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Glow Discharge Plasma-Assisted Preparation of Nickel-Based Catalyst for Carbon Dioxide Reforming of Methane

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A plasma-assisted method was employed to prepare Ni/γ-Al_2O_3 catalyst for carbon dioxide reforming of methane reaction. The novel catalyst possessed higher activity and better coke-suppression performance than those of the conventional calcination catalyst. To achieve the same CH_4 conversion, the conventional catalyst needed higher reaction temperature, about 50 °C higher than that of the N_2 plasma-treated catalyst. After the evaluation test, the deactivation rate of the novel catalyst was 1.7%, compared with 15.2% for the conventional catalyst. Different from the characterization results of the calcined catalyst, a smaller average pore diameter and a higher specific surface area were obtained for the plasma-treated catalyst. The variations of the reduction peak temperatures and areas indicated that the catalyst reducibility was promoted by plasma assistance. The dispersion of nickel was also remarkably improved, which was helpful for controlling the ensemble size of metal atoms on the catalyst surface. The modification effect of plasma-assisted preparation on the surface property of alumina supported catalyst was speculated to account for the concentration increase of absorbed CO_2. An enhancement of CO_2 adsorption was propitious to the inhibition of carbon formation. The coke amount deposited on plasma treated catalyst was much smaller than that on the conventional catalyst.

Key words: Nickel-based catalyst, Plasma, CO_2 reforming of CH_4, Coke, Adsorption of CO_2

I. INTRODUCTION

With carbon dioxide reforming of methane reaction, the two greenhouse gases can be catalytic transformed into synthesis gas, which is utilized in the Fisher-Tropsch synthesis to produce liquid hydrocarbons or in other systems of chemical energy transmission [1]. The Ni/γ-Al_2O_3 catalyst is found to exhibit promising catalytic activity for this reaction and is cheaper than noble metal catalysts. But the main problem which prevents this process from being used industrially is that supported Ni catalysts deactivate easily due to carbon deposition and/or metal sintering [2-5]. The coke formation is a structure-sensitive process. It depends on the surface Ni species, particle size, and electron density. The metal sintering is often caused by heat treatment with high temperature. It has been found that the preparation method, catalyst structure, and Ni dispersion exerted important influences on the catalytic activity of Ni in CH_4 reforming with CO_2 [6]. Various methods have been developed for the sake of improving catalyst performances and anti-coking [7,8].

Plasma consists of highly excited atoms, ions, electrons, radicals, and so on. As a novel molecule activation technology, it is effective in catalyst preparation.

Liu et al. concluded that the plasma enhanced preparation or plasma modification of catalysts had several advantages compared to conventional catalyst preparation, including: (i) a highly distributed active species; (ii) reduced energy requirements; (iii) enhanced catalyst activation, selectivity, and lifetime; (iv) shortened preparation time [9]. Because of these advantages, plasma assisted preparation of new catalysts has been introduced into many reactions [10-18]. Chu et al. reported better catalytic performances for the plasma-activated Fischer Tropsch cobalt catalyst [10]. Tang et al. discovered that the microstructure and surface functional groups of Vulcan XC-72 carbon black were significantly changed after plasma treatment, and that the new Pt/C catalyst using plasma treated carbon as support showed a promoted catalytic activity [11]. Liu et al. reported that a novel Pd/HZSM-5 catalyst with high activity and good stability was obtained by plasma for methane combustion [12]. Guo et al. investigated the effect of the plasma introduction mode on the catalytic performance of Ni/γ-Al_2O_3 catalysts for CO_2 methanation reaction [14]. The catalyst treated with plasma followed by reduction exhibited a high low-temperature activity. Zhao et al. found that argon glow discharge plasma could effectively reduce the Al_2O_3 supported Ir catalyst without the use of any conventional reducing chemicals [17]. An enhanced dispersion and high conversions was achieved on this catalyst for CO_2 reforming of CH_4. Liu et al. also reported that there were two techniques regarding plasma enhanced preparation or plasma modification of a catalyst: plasma heat

