

Effects of Nickel Precursor and Calcination Temperature on the Performance of Ni/MgAl₂O₄ Catalysts for Syngas Production by CO₂ Reforming of Coke Oven Gas

Huijie Zhou¹, Hongwei Cheng^{1,*}, Cheng Wu¹ and Xionggang Lu^{1,*}

¹State Key Laboratory of Advanced Special Steel & School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China

*Email: hwcheng@shu.edu.cn; luxg@shu.edu.cn

Tel: +86-21-56335768

Abstract. The CO₂ reforming of coke oven gas (COG) to product syngas at 750°C over 10 wt% Ni loaded on spinel MgAl₂O₄ (10Ni/MA) catalyst supported different nickel precursors was researched, including nickel nitrate, nickel acetate, nickel chloride and nickel acetylacetonate. Moreover, the calcination temperature of catalysts was also studied to investigate the activity and stability. The catalysts were analyzed by XRD, BET, CO₂-TPD, H₂-TPH and TEM. It was observed that MA (calcined at 800°C) supported nickel nitrate has the largest surface area, the most uniform pore diameter and the ratio nickel species owned higher bounding strength with support was the best. In addition, the results showed that catalysts supported nickel nitrate demonstrated the highest catalytic activity in which the conversion of CH₄ and CO₂ were up to 81.4% and 94.5%, respectively, and the selectivity of H₂ and CO were 71.3% and 88.8%, respectively.

1. Introduction

COG (mainly H₂, CH₄, CO and CO₂) is a by-product in steel company and normally burst or just discharged into our environment, where CO₂ and CH₄ are two major kind of greenhouse gases which could lead to global warming. In recent years, the CO₂ reforming of COG or dry reforming to syngas (H₂ and CO) has caused a hot research. Syngas could be further converted into liquid fuels and COG dry reforming reaction can not only achieve environmental protection, but also convert the two greenhouse gases into two energy gases to make the energy utilization [1-3].

The catalysts used for COG dry reforming consist of support, promoter and active metal. The non-noble metals in Group VIII of Ni based catalysts have been researched widely because of low cost and relatively high activity in COG dry reforming. Whereas, the easier carbon deposition is a serious drawback in Ni based catalysts because it will decrease the activity of catalysts. Accordingly, it is necessary to modify the catalyst for the resistance to carbon formation. Nowadays, on the one hand, researchers found that different nickel precursors, even based on the same support, present a big difference in carbon deposition and catalytic activity. On the other hand, the activity of catalysts is significantly influenced by support which provides high surface area, suitable alkalinity, thermostability and mechanical stability [4,5]. Therefore, it is very important to seek suitable active metal precursor and support for COG dry reforming. Spinel structure oxide with face-centered cubic is a kind of compound metal oxide and the common structure is AB₂X₄. It is suitable for high temperature reaction catalyst carrier and becomes a hot research topic gradually in recent years [6,7]. Furthermore, the calcination temperature of the catalysts directly plays an important role in the size and dispersion of active metal and the interaction with supports. Sanjay K. and Hasan Ö. et al.



investigated the effect of calcination temperature on structure, stability, activity and catalytic properties of Ni/MgAl₂O₄ catalyst. Eventually, there exists a big influence on the activity and stability of the catalysts [8].

In this work, we study the influence of different nickel precursor and the calcination temperature of MA on 10Ni/MA in the COG dry reforming, devoting to get an appropriate nickel precursor and calcination temperature for 10Ni/MA catalyst in COG dry reforming. Moreover, several characterization were performed to investigate the surface and textural properties of the supports, fresh and used 10Ni/MA.

2. Results and discussion

2.1. Sample characterization

XRD patterns of the calcined 10Ni/MA catalysts with different nickel precursors are shown in figure 1.a. It is observed that the typical MgAl₂O₄ phase of (111), (200), (220), (311) and (222) exists in all samples, but the diffraction peaks of NiO ((111), (200), (220)) could not be obviously detected on 10Ni/MA-800 (a), indicating NiO is well dispersed on MgAl₂O₄ in 10Ni/MA-800 (a). Figure 1.b depicts the XRD pattern of the calcined 10Ni/MA catalysts with different calcination temperature of MA. When the calcination temperatures of MA are 600°C and 700°C, the diffraction peaks of MgAl₂O₄ become small and weak. The crystallinity of MgAl₂O₄ is higher as the calcination temperature increases, and the characteristic peaks of NiO could not be detected almost.

