Effect of Ni content on hydrogen production via steam reforming of methane over Ni/GDC catalysts

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ABSTRACT

Steam reforming of methane was studied over gadolinia-doped ceria (GDC) supported Ni catalysts. Ni content varied from 1 to 10 wt% and molar ratio of H_2O to CH_4 was 2 in feed. A Ni content of about 5 wt% leads to highest formation rates of both hydrogen and CO_2. Over 1 wt% Ni/GDC catalyst at 700 °C, the hydrogen yield equals almost 4 for complete CO_2 formation. Increasing Ni content leads to decreasing hydrogen yield. A Ni content of about 5 wt% or lower is beneficial for high CO_2 selectivity and low carbon deposition associated with high methane conversion. Increased Ni content results in larger Ni particle size and increased carbon deposition.

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1. Introduction

Steam reforming of methane has been employed for large scale production of hydrogen [1]. Recently, steam reforming of methane becomes increasingly important as the fuel processing technology for fuel cells [2]. The reactions for steam reforming of methane are considered as:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$

For the produced hydrogen to be used in the proton-exchange membrane fuel cells, CO is a poison. To reduce the CO amount, the process of steam reforming of methane is usually followed by treatments of high-temperature and low-temperature water-gas shift reactions as well as preferential CO oxidation. If the CO_2 selectivity of steam reforming of methane is high enough, that is, the CO concentration is low enough, only preferential CO oxidation is needed and thus the hydrogen production cost can be reduced substantially. Therefore, the CO_2 selectivity is an important factor for steam reforming of methane to produce hydrogen.

Nickel catalyst has been found to exhibit promising catalytic performance for steam reforming of methane [1,3], with methane decomposition as a reaction step. Methane decomposition over the nickel catalyst is well known to be associated with carbon depo-

sition (coking) [4], which may lead to serious deactivation of the catalyst. Recently, Huang et al. [5–7] demonstrated that, with doped ceria as the support, the supported nickel catalyst may have a self de-coking capability, that is, the removal of the deposited carbon species via gasification by the O species supplemented from the lattice oxygen of the catalyst itself, in the absence of gaseous oxygen. Of the doped ceria, gadolinia-doped ceria (GDC) has been used as a support material of the nickel catalyst for steam reforming of methane [6,8]. Therefore, GDC-supported Ni catalysts can have minor coking problem with methane as reactant. However, this is considered to depend on the Ni content of the Ni/GDC catalysts since higher Ni content can cover up more GDC surface to reduce its self de-coking capability. Additionally, the lattice oxygen of GDC may enhance the oxidation reaction of the C species to form CO_2 [9,10]; this is beneficial to the CO_2 selectivity. Therefore, the CO_2 selectivity may also be affected by the Ni content.

In this work, the effects of Ni content on hydrogen yield, CO_2 selectivity and carbon deposition during hydrogen production via steam reforming of methane over Ni/GDC catalysts were studied. An optimum Ni content for hydrogen production and CO_2 formation was observed.

2. Experimental

2.1. Preparation of Ni/GDC catalysts

GDC was prepared by a co-precipitation method. The details of the method have been reported elsewhere [5]. GDC prepared in this work was $(GdO_{1.5})_{0.1}(CeO_2)_{0.9}$.

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The Ni/GDC catalyst was prepared by impregnating the GDC powders (325–270 mesh, i.e., 44–53 μm diameter) with an aqueous solution of nickel nitrate (98% purity) in a ratio to make 1–10 wt% Ni with respect to GDC. The mixture was heated with stirring to remove excess water and then place in a vacuum oven to dry overnight. The dried Ni/GDC powder was heated to 800 °C and held for 4 h, and then cooled down.

2.2. Activity tests

The activity of the catalyst for steam reforming of methane to produce hydrogen was measured under atmospheric pressure in a continuous flow reactor charged with 1 g of catalyst. The details of the reactor setup have been reported elsewhere [9]. The catalyst sample was reduced at 400 °C with 10% H_2 in Ar for 1 h, then purged by Ar, and then heated to the test temperature with a heating rate of 10 °C/min. Then, the activity test of steam reforming of methane was carried out with feeding of 100 ml/min of a gas mixture of CH_4:H_2O:Ar = 10.5:21:68.5; that is, the molar ratio of H_2O:CH_4 in feed is 2, which is the ratio of a stoichiometric reaction for steam reforming of methane with complete CO_2 formation. The reactor outflow was analyzed on-line by two gas chromatographs (GCs, China Chromatography 8900), and CO-NDIR and CO_2-NDIR (non-dispersive infrared, Beckman 880) analyzers.

