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Steam Reforming of Coke Oven Gas for Hydrogen Production over a NiO/MgO Solid Solution Catalyst

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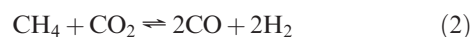
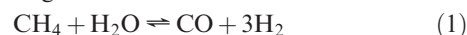
The steam reforming of coke oven gas (COG) for hydrogen production was investigated over the NiO/MgO solid solution catalysts reduced at high temperatures. It was found that the NiO/MgO catalyst possessed good catalytic activity, and the conversions of CH₄ and CO₂ were greatly affected by the reaction temperature and steam/carbon (S/C) mole ratio. During the tested period of 100 h under a low S/C ratio of 1.0 at 875 °C, the conversions of CH₄ and CO₂ kept constant values around 97.6 and 44.3%, respectively, and the hydrogen volume content was enhanced from 58.2% in the original COG to 77.7% by 1.5 times. The catalyst characterization results of X-ray diffraction (XRD), transmission electron microscopy (TEM), and thermogravimetry (TG) after the reaction showed that the Ni nanoparticle sizes had a slight increase and the amount of the coke deposition was ca. 1%. These results showed that the NiO/MgO catalyst was efficient and stable for the steam reforming of COG to amplify hydrogen in COG. This research will be of importance in hydrogen production from COG.

1. Introduction

The environmental pollution produced by the delivery of massive energy through the combustion of fossil fuels has made it necessary to develop new alternatives based on sustainable power carriers. Hydrogen sounds like an excellent solution, because it is the most abundant element in the universe, and when combined with oxygen to create electricity in a fuel cell, it produces only water. However, a major problem is that hydrogen does not exist on earth in an unbound form.^{1–5}

Coke oven gas (COG), a byproduct in the coke-making process, which mainly consists of about 58% H₂, 27% CH₄, and small amounts of CO, CO₂, N₂, etc., is attracting much attention as a high-potential raw material for low-cost hydrogen production.^{6–8} In 2007, the coke output of above 3.22 billion tons in China, which was about 60% of the world production (5.45 billion tons), ranked first in the world, and the yield of COG amounted to 1190 billion N m³. Nowadays, only about 20% of the produced COG is simply used as fuel, while most of the rest is directly burnt at the end of an opened chimney and discharged into atmospheres, causing serious environmental pollution.

Recently, there are a few reports on hydrogen amplification of COG by means of the partial oxidation or CO₂ steam reforming of CH₄ in COG.^{9,10} These catalytic reaction technologies generally required pure oxygen or CO₂, which was expensive, and achieved relatively lower hydrogen augments in the resulting mixture. Steam reforming of COG, which can make hydrogen 3-fold amplification, is one of the important economic processes for the production of hydrogen and synthesis gas.¹¹ The reforming process of COG might mainly contain the following reactions:



Conventional steam reformers could deliver relatively high concentrations of hydrogen with high fuel conversion.^{12,13} However, the steam/carbon (S/C) mole ratio used was usually more than 2.5:1. Excess steam is used to help force the reaction to completion and to inhibit coke and soot formation, while additional heat must be added at the same time. A lower S/C mole ratio is desired to improve cycle efficiency from an industrial viewpoint.

A reduced S/C mole ratio to reduce the heat consumption with carbon deposition on the catalyst is one of the important problems associated with the low S/C mole ratio.¹⁴ Recently,

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NiO/MgO solid solution catalysts have widely been investigated for their good activity and excellent anti-coking performance in the reforming of methane.^{15–17} High Ni metal dispersion over catalysts, use of basic support, addition of metal oxides as alkali or alkali earth metal oxides in the catalyst, and also, during reactivity, a strong interaction between the reduced metal, the support, and the nonreduced metal could reduce coke formation.^{18,19}

In this paper, we report a new technology for hydrogen amplification through the direct steam reforming of COG over the NiO/MgO solid solution catalyst in a low ratio of steam/carbon and investigate the effect of reaction conditions on the catalytic performance in the steam reforming of the simulated COG.

2. Experimental Section

2.1. Catalyst Preparation. The NiO/MgO catalyst was prepared by impregnating MgO ($\geq 98.5\%$, purchased from Sino-pharm Chemical Reagent Co., Ltd.) with an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 98.0\%$, purchased from Shanghai Hengxin Chemical Reagent Co., Ltd.). The paste thus obtained was dried at 110°C in air and then decomposed and calcined at 800°C in air for 5 h. Before use, all of these catalysts were pressed into tablets and crushed to 20–40 mesh particles.

