Available online at www.sciencedirect.com
SCIENCE DIRECT®

ELSEVIER

Catalysis Communications 6 (2005) 796–801

CATALYSIS
COMMUNICATIONS

www.elsevier.com/locate/catcom

Low-temperature catalytic combustion of methane over Pd/CeO_2 prepared by deposition–precipitation method

Li-hua Xiao [a], Kun-peng Sun [b], Xian-lun Xu [b], Xiao-nian Li [a],*

[a] Resources and Environment Catalysis Institute of Zhejiang University of Technology, State Key Laboratory Breeding Base of Green-chemistry Synthesis Technology, Zhaohui District 6, Hangzhou 310032, PR China
[b] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou 730000, PR China

Received 29 January 2005; accepted 22 July 2005
Available online 19 September 2005

Abstract

Ceria supported 2 wt% Pd catalysts for low-temperature methane combustion were prepared by the impregnation (IM) and deposition–precipitation (DP) methods, which are denoted as Pd–IM and Pd–DP, respectively. DP was found to be an available method for achieving high activity and stability of the Pd/CeO_2 catalyst. The temperatures for methane ignition ($T_{10\%}$) and total conversion ($T_{100\%}$) over Pd–DP are 224 and 300 °C at GHSV of 50,000 h^{-1}, which are 83 and 110 °C lower than the corresponding temperatures of Pd/Al_2O_3. X-ray diffraction (XRD), Raman and X-ray photoelectron spectroscopy (XPS) analyses show that palladium species in Pd–DP is highly dispersed, positively charged and difficultly reduced. Raman spectra disclosed that the largest concentration of defects and/or oxygen vacancies was formed in Pd–DP catalyst. A kind of cationic $PdO^{\delta+}$ sites with higher binding energies than PdO are in close vicinity to the oxygen vacancies in the CeO_2 support and might act as the active centers for methane oxidation. Furthermore, the deactivation and steam aging tests for Pd–DP showed that the performance of this type of palladium was very stable and could be repeatedly recovered after several long time aging tests.

Keywords: Pd/CeO_2; Methane; Catalytic combustion; XPS; Raman

1. Introduction

The catalytic combustion of methane has been extensively studied over either noble metals or transition metallic oxides during the last decades in view of developing catalytic combustion applications. It is an alternative to conventional thermal combustion in gas turbines, boilers, incinerators and so on, due to its advantage for generation of power while simultaneously reducing UHC, CO and NO_x pollutions [1]. It is also attractive for the abatement of dilute methane emissions from natural gas or methane combustion devices at considerably low temperatures. For the latter applications, it is clear that the thermal stability of catalyst is out of concern. The main objective is rather to design catalytic materials exhibiting the highest activity at the lowest temperature and the best resistance to poisons present in exhaust gases [2].

Supported palladium catalysts have been extensively studied for the catalytic combustion of methane during the past decades because palladium is more active for methane combustion than other noble metals [3], and most of the work has been focusing on palladium supported on alumina, ziconia, and silica [4–12]. For a more active combination of Pd and the support, recently, the catalytic performance of PdO catalysts supported on various metal oxides (MO_x; M = Al, Ga, In, Nb, Si, Sn, Ti, Y, Zr, Ni) was studied by Eguchi and Arai [3]. Highest activity was achieved on the most dispersed catalysts, i.e. Pd/Al_2O_3–36NiO and Pd/SnO_2, which took a particle size of above 30 nm and gave a light-off ($T_{10\%}$) temperature of around

---

* Corresponding author.
E-mail address: xnli@zjut.edu.cn (X.-n. Li).

1566-7367/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2005.07.015

310 °C and a $T_{90\%}$ conversion of around 450 °C. Due to the strong interaction between Pd and SnO_2 [13], mixed oxide supports SnO_2–MO_x (M = Al, Ce, Fe, Mn, Ni, and Zr) were prepared and the catalytic activity of PdO supported on these supports was studied [14]. But no further improvement of the activity could be obtained by the use of mixed oxide supports compared to commercial SnO_2.

Ceria is a well-known promoter in automotive catalysts due to its enhanced oxygen storage capacity (OSC). Indeed, ceria supported Pd catalysts have been proved to be effective for CO/CO_2 hydrogenation, low-temperature methanol synthesis, and methanol decomposition reactions [15–18]. In particular, the Pd/CeO_2 catalyst prepared by a deposition–precipitation method was reported to be highly active for the methanol decomposition to carbon monoxide and hydrogen at 160–220 °C [17] and extremely stable for hydrodechlorination of chlorobenzene [19] compared with the impregnated sample. The formation of a kind of cationic palladium species was proposed to explain the excellent property of the Pd/CeO_2 catalyst prepared by deposition–precipitation method. However, no similar work has been performed on methane combustion reaction. It will be interesting to investigate what will happen when this type of cationic palladium species acts as the active centers for methane oxidation.

