Effect of La$_2$O$_3$ promoter on NiO/Al$_2$O$_3$ catalyst in CO methanation

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Abstract−A series of NiO/Al$_2$O$_3$ catalysts promoted by different La$_2$O$_3$ contents were prepared by impregnation method. The physicochemical properties of NiO-La$_2$O$_3$/Al$_2$O$_3$ were characterized by N$_2$ adsorption-desorption, X-ray diffraction (XRD), H$_2$ temperature programmed reduction (H$_2$-TPR) and H$_2$ chemisorption. The effect of La$_2$O$_3$ on the activity of NiO/Al$_2$O$_3$ for CO methanation was investigated in a fixed bed reactor. A lifetime test, as well as thermogravimetric (TG) analysis, was performed to investigate the stability performance and anti-carbon deposition of catalysts. The results showed that the addition of La$_2$O$_3$ can restrain the growth of NiO particles, increase the H$_2$ uptake and Ni dispersion, and therefore enhance the activity of catalysts. When the La$_2$O$_3$ content was 3 wt%, a CO conversion of 98% and a selectivity to CH$_4$ of 96% were obtained at 400 °C. Furthermore, the catalyst NiO-La$_2$O$_3$/Al$_2$O$_3$ with 3 wt% La$_2$O$_3$ content displayed highly stable performance in long-term tests, especially exhibiting good anti-carbon deposition property.

Keywords: CO Methanation, La$_2$O$_3$ Promoter, NiO/Al$_2$O$_3$ Catalyst, Stability

INTRODUCTION

The proportion of natural gas in the energy consumption structure is gradually increasing, which is attributed to its advantages such as high calorific value, complete combustion and being smoke-free [1-3]. The natural gas resource meets the needs of environmental protection and economic development, and the production of synthetic natural gas (SNG) from coal and solid dry biomass has been a concern due to the rising price and exhaustion of natural gas [4,5]. As one of the most essential steps in the production of SNG, the CO methanation reaction (CO+3H$_2$=CH$_4$+H$_2$O) has received considerable attention since Sabatier and Senderens first discovered it, due to its wide applications in the chemical industry such as removal of trace amounts of CO from H$_2$-rich feed gas, purification of the reformate gas for fuel cell, and processes in relation to Fischer-Tropsch synthesis, and so on [6-10]. The catalyst of methanation has a crucial effect on CO conversion and CH$_4$ selectivity. There are many reports focusing on the alumina supported Ni-based catalysts for the methanation reaction due to its excellent activity [11-13]. As well, the addition of different promoters such as metal oxide and noble metals could promote the activity of the Ni-based catalyst greatly. Typically, lanthanum was reported to promote the formation of new active sites and enhance metal dispersion effectively [14-17]. However, to our knowledge, the effects of lanthanum on physicochemical properties, catalytic performance, particularly the stability behavior of NiO/Al$_2$O$_3$ catalyst, as well as their anti-carbon deposition properties in CO methanation reaction have not been reported, and need a comprehensive investigation.

We prepared a series of NiO/Al$_2$O$_3$ catalysts promoted with different lanthanum contents with impregnation method. The catalytic activity of catalysts was studied in CO methanation, as well as their stability performance. The prepared catalysts were characterized by N$_2$ adsorption-desorption, X-ray diffraction (XRD), H$_2$ temperature programmed reduction (H$_2$-TPR) and H$_2$ chemisorption; the spent catalysts were characterized with thermogravimetry (TG). The paper aims to reveal the effect of the lanthanum content on the catalytic activity, lifetime performance, and the anti-carbons of NiO/Al$_2$O$_3$ catalysts. Catalysts of high activity and stability were obtained for CO methanation, providing basic data for further industrial expansion.

EXPERIMENTAL

1. Preparation of NiO-La$_2$O$_3$/Al$_2$O$_3$ Catalyst

A typical preparation procedure of La$_2$O$_3$/Al$_2$O$_3$ was as follows. A certain amount of lanthanum nitrate hexahydrate (La(NO$_3$)$_3$·6H$_2$O) was dissolved into the deionized water to keep the concentration of solution at 0.2 mol/L. The γ-Al$_2$O$_3$ was added to the solution and stirred for 2 h, and then the slurry was aged for 12 h at 25 °C. The samples were dried at 110 °C for 12 h in vacuum drying oven and further calcined at 600 °C for 6 h. Then La$_2$O$_3$/Al$_2$O$_3$ was obtained.

