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Short Communication

Low-temperature combustion of methane using PdO/Al_2O_3 catalyst: Influence of crystalline phase of Al_2O_3 support

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ABSTRACT

Palladium oxide (PdO) catalysts supported on various alumina supports (θ-, δ-, κ-, η-, and γ-Al_2O_3) were prepared and the effect of the crystalline phases of the supports on the catalytic performance in methane combustion was investigated. Among the catalysts examined, the PdO/θ-Al_2O_3 catalyst, which showed the lowest reduction temperature in the temperature-programmed reduction of methane and the highest oxygen capacity in methane pulse experiments, exhibited the highest CH_4 conversion and stability for methane combustion. However, all the catalysts were deactivated because of the growth of PdO particles and strong adsorption of water vapor.

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1. Introduction

Methane combustion has been extensively studied from the viewpoints of both environmental protection and power generation. High catalytic activity and thermal stability are required for a catalyst to achieve efficient methane combustion. In general, palladium based catalysts are regarded as the most active for methane combustion [1–3]. It is commonly accepted that either crystalline palladium oxide (PdO), or a combination of Pd and PdO, is more active compared to metallic Pd [4]. The amounts of PdO, Pd dispersion and Pd-support interaction in the supported Pd catalysts play an important role in determining the catalytic activity. The investigations of these parameters have been carried out by many researchers [1,5,6]. Furthermore, different polymorphic structures of the oxide support can affect the activity and stability because of the difference in the degree of interaction based on the support. Yang et al. [7] reported that the activity of Pd/m-ZrO_2 (monoclinic) catalyst was better than that of the corresponding $Pd/t + m$-ZrO_2 (mixed phase of tetragonal and monoclinic) catalyst for methane combustion.

Aluminum oxides, especially γ-Al_2O_3, have been widely employed as supports for methane combustion because of their high surface area, moderate chemical activity, and low cost [8,9]. At high temperatures, α-Al_2O_3 has been used as a support for the Pd catalyst to lower the influence of metal-support interactions [10]. However, no comparative study on the effect of different polymorphic structures of alumina on the catalytic activity for methane combustion has been reported in detail hitherto. Therefore, it is interesting to study the effect of different crystalline structures of alumina on the activities of the catalysts.

In this work, the PdO catalysts supported on various aluminum oxides (θ-, δ-, κ-, η-, and γ phases) were prepared and the effect of the crystalline phases of the PdO/Al_2O_3 catalysts on the structural characteristics and their catalytic performance in methane combustion were investigated.

2. Experimental

2.1. Preparation of catalysts

Single-phase aluminum oxides were prepared by thermal decomposition of boehmite, gibbsite and bayerite [11]. Boehmite (CONDEA), and gibbsite (Samchun) were purchased, while bayerite was prepared using a previously reported procedure [12]. Commercial γ-Al_2O_3 (Procatalyse, $S_{BET} = 194\ m^2\ g^{-1}$) was also used as a support. δ-Al_2O_3 was prepared by calcination of boehmite at 900 °C for 6 h. η-Al_2O_3 was obtained from bayerite by calcination at 600 °C for 4 h. κ-Al_2O_3 was prepared by the calcination of gibbsite at 1000 °C for 4 h. θ-Al_2O_3 was obtained by the calcination of commercial γ-Al_2O_3 at 1050 °C for 2 h.

The PdO/x-Al_2O_3 catalysts were prepared by the impregnation method using palladium nitrate ($Pd(NO_3)$) solution, followed by calcination at 400 °C for 2 h under flowing air. The PdO loading was fixed to 2.0 wt.% for all PdO/x-Al_2O_3 catalysts.