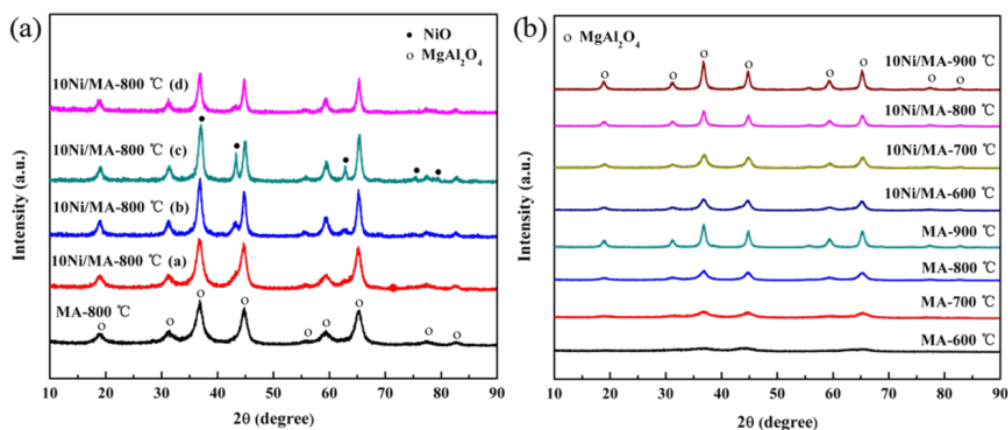


Figure 1. XRD of the support and calcined catalysts with different (a) Ni precursor and (b) calcination temperature of support

The physic-chemical properties of 10Ni/MA catalysts with different nickel precursor and calcination temperature of MA are shown in table 1. The BET surface area and pore volume of 10Ni/MA supported nickel nitrate are 84.89m²/g and 0.34cm³/g respectively, which are higher than those of 10Ni/MA supported nickel acetylacetonate. Moreover, the BET surface area was decreased as the calcination temperature of MA raised.

Figure 2.a is the CO₂-TPD profiles of the calcined 10Ni/MA catalysts with different nickel precursors. It is well known that low temperature corresponds to weak basic sites and high temperature corresponds to strong basic sites, as well as the area of the CO₂ desorption peaks means the relevant number of basic sites in the CO₂-TPD profiles, so that the more easily the catalyst adsorbs CO₂, the higher conversion rate of CH₄ and CO₂. There are three separated CO₂ desorption peaks in 10Ni/MA-800 (a) and 10Ni/MA-800 (b). The area of the desorption peaks of 10Ni/MA-800 (c) and 10Ni/MA-800 (d) is significantly lower than that of the previous two catalysts, and they only have two separated CO₂ desorption peaks. Furthermore, 10Ni/MA-800 (d) has a CO₂ desorption peak around 900°C which is higher than the temperature of catalytic reaction, showing that CO₂ could not be largely adsorbed during the CO₂ reforming [9,10]. The CO₂-TPD profiles of the calcined 10Ni/MA

catalyst with different calcination temperature of MA are shown in figure 2.b. There are two distinct CO₂ desorption peaks, meaning that there were two different basic positions and corresponding strength on the surface of catalyst. As the calcination temperature of MA becomes higher, the number of weak and strong basic sites was all decreased. In addition, there is a weak desorption peak at 533 °C corresponding to a strong basic site with low content.

