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# Enhanced Activity of Bimetallic Pd-Based Catalysts for Methane Combustion

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**Abstract** In this work, the bimetallic Pd catalysts containing Ag, Cu, Co and Ni were prepared via the glow discharge plasma treatment followed by calcination thermally. The X-ray photoelectron spectroscopy (XPS) analysis confirms that the plasma treatment can reduce $Pd^{2+}$ effectively. The calcination of the plasma formed Pd clusters enhances the formation of PdO that was identified as the active species for methane combustion. Compared to the conventional catalysts, all the plasma prepared samples show an enhancement in the activity at the same temperature. Among the investigated catalysts, the Pd–Ag/HZSM-5 sample exhibits the best activity for methane combustion.

**Keywords** Palladium · Bimetallic catalyst · Glow discharge · Plasma · Methane combustion

## 1 Introduction

The catalytic combustion of hydrocarbons has potential applications in the clean power generation and also in the reduction of emissions of volatile organic compounds (VOCs). It thus attracts more and more attentions recently [1–8]. Among all the hydrocarbons, methane combustion is normally used as the model reaction for the catalytic combustion investigations. The supported Pd catalyst has been found to be the most active catalyst for methane combustion [2–9]. However, the supported Pd catalysts normally have a poor stability. To improve the stability of the supported Pd catalysts, a second metal or a co-metal was added, forming a bimetallic catalyst [8–10]. For example, Narui et al. [8] reported that the addition of Pt to the $PdO/Al_2O_3$ catalyst was effective in preventing the catalyst deactivation in methane combustion. Persson et al. [9] reported that, with the addition of Co, Ni, Cu, Ag, Au and Ir, the catalysts showed improved stability.

Previously, we found that the calcination of the glow discharge plasma treated Pd/HZSM-5 catalyst can lead to a significantly improved stability for methane combustion [4, 7, 11]. It was observed that, during the plasma treatment, the impregnated Pd ion was reduced into metallic state. The calcination of such plasma reduced Pd/HZSM-5 generates specific tetragonal PdO particles [7], which remains stability during methane combustion [4, 7, 11]. In this work, we attempt to extend the plasma treatment method for the preparation of bimetallic palladium-based catalysts. We aim to exploit the effect of the co-metal on the activity of the plasma prepared palladium catalysts for methane combustion.

## 2 Experimental

### 2.1 Catalyst Preparation

The Pd–M (M = Co, Ni, Cu, Ag)/HZSM-5 catalysts were prepared by incipient wetness impregnation methods including the following steps: impregnation, glow discharge plasma treatment and thermal calcination. For the purpose of comparison, catalysts were also prepared without the step of plasma treatment. The bimetallic catalysts were accomplished by co-impregnation of the second metal by mixing solutions of $Pd(NO_3)_2$ and the co-metal nitrate, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$ and $AgNO_3$.

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HZSM-5 (Zeolite Plant of Nankai University, Tianjin, China) was commercially obtained with a $SiO_2/Al_2O_3$ ratio of 50. After impregnation for 12 h, the obtained samples were then treated with glow discharge plasma [4, 7, 11–14]. The Pd–M/HZSM-5 samples were held in a discharge chamber with two electrodes connected to a high voltage amplifier (Trek, 20/20B). The signal input for the high voltage amplifier was supplied by a function/arbitrary waveform generator (Hewlett Packard, 33120A) with a 100 Hz square wave. When the pressure was evacuated to 100 Pa, the glow discharge plasma was generated by applying 1000 V to the electrode with argon (>99.999%) as the plasma-forming gas. The powders were treated for 6 times, lasted 10 min each time at room temperature. Then the obtained samples were calcined at 600 °C for 6 h. The Pd loading amount was 1 wt% while the second metal added was 0.5 wt%.

