Plasma treatment of Ni catalyst via a corona discharge

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Abstract

In this paper, plasma treatment of Ni catalyst for partial oxidation of methane to syngas was investigated by using plate–plate discharge model via a corona discharge by flowing argon under atmospheric pressure and room temperature. The catalytic activity and stability for partial oxidation of methane (POM) process were measured for the catalyst before and after plasma treatment. It was found that after plasma treatment, methane conversion increased 5–10% and the syngas selectivity kept the same as before treatment. Also, these catalysts were characterized by thermogravimetric analysis and XPS measurement. It was found that the argon plasma treatment can improve the catalytic stability by preventing the carbon deposition on the Ni catalyst.
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1. Introduction

The catalytic partial oxidation of methane is an attractive way to produce syngas. Of the reported catalysts, a supported Ni catalyst is a promising catalyst for partial oxidation of methane (POM) process since it has a high activity and a low price [1–4]. However, the catalytic stability of Ni catalysts is not so desirable and the catalyst deactivates with time by the carbon deposition, the nickel sintering and loss, and by the phase transformation, which limits its further industrial application. In the past years, many researchers managed to improve the catalytic stability of Ni catalyst by addition of promoters to Ni catalyst or modifying the catalyst preparation method [5–8] but no breakthrough was obtained.

The field of materials surface modification by cold plasma treatment has been used in the surface modification of polymers, for which there now exist numerous industrial applications. So, using plasma to treat catalyst surface to improve catalytic activity and stability is considered reasonable. In this paper, plasma treatment of Ni catalyst for POM to syngas was investigated by using plate–plate discharge model via a corona discharge by flowing Ar.

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2. Experimental

2.1. Catalyst preparation

The catalyst was prepared by an impregnation method. The required amount of Ni(NO$_3$)$_2$·6H$_2$O was slowly added to the support (diameter of 3–5 mm) to obtain the catalyst. After impregnation, the sample was dried at 120 °C for 2 h and calcined at 400 °C for 4 h, and then calcined at 800 °C for 8 h. Finally, the sample was reduced at 500 or 800 °C by hydrogen for 2 h.

2.2. Plasma treatment

The plasma treat experiment of Ni catalyst for partial oxidation of methane to syngas was carried out in a continuous system by using plate–plate ac discharge model under atmospheric pressure and room temperature by flowing argon. The breakdown voltage for Ar corona was 20 kV and the discharge voltage is 40 kV for plasma treatment. The flow rate of Ar is 20 ml/min. The plates were inserted into a quartz tube with inner diameter of 14 mm. The distance between the two plates was 30 mm. Each time 3.0 g catalyst was treated for 4 min by plasma technique.

2.3. Catalyst evaluation

A quartz tube of dimension of 5 mm o.d. × 3 mm i.d. × 300 mm length was used as a reactor. The catalyst amounts were 60 mg. The reaction temperature was 800 °C and the space velocity was $1.0 \times 10^5\,h^{-1}$ with the mole ratio of CH_4:O_2:N_2 as 2:1:1. High purity Ar was used as the carrier gas for GC analysis of the inlet and outlet gas mixtures. The conversion and selectivity were calculated from the GC analysis results based on 100% C, H, O, and N mass balance.

2.4. TPR, TPO measurement and chemisorption

Temperature programmed reduction (TPR) experiments were performed using an automatic TPR/TPD 2910 adsorption instrument by passing 10 vol.% H_2/Ar mixed gas with a flow rate of 20 ml/min. Temperature programmed oxidation (TPO) experiment was performed by passing 5 vol.% O_2/He mixed gas with a flow rate of 20 ml/min. The amount of catalysts used was 100 mg and the temperature was increased at a rate of 10 °C/min to 900 °C.

H_2 chemisorption on reduced Ni catalyst was measured by titration 5% H_2/Ar mixed gas. The Ni dispersion on the support can be calculated from H_2 chemisorption amount.

2.5. Thermogravimetric (TG) analysis

Thermogravimetric experiments were carried out in a TA-50 thermal analysis system. The experiment was conducted using N_2 gas (99.99%) and air (99.99%) at flow rates of 20 and 30 ml/min, respectively. Samples (about 20 mg) were loaded into the thermobalance and heated to 800 °C at a controlled heating rate of 10 °C/min until a constant weight was achieved. The weight loss rate was recorded simultaneously.