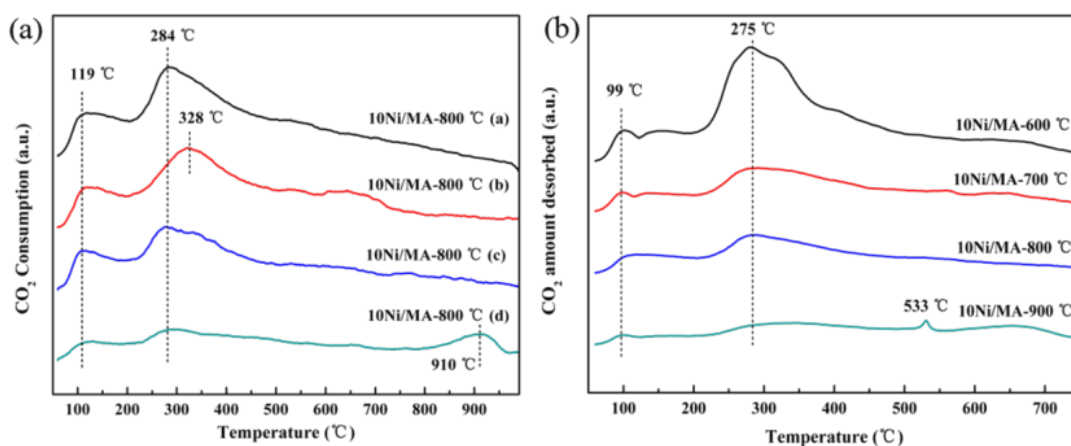


Figure 2. CO₂-TPD spectra of 10Ni/MA catalysts with different (a) Ni precursors and (b) calcination temperature of support

2.2. Effect of different nickel precursors on the performance of 10Ni/MA catalysts

The activity and stability of the 10Ni/MA with different nickel precursors reacting for 24 h in the CO₂ reforming are shown in figure 3. Although the carbon deposition content of 10Ni/MA-800 (d) is nearly 0 and it is highly selective to H₂ and CH₄, CO₂ conversion rates and the CO selectivity are all low. On the whole, the comprehensive catalytic performance of 10Ni/MA-800 (d) is weak. This is consistent with CO₂-TPD that MA supported nickel acetylacetonate owns weak bounding strength and its basic sites are also weak and less in quantity. The other three kinds of catalyst supported different nickel precursors have better catalytic performance than nickel acetylacetonate. Additionally, 10Ni/MA-800 (a) has the highest activity and stability. Its conversions of CH₄ and CO₂ are up to 81.5% and 94.5% respectively, the CO selectivity is the highest (88.77%) and the selectivity of hydrogen is 71.3% with a low carbon deposition rate of 3.2%.

Table 1. Physico-chemical properties of the 10Ni/MA catalysts with different Ni precursor and calcination temperature of MA

Catalysts	Precursor	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
10Ni/MA-800 (a)	Ni(NO ₃) ₂ · 6H ₂ O	84.89	0.34	16.20
10Ni/MA-800 (b)	C ₄ H ₆ NiO ₄ · 4H ₂ O	62.38	0.34	21.10
10Ni/MA-800 (c)	NiCl ₂ · 6H ₂ O	51.94	0.30	22.73
10Ni/MA-800 (d)	C ₁₀ H ₁₄ NiO ₄	37.53	0.16	17.21
10Ni/MA-600	Ni(NO ₃) ₂ · 6H ₂ O	131.14	0.30	9.03
10Ni/MA-700	Ni(NO ₃) ₂ · 6H ₂ O	94.05	0.31	13.03
10Ni/MA-900	Ni(NO ₃) ₂ · 6H ₂ O	58.58	0.25	16.74

2.3. Effect of calcination temperature of MA on the performance of 10Ni/MA catalysts

The influence of calcination temperature of MA on the activity is also studied as shown in figure 4. It can be seen that the CH₄ and CO₂ conversion rates of catalyst calcinated at 800°C are the best, H₂ and CO are the most selective, which is compared with 600°C, 700°C, 900°C. The conversion of CH₄ and CO₂ increased from 74.6% and 92.0% to 81.4% and 94.5%, as the calcination temperature rose from 600°C to 800°C, but decreased when the calcination temperature further rose to 900°C. Low

calcination temperature leads to low crystallinity as XRD detected and weak interaction with Ni species which results in large amount of carbon deposition. High calcination temperature of MA above 800°C may lead to strong interaction with Ni species which is hard to reduce, indicating less active metallic Ni involved in the CO₂ reforming. Therefore, the support MA calcinated at 800°C is beneficial to the activity of catalyst.

