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Article

Catalytic performance enhancement by alloying Pd with Pt on ordered mesoporous manganese oxide for methane combustion



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ABSTRACT

Ordered mesoporous Mn_2O_3 (meso- Mn_2O_3) and meso- Mn_2O_3 -supported Pd, Pt, and Pd-Pt alloy $x(\text{Pd},\text{Pt})/\text{meso-}\text{Mn}_2\text{O}_3$; $x = (0.10\text{--}1.50)$ wt%; Pd/Pt molar ratio (y) = 4.9–5.1 nanocatalysts were prepared using KIT-6-templated and poly(vinyl alcohol)-protected reduction methods, respectively. The meso- Mn_2O_3 had a high surface area, i.e., $106 \text{ m}^2/\text{g}$, and a cubic crystal structure. Noble-metal nanoparticles (NPs) of size 2.1–2.8 nm were uniformly dispersed on the meso- Mn_2O_3 surfaces. Alloying Pd with Pt enhanced the catalytic activity in methane combustion; 1.41(Pd_{5.1}Pt)/meso- Mn_2O_3 gave the best performance; $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$ (the temperatures required for achieving methane conversions of 10%, 50%, and 90%) were 265, 345, and 425 °C, respectively, at a space velocity of 20000 mL/(g·h). The effects of SO_2 , CO_2 , H_2O , and NO on methane combustion over 1.41(Pd_{5.1}Pt)/meso- Mn_2O_3 were also examined. We conclude that the good catalytic performance of 1.41(Pd_{5.1}Pt)/meso- Mn_2O_3 is associated with its high-quality porous structure, high adsorbed oxygen species concentration, good low-temperature reducibility, and strong interactions between Pd-Pt alloy NPs and the meso- Mn_2O_3 support.

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1. Introduction

Methane is widely considered to be the cleanest available hydrocarbon energy source for transportation and industrial applications [1]. Methane itself, however, is a greenhouse gas, with a global warming effect 21–23 times greater than that of CO_2 [2], and more serious pollutants (e.g., CO, nitrogen oxides, and unburned hydrocarbons) are always detected in the outlets of methane flame combustion [3]. Catalytic combustion of methane has many advantages over conventional flame combus-

tion, e.g., suppression of NO_x and CO and emissions and more efficient energy use. Pd-based catalysts are commonly used for methane combustion because of their excellent low-temperature catalytic activities [4,5]. PdO is believed to be an important activity-controlling factor in catalyzing the oxidation of hydrocarbons, and the reduction of PdO to metallic Pd⁰ at high temperatures decreases the catalytic activity [6,7]; for example, Hellman et al. [8] found that the PdO (101) facet was more reactive than metallic Pd⁰ in methane combustion. Pd-based catalysts, however, have some major drawbacks: (1)

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they often have poor stability in steady-state methane combustion processes [9,10], and (2) their exposure to water or sulfur-containing compounds can significantly reduce the activity via formation of inactive $\text{Pd}(\text{OH})_2$ and stable palladium sulfate phases [5,11,12]. These problems can be overcome by adding a second metal to generate a bimetallic alloy catalyst. Pt-based catalysts are also good catalysts for the combustion of hydrocarbons. The addition of Pt can increase the low-temperature methane combustion activity or hinder the growth of Pd or PdO particles [13]. Doping of a supported Pd catalyst with a small amount of Pt improves the thermal stability [14,15] and enhances resistance to sulfur or water-vapor poisoning [12].

Transition-metal oxides (e.g., Mn [16,17], Co [18], Cu, Cr, and Ni [19]) have also been used as catalysts in methane combustion; they are cheaper, more stable at high temperatures [11], and more resistant to sulfur poisoning [19] than supported noble-metal catalysts. Among the transition-metal oxide catalysts developed so far, manganese oxides have been widely studied as possible alternative catalysts for methane combustion because of their varied and multiple oxidation states and oxygen-storage capacities [20]. Han's group [17] reported complete conversion of methane over $\alpha\text{-Mn}_2\text{O}_3$ at ca. 600 °C, and this catalyst has ultrahigh stability. Machocki and coworkers [21] found that Ag-loaded manganese-lanthanum oxides showed good catalytic activities in methane combustion, and the reaction rate was related to the surface $\text{Mn}^{4+}/\text{Mn}^{3+}$ molar ratio.