2.6. XPS characterization

XPS analyses employed a multi-pass analyzer (PHI 1600) with pass energy of 188 eV for survey spectra and 29 eV for high-resolution spectra. X-rays were generated using a Mg Kα X-ray source.

2.7. XRD measurement

XRD measurement was done using D/max-2500 XRD instrument. X-ray source was Cu Kα. The voltage is 50 kV and the electric current is 200 mA. The scanning rate is 4–8°/min and the scanning range is $2\theta = 3$–80°.

3. Results and discussion

3.1. Catalytic performance

The catalytic activity of Ni catalyst after Ar plasma treatment was measured and shown in Figs. 1 and 2. It was found that the methane conversion increased after plasma treatment while the CO selectivity kept the same value as before treatment. In order to know what change occurred on the Ni catalyst surface after plasma treatment, a series characterization were made and discussed in the following parts.

3.2. XRD results

XRD measurement for three catalysts before and after Ar plasma treatment were shown in Fig. 3. It can be seen that the XRD spectra after plasma treatment is nearly same as before plasma treatment. No apparent change was observed from XRD results. The reason is that during the plasma treatment the temperature is kept about room temperature, which could not result in the crystal change of the catalyst.

3.3. TPR, TPO results and H_2 chemisorption

TPR and TPO profile shown in Fig. 4 proved that the oxidative and reductive performance of the catalyst has little change after Ar plasma treatment. Table 1 shows that after Ar plasma treatment, H_2 chemisorption amount and Ni dispersion increased, which is one of the reasons result in the
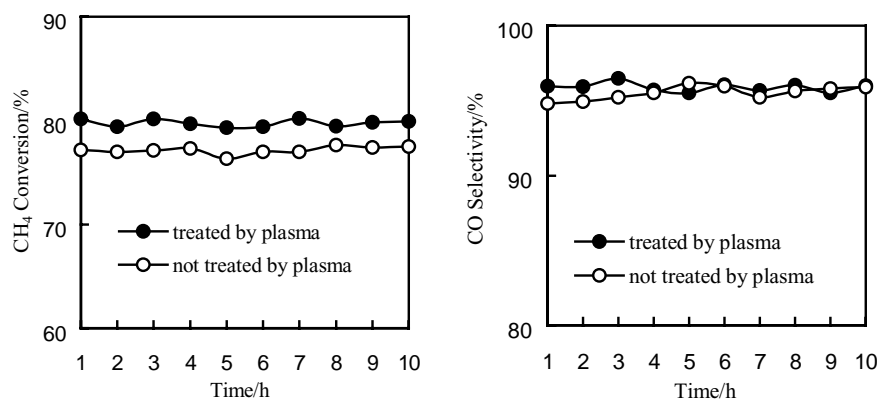

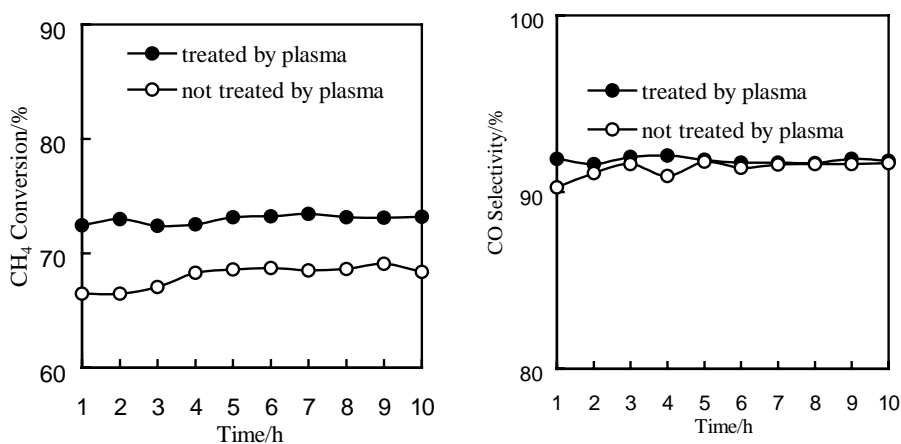Fig. 1. Methane conversion and CO selectivity on 10% Ni/pellet γ-Al_2O_3 catalyst.