All tests were carried out at the designated temperature with 900 min feeding of $CH_4 + H_2O + Ar$ gas mixture and then switching to 100 ml/min of pure Ar for 100 min. Then, for the 700 °C tests, the catalyst sample was heated to 800 °C with a heating rate of 10 °C/min. Afterwards, 100 ml/min of a gas mixture of 20% O_2 in argon was introduced to remove deposited carbon, if any, until no CO_2 or CO can be detected in the reactor outflow. The carbon removal operation was carried out at 800 °C except for the 900 °C test, for which the carbon removal operation was carried out at 900 °C.

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows that, with increasing Ni content, the BET area of the Ni/GDC catalyst decreases while the size of the GDC-supported NiO particle increases. Notably, the NiO particle size was calculated via Scherrer's formula from the XRD diagrams; however, for the 1 and 3 wt% Ni catalysts, the NiO particles are too small to be detectable, as shown in Fig. 1. The variation of the BET area is consistent with that of the NiO particle size; that is, when the NiO particle size increases, the BET area decreases. Notably, with reduction at 400 °C with 10% H_2, the NiO supported over doped ceria can be completely reduced to Ni [11]; larger NiO particle should result in larger Ni particle.

The above-described results reveal that an increased Ni content results in both decreased BET area and increased NiO particle size; additionally, the decrease of the BET area is associated with the
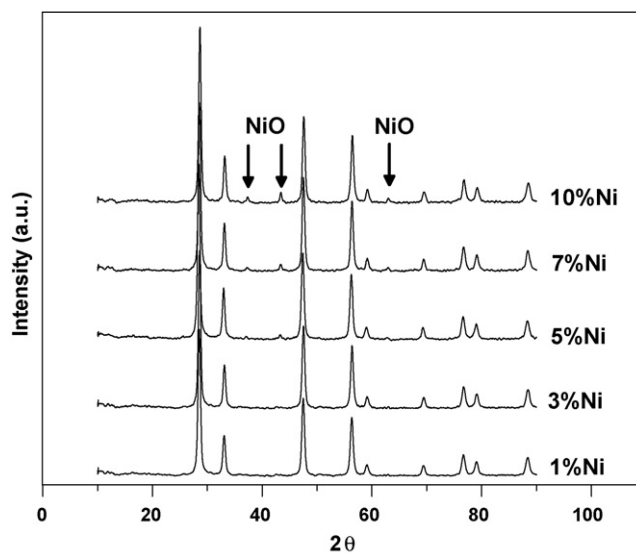

Fig. 1. XRD diagrams of Ni/GDC catalysts with varying Ni content.

increase of the NiO particle size. This is because an increase in NiO particle size can lead to an increased plugging of the pores, which causes a decrease of the accessible pore area for the reactant gas. Notably, the NiO species are in the pores of the GDC support. This plugging of the pores, especially the inner and smaller pores, may also occur when the NiO particle size is too small to be detectable by XRD; that is, the BET area decreases when loading Ni into GDC with a Ni content of only 1 wt% and when the Ni content increases from 1 to 3 wt%, both shown in Table 1.

3.2. Effect of Ni content on hydrogen yield

Fig. 2 shows the profiles of hydrogen, CO and CO_2 formation rates as well as methane conversion rate over 5 wt% Ni/GDC at 700 °C. The rates go up and then down to steady-state or stable values; for methane conversion, the rate is quite constant after about 140 min of operation. However, the product formation rates oscillate during the stable states. The inset in Fig. 3 shows that the formation rate of CO goes down when that of CO_2 goes up or vice versa. This

Table 1
Effect of Ni content on BET area and GDC-supported NiO particle size

	BET area (m²/g)	NiO particle size[a] (nm)
GDC	47.7	–
1% Ni/GDC	37.9	–[b]
3% Ni/GDC	31.4	–[b]
5% Ni/GDC	29.9	24.5
7% Ni/GDC	26.8	29.2
10% Ni/GDC	19.4	31.7