NiO-La$_2$O$_3$/Al$_2$O$_3$ catalysts were prepared by impregnation method. A certain amount of nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) was dissolved into the deionized water to obtain a clear solution with the concentration of 0.2 mol/L. The as-prepared La$_2$O$_3$/Al$_2$O$_3$ samples were added to the solution and stirred for 2 h at 25 °C, and then the slurry was aged for 12 h. The samples were dried at 110 °C for 12 h and calcined at 500 °C for 2 h. The obtained catalysts were marked as La0, La1, La3, La5 and La8, which corresponded to the lanthanum content of 0, 1, 3, 5 and 8 wt%, respectively. In all of the catalysts, the nickel loading was 15 wt%. The powder catalysts were pressed into pellets which were further crushed into particles of 60-80 mesh for the following characterizations and activity evaluations.

2. Activity Test

The activity of catalysts was conducted on a fixed-bed reactor equipped with a stainless steel tubular reactor of 10 mm in diameter. A thermocouple (type K-161) was inserted into catalyst bed to

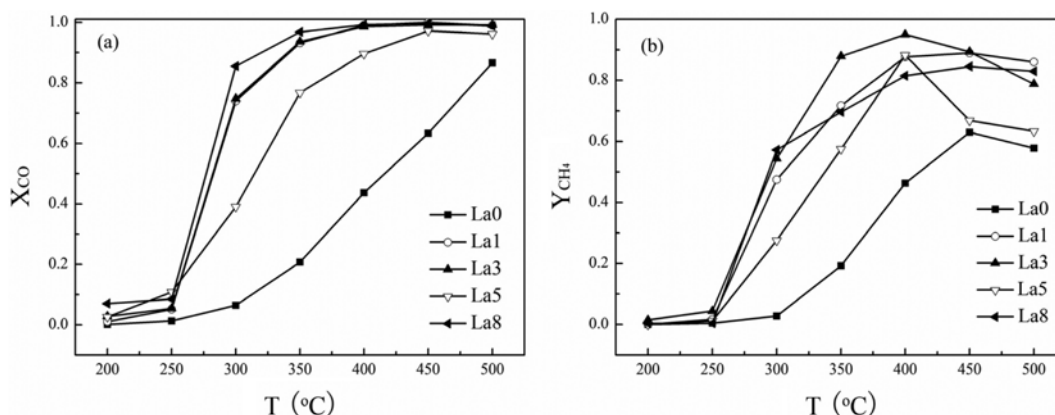[†]To whom correspondence should be addressed.
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Fig. 1. Effect of La$_2$O$_3$ on X$_{CO}$ (a) and Y$_{CH_4}$ (b) for CO methanation (reaction conditions: T=200-500 °C, P=1.5 MPa, GHSV=10,000 h^{-1}, H$_2$: CO : CH$_4$=0.6 : 0.22 : 0.14).

measure the temperature of catalyst bed accurately; the temperature of furnace was precisely controlled by a temperature controller. About 0.2 g catalyst was reduced at 600 °C for 2 h under H$_2$ flow of 50 mL/min, and then cooled to 200 °C in N$_2$ atmosphere. Then, the feed gas H$_2$, CO and CH$_4$ was introduced into the reactor with volume ratio of 0.6 : 0.22 : 0.14. CO methanation reaction was carried out under P=1.5 MPa and GHSV (gas hour space velocity)=10,000 h^{-1}. The temperature range was 200-500 °C, with 50 °C as the interval. The products were analyzed online by the gas chromatograph (type GC900A).