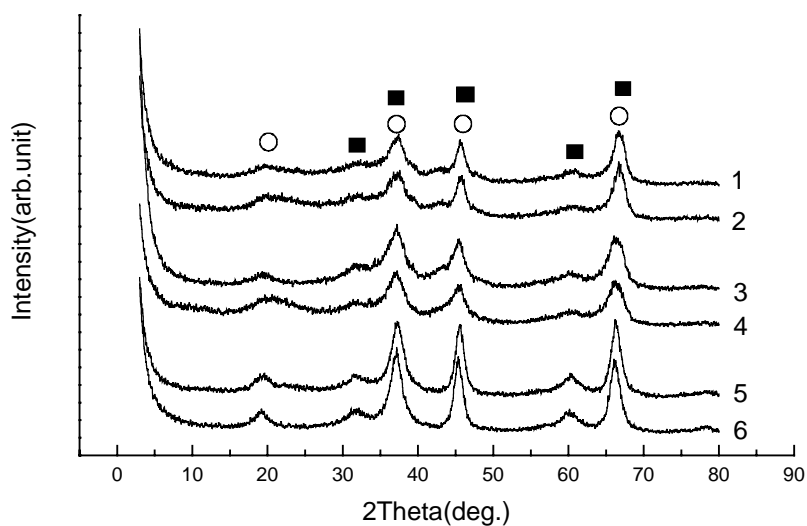Fig. 2. Methane conversion and CO selectivity on 5% Ni/pellet γ-Al$_2$O$_3$ catalyst.

Fig. 3. XRD spectra of Ni/γ-Al$_2$O$_3$ catalyst before and after Ar plasma treatment: ($\blacksquare$) NiAl$_2$O$_4$; ($\bigcirc$) γ-Al$_2$O$_3$; (1) 5% Ni/pellet γ-Al$_2$O$_3$ not treated by plasma; (2) 5% Ni/pellet γ-Al$_2$O$_3$ treated by plasma; (3) 10% Ni/pellet γ-Al$_2$O$_3$ not treated by plasma; (4) 10% Ni/pellet γ-Al$_2$O$_3$ treated by plasma; (5) 10% Ni/powder γ-Al$_2$O$_3$ not treated by plasma; (6) 10% Ni/powder γ-Al$_2$O$_3$ treated by plasma.

increase of methane conversion. Also, the increase of Ni dispersion may be beneficial for the catalytic stability, which was further proved by TG results.

3.4. Carbon deposition by TG results

The weight loss data for different catalysts after the POM reaction are listed in Table 2. It can be seen that the

carbon deposition decreased after the catalyst was treated by Ar plasma. Fig. 5 shows the weight loss rate of 10% Ni/γ-Al$_2$O$_3$ catalysts after POM reaction. After plasma treatment, the 10% Ni/γ-Al$_2$O$_3$ catalyst showed a lower and narrower temperature peak. Other catalysts showed the similar results. These results proved that the plasma treatment is beneficial for preventing the carbon deposition on the Ni catalyst.