All the bimetallic catalysts prepared thermally without the plasma treatment are denoted as C-Pd–M (M = Co, Ni, Cu, Ag)/HZSM-5. The samples after plasma treatment are denoted as PT-Pd–M/HZSM-5, and the calcined PT-Pd–M/HZSM-5 samples are denoted as PC-Pd–M/HZSM-5.

### 2.2 Activity Tests

The catalytic activities for methane combustion over the catalysts were tested in a quartz tube reactor (i.d., 4 mm) at atmospheric pressure. Typically, 0.1 g of sample was placed in the tube. The temperature was increased at a rate of 10 °C/min from room temperature to 300 °C in flowing pure argon (30 mL/min). Then a gaseous mixture containing 1.5 vol.% $CH_4$ and 6 vol.% $O_2$ in argon was fed into the reactor at a space velocity of 60,000 mL $h^{-1}$ $g^{-1}$. The methane conversion was measured as a function of temperature between 300 °C and 650 °C with successive heating steps of 50 °C, maintaining 90 min duration at each temperature. The effluent gas from the reactor went through an ice-cold trap firstly to remove the condensable water. The composition of the product gas containing $CH_4$, $O_2$ and $CO_2$ was analyzed by a online gas chromatograph (Agilent 4890D) equipped with a thermal conductivity detector (TCD) using a Paropak Q pack column.

### 2.3 Catalyst Characterization

The phase structure of the catalyst samples were analyzed by X-ray diffraction, using a Rigaku D/max 2500v/pc diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å, 40 kV, 200 mA) at a scanning rate of 8°/min within the $2\theta$ range of 10–90°. The phase identification was made by comparison with the Joint Committee on Powder Diffraction Standards (JCPDSs).

XPS analysis was performed using a PHI-1600 spectrometer operated at $1.2 \times 10^{-8}$ Torr with Mg Kα radiation (1253.6 eV). The contaminative C1s peak at 284.6 eV was used for calibration.

## 3 Results and Discussion

### 3.1 Characterization of the Plasma Treated Samples

As reported previously [11–14], the metal ions with positive standard electrode potential can be reduced into metallic species during the argon glow discharge plasma treatment. The present investigation also confirms that the $Pd^{2+}$ and $Ag^{+}$ can be reduced by the argon glow discharge plasma, according to the XPS analyses. Because the active palladium species for methane combustion is PdO [2–11], the plasma reduced catalysts were calcined to generate the PdO species.

Figure 1 shows the XRD patterns of the C-Pd–M/HZSM-5 catalysts. A highly dispersed PdO species can be identified. Figure 2 exhibits the XRD patterns of PC-Pd–M/HZSM-5. Similarly, a highly dispersed PdO species can be observed clearly. From Figs. 1 and 2, the Pd–Ag and Pd–Cu catalysts have comparatively more intense PdO peaks. Especially, the PC-Pd–Ag/HZSM-5 catalyst presents a peak at near

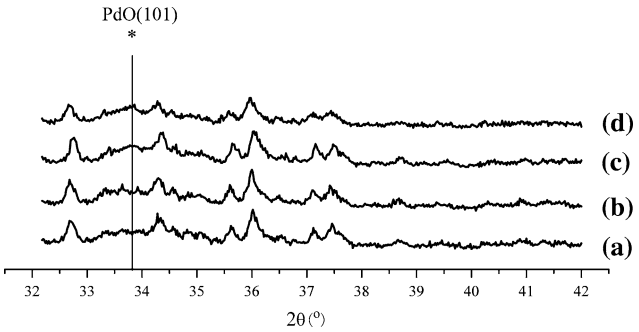


**Fig. 1** XRD patterns of conventional bimetallic catalysts. (**a**) Pd–Ni/HZSM-5; (**b**) Pd–Co/HZSM-5; (**c**) Pd–Cu/HZSM-5; (**d**) Pd–Ag/HZSM-5