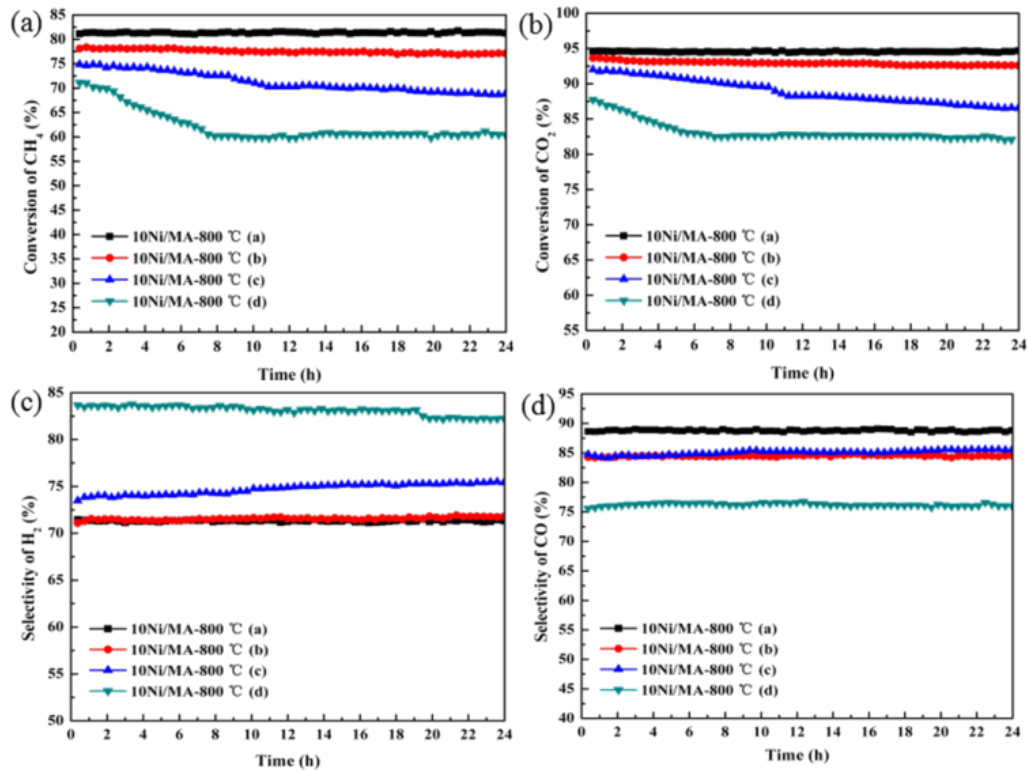


Figure 3. Influence of different Ni precursor on the catalytic performance over 10Ni/MA-800 catalysts. CH₄/CO₂ molar ratio=1, T=750°C, V=24000 mL/(g h)

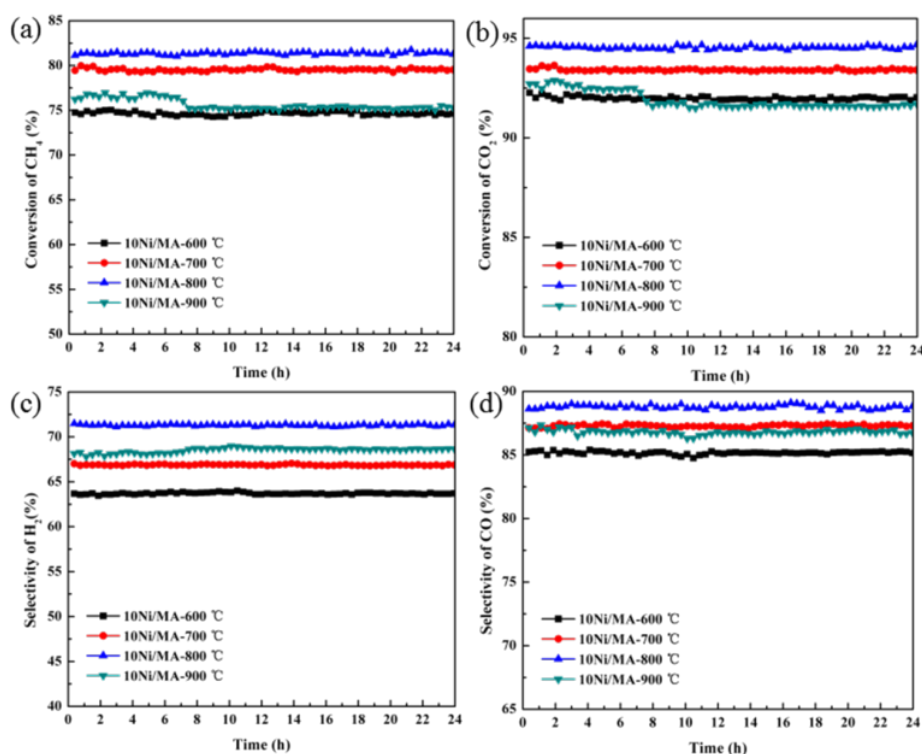


Figure 4. Influence of different calcination temperature of support on the catalytic performance over 10Ni/MA-*t* catalysts. CH₄/CO₂ mol-ar ratio=1, T=750°C, V=24000 mL/(g h)

