Effect of Preparation Method on the Performance of 10Ni/MgAl$_2$O$_4$ for Dry Reforming of Coke Oven Gas

Cheng WU[1,2], Hong-Wei CHENG[1,2,a,*], Yuan-Zhi WANG[1,2] and Xiong-Gang LU[1,2,b]

[1] School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

[2] State Key Laboratory of Advanced Special Steel, Shanghai University, Shanghai 200072, China

[a]hwcheng@shu.edu.cn, [b]luxg@shu.edu.cn

*Corresponding author: Hongwei Cheng

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Abstract. MgAl$_2$O$_4$ spinel, as support of the 10Ni/MgAl$_2$O$_4$ catalyst which used for coke oven gas dry reforming, was prepared by sol-gel, coprecipitation and urea hydrolysis method. The catalysts were prepared by impregnation. The MgAl$_2$O$_4$ and 10Ni/MgAl$_2$O$_4$ were both calcined at 800 ^{o}C for 5 h and the samples were characterized by BET, XRD, TG-DSC techniques. The MgAl$_2$O$_4$ prepared by coprecipitation showed higher performance in comparison with other two methods which performed high conversion of reactant gas and selectivity of syngas at 700 ^{o}C for 24 h.

Introduction

Syngas is an important raw material for the organic energy production, converted from carbonaceous minerals, mainly consisted of H$_2$ and CO [1-3]. The most widely used is for methanol synthesis when the H$_2$/CO ratio is 2 [4]. Nowadays, the methane reforming is used for the preparation of syngas through partial oxidation, steam reforming or dry reforming [5,6]. Coke oven gas (COG) is a by-product and surplus gas in the steel industry, which consist of H$_2$ (57-60 %), CH$_4$ (23-27 %), CO (5-8 %) and CO$_2$ (< 3 %), if only just burnt away may be harmful to the environment [7]. Dry reforming, especially COG dry reforming is that two major greenhouse gas converted into two energy gas (CH$_4$+CO$_2$ ↔ 2CO+H$_2$), the H$_2$/CO ratio is 2. The core of the COG dry reforming reaction is the stability and activity of the catalysts.

The catalyst used for COG dry reforming is consisted of active metal component, support and assistant. Most of the metal component in Group VIII have been examed to be the suitable catalyst over large amounts of supports resulting in good catalytic stability and activity. Precious metals having excellent activity and good resistance to carbon deposition such as Ru, Rh, Pd and Pt, but they are expensive and not easy to available. Ni-based catalysts present quite good catalytic activity and low price with wide application in the industry [8]. MgAl$_2$O$_4$ is composite oxide widely used as support in methane dry reforming with acidic and alkaline center which can have good adsorption of methane and carbon dioxide. MgAl$_2$O$_4$ with spinel structure is stable and resistance on sintering at high temperature. MgAl$_2$O$_4$ is easily available and can improve dispersion of active metal, reduce the size of the particles and increase of CH$_4$ and CO$_2$ adsorption and decomposition, but different preparation methods of support have big influence on the stability and activity of the catalyst and there was few research on it. Koo et al. [9] also obtained that 10Ni-5Ca/MgAl$_2$O$_4$ catalyst was better than other Ni/Ca ratio in activity and stability which MgAl$_2$O$_4$ support can provide high structure stability at 900 ^{o}C. Naeem et al. [10] used the polyol and surfactant-assisted methods to synthesize Ni-based and found that surfactant-assisted catalysts presented high resistance on carbon deposition.

The present work is focus on the effect of preparation method on the catalytic performance of 10Ni/MgAl$_2$O$_4$ for dry reforming of COG. The support MgAl$_2$O$_4$ is prepared by sol-gel, coprecipitation and urea hydrolysis method.

Experimental

Catalyst Preparation

The $MgAl_2O_4$ (named as MA) support was synthesized by sol-gel, coprecipitation and urea hydrolysis with the molar ratio $Mg^{2+}/Al^{3+} = 0.5$ [11,12], which calcined in air at 800 ^oC for 5 h and denominated as MA-x (x = s, c, h), respectively.

The catalysts were prepared by impregnation (named as 10Ni/MA-x), which contained 10 wt%Ni and nickel precursor was nickel nitrate. The catalysts were calcined in air at 800 ^oC for 5 h. Prior to reacting, the catalysts (0.25 g) were reduced in a 15 mol% H_2/N_2 steam atmosphere for 2 h at 800 ^oC.