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treatment and plasma chemical modification [9]. The catalysts prepared by the plasma heat treatment were different from those calcined conventionally. The active plasma species would flow to, and physically or chemically react at, the catalyst surface [19]. Therefore, the effect of plasma chemical modification could not be ignored during the plasma heat treatment. Sugiyama *et al.* researched a plasma heat-treated Nb_2O_5 catalyst for the vapor-phase Beckmann rearrangement reaction [20]. The catalyst showed weakened acid strength and better selectivity. XPS characterization and catalyst color confirmed that the catalyst surface was modified.

In this work, compared with the conventional catalyst prepared by calcination thermally, a novel catalyst activated by N_2 glow discharge plasma was employed in CO_2 reforming of CH_4 reaction. The Ni-based catalysts were characterized by BET, H_2-Temperature-programmed reduction (TPR), X-ray powder diffraction (XRD), CO_2-Temperature-programmed desorption (TPD) and thermo-gravimetric analysis (TGA) techniques.

II. EXPERIMENTS

A. Sample preparation

The precursor of $10\%Ni/\gamma-Al_2O_3$ catalyst was prepared by impregnation and divided into two parts. One part was calcined in air at 550 °C for 300 min and labeled NA-C. The other part was put into the discharging tube and activated by N_2 glow discharge plasma. The plasma generator was GP06-DL3 type coupled with a high-frequency plasma generator. The discharge parameters were as follows: frequency 13.56 MHz, discharge voltage 100 V, anodic current 100 mA, total treatment time 120 min and a vacuum between 2 and 200 Pa. The novel catalyst prepared by this way was labeled NA-P.

B. Characterization

The H_2-TPR experiment was conducted in a fixed-bed reactor. The catalyst was reduced with 4.2% H_2/N_2 at a flow rate of 30 mL/min. The temperature was raised to 800 °C at a rate of 10 °C/min.

The specific surface area of catalyst was determined by N_2 adsorption experiment at −196 °C on a Quantachrome NOVA 1000e apparatus. Before each measurement, the sample was degassed in vacuum at 300 °C for 180 min. The specific surface area was calculated using the BET method while the pore size distribution was obtained from the adsorption isotherm by the BJH method.

The XRD pattern was recorded on a DX-2000 diffractometer using Cu Kα (λ=1.54056 Å) radiation between 15° and 90°. The voltage and anode current were 40 kV and 30 mA, respectively.

The amount of carbon deposited on the catalyst was determined by TGA analysis. With a TGA Q500 apparatus, the TGA analysis was performed in flowing air from room temperature to 800 °C at a heating rate of 10 °C/min.

The TPD experiment of CO_2 was carried out in a fixed-bed reactor equipped with an on-line mass spectrometer using the following steps: each catalyst was first reduced at 700 °C in H_2 for 60 min, then cooled to room temperature and exposed to CO_2 for 30 min. After being purged by Ar, the catalyst was heated linearly to 650 °C at the rate of 10 °C/min. Amounts of CO_2 (m/e=44) in effluent were measured by mass spectrometer and recorded as functions of temperature.

C. Catalytic performance test

The catalytic evaluation tests were carried out in a continuous quartz micro-reactor under 700 °C with a mixture gas of CH_4 and CO_2. The molar ratio of CH_4 to CO_2 was 1:1 and GHSV was 35 L/(g-cat·h). Prior to each reaction, the catalyst was reduced *in-situ* at 700 °C for 60 min in H_2 flow. The outlet products were analyzed by a gas chromatograph (GC1690) using the thermal conduct detector.