The catalytic performance of catalysts was evaluated by CO Conversion (X$_{CO}$), CH$_4$ Selectivity (S$_{CH_4}$), and CH$_4$ Yield (Y$_{CH_4}$) with Eqs. (1), (2) and (3), respectively.

$$\text{CO Conversion (\%)} = \frac{n_{CO,in} - n_{CO,out}}{n_{CO,in}} \times 100\% \tag{1}$$

$$\text{CH}_4 \text{ Selectivity (\%)} = \frac{n_{CH_4,out} - n_{CH_4,in}}{n_{CO,in} - n_{CO,out}} \times 100\% \tag{2}$$

$$\text{CH}_4 \text{ Yield (\%)} = \text{CO Conversion} \times \text{CH}_4 \text{ Selectivity} \tag{3}$$

where n$_{CO,in}$ and n$_{CO,out}$ respresent the molar concentration of CO in the feed and product mixture, respectively; n$_{CH_4,in}$ and n$_{CH_4,out}$ represents the molar concentration of CH$_4$ in the feed and product mixture.

3. Catalyst Characterization

N$_2$ adsorption-desorption of samples was performed on Nova 2200e apparatus at 77 K. The pore size and pore volume were calculated by the desorption branch of isotherms using Barrett-Joyner-Halenda (BJH) method. The specific surface areas were evaluated by Brunauer-Emmett-Teller (BET) equation.

XRD patterns were recorded on D/MAX-2500 X-ray diffractometer at 40 kV and 40 mA, with CuKα as radiation source. The catalysts were scanned from 10° to 80° at room temperature, with 5°/min as the scanning step. The NiO average crystallite sizes were calculated by Scherrer equation.

H$_2$-TPR was carried out on the AutoChem2910 instrument. The samples were pretreated in He gas at 200 °C for 1 h and cooled to room temperature. Then, the catalysts were reduced by 10% H$_2$/Ar from room temperature to 900 °C, with the heating rate of 10 °C/min.

H$_2$ chemisorption was tested on AutoChem2910 equipment, which

was employed to evaluate the dispersion property of active component on the catalysts. Ni dispersion was calculated according to chemisorbed H$_2$, which was studied by pulse chemisorption of 5% H$_2$/Ar gas until saturated.

TG was carried out on the Pyris Diamond thermogravimetric analyzer used to study the amount of carbon deposition on the catalyst after a long-term reaction. The catalysts were treated in 50 mL/min air; the patterns were registered from room temperature to 800 °C, with 10 °C/min as heating rate.

RESULTS AND DISCUSSION

1. Effect of Lanthanum Content on CO Methanation

Fig. 1 shows the effect of La$_2$O$_3$ content on the CO conversion (a) and CH$_4$ yield (b) of NiO-La$_2$O$_3$/Al$_2$O$_3$ catalysts. Obviously, the CO conversion and CH$_4$ yield of all catalysts increase with increasing the reaction temperature; as well, the catalysts show good catalytic performance in 350-450 °C. As seen in Fig. 1(a), the catalysts La1, La3, La5 and La8 exhibit higher CO conversion than La0 in the temperature region of 200-500 °C, indicating that the addition of lanthanum can greatly improve the reaction rate of CO methanation, which is in accordance with the literature [9]. It is seen from Fig. 1(b) that CH$_4$ yield increases with the increasing of La$_2$O$_3$ content, reaching the maximum for La3; then, CH$_4$ yield does not change but even decreases with further increasing La$_2$O$_3$ content. Typically, La3 catalyst exhibits the highest CH$_4$ yield of 94.9% when the temperature is as high as 400 °C. These results reveal that the catalyst with La$_2$O$_3$ content of 3 wt% has the highest catalytic performance.

Moreover, CO$_2$ is detected in the effluent gas when the reaction temperature is above 350 °C, which is not shown here; CO$_2$ production is gradually increased with increasing the temperature. The CO$_2$ may come from WGS (water gas shift) reaction by the produced steam and CO feed; WGS reaction is CO+H$_2$O →CO$_2$+H$_2$, which will be accelerated at high temperature. Therefore, increasing the reaction temperature will lead to the increasing of CO$_2$ byproducts and decreasing of the CH$_4$ production. Hence, it is important to choose a suitable temperature region for improving the catalytic activity. It is clear that from Fig. 1 the optimal temperature region for CO methanation reaction is 350-450 °C.