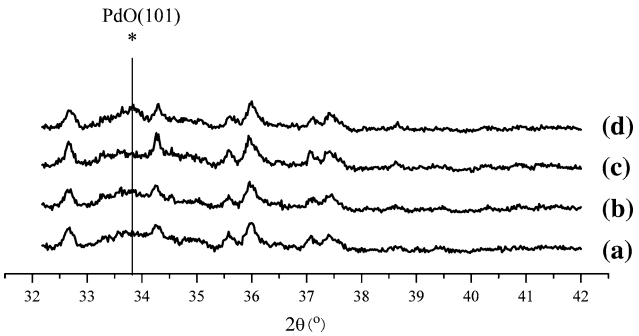


**Fig. 2** XRD patterns of plasma treated bimetallic catalysts. (**a**) Pd–Ni/HZSM-5; (**b**) Pd–Co/HZSM-5; (**c**) Pd–Cu/HZSM-5; (**d**) Pd–Ag/HZSM-5

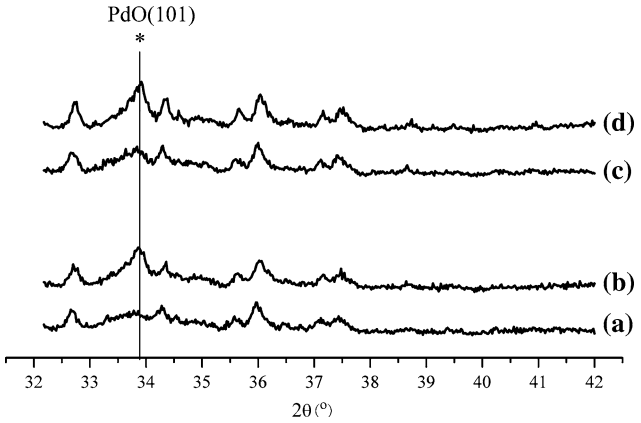


**Fig. 3** XRD patterns of (**a**) fresh C-Pd–Ag/HZSM-5; (**b**) used C-Pd–Ag/HZSM-5; (**c**) fresh PC-Pd–Ag/HZSM-5; (**d**) used PC-Pd–Ag/HZSM-5

$2\theta = 33.8°$, assigned to PdO(101), while the conventional C-Pd–Ag/HZSM-5 sample shows a smaller peak of PdO(101). As shown in Fig. 3, the PdO peaks of Pd–Ag/HZSM-5 catalysts will be further enhanced after the methane combustion at the reaction condition aforementioned. According to previous investigations [4, 7], the formation of the bulk PdO is very helpful to enhance the catalyst activity for methane combustion. From the present studies, all the plasma treated bimetallic Pd/HZSM-5 catalysts show an enhanced formation of PdO, which could explain the reason of the better low-temperature activity obtained over the plasma treated catalysts, as discussed below.

Table 1 summarizes the atomic composition of the surface of C-Pd–Ag/HZSM-5 and PC-Pd–Ag/HZSM-5. The $Pd_{3d5/2}$ binding energy of both C-Pd–Ag/HZSM-5 and PC-Pd–Ag/HZSM-5 is 337.5 eV, which indicates the existence of PdO, consistent with the XRD results. Although the surface Pd species concentration is the same on the conventional catalysts and the plasma treated samples, the intensity ratios of Pd/Si of the PC-Pd–Ag/HZSM-5 are higher than those of C-Pd–Ag/HZSM-5. The Pd/Ag atomic ratios derived from XPS intensity data obviously shows the surface enrichment of Ag in the Pd–Ag catalysts. All the ratios of Ag/Pd on the catalysts surface are higher than those of the catalysts as prepared. The surface enrichment of Ag has been already reported and attributed to the lower surface energy of Ag with respect to Pd [15, 16].