[a] Calculated via Scherrer's formula from the XRD diagrams.
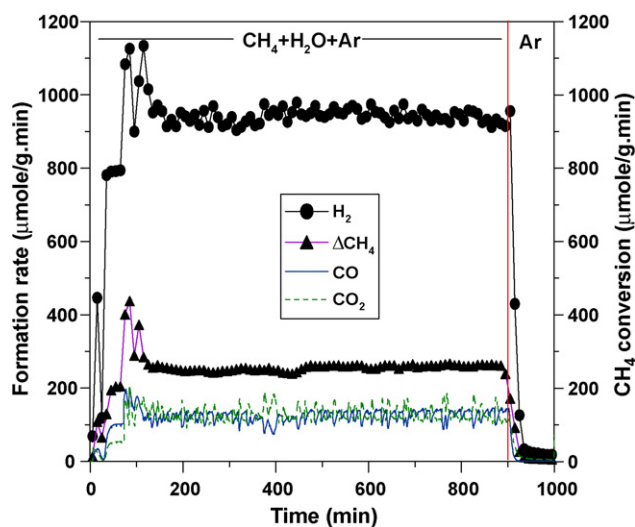[b] NiO particle size too small to be detectable by XRD.

Fig. 2. Product formation rates and methane conversion over 5 wt% Ni/GDC at 700 °C.

Table 2
Effect of Ni content on steady-state product formation rates

Catalyst	Test temperature (°C)	H_2 (μmol/g min)	CO_2 (μmol/g min)	CO (μmol/g min)
1% Ni/GDC	700	290	70.4	0.62
1% Ni/GDC	800	384	89.7	9.45
1% Ni/GDC	900	543	115	28.5
3% Ni/GDC	700	635	124	51.2
5% Ni/GDC	700	948	130	125
7% Ni/GDC	700	945	118	125
10% Ni/GDC	700	912	115	123

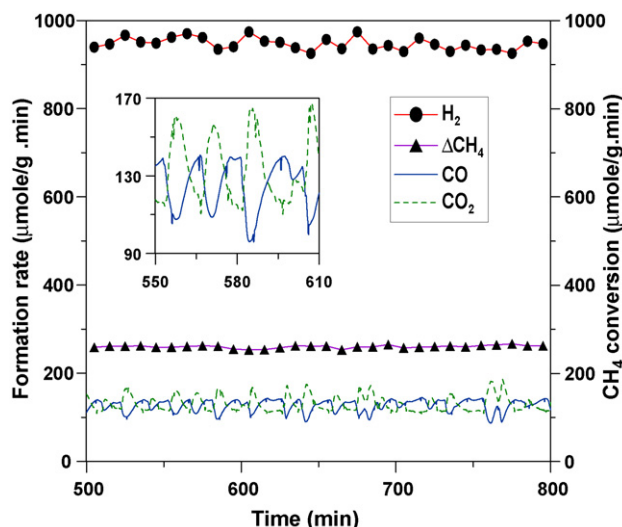Averaged values of formation rates from 400 to 800 min.

Fig. 3. Steady-state product formation rates and methane conversion over 5 wt% Ni/GDC at 700 °C.

indicates that the reactions for CO and CO_2 formations are closely related to each other. However, further studies are needed to see the merit of this oscillatory behavior on the reaction kinetics and/or mechanism of steam reforming of methane. In this work, only the averaged formation rates are considered and termed steady-state rates, although they are better described as pseudo-steady-states; Fig. 3 presents an example for the profiles of these steady-state rates.

Table 2 shows that, at 700 °C, the steady-state hydrogen formation rate is the highest over the 5 wt% Ni/GDC catalyst. Additionally, both CO_2 and CO formation rates are also the highest over 5% Ni/GDC. This indicates that 5% Ni leads to an optimum activity for methane conversion to produce hydrogen. Table 3 shows that the methane conversion barely increases with Ni content higher than 5 wt%.

Table 3 also shows that the hydrogen yield equals almost 4 over the 1 wt% Ni/GDC catalyst at 700 °C. This indicates the occurrence

of the following reaction, indicating complete CO_2 formation from steam reforming of methane via reactions (1) and (2):

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \tag{3}$$

which leads to the highest hydrogen yield. This almost complete CO_2 formation may be associated with the almost completion of the water-gas shift (WGS) reaction (2) at 700 °C. Table 3 also shows that, with increasing temperature, the hydrogen yield decreases. This is consistent with the exothermic feature of the WGS reaction, which decreases the WGS activity with increasing temperature [12].

The above-described almost complete CO_2 formation may also be associated with the relatively low methane conversion over the 1 wt% Ni/GDC catalyst at 700 °C; that is, reaction (1) consumes only relatively small amount of H_2O and thus the amount of H_2O for WGS reaction can be relatively plentiful, which can result in its almost completion. This may also explain the decrease of the H_2 yield with increasing temperature, which leads to increasing CH_4 conversion and thus decreasing amount of H_2O for WGS reaction. Additionally, with increasing Ni content, Table 3 shows decreasing H_2 yield; this may also be associated with increasing CH_4 conversion.