2.2. Characterization. Transmission electron microscopy (TEM) was performed on a JEM-200CX electron microscope. The sample was ground and dispersed in ethanol, then dropped in copper grids, and finally dried at 60°C .

Brunauer–Emmett–Teller (BET) surface areas of the catalysts were measured by N_2 adsorption at a liquid nitrogen temperature of -196°C using a Micromeritics ASAP 2020. The X-ray diffraction (XRD) was performed with a D/Max-2200 X-ray diffractometer, using $\text{Cu K}\alpha$ radiation at 40 kV and 200 mA.

A thermogravimetric analyzer (Cahn Thermax 700) was used to detect the coke deposited on catalysts after the catalytic reaction. About 400 mg of the used catalyst was loaded into an alumina pan and dried under an air atmosphere at 110°C for 8 h. The thermogravimetric temperature-programmed oxidation (TG-TPO) experiment was carried out with a 10 mol % O_2/Ar flow rate of 30 mL min^{-1} and a ramp of 10°C/min in a temperature range from 25 to 1100°C .

2.3. Activity Test. The steam reforming of COG was carried out on an atmospheric fixed-bed reactor. A preheater filled with quartz balls with a set temperature of 350°C , in which water was vaporized and fully mixed with the simulated COG (H_2 , 58.2 vol %; CH_4 , 31.5 vol %; CO , 7.4 vol %; and CO_2 , 2.9 vol %), was connected to the reactor. A total of 1 g of catalyst was placed at the middle portion of the quartz tube reactor with an internal diameter of 10 mm and a length of 1000 mm. The catalyst was first reduced in a 10 vol % H_2/Ar flow rate of 50 mL min^{-1} at 875°C for 1 h. The effluent gas was cooled in an ice-water trap and then analyzed using an online gas chromatograph. The conversions (X) of CH_4 and CO_2 were calculated as follows:

$$X_{\text{CH}_4} (\%) = \frac{F_{\text{CH}_4}^{\text{in}} - F_{\text{CH}_4}^{\text{out}}}{F_{\text{CH}_4}^{\text{in}}} \times 100\%$$

$$X_{\text{CO}_2} (\%) = \frac{F_{\text{CO}_2}^{\text{in}} - F_{\text{CO}_2}^{\text{out}}}{F_{\text{CO}_2}^{\text{in}}} \times 100\%$$

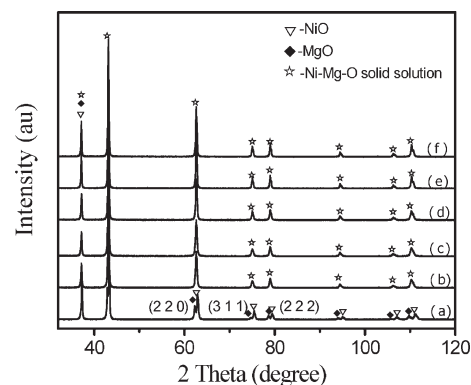


Figure 1. XRD patterns of the 34.5 wt % NiO/MgO calcined at (a) NiO/MgO mechanical mixture, (b) 700°C , (c) 800°C , (d) 900°C , (e) 1000°C , and (f) 1100°C .

Table 1. BET Surface Areas of the NiO/MgO Catalysts with Different Ni Loadings

Ni loading (wt %)	0	6.9	13.4	24.9	30.0	34.8	43.4
S_{BET} (m^2/g)	25	34.9	33.8	24.8	23.3	15.8	11.7

where F_i^{in} and F_i^{out} are the mole flow rates of the inlet and outlet gas, respectively.

3. Results and Discussion

3.1. Textural Properties. The XRD patterns of MgO are very similar to those of NiO. For MgO, the peak positions corresponding to the (220), (311), and (222) faces are at $2\theta = 62.28^\circ$, 74.67° , and 78.61° , respectively. For NiO, the corresponding peaks are at $2\theta = 62.94^\circ$, 75.43° , and 79.37° , respectively. The above three diffraction lines can be used to identify the formation of a solid solution. Figure 1 shows the XRD patterns of both the mechanical mixtures and the prepared 35 wt % NiO/MgO catalyst calcined at different temperatures. Three double peaks corresponding to the (220), (311), and (222) faces are present for the mechanical mixtures. In contrast, only three single peaks at $2\theta = 62.60^\circ$, 74.99° , and 79.04° , respectively, are observed for the NiO/MgO catalyst calcined in the range of 700 – 900°C . This indicates that the NiO/MgO solid solution was formed in the preparation process.¹⁵

The BET surface areas of the catalysts with different Ni loadings are listed in Table 1. The NiO/MgO catalysts possess larger specific surface areas between 34.9 and $11.7\text{ m}^2/\text{g}$. The surface areas decrease with increasing Ni loading.

