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Reduction of Pd/HZSM-5 Using Oxygen Glow Discharge Plasma for a Highly Durable Catalyst Preparation

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Abstract Pd/HZSM-5 catalyst prepared via glow discharge plasma reduction followed by calcination thermally showed enhanced stability for methane combustion. In order to investigate the plasma catalyst preparation mechanism, oxygen glow discharge, initiated at room temperature, has been employed for reduction of Pd/HZSM-5 catalyst. The catalyst characterization using XRD and XPS analyses demonstrates that oxygen glow discharge plasma is also able to reduce Pd/HZSM-5 catalyst. This suggests that the electronic effect plays an important role in the treatment of catalyst using glow discharge. This also confirms that the thermal effect of the glow discharge reduction can be ignored. A highly durable catalyst for methane combustion has been obtained from calcination of the glow discharge reduced sample.

Keywords Pd/HZSM-5 · Glow discharge · Oxygen plasma · Methane combustion

1 Introduction

The catalytic combustion of methane has been considered as one of the major techniques for reducing NO_x emission and also for the complete oxidation of unburned methane effluents of natural gas fueled vehicles. Palladium supported catalysts, esp., the zeolite supported catalysts, have been found to be the most active catalyst for the catalytic combustion of methane [1–9]. However, the low temperature activity and stability of the developed palladium catalysts still need to be further improved. Most reported improvements were conducted using promoter elements [3, 4, 6, 8]. Previously Liu et al. [7] reported that glow discharge plasma reduction followed by calcinations thermally significantly improves the low-temperature activity and stability of Pd catalysts. Argon was previously used as the plasma forming gas. During the plasma catalyst treatment, Pd species was first reduced into metallic Pd species by argon plasmas [7, 10, 11]. A highly dispersed Pd catalyst was then obtained after further calcination thermally [7]. A temperature measurement of plasmas has also been conducted using IR imaging, which confirms that the temperature of catalyst powder during glow discharge plasma treatment remains around the room temperature. This means no thermal effect on catalyst during glow discharge reduction. Only electronic effect needs to be considered. It is reasonable to think that, if oxidative gas, like oxygen, is used as the plasma forming gas, it would be an excellent way to evaluate the electronic mechanism of the plasma catalyst treatment at room temperature. Therefore, in this work, we attempt to reduce Pd/HZSM-5 catalyst using oxygen glow discharge plasma. A plasma reduction of catalyst is indeed observed. The further calcination of this oxygen plasma reduced catalyst leads to a highly stable catalyst too for methane combustion.

2 Experimental

2.1 Catalyst Preparation

The preparation of Pd/HZSM-5 catalyst includes the following steps: impregnation, glow discharge reduction

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using oxygen glow discharge and thermal calcination. The procedure is the same as the method reported previously [7, 10, 11]. The HZSM-5 powder (SiO_2/Al_2O_3 = 50, purchased from the Catalyst Plant of Nankai University, Tianjin, China) is first impregnated with an aqueous solution of $PdCl_2$ and hydrochloric acid over night, and then dried at 50 °C for 4 h. The amount of Pd-loading was 0.5, 1 and 2 wt.%. After that, the glow discharge reduction is conducted. During the glow discharge reduction, the Pd/HZSM-5 sample is held in a discharge tube with one electrode connected to a DC high-voltage generator (made in Tianjin Cutting and Welding Setup Inc. Ltd., China; alternatively, a TREK 20/20C high-voltage amplifier with HP 33120A signal generator can also be applied). The catalyst powder is located at the region of "positive column" of glow discharge. Before the generation of the discharge, the system is evacuated to 100–200 Pa. The plasma reduction time is ranged from 30 min to 60 min. The plasma reduced Pd/HZSM-5 sample is then calcined under air at 500 °C for another 4 h.