III. RESULTS AND DISCUSSION

Table I presents the activities of Ni-based catalysts. The results indicate that the plasma-treated catalyst had higher activity than that of the conventional catalyst calcined at high temperature. The initial conversions of CH_4 and CO_2 over the NA-P catalyst were 68.4% and 80.0%, respectively, which were more than 13% higher each compared to those over the NA-C catalyst. After the 360 min experiment, the final CH_4 conversion of the NA-C catalyst decreased to 51.2%, while that of the NA-P catalyst was 67.2%. The CO yield of the NA-P catalyst was 68.0%, which was 1.25 times higher than that of the NA-C catalyst. The deactivation rate of the NA-P catalyst was 1.7%, compared with 15.2% for the NA-C catalyst. It is apparent that the N_2 plasma treated catalyst possessed better stability.

The reforming of CH_4 is highly endothermic; hence the increase in temperature facilitates to increase the conversions of CH_4 and CO_2. Figure 1 shows the catalytic performances of two typical catalysts at different temperatures. With the reaction temperature varying from 550 °C to 700 °C, the conversions of feed gases over the novel NA-P catalyst were always higher than those over the NA-C catalyst. To achieve the same CH_4 conversion, the conventional catalyst needed higher reaction temperature, about 50 °C higher than that of the plasma-treated catalyst. For example, CH_4 conver-

TABLE I Activities of Ni based catalysts for carbon dioxide reforming of methane.

Catalyst	Initial conversion[a]/%		Final conversion[b]/%		Yield of CO[b]/%	H_2/CO[b]	Deactivation rate[c]/%
	CH_4	CO_2	CH_4	CO_2			
NA-C	60.4	70.7	51.2	60.0	54.3	1.04	15.2
NA-P	68.4	80.0	67.2	81.5	68.0	1.07	1.7

[a] Initial conversion: measured at l0 min on stream.
[b] Final conversion: measured at 360 min on stream.
[c] Defined as (initial CH_4 conversion−final CH_4 conversion)/initial CH_4 conversion.
Reaction conditions: Ni content 10 wt%; catalyst mass 100 mg, T=700 °C; GHSV=35 L/(g-cat·h), CH_4:CO_2=1:1, P=101.3 kPa.
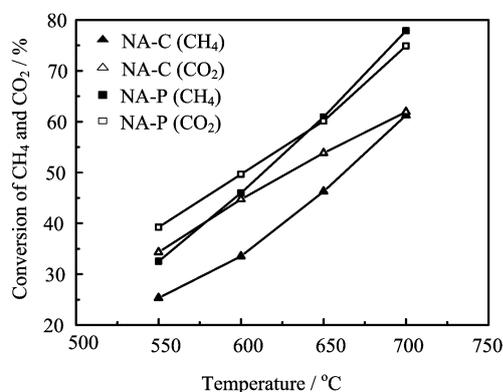

FIG. 1 CH_4 and CO_2 conversions over Ni/γ-Al_2O_3 samples at different temperatures reaction conditions: the same as Table I.

sion over the NA-P catalyst was 60.9% at 650 °C, and that over the NA-C catalyst could reach 61.2% only at 700 °C. It was known that the CO_2 reforming of CH_4 reaction was always carried out at high temperature, but high-energy input might induce an extra CO_2 emission for energy generation in industrial application. Consequently, it is desirable to operate the reaction at lower temperatures. As expected, the plasma technique significantly enhanced the low-temperature activity of Ni-based catalyst in this reaction.