Catalyst Characterization

The BET surface area and pore-size distribution of the samples were detected in N_2 atmosphere at -196 ^oC. They were detected through N_2 adsorption/desorption methods by Micromeritics ASAP 2020 physisorption anaiyzer. The samples were outgassed at 300 ^oC for 5 h in N_2 flowing before testing.

The phase compositions of the samples were recorded on a Rigaku D/Max-2200 diffractometer with Cu/Kα radiation (40 mA, 45 kV). The $2\theta = 10^o$ - 90° range and the scan rate was 6°/min.

The amount of carbon deposition of the used catalysts was obtained by Netzsch SAT 449 F3 thermal analyzer under 10 mol% O_2/N_2 steam (40 ml/min), and began from room temperature to 1000 ^oC with a liner heating rate of 10 ^oC/min.

COG Dry Reforming

The COG (58% H_2, 31.5% CH_4, 3.1% CO_2, 7.4% CO) and CO_2 were 77.88 mol% and 22.12 mol% of the total reaction gas to ensure that the molar ratio $CH_4/CO_2 = 1$. COG dry reforming reactions were performed in a fixed-bed quartz reactor under atmospheric pressure and the gas was detected by GC-9160. The reduced catalysts were reacted in the COG dry reforming for 24 h, gas hourly space velocity (GHSV) was 24000 ml/(h·g) and the reacting tempreture was 700 ^oC. The conversion and selectivity were calculated as our previous work [13,14].

Results and Discussion

Fig. 1(a) shows the N_2 adsorption/desorption isotherms and the pore size distributions of 10Ni/MA catalysts. Table. 1 shows the BET surface areas. From the results, It can be seen that all catalysts presented type IV isotherms with a H1-type hysteresis loop and these were typical mesoporous materials [8,15]. The 10Ni/MA-c owned largest BET surface area, pore volume and average pore diameter.
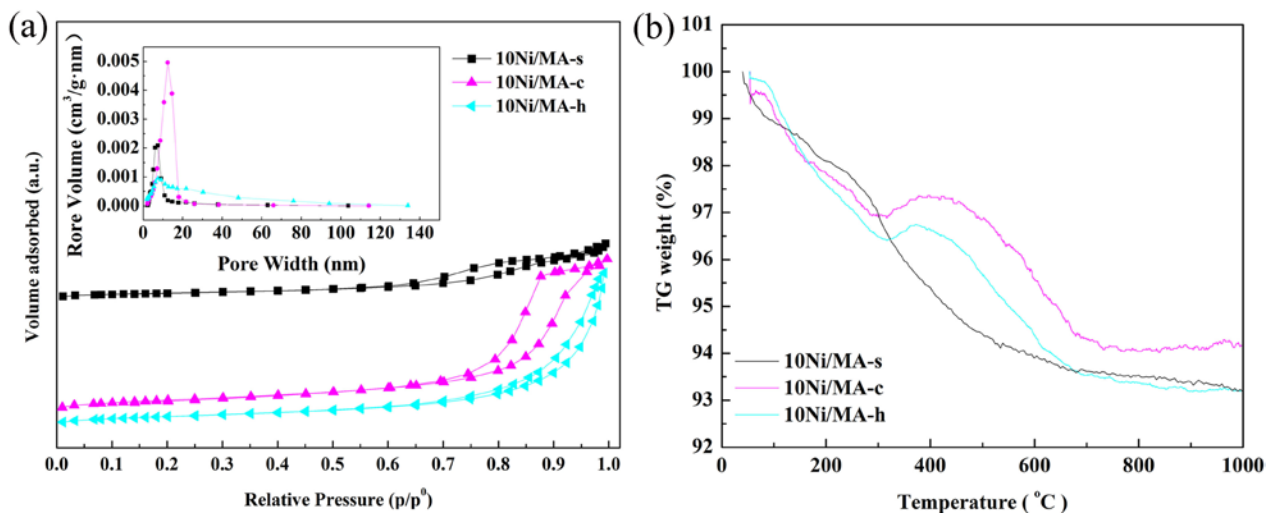

Fig. 1(a). N_2 adsorption/desorption isotherms and the pore size distribution of 10Ni/MA catalysts, Fig. 1(b). TG values of the used 10Ni/MA catalysts after 24 h reaction.

Table 1. The physical properties of 10Ni/ $MgAl_2O_4$ catalysts prepared by different methods.