2.4. Carbon deposition characterization

The activity and stability of the 10Ni/MA catalysts are significantly affected by the amount of carbon deposition. The XRD patterns of the reduced and used 10Ni/MA catalysts are shown in figure 5. The structures of the catalysts are stable after reacting for 24 h during the CO₂ reforming. The diffraction peaks of Ni around $2\theta=45.35^\circ$, 51.88° and 76.39° correspond to the (111), (200) and (220). There exists the diffraction peaks of carbon only in the 10Ni/MA-800 (c) as shown in figure 5.a, indicating resistance of carbon deposition on 10Ni/MA catalyst with nickel chloride is quite weak. Furthermore, the large amount of carbon deposition may result in the decreased catalytic activity. Figure 5.b displays the diffraction peaks of Ni and the carbon peaks are not observed, meaning the nickel had been reduced.

The H₂-TPH profiles are shown in figure 6 reflecting the type of the carbon deposition. The temperature of reduction peak below 400°C reflects active carbon species namely CH_x, mainly including C_α species of completely dehydrogenation and C_β species with part of the dehydrogenation. The high temperature of reduction peak around 520°C indicates stable carbon corresponding to C_γ, which normally clogs the activity center of catalysts. The carbon deposition type of 10Ni/MA-800 (a) and 10Ni/MA-800 (c) are mainly C_α and C_γ, and 10Ni/MA-800 (c) is mainly C_γ. Also the type of carbon deposition of 10Ni/MA-800 (d) is C_α and its peak area is very low showing less carbon deposition, which is supported by the amount of carbon measured by TG.

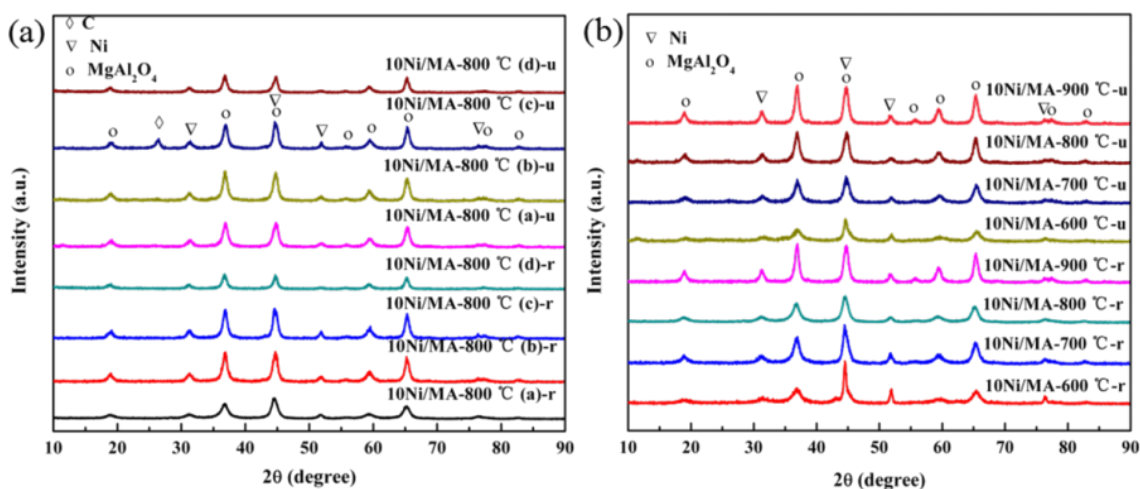


Figure 5. XRD of 10Ni/MA catalysts after reduced and used: different (a) Ni precursor, (b) different calcination temperature of supports

The TG profiles of 10Ni/MA catalysts are shown in figure 7. The loss in mass below 100 °C is due to the evaporation of the adsorbed water. The mass gain in the range of 200–450 °C is ascribed to the metallic Ni oxidation and the mass loss above 450 °C is attributed to the carbon oxidation [11]. The mass of 10Ni/MA-800 (d) is not lost reflecting almost no carbon deposition which corresponds to the H₂-TPH results, besides the amount of carbon deposition of 10Ni/MA-800 (b) is only about 3.2 wt.%, but for 10Ni/MA-800 (c) is about 6.9 wt.%. Additionally, the amount of carbon deposition decreases from 12.8 wt.% to 3.2 wt.% as the calcination temperature raised from 600 °C to 800 °C and increases to 7.2 wt.% as calcination temperature further raised to 900 °C.

