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Mesoporous Pd$_x$Pt alloys: High-performance catalysts for methane combustion

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Xingtian Zhao, Yuxi Liu*, Jiguang Deng*, Peng Xu, Jun Yang, Kunfeng Zhang, Zhuo Han, Hongxing Dai*

Beijing Key Laboratory for Green Catalysis and Separation, Key Laboratory of Beijing on Regional Air Pollution Control, Laboratory of Catalysis Chemistry and Nanoscience, Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China

ABSTRACT

Mesoporous cubic Pd$_x$Pt (x = 0.43–8.52) alloys with surface areas of 26–32 m^2/g were synthesized using the KIT-6-templating method. Physicochemical properties of the materials were characterized by means of various techniques, and their catalytic activities were evaluated for methane combustion. It is found that the Pd and Pt were uniformly distributed in the Pd$_x$Pt alloys. The addition of Pt to Pd exerted a significant effect on the redox property of Pd. The Pd$_x$Pt alloys possessed a higher methane activation ability than the monometallic Pd. The oxidized Pd–Pt (i.e., PdO–PtO$_2$) were more active than the metallic Pd^0–Pt^0. The Pd$_{2.41}$Pt sample performed the best for methane combustion ($T_{10\%}$, $T_{50\%}$, and $T_{90\%}$ were 272, 303, and 322 °C at SV = 100,000 mL/(g h); TOF$_{Pd}$, TOF$_{Pt}$, TOF$_{Pd+Pt}$, and specific reaction rate at 280 °C were 0.85 × 10^{-3} s^{-1}, 1.98 × 10^{-3} s^{-1}, 0.59 × 10^{-3} s^{-1}, and 4.46 μmol/(g$_{cat}$ s), respectively). The deactivation of the Pd$_{2.41}$Pt sample induced by 2.5–5.0 vol% CO$_2$ or H$_2$O addition was reversible, but its deactivation due to 100 ppm SO$_2$ introduction was irreversible. It is concluded that the excellent catalytic performance of the Pd$_{2.41}$Pt sample was associated with its good mesoporous structure, Pd–Pt alloy and PdO–PtO$_2$ coexistence, and good methane and oxygen activation ability.

1. Introduction

Methane is widely used in industrial and transportation activities as it is the main component of natural gas. Due to its tough combustion, however, unburned methane at low temperatures always exists in the exhaust. It is generally accepted that methane induces a strong greenhouse effect with a global warming potential 20 times higher than that of CO$_2$ [1]. Therefore, much attention has been paid on reducing the emission of methane. Flame combustion of methane at high temperatures often results in the emissions of nitrogen oxides (NO$_x$) and CO that are harmful to the environment. Compared to the conventional flame combustion, catalytic combustion of methane is regarded as an efficient and green pathway, in which the key issue is the availability of high-performance catalysts at low temperatures. Therefore, it is highly desirable to design and prepare novel catalysts with excellent low-temperature activity and stability.

In the past years, the Pd-based catalysts have been investigated intensively and extensively due to their good catalytic performance for methane combustion [2–5]. For example, PdO or Pd–PdO mixture were recognized as the active phase of the supported Pd catalysts at low temperatures, but the metallic Pd^0 was the active phase at high temperatures [1–3,6,7]. The performance of the Pd-based catalysts for methane lean-burn combustion at low temperatures could be improved if the Pd was alloyed with other metals (e.g., Pt [8]). The Pt was found to be more active under the rich-burn conditions (O$_2$/CH$_4$ molar ratio <2) [9]. Although monometallic Pt catalysts were less active than the monometallic Pd catalysts under lean-burn conditions [9], some researchers [10–14] have pointed out that substituting Pt for Pd could generate a catalyst that showed enhanced catalytic activity and stability. The influence of Pt on catalytic activity of a bimetallic catalyst, however, is still a debated issue. For instance, Strobel et al. [15] investigated the combustion of methane over the supported Pd–Pt catalysts with different amounts of Pt and Pd, and observed a positive effect on catalytic performance over the supported Pd–Pt catalysts with smaller Pt amounts, but a negative effect on catalytic activity was observed over the supported Pd–Pt catalysts with higher Pt loadings. Such a phenomenon was also reported by Persson et al. [16], who claimed

that the Pt could act either as a promoter or as an inhibitor for methane combustion. Castellazzi et al. [13] attributed this result to the extent of PdO formation, the strength of the metal–support interaction, and the stabilization of metallic Pd^0.

Recently, the materials consisting of mesoporous networks have been found to be highly active for some reactions. These porous materials possess large specific surface areas, high structural stability, and good catalytic durability due to their nanoscale skeletons and inter-connected hollow channels that are favorable for easy mass transfer and high electron conductivity [17,18]. In the past years, porous noble metal nanostructures have gained enormous attention [19–24]. For example, the 3D porous architecture could not only maximize the availability of electron transfer within nanosized surface but also provide better mass transfer of reactants to the catalyst [18]. Xu and coworkers [22,24] conducted a systematic investigation on the catalytic properties of nanoporous gold, and found that the porous Au catalysts performed well in the oxidation of CO.

It has been generally accepted that the metal–support interaction plays an important role in improving the catalytic activity of a supported noble metal catalyst. In order to leave out the effect of the metal-support interaction, only noble metals can be used as catalyst to investigate their catalytic performance and hence clarify the active sites. Up to now, however, there have been no reports on the preparation and catalytic applications of mesoporous Pd_xPt alloys for methane combustion. In the present work, we used the mesoporous silica (KIT-6) as hard template to fabricate the mesoporous Pd, Pt and Pd_xPt alloys, characterized their physicochemical properties, and evaluated their catalytic performance for methane combustion. It is found that the Pd_xPt alloys showed much better catalytic activity than the monometallic Pd or Pt.