The textural properties of the catalysts are listed in Table 1. The

**Table 1. Surface area, pore volume, BJH pore size and NiO crys-
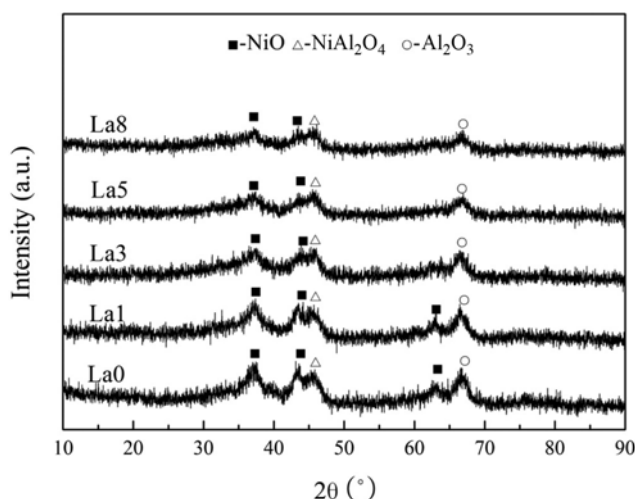talline size of samples**

Samples	Surface area (m^2/g)	Pore volume (cm^3/g)	BJH pore size (nm)	NiO particle size (nm)[a]
Al_2O_3	234.2	0.565	9.7	-
La0	164.5	0.349	9.8	15.7
La1	157.8	0.345	7.9	10.7
La3	159.0	0.289	5.6	9.3
La5	162.3	0.257	4.9	-
La8	148.3	0.239	5.6	-

[a]Calculated from Scherrer formula

**Table 2. H_2 uptake and Ni dispersion of catalyst by H_2 chemisorp-
tion**

Catalyst	H_2 uptake (mL/g)	Ni dispersion[a] (%)
La0	0.25	0.65
La1	0.27	0.69
La3	0.37	0.94
La5	0.30	0.77
La8	0.12	0.30

[a]Calculation formula of dispersion: D=Ni atoms on the catalyst/Total Ni atoms in the catalyst

Al_2O_3 support behaves as the largest surface area and pore volume. Then, the catalysts exhibit an evident drop when supported by La_2O_3 and NiO, which suggests that the pores of Al_2O_3 were filled and partly blocked by La_2O_3 and NiO particles during the preparation process. As for the catalysts promoted by lanthanum, as the La_2O_3 content increases, a decreasing trend of pore volume and BJH pore size is observed, assigned to the entering of the precursor into porous structure; however, they do not show any significant change with each other in the surface area.

Combined with the data of Fig. 1 and Table 1, it can be concluded that structural properties of catalysts such as surface area and pore structure parameters are not the key factors that affect the activity of catalysts. Such is in good agreement with the previous work, and their evaluation results showed that the surface area of catalysts is not directly related to their catalytic activity [18,19]. It is the chemical properties, rather than the physical properties, which mainly determine the catalytic performance of catalysts in the CO methanation.

The XRD patterns of the NiO-La_2O_3/Al_2O_3 catalysts are shown in Fig. 2. No characteristic peaks corresponding to lanthanum or its compounds are detected in the catalysts La1, La3, La5 and La8, indicating the lanthanum is highly dispersed on the catalysts. The characteristic peak of $NiAl_2O_4$ is observed in all catalysts suggesting its existence of strong metal-support interaction. It is evident

the NiO peaks are getting more diffuse with increasing La_2O_3 content. The NiO crystalline sizes of the catalysts are estimated by the Scherrer formula [7] according to the XRD patterns as shown in Table 1. NiO crystalline size of the catalyst La0 is 15.7 nm, while the crystalline sizes in the catalysts promoted by La_2O_3 are smaller. This suggests introducing La_2O_3 to the NiO/Al_2O_3 catalyst can restrain the growth of NiO crystalline size. It has been reported that the catalytic activity of Ni-based catalysts depends on the active crystalline size [8]. Therefore, adding La_2O_3 to the catalyst can make the NiO particles smaller, improving the catalytic performance for CO methanation.

Table 2 shows the results of H_2 uptake and Ni dispersion by H_2 chemisorption. As shown in Table 2, the catalyst La1 exhibits a significant improvement in H_2 uptake and Ni dispersion than La0, confirming the little amount addition of lanthanum plays a positive role in improving the catalytic performance of CO methanation. Considering the La_2O_3 content effects, H_2 uptake and Ni dispersion of the catalysts increase initially and then decrease with increasing La_2O_3 content. When the La_2O_3 content is as high as 3 wt%, the H_2 uptake and Ni dispersion reach the maximum, which are 0.37 mL/g and 0.94%, respectively, contributing to the highest catalytic activity.