The N_2 adsorption-desorption isotherms and pore size distributions of the fresh NA-C and NA-P catalysts are illustrated in Fig.2. The isotherms of two catalysts can be classified as Langmuir IV type according to the IUPAC classification, which is a typical feature of meso-porous material. The relative pressure range in which characteristic capillary condensation occurred was shifted from P/P_0=0.6-0.9 for NA-C to P/P_0=0.4-0.8 for NA-P. The phenomenon indicates that the plasma treatment decreased the pore diameter size. The average pore diameter from 10.91 nm for the NA-C sample shifted to a smaller one of 7.86 nm for the NA-P catalyst. Furthermore, the specific surface area increased from 144.8 m^2/g of the conventional NA-C to 184.2 m^2/g of NA-P catalyst. Ref.[21] had suggested that the higher surface area of catalyst influenced the reaction activity in two ways: (i) highly-dispersed ac-
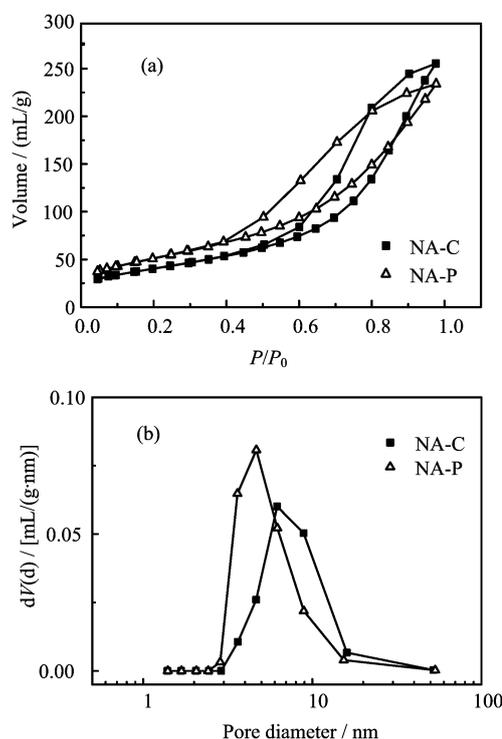

FIG. 2 N_2 adsorption-desorption isotherms (a) and pore size distributions (b) of the fresh NA-C and NA-P catalysts.

tive sites were formed; (ii) accessibility of reactants to active sites was high and thus resulted in high reactivity. Hou *et al.* reported that the reforming activity increased with the surface area of the catalysts and decreased with the Ni particle size, while the coke formation rate decreased with the surface area and increased with the Ni particle size [6]. In this work, a smaller average pore diameter and a higher specific surface area were obtained by the plasma treatment, which was a benefit for the good performance of the NA-P catalyst.

The H_2-TPR profiles of the NA-C and NA-P catalysts are depicted in Fig.3. The NA-C and NA-P catalysts exhibited two reduction peaks. The first peak with a lower reduction temperature of the conventional catalyst represented the reduction of NiO, and the second peak with high reduction temperature corresponded to
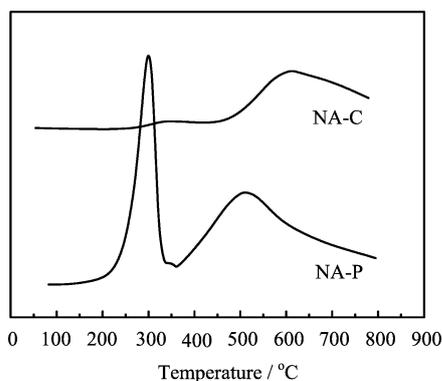

FIG. 3 H$_2$-TPR profiles of the NA-C and NA-P catalysts.

FIG. 4 XRD spectra of the reduced NA-C (a) and NA-P (b) catalysts.

the reduction of NiAl$_2$O$_4$ [22]. Compared with the reduction behaviors of NA-C catalyst, the reduction temperatures of NA-P catalyst were systematically shifted to lower regions. The reduction temperatures of the two peaks decreased about 45 and 95 °C, respectively. Moreover, the peak areas were bigger than those of the NA-C catalyst.

Zou *et al.* reported that the cold plasmas were often used to dissociate relatively unreactive chemicals into reducing agents or accelerate the transformation of chemicals to reducing agents, thus shortening the reduction time [23]. The glow discharge plasma is one kind of cold plasma. The variations of the reduction peak temperatures and areas indicate that the catalyst reducibility was improved by plasma treatment. This meant that more active species could be reduced easily to form reaction sites.