3.3. Effect of Ni content on CO_2 selectivity

Table 3 shows that, with increasing Ni content, the CO_2 selectivity decreases, which may also be associated with the above-described effect of decreasing amount of H_2O for WGS reaction. Notably, WGS reaction produces both H_2 and CO_2 and thus a higher rate of WGS reaction results in an enhancement of both H_2 yield and CO_2 selectivity.

For Ni content of 5% and higher, the CO_2 formation rate decreases slightly; this is consistent with slightly increasing CH_4 conversion and thus slightly decreasing amount of H_2O for WGS reaction. As the Ni content increases to higher than 5%, Table 2 shows that the steady-state formation rate of CO_2 becomes smaller than that of CO, as also shown in Fig. 4. Additionally, Fig. 4 shows that, as the Ni content increases from 1% to 5%, the steady-state CO formation rate increases sharply; however, for Ni content of 5% and higher, the CO rate is kept almost constant. Consequently, the CO_2 selectivity decreases only slightly with increasing Ni content over 5%. There-

Table 3
Effect of Ni content on steady-state CH_4 conversion, H_2 yield and CO_2 selectivity

Catalyst	Test temperature (°C)	CH_4 conversion (%)	H_2 yield[a]	CO_2 selectivity[b]
1% Ni/GDC	700	17.0	3.98	0.991
1% Ni/GDC	800	23.8	3.76	0.905
1% Ni/GDC	900	34.7	3.65	0.801
3% Ni/GDC	700	43.1	3.44	0.708
5% Ni/GDC	700	65.2	3.39	0.510
7% Ni/GDC	700	65.5	3.37	0.486
10% Ni/GDC	700	65.6	3.24	0.483

[a] H_2 yield is defined as (H_2 formation rate/CH_4 conversion rate) during steady-state.
[b] CO_2 selectivity is defined as [(CO_2/(CO + CO_2))] in steady-state formation rates.
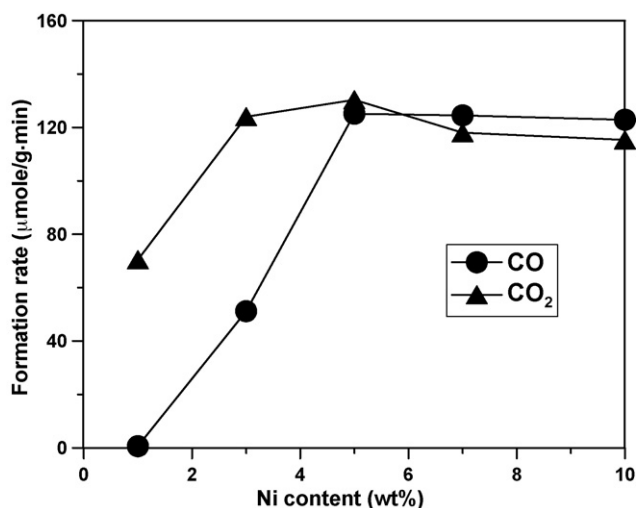
Fig. 4. Effect of Ni content on steady-state CO and CO_2 formation rates at 700 °C.

fore, a Ni content of about 5% or lower is beneficial for high CO_2 selectivity associated with high CH_4 conversion.

3.4. Effect of Ni content on carbon deposition

As the Ni content increases to higher than 5%, CH_4 conversion increases but H_2 formation rate decreases, as shown in Tables 3 and 2, respectively. This may indicate the formation of deposited carbon via methane decomposition [13]:

$$CH_4 \rightarrow C + 2H_2 \tag{4}$$

Via a carbon balance:

$$\Delta CH_4 = \Delta CO_2 + \Delta CO + \Delta C \tag{5}$$

Notably, ΔCO_2 is equivalent to $4\Delta H_2$ according to reaction (3), ΔCO is equivalent to $3\Delta H_2$ according to reaction (1), and ΔC is equivalent to $2\Delta H_2$ according to reaction (4). Thus, based on the carbon balance of Eq. (5), an equation for the amount of hydrogen production can be derived as

$$\Delta H_2 = 4\Delta CO_2 + 3\Delta CO + 2\Delta C \tag{6}$$

According to Eq. (6), with the same CH_4 conversion, H_2 formation rate decreases with increasing formation of CO and further decreases with increasing formation of deposited carbon. Notably, increasing formation of CO means decreasing CO_2 selectivity, which is defined as $[(CO_2/(CO+CO_2)]$ in steady-state formation rates; in other words, the formation of CO is against that of CO_2 with the same CH_4 conversion. Tables 3 and 2 show that, as the Ni content increased from 5% to 7%, CH_4 conversion increases but the CO_2 rate decreases and the CO rate remains the same; according to Eq. (5), this should indicate carbon deposition, which results in decreasing H_2 formation rate.