After reaction, the surface palladium composition decreases from 0.2% to 0.1% over Pd–Ag/HZSM-5. Especially, the intensity ratios of Pd/Si and Pd/Al in PC-Pd–Ag/HZSM-5 are both higher than those in the conventional catalysts. It may suggest an aggregation of palladium species on the conventional catalysts during reaction. The aggregated palladium species would block the pore of the zeolite and induce a deactivation of the catalyst. On the other hand, the ratios of Ag/Pd increase, suggesting a selective shift effect during the reaction.

### 3.2 Activity Test

Figs. 4–7 present the activity results of all the catalysts. With the addition of a second metal such as Ag, Cu, Co or Ni, all the plasma treated bimetallic catalysts show an enhanced activity. Obviously, to gain the same activity, the plasma treated catalysts need lower temperature. Among all the catalysts tested, Pd–Ag/HZSM-5 catalyst possesses the best low-temperature activity.

As shown in Figs. 4–7, the bimetallic catalysts exhibit the activity sequence as: Pd–Ag/HZSM-5 > Pd–Cu/HZSM-5 > Pd–Co/HZSM-5 > Pd–Ni/HZSM-5. Even the catalysts

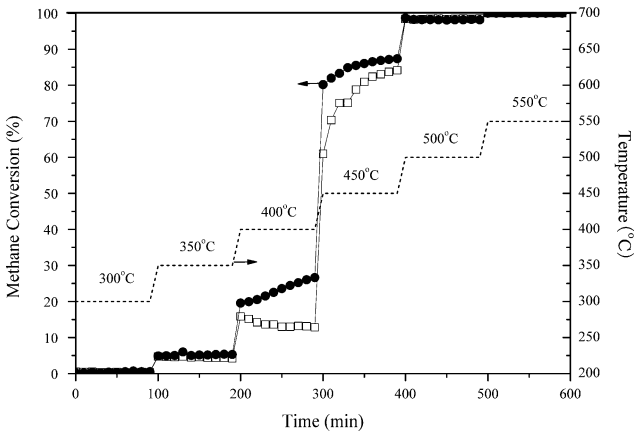


**Fig. 4** The activity tests of Pd–Ag/HZSM-5 □: C-Pd–Ag/HZSM-5; ●: PC-Pd–Ag/HZSM-5

**Table 1** The surface atomic composition of Pd–Ag/HZSM-5

| Sample | Surface atomic composition (%) | | | | | | Intensity ratio (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | C | O | Si | Al | Pd | Ag | Pd/Si | Pd/Al | Pd/Ag |
| C-Pd–Ag/HZSM-5 | 33.1 | 44.0 | 21.3 | 0.6 | 0.2 | 0.8 | 0.94 | 33.33 | 25.00 |
| Used C-Pd–Ag/HZSM-5 | 47.1 | 33.5 | 18.3 | 0.8 | 0.1 | 0.2 | 0.55 | 12.50 | 50.00 |
| PC-Pd–Ag/HZSM-5 | 37.7 | 40.9 | 19.8 | 0.8 | 0.2 | 0.6 | 1.01 | 25.00 | 33.33 |
| Used PC-Pd–Ag/HZSM-5 | 50.5 | 32.2 | 16.4 | 0.7 | 0.1 | 0.1 | 0.61 | 14.29 | 100.00 |
| PT-Pd–Ag/HZSM-5 | 39.1 | 39.5 | 19.9 | 0.8 | 0.2 | 0.5 | 1.01 | 25.00 | 40.00 |