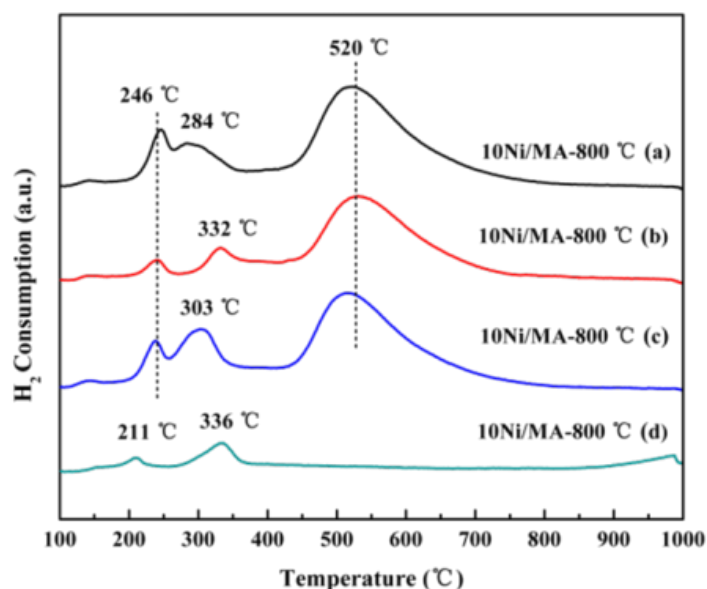


Figure 6. H₂-TPH profiles of the 10Ni/MA catalysts with different Ni precursor

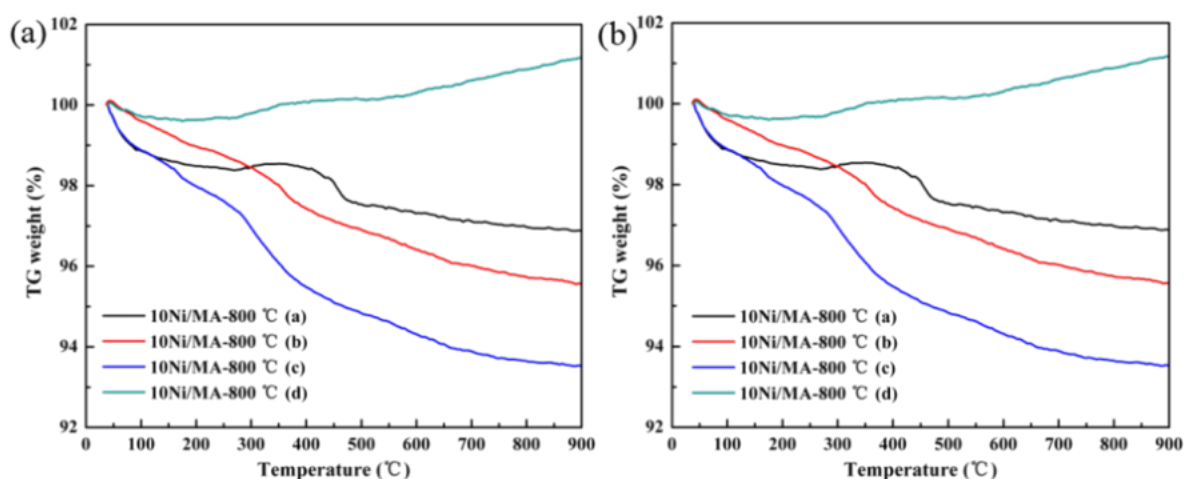


Figure 7. TG profiles of the 10Ni/MA catalysts after 24 h reaction: (a) different Ni precursor, (b) different calcination temperature of support

In order to further study the amount of the carbon deposition after reaction, the TEM images of 10Ni/MA are shown in figure 8. There exists lots of carbon nanotubes on the 10Ni/MA catalyst with nickel chloride, but less carbon deposition on the catalyst supported nickel nitrate. When the calcined temperature of support reaches to 600 °C and 900 °C, the 10Ni/MA catalysts have many carbon nanotubes.