3.2. Effect of the Space Velocity. Figure 2 shows the effect of the space velocity (SV) on the conversion of CH_4 and CO_2 over the NiO/MgO catalyst with 13 wt % Ni loading at 875°C . The catalyst displays a high conversion of more than 96% in a wide range of space velocity from 12 500 to $56\,000\text{ mL g}^{-1}\text{ h}^{-1}$. When the space velocity is further enhanced to $76\,000\text{ mL g}^{-1}\text{ h}^{-1}$, the CH_4 conversion declines to 92%. The CO_2 conversion always decreases with an increasing space velocity. As the space velocity is enhanced to $76\,000\text{ mL g}^{-1}\text{ h}^{-1}$, the CO_2 conversion decreases from 55.4% at $\text{SV} = 12\,600\text{ mL g}^{-1}\text{ h}^{-1}$ to -2.1% , suggesting that more CO_2 is formed at the high space velocity.

3.3. Effect of the Reaction Temperature. Figure 3 shows the effect of the reaction temperature on the catalytic performance of the NiO/MgO catalyst for the reforming of COG at $\text{S/C} = 1.0$. The CH_4 conversion continuously increases from 19.2 to 98.7% with an increasing reaction temperature.

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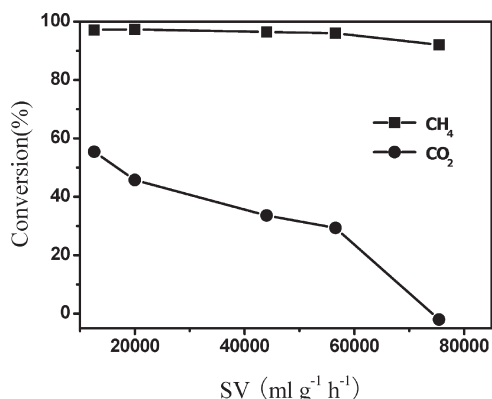


Figure 2. Effect of the space velocity on the catalytic performance. Reaction conditions: catalyst, 1 g; S/C, 1.0 (mol/mol); reaction temperature, 875 °C; pressure, 0.1 MPa.

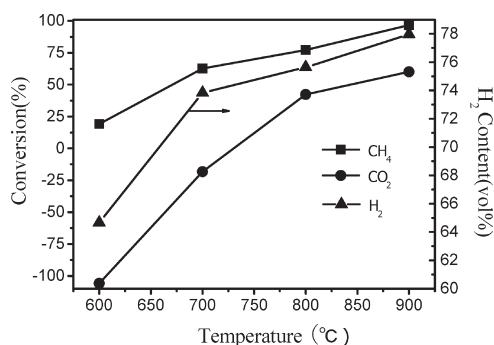


Figure 3. Effect of the reaction temperature on the catalytic performance. Reaction conditions: catalyst, 1 g; S/C, 1.0 (mol/mol); pressure, 0.1 MPa; SV, 12 600 mL g⁻¹ h⁻¹.

However, for CO₂, when the reaction temperature is in the lower range of 600–730 °C, the conversion is a negative value. This implies that the lower temperature is favorable to the water–gas shift reaction (eq 3). When the reaction temperature reaches 730 °C, the CO₂ conversion turns positive and is increased to 60.1% with the increase in the reaction temperature to 900 °C. This can be attributed to the reverse water–gas shift reaction at high temperatures. Correspondingly, the H₂ volume percentage is increased from 58.2 to 78.0% after the reaction.

3.4. Effect of the S/C Ratio. In the steam reforming of CH₄, the S/C ratio had a great influence on the catalytic activity and stability. Generally, the steam reforming of CH₄ was performed with the S/C ratio in the range of 1.9–9.0 because of the coke formation under atmospheric pressure and S/C ratio less than 1.4.^{16,20–22} However, it was found that the steam reforming of COG was rather stable under lower S/C ratios in the range of 0.3–1.5 over the NiO/MgO solid solution catalyst and showed good catalytic activity because of the presence of excessive hydrogen. Figure 4 illustrates the effect of the S/C ratio on the reaction results over the NiO/MgO catalyst at 875 °C. The CH₄ conversion increases from 45.1 to 98.3% with an increasing S/C ratio from 0.3 to 0.9, while CO₂ conversion decreases from 88.4 to 67.2%. This suggests that CH₄ might preferentially react with the steam to form CO and H₂. As the S/C ratio is further