Catalysts	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
10Ni/MA-s	50.3	0.12	9.9
10Ni/MA-c	101.2	0.39	15.2
10Ni/MA-h	71.4	0.24	13.2

Fig. 2(a) shows the XRD of supports and calcined catalysts. The spinel $MgAl_2O_4$ can be synthesized by three different methods and the crystallinity of MA-s was the highest. The characteristic peaks of NiO at $2\theta = 37.04^o$, 43.3^o and 62.78^o were also presented in Fig.2(a) which were correspond to planes (111), (200) and (220). Fig. 2(b) shows the XRD of reduced catalysts. After reduced the NiO were totally converted into metallic Ni, which were present at $2\theta = 45.35^o$, 51.88^o and 76.39^o [12,16].
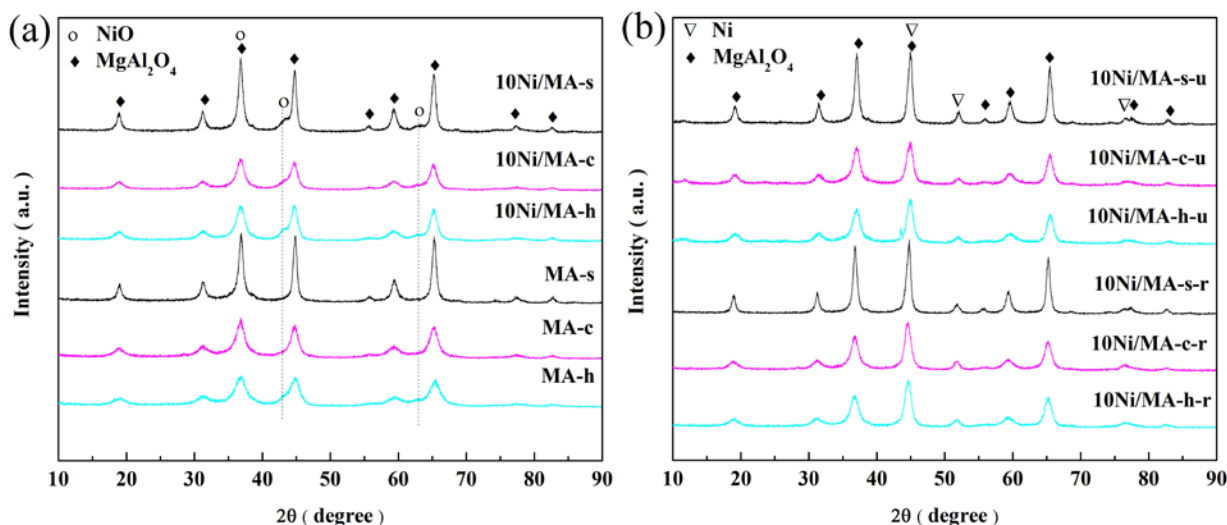

Fig. 2(a). Supports and calcined catalysts, Fig. 2(b). Reduced (r) and used (u) catalysts.

Fig 3 shows the conversion of reactant gas and selectivity of syngas over 10Ni/MA catalysts for COG dry reforming. The catalysts performed good conversion and selectivity after reacting at 700 ^{o}C for 24 h and were stable and active. As for the 10Ni/MA-c catalyst, the conversion of CH_4 and CO_2 were 76.3 % and 89.2 %, the selectivity of H_2 and CO were 84.3 % and 90.3 %. The other two catalysts performed less active than the 10Ni/MA-c catalyst. This may not only because the large BET surface area and average pore diameter but also the the pore size distribution was uniform.

To further investigate the anti-coking properties of the catalysts, the catalysts after the experiment were characterized by XRD and TG. From Fig. 2(b), it can be seen that carbon deposit peak could hardly be presented in the XRD patterns of the catalysts after used, this may because little carbon was deposited on the catalysts after COG dry reforming at 700 ^{o}C for 24 h. Furthernmore, the amount of carbon deposition on the used 10Ni/MA prepared by different methods were shown in Fig. 1(b). The amount of carbon deposit on the 10Ni/MA-c was about 5.5 wt%, but the amount of carbon deposited on 10Ni/MA-s and 10Ni/MA-h performed were almost the same and more than that of 10Ni/MA-c. Zhu. et al. uesd $La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O_3$ catalysts for the COG dry reforming reacted at 800 ^{o}C. Compared with $La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O_3$, 10Ni/MA presented relatively low activity but high resistance to carbon deposition owning to low reacting tempreture of 700 ^{o}C[14].

Therefore, it is found that the 10Ni/MA-c catalyst prepared by coprecipitation method has the best properties based on the catalytic activity and resistance to carbon deposition.

Conclusions

The 10Ni/MA catalysts prepared by different methods were synthesized successfully and the conclusions of this research were as follows:

1.Different preparation methods had significant influences on the activity of the catalysts.