XRD measurements were made for catalysts reduced at 700 °C for 60 min. According to the XRD results of reduced NA-C and NA-P catalysts (shown in Fig.4), the diffraction peaks of nickel over NA-P catalyst were much broader and weaker than those over NA-C catalyst. This suggests that the Ni particle size over NA-P catalyst was smaller than that over NA-C catalyst and an enhanced dispersion was achieved by the plasma treatment. Refs.[12,16,24,25] additionally verified a remarkable improvement of the dispersion on plasma treated catalysts by means of XRD. Cheng *et al.* studied the XRD patterns of the support Al$_2$O$_3$ and fresh plasma treated Ni/Al$_2$O$_3$ catalyst [16]. They could not identify any peaks of nickel species including Ni and NiO from the XRD pattern of plasma treated sample, even with a 9% nickel loading on the support. This implies that nickel particles were highly dispersed on the alumina support. The plasma-assisted preparation could avoid destroying catalyst structure and sintering of active metal that occurred in conventional calcination thermally [9]. As a result, the transference and aggregation of nickel on the catalyst surface were reduced. Theoretically, the ensemble size necessary for carbon formation was larger than the ensemble size for CH$_4$ reforming. One effect of plasma treatment was the
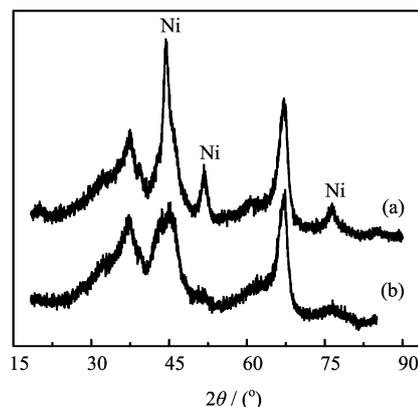
control of metal ensemble size on nickel surfaces. The catalyst with highly dispersed Ni possessed a higher reforming activity and was less sensitive for coke deposition [26].

The concentration of CO$_2$ on the catalyst surface plays an important role in maintaining the catalytic activity for CO$_2$ reforming of CH$_4$ reaction. CO$_2$-TPD experiments were carried out with an on-line mass spectrometer. In Fig.5, the TPD pattern of NA-P catalyst shows two desorption peaks of CO$_2$. The total peak area of NA-P catalyst was bigger than that of NA-C catalyst. This indicates that the plasma treatment increased the adsorption sites for CO$_2$ gas and amount of absorbed CO$_2$ on the catalyst surface. Increasing the concentration of absorbed CO$_2$ would provide more oxygen species on the surface of the catalyst, which was propitious to the inhibition of carbon formation. Alternatively, it could remove intermediate carbonaceous species before they were transformed into inactive carbon species [27]. When the surface area of catalysts increased or the Ni particle size decreased, the absorbed amount of CO$_2$ could be augmented [6]. The results of BET and XRD of NA-P catalyst gave the confirmation. In general, the adsorption and dissociation of CO$_2$ can be promoted by basic catalysts, because CO$_2$ is an acidic gas [28,29]. The explanation for an enhancement of CO$_2$ adsorption on NA-P catalyst was that the plasma treatment could modify the basicity of alumina-supported catalyst. Ref.[30] demonstrated that the plasma was powerful in generating and redistributing the basic sites which were critical to reaction activity and selectivity. It gave the CO$_2$-TPD results of calcined and O$_2$-plasma-treated 1%Pt/Al$_2$O$_3$. O$_2$ plasma generated both strong and medium CO$_2$ adsorption sites.