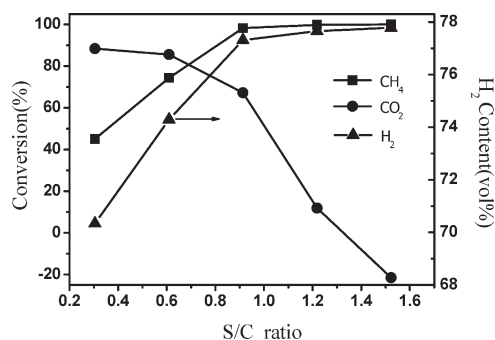


Figure 4. Effect of the S/C ratio on the catalytic performance. Reaction conditions: catalyst, 1 g; pressure, 0.1 MPa; reaction temperature, 875 °C; SV, 12 600 mL g⁻¹ h⁻¹.

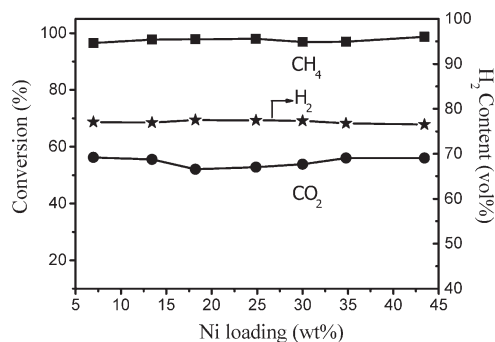


Figure 5. Reforming of COG over the NiO/MgO catalysts with different Ni loadings. Reaction conditions: catalyst, 1 g; S/C, 1.0 (mol/mol); pressure, 0.1 MPa; SV, 12 600 mL g⁻¹ h⁻¹.

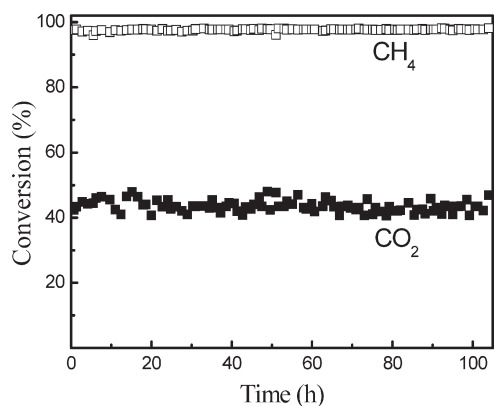


Figure 6. Reforming reaction of COG as a function of the reaction time at 875 °C over 35 wt % NiO/MgO catalyst. Reaction conditions: catalyst, 1 g; S/C, 1.0 (mol/mol); pressure, 0.1 MPa; reaction temperature, 875 °C; SV, 20 000 mL g⁻¹ h⁻¹.

increased to 1.5, the CH₄ conversion is close to 100% but the CO₂ conversion is rapidly decreased to a negative value, indicating that CO₂ is formed by eq 3 because of excessive steam. According to the mass balance based on carbon and oxygen in the feed gas, there was always a trace amount of water nonreacted in the product gas, even when the S/C ratio was less than 1.0. This could be responsible for the equilibrium of the steam reforming reaction (eq 1). As a result, the H₂ volume percentage in the dry resultant mixture is enlarged to 78.0% at 875 °C and S/C = 1.5, as presented in Figure 4.

3.5. Effect of the Ni Loading. A blank test was first used to perform the reforming of COG and had negligible CH₄ conversion (<1.5%) (Figure S1 in the Supporting Information). The NiO/MgO catalysts with less than 5 wt %

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Table 2. Variation of the Component Contents and Flow Rates of the Dry COG before and after Reaction for 100 h at 875 °C

component	before reaction		after reaction	
	content (vol %)	flow rate (mL min ⁻¹)	content (vol %)	flow rate (mL min ⁻¹)
H ₂	58.2	160.9	77.5	399.0
CH ₄	31.5	87.1	0.4	2.3
CO	7.4	20.4	21.4	110.2
CO ₂	2.9	7.9	0.7	3.5
total flow rate		276.3		515.0 (518.4) ^a

^aThe value in parentheses is the total theoretical flow rate.

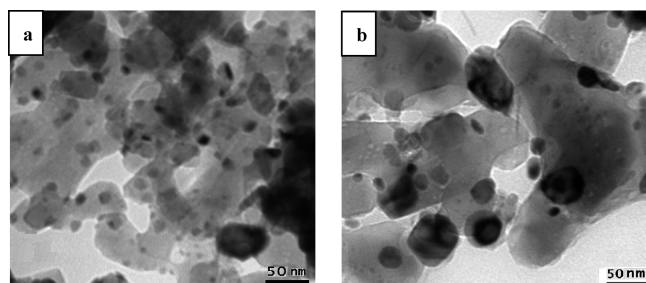


Figure 7. TEM images of the 35 wt % NiO/MgO catalyst before and after the reforming reaction of COG at 875 °C for 100 h: (a) before reaction and (b) after reaction.