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2.2. Catalyst characterization

To identify the crystalline phases, the X-ray diffraction (XRD) patterns were obtained using a Bruker D5000 diffractometer with CuKα radiation at 50 mA and 30 kV. The surface area and pore volume were determined by N_2 sorption at −196 °C using a Micromeritics ASAP2020 apparatus. The Pd particle sizes on the supported catalysts were observed using a transmittance electron microscope (TEM, Tecnai G2 F20) operated at 200 kV. The pulse response experiments after co-adsorption of CH_4 and O_2 were performed at 370 °C using mass spectroscopy (MS, QMS 200 Pfeiffer Vacuum). All catalysts were first pretreated at 400 °C under Ar flow and the subsequent pulse experiments were carried out at 370 °C. Each pulse contained 14.2 μmol of methane. The outlet gases were detected at $m/z = 18$ (H_2O), and 44 (CO_2). The temperature-programmed reduction by methane (CH_4-TPR) was carried out on a fixed-bed quartz reactor (I.D. = 12 mm). 1 vol.% CH_4/N_2 was continuously passed through the reactor with a total flow rate of 50 $cm^3\ min^{-1}$, while the sample was heated from 200 to 400 °C at a rate of 10 °C min^{-1}. The consumption of CH_4 was detected using a nondispersive infrared (NDIR) CH_4 analyzer (Teledyne 7500). MS time response experiments were performed at 370 °C in the same MS reaction apparatus using different gas mixtures ($CH_4/O_2/N_2 = 1/4/95$ and $O_2/N_2 = 4/96$) with a total flow rate of 50 $cm^3\ min^{-1}$ to examine the desorption behavior of reaction products.

2.3. Catalytic performance test

Isothermal and temperature programmed methane combustion (TPMC) were conducted using a fixed-bed quartz reactor (I.D. = 12 mm) under lean conditions. Prior to the tests, 30 mg catalyst was pretreated at 400 °C for 1 h under flowing N_2 (200 $cm^3\ min^{-1}$). After the catalyst cool down to 370 °C, we carried out the performance tests. The total flow rate of reactants (200 $cm^3\ min^{-1}$), consisting of CH_4 (1 vol.%), O_2 (4 vol.%), H_2O (0 or 3 vol.%), and N_2 (balance gas), were continuously passed through the catalyst sample bed. In addition, TPMC was performed at a heating rate 4 °C min^{-1} from 200 to 500 °C in either the presence or absence of water vapor. The effluent gas was analyzed using a nondispersive infrared (NDIR) CH_4 analyzer. Although the data were collected every 2 s, they are shown with an interval of 10 °C to allow for an exact comparison of catalytic performance among the catalysts examined.

3. Results and discussion

3.1. Catalytic combustion of methane

The catalytic performance of the catalysts was investigated as a function of reaction temperature for TPMC in the absence and presence of water vapor (Fig. 1 and Table 1). The temperature at 50 and 90% methane conversions ($T_{50\%}$ and $T_{90\%}$) increased in the following order: PdO/θ-Al_2O_3 < PdO/δ-Al_2O_3 < PdO/κ-Al_2O_3 < PdO/η-Al_2O_3 < PdO/γ-Al_2O_3. In addition, the methane conversions over the PdO/x-Al_2O_3 catalysts are shown as a function of time on stream at 370 °C in Fig. 2 and Table 1. The catalytic performance and stability of the PdO/x-Al_2O_3 catalysts in methane combustion varied with the crystalline phase of the alumina support. The PdO/θ-Al_2O_3 catalyst exhibited the highest methane conversion compared to the other catalysts, and the initial conversion of the catalysts was in the following order: PdO/θ-Al_2O_3 > PdO/δ-Al_2O_3 > PdO/κ-Al_2O_3 > PdO/η-Al_2O_3 > PdO/γ-Al_2O_3. In addition, all the catalysts showed deactivation during the reaction. The PdO/θ-Al_2O_3 catalyst showed a low deactivation rate (20.5%) compared to the other catalysts. However, the methane conversion over the PdO/γ-Al_2O_3 catalyst significantly decreased from 70.0 to 19.4% over 10 h on stream and showed a deactivation rate of 72.3%. To investigate the effect of water vapor on the catalytic performance of the PdO/θ-Al_2O_3 catalyst, an isothermal step-response experiment was performed under both dry and wet reaction conditions (Fig. 3). The methane conversion under dry conditions decreased continuously during the reaction (dry-1). The methane conversion decreased significantly to 40% as soon as the water vapor was introduced into the feed stream (wet). In the case of dry-2, the methane conversion was not restored to that observed in the case of dry-1.