According to the literature [9], the catalytic reaction mechanism of CO methanation is described as the following procedures. The carbon monoxide is first adsorbed on the Ni^0 atoms, subsequently producing carbon atoms by disproportionation reaction, which finally

Fig. 2. XRD profiles of the catalysts with different La_2O_3 content.
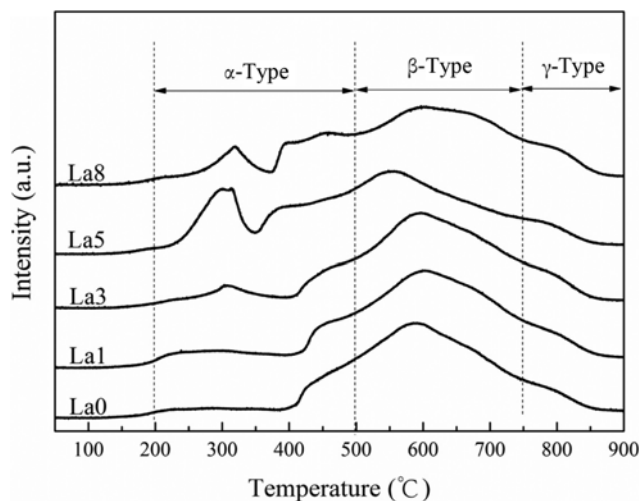
Fig. 3. TPR profiles of the catalysts with different La_2O_3 content.

react with the H atoms to form methane. Thus, the Ni particles with highly dispersed properties will favor the formation of more catalytic active sites. The La3 catalyst with superior H_2 uptake and Ni dispersion is capable of providing sufficient active sites for the catalytic reaction proceeding, exhibiting highest catalytic performance. The results indicate that the addition of a certain amount La_2O_3 to NiO/Al_2O_3 catalyst could promote the Ni dispersion of catalyst, thus providing more active sites and giving higher catalytic performance.

The TPR profiles of the catalysts with different La_2O_3 content are shown in Fig. 3. It has been reported there are three kinds of Ni species (α, β and γ) in Ni/Al_2O_3 catalysts. The α-type NiO species are activated in low-temperature region, with weak metal-support interaction. The β-type NiO species interact more strongly with support than α-type one and show reduction peak in mild-temperature region, and the β-type NiO species favors the catalytic reaction proceeding. The NiAl_2O_4 cannot be reduced until a high temperature of 750-900 °C, which is classified as the γ-type NiO [20,21].

All catalysts show the reduction peak in high-temperature region, indicating the presence of γ-type NiAl_2O_4, in good agreement with XRD results. The La1 exhibits similar TPR shape to La0 attributed to the low content. When the added La_2O_3 content is as high as 3 wt%, two reduction peaks corresponding to α-type temperature region are detected, which are also observed in the catalysts La5 and La8. The region of 410-500 °C may be assigned to the reduction of free NiO state particles. As for the new reduction peak which appears in the extremely low-temperature region, it may be attributed to the surface reduction of LaNiO₃. Since this phase is not observed by XRD, it should be mostly formed by amorphous and disordered particles. There are two controversies about the reduction steps of LaNiO₃. One hypothesis proposes two different processes of the reduction [22]. In the first one, an amorphous phase based on Ni²⁺ (NiO) reduces to Ni⁰ and in the high temperature reduction, LaNiO₃ reacts with the H_2 to form directly Ni⁰ over La_2O_3. Most of the authors [23-25] support another reason, where the reduction of LaNiO₃ is the only process but takes place in two steps. In the first one (low temperature), the Ni³⁺ in the perovskites reduces to a phase based in Ni²⁺. This step would be followed by a second reduction process at higher temperature, where the Ni²⁺ reduces to metallic Ni⁰. And this is also the case in our investigation. When the introduced La_2O_3 is more than 3 wt% (La3, La5 and La8), the La interacts with Ni and O, yielding Ni-O-La, in which the oxygen atoms are easily removed from the lattice of catalysts due to the unsymmetrical distribution of electron cloud in its surroundings, promoting the reducibility of the catalysts. This also interprets the diffuse NiO characterization peaks in XRD profiles and the low dispersion by H_2-chemisorption of La5 and La8; the former is due the existence of LaNiO₃, and the latter is due to the weak metal-support interaction. Then, the follow-up increasing of La_2O_3 content will lead to the increasing of α-type NiO, which is required for the high reducibility performance; however, it is at the cost of the decreasing of β-type NiO species. Only the La3 catalyst possesses more reducible β-type NiO species and intermediate metal-support interaction, having superior reducibility behavior.