The carbon deposition, metal sintering and reoxidation of Ni can lead to catalyst deactivation. In particular, the first one is the main cause. Carbon deposition originates mainly from excessive dehydrogenation of methane and Boudouard reaction. The TGA exper-
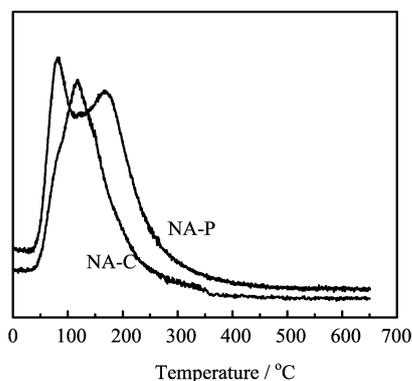
FIG. 5 TPD-MS profiles of CO_2 over NA-C and NA-P catalysts (m/e=44).

iment results of the used catalysts presented a weight loss due to the removal of deposited carbon. Zhang *et al.* reported that three kinds of carbonaceous species formed on the Ni/Al_2O_3 catalyst upon TGA analysis [31]. They were designated as C_α (at 150-220 °C), C_β (at 530-600 °C) and C_γ (at >650 °C). Cheng *et al.* gave an example of the TGA analyses of used catalyst obtained with reaction temperature of 650 °C [16]. There were only C_α and C_β carbonaceous species on the used plasma-treated catalyst. In this work, the used NA-C catalyst presented a similar TGA result to the above example (Fig.6). Two peaks were observed on the DTG curve with weight losses of 6.54% and 11.59%, respectively. However, the DTG curve of the used NA-P catalyst exhibited different peak features compared with that of the used NA-C catalyst. The total weight loss over the NA-P catalyst was 9.0%, which was half of that over the NA-C catalyst. This result agrees well with the experimental data of deactivation rate (listed in Table I). According to thermodynamic calculations, high temperature operation above 870 °C was needed to prevent carbon deposition when the feed gas ratio of CH_4 to CO_2 was 1 and the total pressure was 101.3 kPa [32]. In this work, although the reaction conditions were severe in terms of carbon deposition, the total coke amount formed on the NA-P catalyst was much smaller than that on the used NA-C catalyst. The plasma treatment could remarkably promote the coke-suppression performance of nickel catalyst.

IV. CONCLUSION

In conclusion, the N_2 glow discharge plasma-assisted preparation promoted the catalytic activity of the Ni/γ-Al_2O_3 catalyst and inhibited the coke formation in carbon dioxide reforming of methane reaction. The plasma treatment was responsible for the increased specific surface area and the enhanced adsorption of CO_2. The dispersion of nickel and catalyst reducibility were remarkably improved.
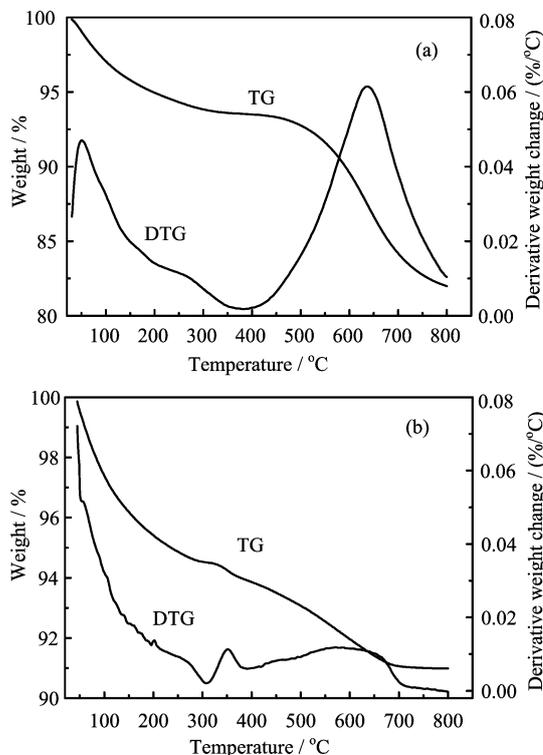

FIG. 6 TGA profiles of NA-C (a) and NA-P (b) catalysts after reaction at 700 °C for 360 min.

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