Ni loading showed certain conversion of CH₄. However, these catalysts were rapidly transformed into powder with a prolonging reaction time (< 5 h), ultimately leading to bed plugging. Therefore, only the conversions of CH₄ and CO₂ over the NiO/MgO catalysts in the Ni loading range of 7.0–43.4 wt % are shown in Figure 5. It can be seen that the catalysts show high CH₄ conversion between 95 and 99% and CO₂ conversion around 53% under a S/C ratio of 1.0 at 875 °C.

3.6. Stability and Characterization of the Catalyst after the Reaction. The 35 wt % NiO/MgO catalyst was chosen to study its stability under a low S/C ratio of 1.0 at 875 °C to avoid catalyst pulverization during the long-time reaction process. The result is shown in Figure 6. During the tested period of ca. 100 h, the conversions of both CH₄ and CO₂ are kept constant, with values at about 97.6 and 44.3%, respectively. Table 2 summarizes the variations of the contents and the flow rates of the components in the dry mixture gases before and after reaction. The CH₄ content decreases from 31.5 to 0.4%. Correspondingly, the total gas volume after the reaction was increased to 515.0 mL min⁻¹ by 1.9 times that of the original mixture, which is very close to the theoretical value of 518.4 mL min⁻¹, and the hydrogen content is increased from 58.2 to 77.5%. As a result, the amount of hydrogen in the product gas is enlarged by 1.5 times.

After the 100 h reaction, the catalyst particles did not have obvious changes and no coke deposition was observed on the catalyst surface. TEM images in Figure 7 showed that Ni nanoparticle sizes on the catalyst surface after the reaction have only a slight increase compared to those before the reaction. This was consistent with that of XRD, shown in Figure 8. All of these demonstrate that the NiO/MgO solid solution catalyst possesses excellent stability for the reforming of COG.

The carbon deposition on the used catalyst was investigated by thermogravimetry (TG), and the profile is shown in Figure 9. A weight augment from 265 to 450 °C is attributed to the Ni metal oxidation, and subsequent weight loss is attributed to removal of deposited carbon. The amount of coke is estimated ca. 1% from 450 to 550 °C in the profile. This implies that the catalyst possesses high resistance to carbon formation.

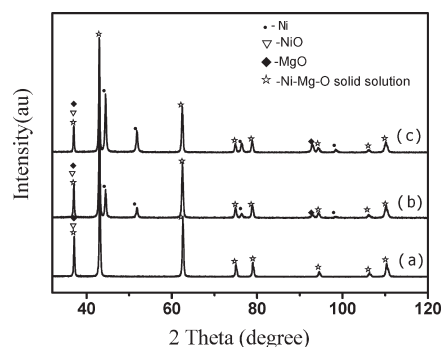


Figure 8. XRD images of the 35 wt % NiO/MgO catalyst before and after the reforming reaction of COG at 875 °C for 100 h: (a) before reaction, (b) reduction, and (c) after reaction.

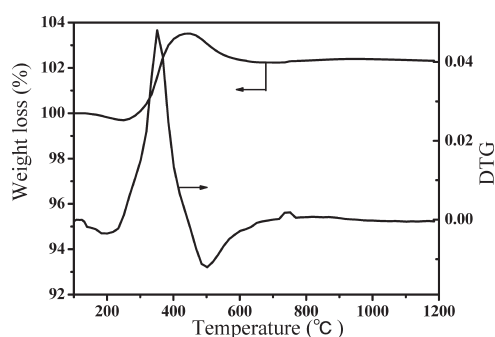


Figure 9. TG and differential thermogravimetry (DTG) profiles of the 35 wt % NiO/MgO catalyst after the reforming reaction of COG at 875 °C for 100 h.

4. Conclusions

The NiO/MgO solid solution catalysts are suitable for the steam reforming of COG to amplify hydrogen in COG under atmospheric pressure and low steam/carbon ratios. A high CH₄ conversion of ca. 97.6% was achieved under a low S/C ratio of 1.0 at 875 °C, and the hydrogen volume content was enhanced from 58.2 to 77.7%. During the 100 h reaction, the 35 wt % NiO/MgO catalyst showed good stability and excellent resistance to carbon deposition.

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Supporting Information Available: Reforming of COG (Figure S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.