2.10Ni/MA-c performed the highest resistance of carbon deposition. The amount of carbon deposit on the three used catalysts were all less than 10 wt% and the carbon deposit amount was only 5.5 wt%. The activity and stability were significant effected by crabon deposit cause the activility center can be blocked by crabon deposit.

3.10Ni/MA-c performed the highest activity, the conversion of CH_4 and CO_2 were 76.3 % and 89.2 %, the selectivity of H_2 and CO were 84.3 % and 90.3 %, which show good application potential in the dry reforming of coke oven gas for syngas production.
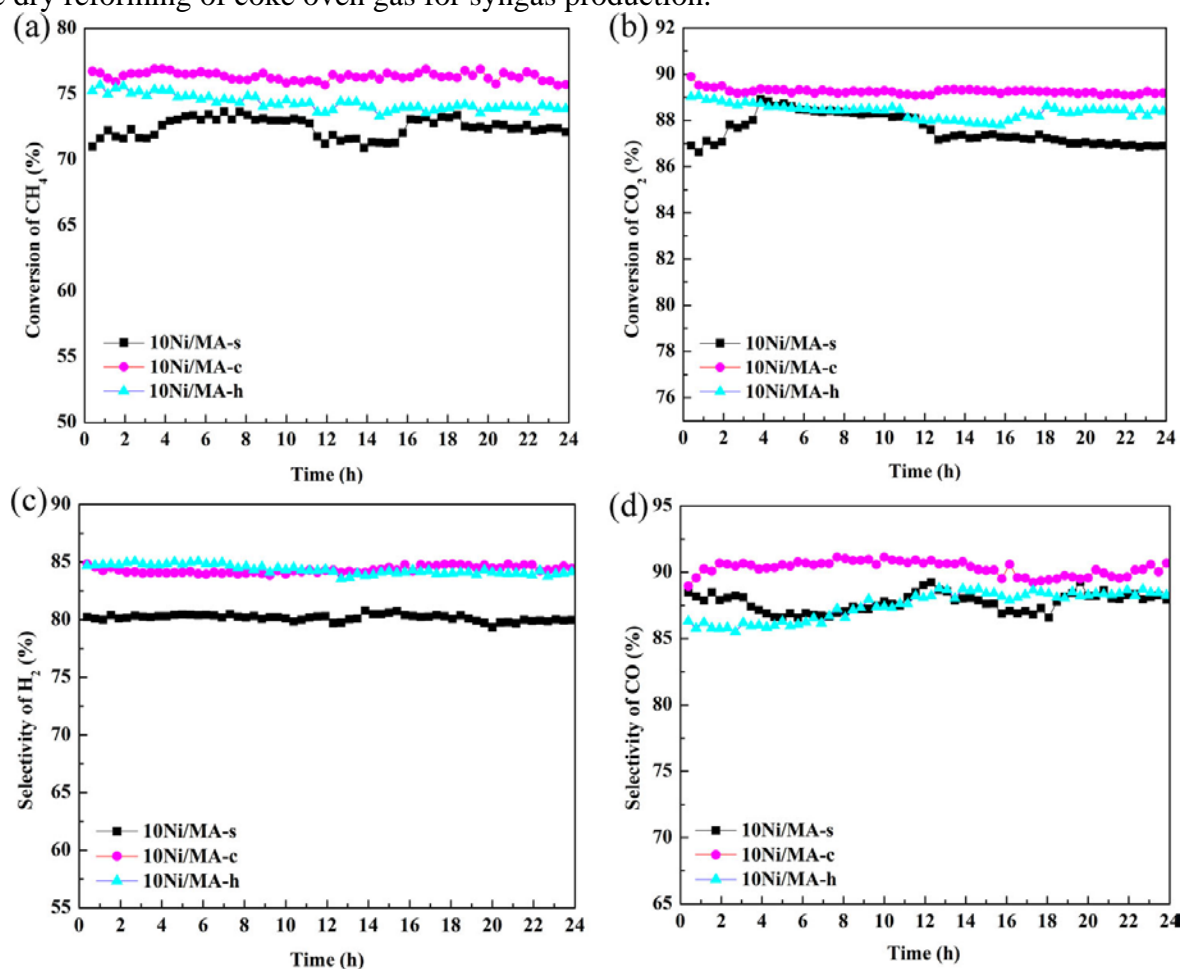

Fig. 3. The conversion of CH_4, CO_2 and the selectivity of H_2, CO over 10Ni/MA prepared by different methods in the COG dry reforming.

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