2. Experimental

2.1. Catalyst preparation

Ordered mesoporous silica (KIT-6) was synthesized under the hydrothermal conditions at 100 °C for 24 h according to the procedure of the previous literature [25]. As confirmed by the small-angle X-ray diffraction pattern (Fig. S1) and transmission electron microscopic image (Fig. S2), the as-synthesized KIT-6 template possessed an ordered mesoporous architecture with an average pore size of 6.8 nm. The mesoporous bimetallic Pd_xPt alloys were prepared using the nanocasting method with KIT-6 as hard template. The typical preparation procedures are as follows: 1.00 g of KIT-6 was added to 40 mL of hexane at room temperature (RT). After being vigorously stirred for 30 min and sonication for another 30 min, a mixture of H_2PdCl_4 (0.56 mol/L) and H_2PtCl_6 (0.56 mol/L) aqueous solution was then added dropwise under stirring. The ratio of the volume of precursor aqueous solution to the pore volume

of silica was 1.0. The hexane solution was sonicated for 1 h. After removing the excessive solution, the obtained brown composite was dried at 120 °C for 24 h. Such an impregnation process was repeated several times to gain a high noble metal incorporation (30–45 wt%) into the mesopores of the KIT-6. After being dried at 120 °C for 24 h, the resulting powders were placed into a three-neck flask at the ambient temperature for 30 min under the protection of N_2. Then, a $NaBH_4$ aqueous solution (0.30 mol/L) was added to reduce the H_2PdCl_4 and H_2PtCl_6 precursors ($NaBH_4$/nobel metal molar ratio = 10.00:1.00). Until no H_2 was released, the black powders were centrifuged and the KIT-6 template was removed using a hydrofluoric acid aqueous solution (10 wt%). After being washed five times with 250 mL of deionized water (50 mL for each time), the sample was dried at 120 °C overnight, and calcined in air at a ramp of 1 °C/min from RT to 400 °C and kept at this temperature for 2 h. By adjusting the molar ratios of H_2PdCl_4 and H_2PtCl_6, the Pd_xPt samples with different Pd/Pt molar ratios (x) were obtained. For comparison proposes, single metal Pd or Pt was also fabricated using the above method. The nominal x value was 9.00, 2.33, 1.00, and 0.43, respectively. The real noble metal contents of the samples were determined by the inductively coupled plasma atomic emission spectroscopic (ICP–AES) technique.

2.2. Catalyst characterization

Physicochemical Properties of the Pd, Pd_xPt, and Pt samples were characterized by means of techniques, such as ICP–AES, X-ray diffraction (XRD), transmission electron microscopy (TEM), high-angle annular dark-field-scanning transmission electron microscopic (HAADF–STEM) and element mapping, N_2 adsorption-desorption (BET), X-ray photoelectron spectroscopy, CO temperature-programmed reduction (CO-TPR), O_2 temperature-programmed desorption (O_2-TPD), CH_4 temperature-programmed desorption (CH_4-TPD), and Fourier transform infrared (FT–IR) spectroscopy. The detailed characterization procedures can be seen in the Supplementary material.

2.3. Catalytic activity evaluation

Catalytic activities of the samples for methane combustion were evaluated in a continuous flow fixed-bed quartz tube microreactor. The reactant mixture was composed of 2.5 vol% CH_4 + 20 vol% O_2 + 77.5 vol% N_2 (balance), and the space velocity (SV) was ca. 100,000 mL/(g h). All of the activity data were collected when the combustion of methane reached a steady state at a given temperature. Catalytic activities of the samples were evaluated using the temperatures ($T_{10\%}$, $T_{50\%}$, and $T_{90\%}$) required for achieving methane conversions of 10, 50, and 90%, respectively. The detailed activity evaluation procedures are put in the Supplementary material.

Table 1
BET surface areas, average pore sizes, pore volumes, average noble metal particle sizes (D), real Pd or Pt contents, and real Pd/Pt molar ratios of the samples.

Nominal sample	Real sample	BET surface area (m^2/g)	Average pore size (nm)	Pore volume (cm^3/g)	XRD result		ICP–AES result		
					Crystal phase	D^a (nm)	Real Pd content[b] (wt%)	Real Pt content[b] (wt%)	Real Pd/Pt molar ratio[b] (mol/mol)
Pd	Pd	30.2	19.8	0.137	Cubic	9.4	100	–	–
Pd_9Pt_1	$Pd_{8.52}Pt$	25.5	18.1	0.131	Cubic	7.9	82.3	17.7	8.52
Pd_7Pt_3	$Pd_{2.41}Pt$	31.9	15.6	0.142	Cubic	7.1	56.8	43.2	2.41
Pd_5Pt_5	$Pd_{0.99}Pt$	29.2	14.9	0.149	Cubic	7.2	35.1	64.9	0.99
Pd_3Pt_7	$Pd_{0.43}Pt$	29.6	14.4	0.147	Cubic	7.4	18.9	81.1	0.43
Pt	Pt	31.1	13.7	0.123	Cubic	6.8	–	100	–

[a] Data were calculated according to the Scherrer equation using the FWHM of the (111) line of cubic Pd or Pt.
[b] Data were determined by the ICP – AES technique.