2. Experimental

2.1. Catalysts preparation

Two kinds of 2 wt% Pd/CeO_2 catalyst samples were prepared by impregnation (IM) and deposition–precipitation (DP) methods, respectively, which are designated as Pd–IM and Pd–DP in the subsequent sections. A 2 wt% Pd/Al_2O_3 catalyst, named as PdA, was prepared by the deposition–precipitation method for a reference. The preparation process of Pd–DP was as follows [17]. An aqueous solution of 0.25 M Na_2CO_3 was added drop-wise to an aqueous mixture of $PdCl_2$ and CeO_2 powder until the pH value reached 10 under vigorous stirring. The resulting suspension was aged for 3 h under stirring, and then washed with distilled water until no chlorine anion was detected in the rinse water with an $AgNO_3$ reagent. The resulting precipitate was filtered, dried at 110 °C, and eventually calcined in air at 400 °C for 3 h. The Pd–IM sample was prepared by impregnation of a commercial CeO_2 powder with an aqueous solution of $PdCl_2$ and then subjected to the same heat treatment as Pd–DP. The palladium loading was 2 wt% for all the catalyst samples.

2.2. Catalysts characterization

X-ray diffraction (XRD) patterns of catalysts were collected on a Rigaku D/Max-2400 diffractometer (Cu Kα radiation, 50 kV, 60 mA). The crystallite sizes of CeO_2 in these supported catalysts were evaluated from the full width at half maximum of the CeO_2 (1 1 1) peak by using the Scherrer equation with a correction for the instrumental broadening. Raman spectra were recorded at room temperature on a Nicolet 910 Raman instrument. XPS were acquired on a PHI 550 photoelectron spectrometer equipped with an Mg Kα ($h\nu = 1253.6$ eV). Binding energies were calculated on the base of C1s at 285.00 eV with a precision of 0.2 eV. The BET surface areas of catalysts were calculated from the nitrogen adsorption isotherm at −196 °C measured in a micromeritics ASAP2010 apparatus.

2.3. Catalytic activity test

The methane combustion reaction was carried out in a conventional fixed-bed flow reactor. Catalyst sample of 0.5 ml (30–60 mesh) was packed in a quartz tube, which was connected with a thermocouple centered in the catalyst bed. Prior to the catalytic activity measurement, catalyst samples were pre-reduced in a H_2 stream at 300 °C for 1 h. Then, reaction gases of 1 vol% CH_4–99 vol% air were flushed through the catalyst bed with an hourly space velocity set at 50,000 h^{-1} under atmospheric pressure. The conversion of methane was measured from 200 to 600 °C and the contents of CH_4 and CO_2 were analyzed by an on-line gas chromatograph equipped with a flame ionization detector (FID) and a methanation oven. No CO formation was detected in this experiment.

3. Results and discussion

3.1. Catalytic activity and stability

Fig. 1 shows the methane conversion curves over Pd–DP, Pd–IM, and PdA catalysts, and Table 1 lists the temperatures for 10%, 50% and 100% conversions of methane as expressed by T_{10}, T_{50}, and T_{100}, respectively. The catalytic activity of Pd–DP for methane combustion is significantly higher than that of Pd/Al_2O_3 as well as Pd–IM.

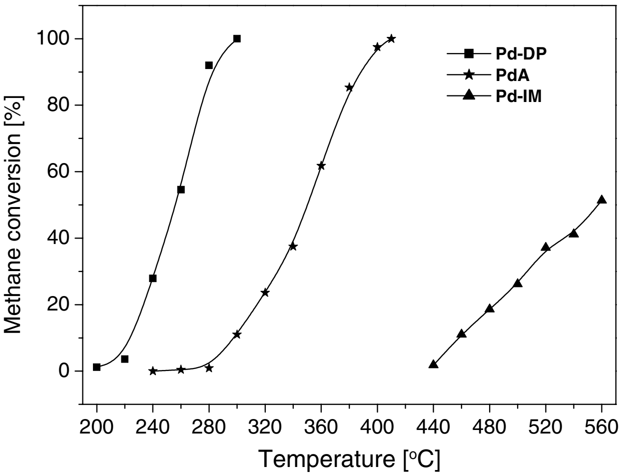

Fig. 1. Methane conversion curves over Pd–DP, PdA, and Pd–IM catalysts.