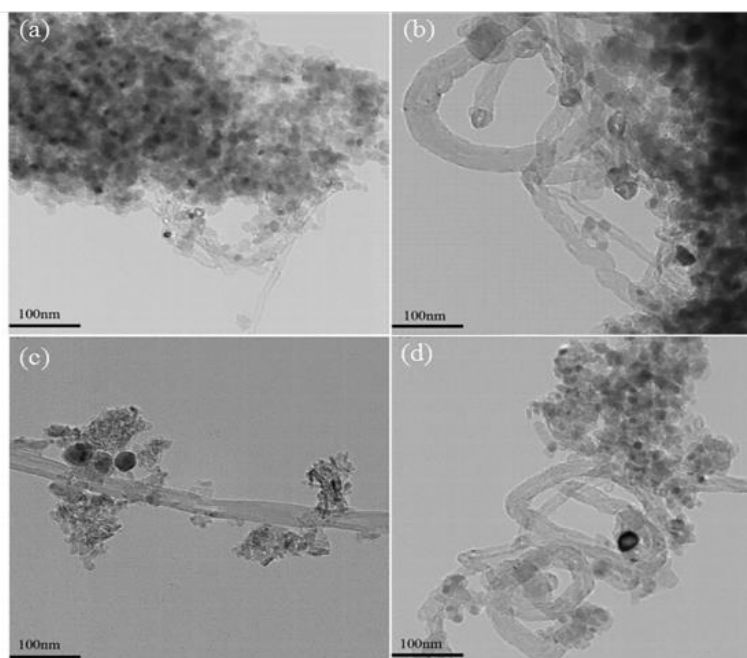


Figure 8. TEM images of the 10Ni/MA catalysts after used: (a) nickel nitrate precursor, (b) nickel chloride precursor, (c) the support calcined at 600°C, (d) the support calcined at 900°C

3. Experimental

3.1. Catalyst preparation

The MgAl_2O_4 was prepared by co-precipitation. The catalyst was synthesized by impregnation which supported 10 wt.% Ni with four kinds of nickel precursor, including nickel nitrate, nickel acetate, nickel chloride and nickel acetylacetonate and the MgAl_2O_4 support was calcined at 800°C named 10Ni/MA-800 (a), 10Ni/MA-800 (b), 10Ni/MA-800 (c) and 10Ni/MA-800 (d) respectively. The

10Ni/MA catalysts which MgAl₂O₄ calcination temperature was 600°C, 700°C, 800°C, 900°C named 10Ni/MA-600, 10Ni/MA-700, 10Ni/MA-800 and 10Ni/MA-900 respectively.

3.2. CO₂ reforming experiment

The CO₂ reforming was carried out in a fixed-bed quartz reactor under atmospheric pressure. The reaction gas were 77.88 mol% COG (58% H₂, 31.5% CH₄, 3.1% CO₂, 7.4% CO) and 22.12 mol% CO₂ to ensure the mole ratio CH₄/CO₂=1. The catalysts were reacted in the CO₂ reforming for 24 h at 750 °C after reduced at 800 °C for 2 h in 30 %H₂/N₂. The conversion of CH₄, CO₂ and selectivity of syngas were calculated as follows [12]:

$$X_{CH_4}\% = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100 \quad ; \quad X_{CO_2}\% = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \times 100 \quad (1)$$

$$S_{H_2}\% = \frac{F_{H_2,out}}{F_{H_2,in} + 2(F_{CH_4,in} - F_{CH_4,out})} \times 100 \quad ; \quad S_{CO}\% = \frac{F_{CO,out}}{F_{CO,in} + (F_{CH_4,in} - F_{CH_4,out}) + (F_{CO_2,in} - F_{CO_2,out})} \times 100 \quad (2)$$

F_{in} and F_{out} represented the gas flow rates of the inlet and outlet gas.