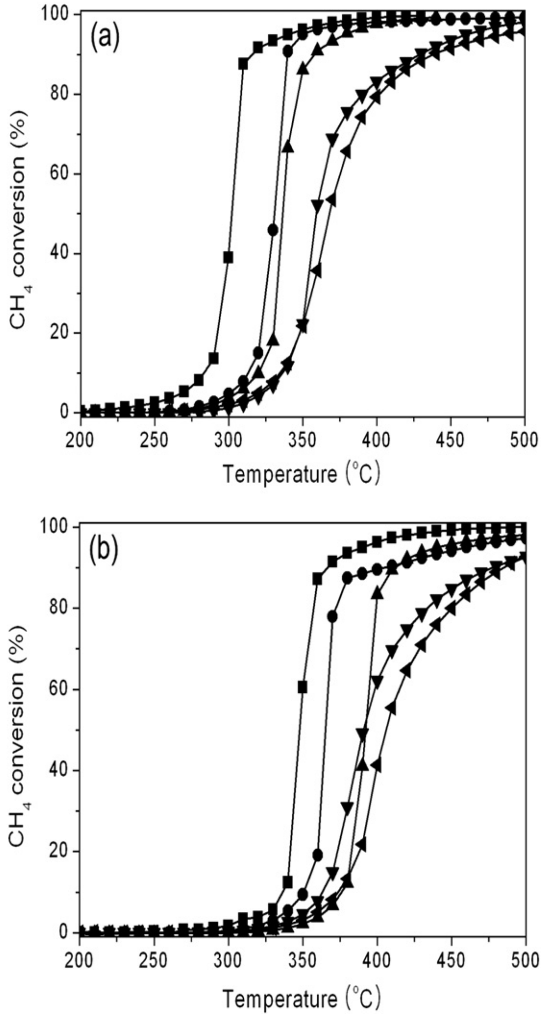

Fig. 1. Catalytic performance for temperature programmed methane combustion as a function of reaction temperature in the (a) absence and (b) presence of water vapor (3%); (■) PdO/θ-Al_2O_3, (●) PdO/δ-Al_2O_3, (▲) PdO/κ-Al_2O_3, (▼) PdO/η-Al_2O_3, and (◄) PdO/γ-Al_2O_3. Reaction conditions: catalyst quantity = 30 mg, $CH_4/O_2/N_2 = 1/4/95$ (dry), Total flow rate = 200 $cm^3\ min^{-1}$, and continuous addition of 3% H_2O vapor (wet).

It has been reported that the deactivation resulted from the transformation of PdO to Pd and the increase in size of the PdO particles [13]. In order to elucidate the reasons for the deactivation phenomena during methane combustion, TEM analysis was performed after the reaction. The results showed that the particle sizes of the catalysts slightly increased after the reactions compared to those before the reaction (Fig. 4 and Table 1). In addition, XPS analysis was carried out to examine the changes in the oxidation state of PdO before and after the 10 h methane combustion under dry conditions (Fig. S1). The Pd3d binding energy (B.E.) in all the fresh catalysts was observed to be centered at ca. 336.7 eV, which corresponded to the Pd^{2+} species [14]. In addition, the Pd3d BE values of the catalysts were almost unchanged after the reaction. This result indicated that the oxidation state in the PdO/x-Al_2O_3 catalysts remained in the form of Pd^{2+} before and after the reaction. From the TEM and XPS results, we concluded that the particle growth and transformation of PdO might have caused the deactivation of the catalysts. It is generally accepted that the water vapor either supplied

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