Table 1
Chemisorption of H$_2$ and Ni dispersion

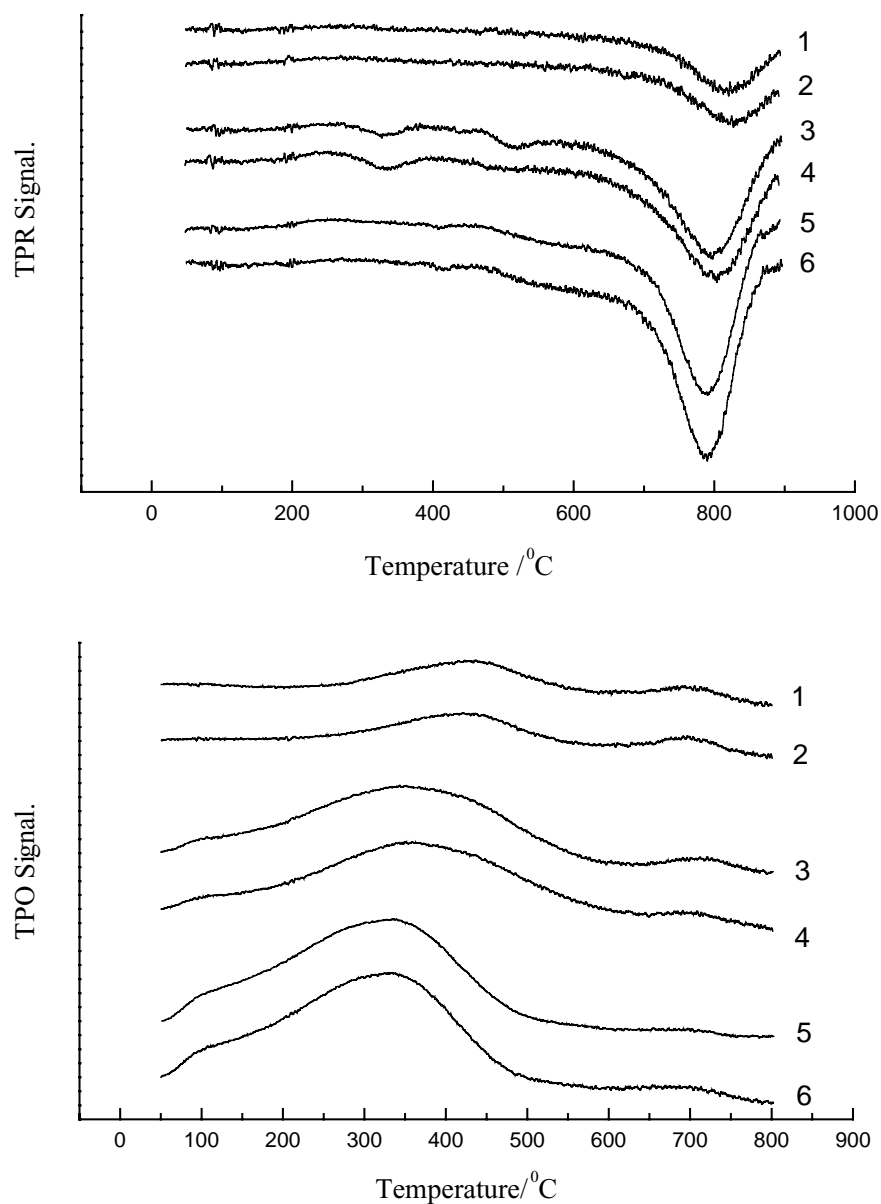| Catalyst	H$_2$ chemisorption (ml/g)		Ni dispersion (%)	
	Not treated by plasma	Treated by Ar plasma	Not treated by plasma	Treated by Ar plasma
10% Ni/powder γ-Al$_2$O$_3$	0.070	0.108	0.3676	0.5664
10% Ni/pellet γ-Al$_2$O$_3$	0.078	0.129	0.4112	0.6770
5% Ni/pellet γ-Al$_2$O$_3$	0.063	0.112	0.6628	1.1756

Fig. 4. TPR and TPO profile of catalyst before and after Ar plasma treatment: (1) 5% Ni/pellet γ-Al$_2$O$_3$ not treated by plasma; (2) 5% Ni/pellet γ-Al$_2$O$_3$ treated by plasma; (3) 10% Ni/pellet γ-Al$_2$O$_3$ not treated by plasma; (4) 10% Ni/pellet γ-Al$_2$O$_3$ treated by plasma; (5) 10% Ni/powder γ-Al$_2$O$_3$ not treated by plasma; (6) 10% Ni/powder γ-Al$_2$O$_3$ treated by plasma.

3.5. The surface modification

Fig. 6 shows the comparison of high-resolution XPS spectra of Ni 2p before and after Ar plasma treatment. It can be seen that the Ni^0 increased after Ar plasma treatment. Since the reduced Ni is the active site for POM reaction, it is obvious that Ni^0 increase on the surface results in the catalytic activity increase.