As expected, the La3 catalyst, which has superior activity and selectivity, is observed under the reaction condition of P=1.5 MPa and GHSV=10,000 h⁻¹, with the optimal reaction temperature region of 350-450 °C. This is because the catalyst is able to produce more
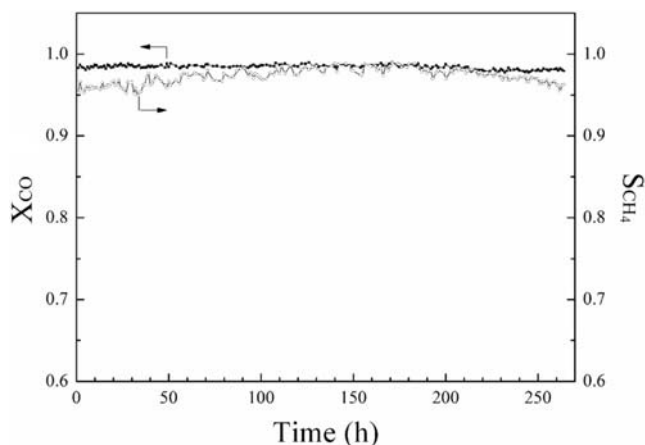

Fig. 4. Long-term test results of La3 catalyst for 264 h (Reaction conditions: T=400 °C, P=1.5 MPa, GHSV=10,000 h⁻¹, H_2 : CO : CH_4=0.6 : 0.22 : 0.14).

reducible β-type NiO particles on the surface with intermediate interaction with the support, which eventually generate relatively small-sized and highly dispersed active Ni particles after reduction, promoting the catalytic performance of catalysts.

2. Stability Test of the Catalyst

The lifetime performance of catalyst is a key consideration in the research and development of catalyst employed in the CO methanation reaction. As we know, the deposited carbon is often an intermediate product during the methanation reaction, which leads to the unsatisfied catalyst deactivation. Fig. 4 shows the stability results of La3 catalyst for 264 hours. The stability of the catalyst is tested on a fixed-bed reactor under the condition of T=400 °C, GHSV=10,000 h⁻¹, P=1.5 MPa. It is evident from Fig. 4 that during the 264 h long-term test, CO conversion remains constant at 98%; in the meantime, CH_4 selectivity shows a slight decrease from 98% to 96%. This indicates that La3 catalyst exhibits good stability in the 264 h long-term run without any distinct catalyst deactivation.

The amount of carbon deposition in La3 catalyst during the long-term reaction is approximately determined by thermogravimetric analysis. The TG analysis results of La3 catalyst after 264 h stability test (the sample weight is 3.76 mg) are shown in Fig. 5. There are
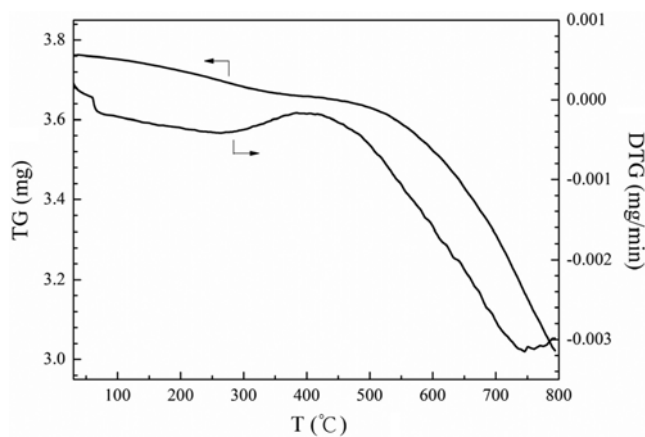

