO<sub>2</sub>-x/y, where x and y indicate the molar ratio of  $C_2H_5NO_2/Ni(NO_3)_2\cdot 6H_2O$  and  $NH_4NO_3/Ni(NO_3)_2\cdot 6H_2O$ , respectively. The metallic Ni loading was 10 wt%. The samples were then crushed and sieved into a 40–60 mesh size for subsequent catalytic tests.

#### 3.2. Catalyst Characterization

Fresh, reduced and spent samples were characterized by several techniques to identify and infer the effects of combustible materials such as  $C_2H_5NO_2$  and  $NH_4NO_3$  on the catalyst morphology and the resulting catalytic performance.  $N_2$  adsorption-desorption isotherms for each sample were collected on a Micromeritics ASAP 2020 system (Micromeritics, Norcross, GA, USA). The surface area, pore size and pore volume were calculated with the N<sub>2</sub> adsorption-desorption isotherms via the conventional Barrett-Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) methods. Prior to the measurements, the samples were outgassed under vacuum for 5 hours at 200 °C. The X-ray diffraction (XRD) patterns of each reduced sample were obtained with a Bruker AXS D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu K $\alpha$  radiation ( $\lambda$ =1.5406 Å) at a scanning rate of 6°/min with the 20 range of 10–90°. The reducibility of the catalyst was studied by the H<sub>2</sub> temperature-programmed reduction ( $H_2$ -TPR) in an auto-controlled flow reactor system of TP-5076, which is equipped with a thermal conductivity detector (TCD, Tianjin Xianquan Co., China). The sample of 50 mg was pretreated in N<sub>2</sub> stream at 200 °C for 1 hour. Additionally, when the temperature cooled down to 30 °C, the sample was heated to 950 °C at a heating rate of 10 °C/min in the  $H_2/N_2$  flow (5 vol.%  $H_2$  in  $N_2$ ) of 30 mL/min. The H<sub>2</sub>-TPR spectra were obtained at the temperature range of 50–950  $^{\circ}$ C. The carbon accumulation in spent samples after reaction for 50 hours was determined by thermogravimetric (TG) analysis on a Mettler–Toledo TGA-1100SF thermogravimetric analyzer (Mettler-Toledo, Greifensee, Switzerland).

#### 3.3. Catalytic Test

The dry reforming of CH<sub>4</sub> with CO<sub>2</sub> was performed at atmospheric pressure in a continuous-flow fixed bed quartz tube reactor with an inner diameter of 9 mm. For the typical experiment, 200 mg of shaped catalyst was filled into the center of the reactor. Before starting the reforming reaction, the catalyst was pre-reduced to 750 °C and atmospheric pressure for 2 hours in an H<sub>2</sub> flow of 60 mL/min with a heating rate of 10 °C/min. After that, the reactor temperature was elevated to 800 °C, and then a flow of gas mixture with a molar ratio of CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> = 9/9/2 was fed with a flow rate of 160 mL/min. The products were analyzed by online gas chromatography (Agilent GC 7820A, Agilent, USA). CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub> and CO were measured by a TCD detector with a 5A molecular sieve column and a Porapak Q column. Additionally, 10% of N<sub>2</sub> was employed as an internal standard. The conversions of CH<sub>4</sub> and CO<sub>2</sub> were calculated with the following formulas:

$$X_{CH4} = (F_{CH4-in} - F_{CH4-out}) / F_{CH4-in} \times 100\%$$
(5)

$$X_{CO2} = (F_{CO2-in} - F_{CO2-out}) / F_{CO2-in} \times 100\%$$
(6)

where *X* and *F* indicate the conversion and flow rate of *i* gas in the feed or the effluent, respectively.

#### 4. Conclusions

In summary, the combustion method was applied to prepare SiO<sub>2</sub> supported Ni catalysts which showed remarkably smaller Ni nanoparticle sizes due to the synergistic effects of C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> and NH<sub>4</sub>NO<sub>3</sub> in the combustion process. This kind of Ni/SiO<sub>2</sub> catalyst exhibits excellent coke-resistance performance and effectively suppresses the side reaction toward RWGS compared to that prepared with the conventional wetness impregnation method. As a result, there is almost no loss of activity with the H<sub>2</sub>/CO molar ratio close to the theoretical value at 1/1 after a 50-hour stability test over the Ni/SiO<sub>2</sub>-2/1 catalyst.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/9/2/183/s1, Figure S1: XRD patterns of fresh Ni/SiO<sub>2</sub> catalysts prepared with the combustion method by using different ratios of  $C_2H_5NO_2$  to  $NH_4NO_3$ , Figure S2: TEM images of spent Ni/SiO<sub>2</sub>-0/0 catalyst ((a) and (b)) and Ni/SiO<sub>2</sub>-2/1 catalyst ((c) and (d)) after 50-hours of reaction, Table S1: The equilibrium conversions of CH<sub>4</sub> and CO<sub>2</sub>, H<sub>2</sub>/CO molar ratio, and selectivity to H<sub>2</sub>O calculated by HSC chemistry 6.0, Table S2: BET surface area of as-prepared Ni/SiO<sub>2</sub> catalysts.

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