2.2 Reaction and Analysis

The catalytic reactions were performed using a quartz tube reactor (I.D. 4 mm) at atmospheric pressure. The loading amount of the catalyst is 220 mg. The gaseous mixture of methane (1.46 vol.%) and oxygen (5.96 vol.%) in argon (GHSV = 36000 h^{-1}) is fed through the reactor. Before reaction, pure argon (20 mL/min) flows through the catalyst bed at a temperature-increasing rate of 5 °C/min until the temperature reaches 300 °C. Then the feed gas is fed through the catalyst bed. The methane conversion is measured as the function of temperature from 300 °C to 500 °C. An on-line GC (Agilent 4890D) equipped with a Paropak Q column was applied for the analyses of the contents of the feed and effluent gases. T_{10}, T_{50} and T_{90} are the reaction temperature when methane conversion reached 10, 50 and 90%, respectively.

2.3 Characterization of Catalyst

XRD characterization was conducted using a Rigaku D/max-2500 diffractometer with Cu Kα radiation. XPS analysis was performed using a PHI1600 XPS system operated at 1.2×10^{-8} Torr under Mg Kα radiation. The binding energy of C_{1s} (284.5 eV) was taken as internal standard for binding energy calibration. The gas temperature of the O_2 plasma during the catalyst treatment is measured by infrared imaging (Ircon, 100PHT).

3 Results and Discussion

Figure 1 exhibits the XRD patterns of the oxygen plasma reduced Pd/HZSM-5 sample and the calcined plasma-reduced catalyst. Evidently, the patterns of the plasma reduced sample present a big peak at near $2\theta = 40°$ that is attributed to the metallic Pd species. The size of the metallic Pd particles is around 4 nm. This means that, even using oxygen plasma, the metal ion can be reduced during glow discharge plasma treatment. This suggests that the electronic effect plays a very important role in the glow discharge plasma treatment of catalyst. Similar to the catalyst treatment using argon plasma, the present investigation confirms again the reduction mechanism of glow discharge treatment preparation. The oxidative effect of oxygen is obviously inhibited under the present glow discharge environment. Since the metal can be oxidized at high temperatures, the observed plasma reduction suggests that the oxygen glow discharge applied in this work would be operated at low temperature. Figure 2 presents IR thermal images to show the gas temperature of the oxygen glow discharge plasma during catalyst treatment. Obviously, the gas temperature is below 25 °C. Under this condition, oxidation is not controlling reaction. The reduction by electrons is the major reaction for the catalyst treatment.

XPS analysis has also been performed in order to make sure the plasma reduction mechanism with oxygen plasma. XPS analysis can give us the information of catalyst surface. Figure 3 exhibits the XPS spectra of Pd_{3d} of the plasma treated sample, calcined catalyst and used catalyst. Two peaks are observed over the plasma reduced sample. The peak with a binding energy of 335.4 eV can be attributed to metallic phase Pd, while the peak with a binding energy of

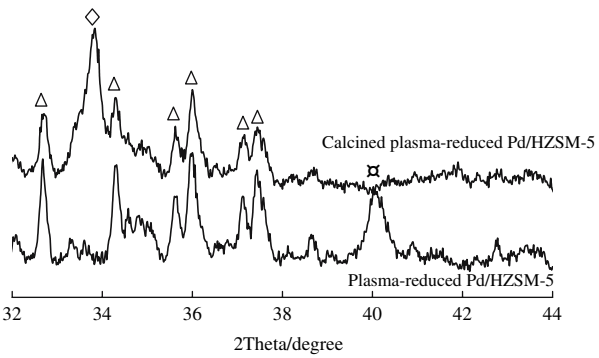

Fig. 1 XRD patterns of plasma reduced Pd/HZSM-5 and calcined plasma-reduced Pd/HZSM-5. (Δ: HZSM-5; ◇: PdO; ¤: Pd; Pd loading: 1 wt.%)