Table 2
TG analysis results—carbon deposition on catalysts after POM reaction

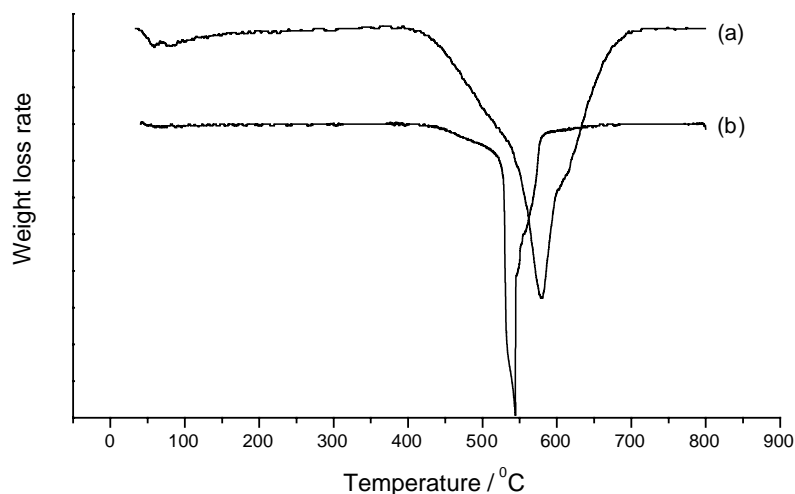|	Catalyst					
	10% Ni/powder γ-Al$_2$O$_3$		10% Ni/pellet γ-Al$_2$O$_3$		5% Ni/pellet γ-Al$_2$O$_3$	
	Non-treated	After plasma treatment	Non-treated	After plasma treatment	Non-treated	After plasma treatment
Carbon deposition (%)	22.06	11.21	32.07	14.42	9.24	5.23

Fig. 5. Weight loss rate profile of the sample: (a) 10% Ni/pellet γ-Al$_2$O$_3$ not treated by plasma; (b) 10% Ni/pellet γ-Al$_2$O$_3$ treated by plasma.
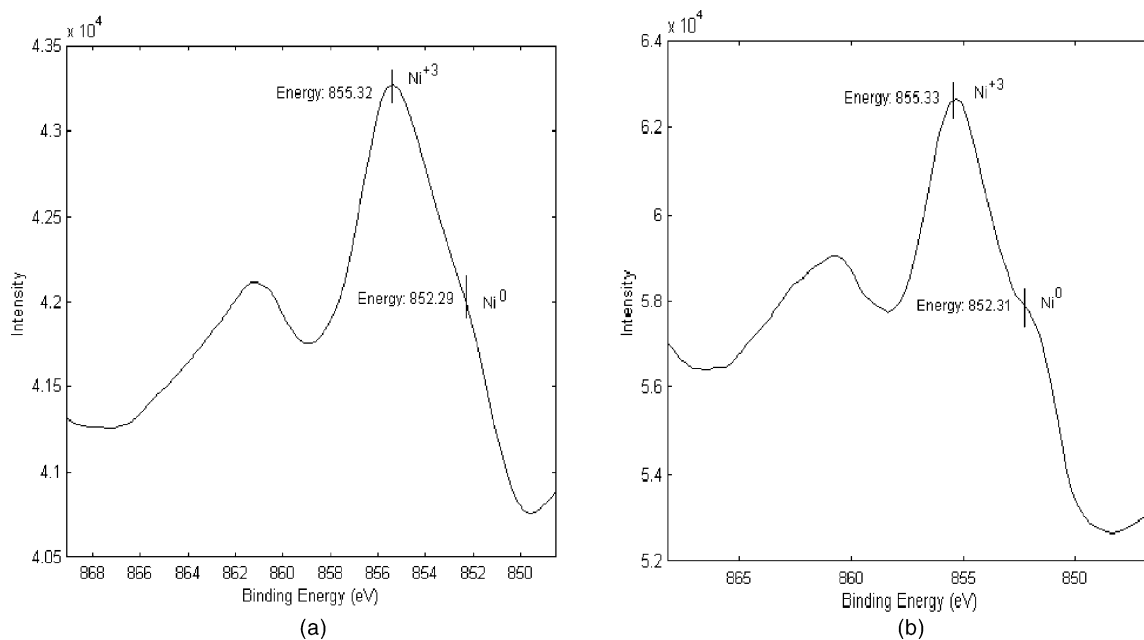

Fig. 6. High-resolution XPS Ni 2p spectra on 10% Ni/pellet γ-Al$_2$O$_3$: (a) before treatment; (b) after Ar plasma treatment.

4. Conclusion

Ar plasma treatment can increase the catalytic activity of Ni catalyst and the Ni dispersion. Also, the plasma treatment improved the catalytic stability by preventing carbon deposition on the Ni catalyst.

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