H_2 formation rate may decrease even further than indicated by Eq. (6). This is due to the deposition of the carbon-containing species such as CH_3, CH_2 and CH, which are possible surface intermediates from methane decomposition [14]. As shown in Fig. 2, after the $CH_4 + H_2O + Ar$ feed was switched to pure Ar, some H_2 and CH_4 were produced for a while; this should indicate the deposition of the CH_3, CH_2 and/or CH species during the period with $CH_4 + H_2O + Ar$ feed. Notably, with GC sampling time of 10 min, blank test showed that no residual methane could be detected after switching to pure argon. Therefore, carbon deposition over Ni/GDC in this work means the deposition of CH_3, CH_2, CH and/or C species.

Table 4
Effect of Ni content on overall carbon deposition

Catalyst	Test temperature (°C)	Amount of deposited carbon[a] (m mol/g)
1% Ni/GDC	700	2.88
1% Ni/GDC	800	4.91
1% Ni/GDC	900	8.19
3% Ni/GDC	700	15.3
5% Ni/GDC	700	38.9
7% Ni/GDC	700	61.6
10% Ni/GDC	700	69.9

[a] Equivalent to the amount of CO_2 formation during the removal of the deposited carbon. Notably, no CO was formed during carbon removal.

Table 4 shows that the amount of deposited carbon increases not only with increasing temperature but also with increasing Ni content. This may be associated with CH_4 conversion. However, as the Ni content increased from 5% to 7%, CH_4 conversion increases only slightly but the amount of deposited carbon increases dramatically; this is considered to be due to largely increased size of the surface Ni particle, as revealed by the results of Table 1. Therefore, increased Ni content results in larger Ni particle size and thus increased carbon deposition. A Ni content of about 5% or lower is beneficial for low carbon deposition with high CH_4 conversion.

The above results indicate that smaller Ni particle is favorable for less coking than larger one. This is because the interaction between the deposited C species over the smaller Ni particle and the oxygen-containing GDC support is closer than that between the C species over the larger Ni particle and the GDC support. Notably, the de-coking reaction is [8]

$$C + O \rightarrow CO \tag{7}$$

where O is the surface O species over Ni or the lattice O species of GDC; then, the O species can be supplemented from H_2O dissociation [6]

$$H_2O \rightarrow H_2 + O \tag{8}$$

Notably, also, the de-coking reaction can produce CO_2 [9]. Notably, also, the Ni surface may be fully covered with the C species and thus H_2O may not be able to be adsorbed onto it to be dissociated; this leads to that the GDC support becomes the only source of the O species for de-coking. Therefore, for GDC to supply the O species for de-coking, i.e., the removal of the deposited C species over Ni, the smaller Ni particle can have a higher rate than the larger one; in other words, the smaller Ni particle has a higher de-coking capability than the larger one.

The above results also indicate that the CH_4 conversions are roughly the same when Ni contents are higher than 5%. This is because the Ni surface has been fully covered with the C species due to relatively high amount of deposited carbon, shown in Table 4; this is also in accordance with the above explanation on the effect of Ni particle size on the de-coking capability; thus, no more CH_4 can be adsorbed until some C species have been removed. Notably, the deposited C species can be removed via reaction with the lattice oxygen of GDC. This may be an indication that the de-coking rate is a determining factor on the CH_4 conversion rate. Therefore, the CH_4 conversion can be kept relatively constant.

4. Conclusions

(1) A Ni content of about 5 wt% leads to highest formation rates of both hydrogen and CO_2.
(2) Over the 1 wt% Ni/GDC catalyst at 700 °C, the hydrogen yield equals almost 4 for complete CO_2 formation.
(3) Increasing Ni content leads to decreasing hydrogen yield.

(4) A Ni content of about 5 wt% or lower is beneficial for high CO_2 selectivity and low carbon deposition associated with high CH_4 conversion.

(5) Increased Ni content results in larger Ni particle size and increased carbon deposition.

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