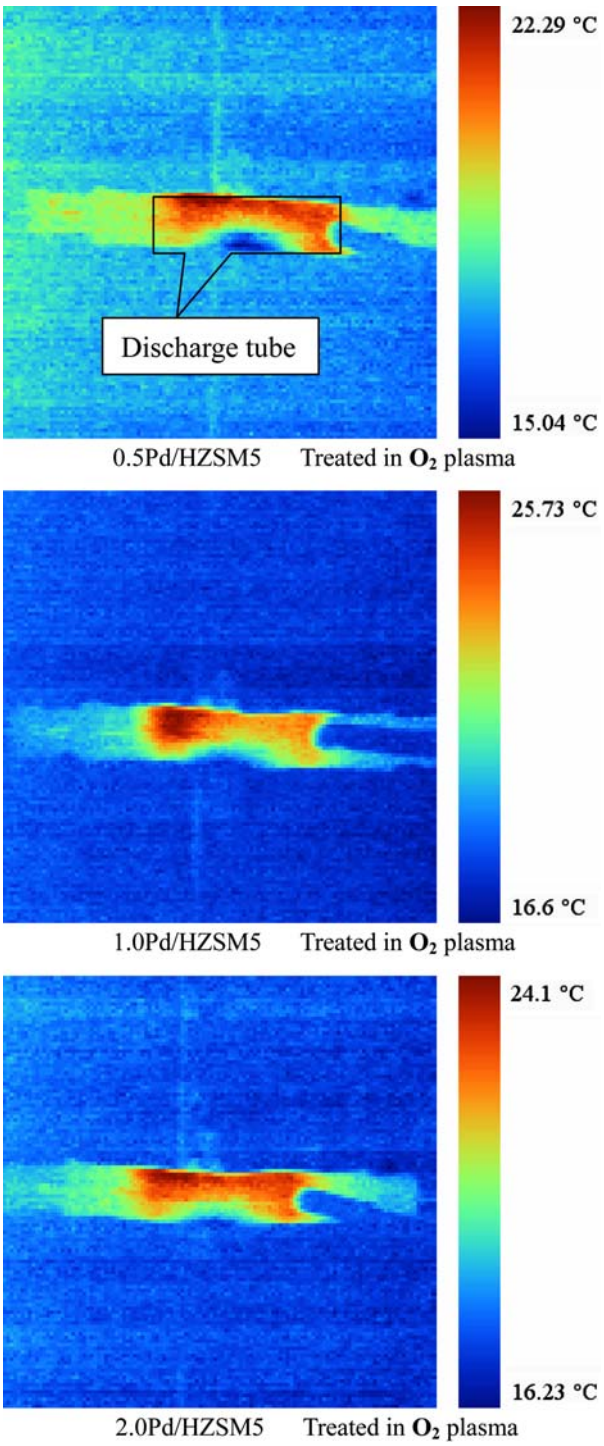

Fig. 2 IR thermal image of O_2 glow discharge plasma during the catalyst treatment

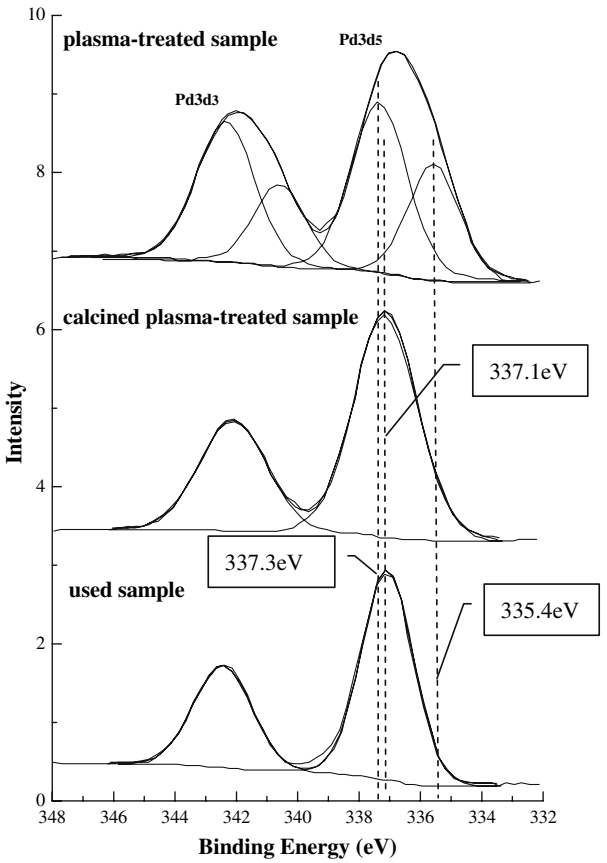

Fig. 3 XPS Pd_{3d} spectra of plasma reduced, calcined plasma reduced and used Pd/HZSM-5 samples; Pd loading: 1 wt.%