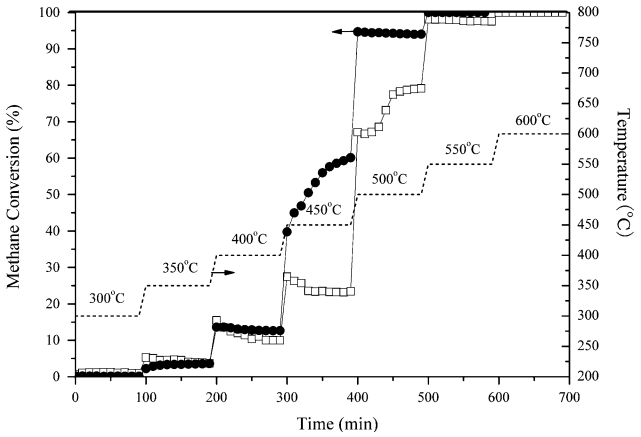


**Fig. 5** The activity tests of Pd–Cu/HZSM-5 □: C-Pd–Cu/HZSM-5; ●: PC-Pd–Cu/HZSM-5

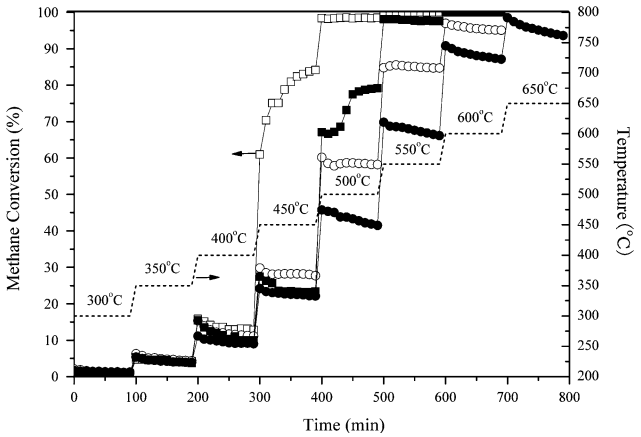


**Fig. 6** The activity tests of conventional bimetallic catalysts ●: Pd–Ni/HZSM-5; ○: Pd–Co/HZSM-5; ■: Pd–Cu/HZSM-5; □: Pd–Ag/HZSM-5

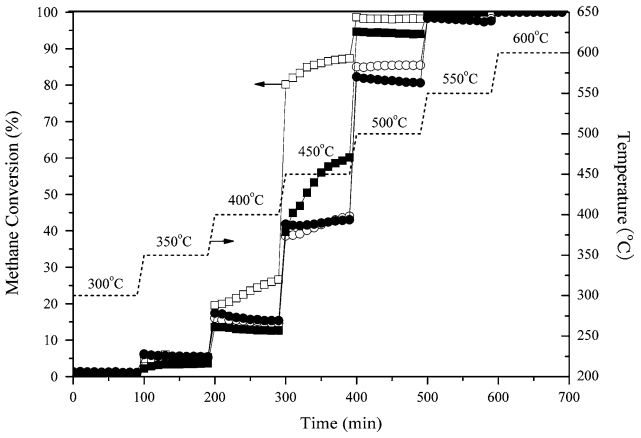


**Fig. 7** The activity tests of plasma treated bimetallic catalysts ●: Pd–Ni/HZSM-5; ○: Pd–Co/HZSM-5; ■: Pd–Cu/HZSM-5; □: Pd–Ag/HZSM-5

with plasma treatment have the same activity sequence. The catalysts prepared by plasma methods exhibit a higher activity at the same temperatures, compared to the conventional catalysts. The difference of activity is deduced by the PdO species on the catalyst surface. Further investigation is being conducted to better understand how the plasma treatment affects the formation of the bulk PdO.

## 4 Conclusions

In this work, we confirm that the addition of the second metal to Pd/HZSM-5 catalysts induces an increase in the light off temperature for methane combustion, which is useful for various applications. Among the four bimetallic palladium catalysts tested, the Pd–Ag/HZSM-5 sample exhibits the lowest light off temperature while the Pd–Ni/HZSM-5 catalyst shows the highest light off temperature. The present studies also demonstrate that the plasma treatment, followed by thermal calcination, significantly enhances the activity of all the bimetallic Pd/HZSM-5 catalysts for methane combustion. At the same temperature, the plasma prepared catalysts show a higher activity compared to the conventional samples.

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