3.3. Catalysts characterization

The phase composition of catalysts after calcined, reduced and used were detected on a Rigaku D/MAX-2200 diffractometer apparatus and the BET surface area, pore volume and average pore diameter were measured by Micromeritics ASAP 2020 physisorption analyzer using N₂ adsorption/desorption technique. The strength and amount of basic sites were measured by temperature-programmed desorption (CO₂-TPD). The species and amount of carbon deposition of used catalysts were measured through temperature-programmed hydrogenation (H₂-TPH) also on AutoChem II 2920 apparatus. The amount of carbon deposition on the catalysts after used was measured by thermogravimetry-differential scanning calorimetry (TG-DSC) and the morphology of catalysts after reduced and used were detected through TEM on the JEOL JEM-200CX microscope (100 kV).

4. Conclusions

The CO₂ reforming was reacted for 24 h at 750 °C on the 10Ni/MA catalysts which were prepared by co-precipitation. The results demonstrated that nickel precursor and calcination temperature of MA have deep influence on the activity and stability of 10Ni/MA catalysts by affecting the metallic Ni dispersion and carbon deposition. Furthermore, the MA (calcined at 800°C) supported nickel nitrate performs best and owns high metallic Ni dispersion and small amount of carbon deposition. Its conversion of CH₄ and CO₂ is up to 81.4% and 94.5%, respectively, while the selectivity of H₂ and CO reaches to 71.3% and 88.8%, respectively, which shows a promising application in CO₂ reforming of COG to product syngas.

5. Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 51674164 and 51474145) and the Shanghai Rising-Star Program (No. 15QA1402100).

6. References

- [1] Bermúdez J, Arenillas A and Menéndez J Syngas from CO₂ reforming of coke oven gas: synergetic effect of activated carbon/Ni-γAl₂O₃ catalyst 2011 Int. J. Hydrogen Energy 36 13361-68
- [2] Tóth A, Halasi G, Bánsági T, Solymosi F Reactions of propane with CO₂ over Au catalysts 2016 J. Catal. 337 57-64
- [3] Simonov M, Rogov V, Smirnova M and Sadykov V Pulse microcalorimetry study of methane dry reforming reaction on Ni/ceria-zirconia catalyst 2017 Catalysts 7 268
- [4] Cheng H, Feng S, Ta W, Lu X, Yao W, Li G and Zhou Z Effects of noble metal-doping on Ni/La₂O₃-ZrO₂ catalysts for dry reforming of coke oven gas 2014 Int. J. Hydrogen Energy 39 12604-12
- [5] Ha Q, Armbruster U, Atia H, Schneider M, Lund H, Agostini G, Radnik J, Vuong, H and Martin A

- Development of active and stable low nickel content catalysts for dry reforming of methane 2017 Catalysts 7 157
- [6] Sanjay K, Abhishek G, Goutam D, Deepak K Effect of calcination temperature on stability and activity of Ni/ MgAl₂O₄ catalyst for steam reforming of methane at high pressure condition 2016 Int. J. Hydrogen Energy 41 14123-32
- [7] Hafizi A and Rahimpour M Inhibiting Fe-Al spinel formation on a narrowed mesopore-sized MgAl₂O₄ support as a novel catalyst for H₂ production in chemical looping technology 2018 Catalysts 8 27
- [8] Hasan Ö, Faruk Ö, M. A Effect of the calcination temperature on Ni/MgAl₂O₄ catalyst structure and catalytic properties for partial oxidation of methane 2014 Fuel 116 63-70
- [9] Barroso M, Galetti A, Gomez M, Arrua L, Abello M Ni-catalysts supported on Zn_xMg_{1-x}Al₂O₄ for ethanol steam reforming: influence of the substitution for Mg on catalytic activity and stability 2013 Chem. Eng. J. 222 142-49
- [10] Koo K, Lee S, Jung U, Roh H, Yoon W Syngas production via combined steam and carbon dioxide reforming of methane over Ni–Ce/MgAl₂O₄ catalysts with enhanced coke resistance 2014 Fuel Process. Technol. 119 151-57
- [11] Cheng H, Li G, Zhao H, Lu X, Xu Q and Tao W Effects of preparation technique and lanthana doping on Ni/La₂O₃-ZrO₂ catalysts for hydrogen production by CO₂ reforming of coke oven gas 2017 Catalysis Today <http://dx.doi.org/10.1016/j.cattod.2017.11.017>
- [12] Tao W, Cheng H, Yao W, Lu X, Zhu Q and Li G 2014 Syngas production by CO₂ reforming of coke oven gas over Ni/La₂O₃-ZrO₂ catalysts Int. J. Hydrogen Energy 39 18650-58