337.3 eV should be assigned as palladium ion (+2) species. The XPS analysis also confirms the reduction mechanism of glow discharge treatment. Based on our EXAFS studies [12], the plasma decompose the Pd salt impregnated over supports ($PdCl_2$ in this work) into Pd ions firstly. Simultaneously, the ions capture the abundant electron in plasma and are reduced to metallic Pd. Therefore, there are two Pd-related species in the plasma-treated sample. The one is Pd ions, other one is the partly reduced metallic Pd.

The XRD patterns of calcined plasma-reduced catalyst present a sharp peak at near 33.8° that is attributed to the tetragonal PdO crystal, as shown in Fig. 1. The XPS analysis gives us a further evidence for the excellent production of PdO from the PR&C preparation with oxygen plasma reduction, as shown in Fig. 3. The peak with a binding energy of 337.1 eV is characterized as PdO species. Since PdO represents as the active species for methane combustion, it can be expected that this plasma prepared Pd/HZSM-5 catalyst would present an excellent catalytic performance for it.

Table 1 and Fig. 4 present a comparison of catalytic activity and stability of the Pd/HZSM-5 catalysts with various metal loading (0.5, 1 and 2 wt.%) at 425 °C. Obviously, the calcined plasma-reduced catalysts shows a very stable activity for methane combustion, even at 100% conversion. This confirms again that the glow discharge plasma reduction followed by calcination thermally can induce a very stable catalyst preparation. Compared to the reported work, a better low-temperature activity has also

Table 1 The effect of reaction temperature on the catalytic activity

Pd loading content/wt.%	T_{10}/°C	T_{50}/°C	T_{90}/°C
0.5	360	391	420
1.0	328	360	400
2.0	324	349	377

Reaction condition: CH4/O2/Ar = 1.46:5.96:92.6, GHSV = 36000 h^{-1}

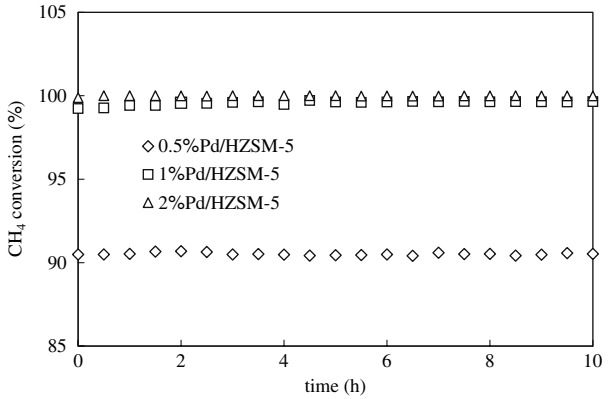

Fig. 4 The stability test of catalysts. (Reaction condition: $CH_4/O_2/Ar = 1.46:5.96:92.6$; reaction temperature = 425 °C; GHSV = 36000 h^{-1})

been achieved over this plasma prepared Pd/HZSM-5 catalyst.

4 Conclusions

The present investigation confirms that glow discharge plasma treatment of Pd/HZSM-5 catalyst will lead to reduction of catalyst, even using the oxygen as the plasma-forming gas. This further confirms the proposed electron reduction mechanism for plasma treatment using glow discharge. The calcination of oxygen glow discharge-reduced catalyst generates too a highly stable catalyst for methane combustion. The prepared catalyst also exhibits very good low-temperature activity.

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