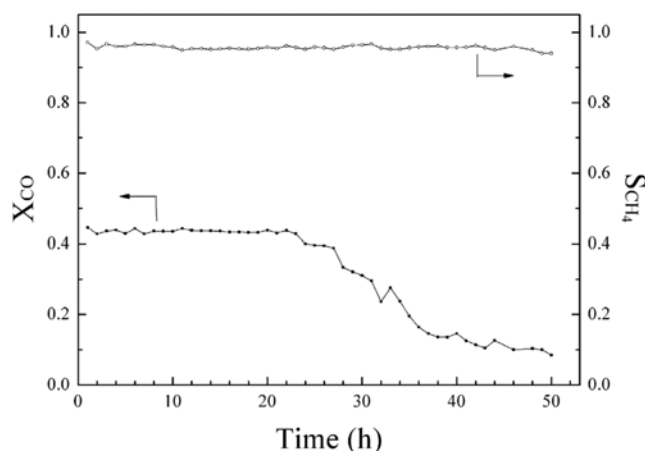Fig. 5. TG/DTG curve of La3 catalyst after 264 h reaction.

Fig. 6. Long-term test results of La0 catalyst (reaction conditions: T=400 °C, P=1.5 MPa, GHSV=10,000 h^{-1}, H$_2$: CO : CH$_4$= 0.6 : 0.22 : 0.14).

two significant weight loss regions in 200-400 °C and 400-800 °C, respectively. The carbon deposition in the region of 200-400 °C is 0.0991 mg with the carbon deposition percent of 2.63%; meanwhile, the values are 0.0643 mg and 17.1% in the region of 400-800 °C. According to the literature [26], the carbon deposition species in the range of 200-400 °C that correspond to surface carbon species formed in the CO disproportionation have catalytic activity and could be removed easily; while in the region of the 400-800 °C, the carbon species correspond to the graphite carbon that is difficult to be removed and can accumulate on the catalyst surface, resulting in covering the active sites and decreasing the activity of catalyst.

To compare and illustrate the promoted behavior of modified catalyst in stability performance, a long-term test is also carried out using La0 at 400 °C. It is evident from Fig. 6 that CH$_4$ selectivity remains constant at 95%; in the meantime, CO conversion shows a huge decrease from 43% to 8%. It is clear from Fig. 4 and Fig. 6 that, La3 shows both higher CH$_4$ yield and superior stability performance than La0 under the same reaction condition. Notably, the La0 displays a significant down trend as time goes.

These results indicate that La3 catalyst performs good stability with resistance to carbon formation. The high resistance to carbon formation of the catalysts may be attributed to the fine dispersion and high reducibility of active components, associated with the fact that the introduction of La$_2$O$_3$ increases the reducible β-type NiO particles with the appropriate metal-support interaction, and thus increases the catalytic active centers favoring the reaction proceeding. It would be more promising and practical to explore the application of the obtained La3 catalyst to realize the CO methanation reaction.

CONCLUSIONS

A series of La$_2$O$_3$ promoted Ni-based catalysts were prepared by impregnation method, and the effect of La$_2$O$_3$ on the catalysts for methanation reaction was investigated. The results showed that the addition of La$_2$O$_3$ as promoter to Ni-based catalyst can significantly enhance the catalytic activity for CO methanation. Under the conditions of T=400 °C, GHSV=10,000 h^{-1}, P=1.5 MPa, as La$_2$O$_3$

content increases, CH$_4$ yield increases and then changes slightly with further increasing La$_2$O$_3$ content. La3 catalyst with La$_2$O$_3$ content of 3 wt% has the best catalytic activity, with CO conversion of 98% and CH$_4$ selectivity of 96%. Moreover, the La3 catalyst is highly stable with little carbon deposit after the long-term test for 264 h. From the characterization analysis, the addition of La$_2$O$_3$ with a small amount inhibits the growth of NiO particles, favors the formation of highly dispersed active particles with appropriate metal-support interaction and reducibility performance, resulting in the high catalytic activity and excellent stability performance of catalyst. This work would, therefore, be important for developing highly efficient NiO-La$_2$O$_3$/Al$_2$O$_3$ catalyst with superior activity and excellent stability, and also provides scientific understanding of the CO methanation reaction.

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