Recently, our group investigated a number of nanosized or porous catalysts (e.g., Au-Pd/meso- Co_3O_4 [22], Au-Pd/3DOM Co_3O_4 [23], Au-Pd/3DOM Mn_2O_3 [24], Au/3DOM Mn_2O_3 [25], Au/meso- Mn_2O_3 [26], Au-Pd/meso- Cr_2O_3 [27], and Ag/ Mn_2O_3 nanowires [28]), and found that most of them (especially the bimetallic catalysts) performed well in the oxidation of typical volatile organic compounds and/or CO. We introduced a small amount of Pt to generate Pd-Pt alloy nanoparticles (NPs) and loaded them via a poly(vinyl alcohol) (PVA)-protected reduction route on KIT-6-derived ordered mesoporous Mn_2O_3 (meso- Mn_2O_3) with specific redox properties to overcome the drawbacks of Pd-based catalysts. We investigated their physicochemical properties and evaluated their catalytic performances in methane combustion. Ordered meso- Mn_2O_3 has a good-quality porous structure and a high surface area, therefore its use as a support for metal alloy catalysts with a uniform particle distribution improves the catalytic activity and stability. To the best of our knowledge, there have been no reports of the preparation of three-dimensional ordered meso- Mn_2O_3 -supported metal alloy catalysts and their use as methane combustion catalysts.

2. Experimental

2.1. Catalyst preparation

Mesoporous silica (KIT-6) and ordered meso- Mn_2O_3 were synthesized using previously reported procedures [29,30]. In a typical synthesis, KIT-6 (1.0 g) was suspended in toluene (50 mL). The mixture was stirred at 65 °C for 0.5 h and $\text{Mn}(\text{NO}_3)_2$

aqueous solution (50 wt%, 20.00 mmol) was added under vigorous stirring. The mixture was stirred at 65 °C for 3 h. A powder was obtained by filtration and drying the residue at room temperature (rt). The precursor@silica composite was placed in a crucible and calcined in a muffle furnace from rt to 600 °C at a ramping rate of 1 °C/min; this temperature was maintained for 6 h. The silica template was removed by etching twice with hot NaOH aqueous solution (2.00 mol/L). Template-free meso- Mn_2O_3 was obtained by centrifugation, washing with deionized water and ethanol, and drying at 80 °C.

Ordered meso- Mn_2O_3 -supported Pd-Pt alloy catalysts were prepared via a PVA ($MW_{\text{aver.}} = 10000$ g/mol)-protected reduction route with NaBH_4 as a reducing agent [31]. The typical preparation procedure was as follows. A desired amount of PVA was added to an aqueous solution of PdCl_2 and H_2PtCl_4 (100 mg/L, Pd/Pt molar ratio = 5.0) in an ice bath; the mixture was stirred vigorously for 20 min. A certain amount of NaBH_4 aqueous solution (0.1 mol/L) was quickly added to the mixed solution, generating a dark-brown noble-metal sol. A desired amount of meso- Mn_2O_3 powder was added to the noble-metal sol (theoretical Pd-Pt loadings = (0.1, 1.0, and 1.5) wt%) and the mixture was stirred for 6 h. The mixture was filtered, washed with deionized water, and dried at 80 °C for 12 h. The dried powders were calcined in a muffle furnace from rt to 600 °C, at a ramping rate of 1 °C/min, and then this temperature was maintained for 6 h; $x(\text{Pd}_y\text{Pt})/\text{meso-}\text{Mn}_2\text{O}_3$ samples were obtained. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) showed that the actual loadings (x) of the noble metals were (0.07, 0.72, and 1.41) wt%, respectively, and the corresponding y values were 4.9, 5.1, and 5.1.

For comparison, $x\text{Pd}/\text{meso-}\text{Mn}_2\text{O}_3$, $x\text{Pt}/\text{meso-}\text{Mn}_2\text{O}_3$, and $x(\text{Pd}_y\text{Pt})/\text{bulk-}\text{Mn}_2\text{O}_3$ samples were also prepared using the same method. ICP-AES showed that the actual Pd, Pt, and Pd-Pt loadings (x) were (1.40, 1.42, and 0.70) wt% in $x\text{Pd}/\text{meso-}\text{Mn}_2\text{O}_3$, $x\text{Pt}/\text{meso-}\text{Mn}_2\text{O}_3$, and $x(\text{Pd}_y\text{Pt})/\text{bulk-}\text{Mn}_2\text{O}_3$, respectively; the actual Pd/Pt molar ratio (y) in $x(\text{Pd}_y\text{Pt})/\text{bulk-}\text{Mn}_2\text{O}_3$ was 4.9.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the samples were recorded using a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation and a Ni filter ($\lambda = 0.15406$ nm). Elemental analyses of the noble-metal loadings were performed using ICP-AES (Thermo Electron IRIS Intrepid ER/S spectrometer). Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) were performed using a JEOL-2010 instrument operated at 200 kV. High-angle annular dark-field and scanning transmission electron microscopy (HAADF-STEM) were used to acquire HAADF and element mapping images (FEI G2 80-200/Chemi-STEM Cs-corrected transmission electron microscope with probe corrector). The Brunauer-Emmett-Teller (BET) surface areas of the samples were determined based on N_2 adsorption at -196 °C (Micromeritics ASAP 2020 analyzer); the samples were outgassed at 250 °C for 2.5 h under vacuum before the measurements. Their pore-size distributions were calculated based on the desorption branches

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