



Review

Catalytic combustion of methane at high temperatures: Cerium effect on PdO/Al₂O₃ catalysts

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ABSTRACT

PdO/Al₂O₃ and PdO/CeO₂/Al₂O₃ catalysts were prepared in order to investigate the role of palladium precursors and cerium addition on the catalytic properties of these systems and on the thermal stability of PdO (active phase) in the catalytic combustion of methane at high temperatures (above 600 °C). The catalysts were obtained from different palladium precursors and presented distinct interactions with CeO₂/Al₂O₃, thermal stability of PdO and catalytic activity. The use of cerium improved PdO thermal stability and the cerium effect was more pronounced on the catalyst prepared from acetylacetonate indicating that a PdO–CeO₂ interaction is more favorable in this system.

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Contents

| | |
|--|---|
| 1. Introduction | 2 |
| 2. Experimental | 3 |
| 2.1. Reagents | 3 |
| 2.1.1. Preparation of the catalysts | 3 |
| 2.1.2. Characterization | 3 |
| 2.1.3. Temperature programmed catalytic activity tests | 3 |
| 3. Results and discussion | 3 |
| 4. Conclusions | 7 |
| Acknowledgements | 7 |
| References | 7 |

1. Introduction

In recent decades catalytic combustion has been widely investigated as an alternative to conventional combustion due to its many practical applications both for pollution abatement and power generation. Catalytic combustion offers the possibility of producing heat and energy at much lower temperatures than conventional thermal combustion, thus reducing the emission of pollutants such as CO, NO_x and unburned hydrocarbons (UHCs) [1–9].

Noble metals display considerable activity in hydrocarbon oxidation and palladium has been widely reported in the literature

[2–5,7,8,10–12] as the catalyst of choice in methane combustion. Some of the reasons for this include: first, palladium-based catalysts are extremely active in methane oxidation which guarantees ignition at low temperatures, below 400 °C; second, palladium species formed under reaction conditions (up to 800 °C) present low volatility; finally, these systems have the unique capability of temperature self-control associated with the reversible PdO (active)/PdO (inactive) transformation.

Catalytic combustion at high temperatures (over 600 °C) requires thermally stable catalysts, resistant not only to support sintering but also resistant to decomposition and/or sintering of the active phase. There is general agreement in the literature [1–12] that the active phase of palladium catalysts is palladium oxide, PdO. This, in turn, is only thermodynamically stable at temperatures below 600 °C. Above 600 °C PdO decomposes into metallic palladium which is thermodynamically stable in the high

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temperature range. As metallic palladium is much less active than palladium oxide in methane combustion, this decomposition implies a loss of catalytic activity.

The use of rare earth oxides has been described in the literature [9,11–16] as one of the best alternatives for stabilization of the support and the active phase. According to these studies, while La_2O_3 is an excellent stabilizer of the specific area of supports such as Al_2O_3 and ZrO_2 , CeO_2 is an excellent alternative to stabilize PdO since it hinders PdO reduction and promotes Pd re-oxidation when PdO– CeO_x contact is favorable.

In this work the characterization and reactivity of cerium–alumina-supported Pd catalysts in the catalytic combustion of methane are investigated. In particular, the effect of a palladium precursor on reactivity and PdO thermal stability of Pd-supported catalysts is considered. In order to better understand the CeO_2 effect PdO/ Al_2O_3 and PdO/ CeO_2 / Al_2O_3 samples were prepared from different Pd precursors (chloride, nitrate, and acetylacetonate). The samples were characterized by means of different techniques (see Section 2) and tested in the combustion of methane.

2. Experimental

2.1. Reagents

The alumina Pural SB (BET surface area of $193 \text{ m}^2\text{g}^{-1}$) used as support was supplied by Condea. This support was calcined at 600°C for 10 h before use. High purity palladium reagents, $\text{Pd}(\text{NO}_3)_2$, $\text{Pd}(\text{C}_5\text{H}_7\text{OO})_2$ and PdCl_2 , supplied by Merck, were used as precursors.

2.1.1. Preparation of the catalysts

PdO/ Al_2O_3 catalysts with nominal Pd loading near 3% (w/w) were prepared from alumina impregnation with solutions of $\text{Pd}(\text{NO}_3)_2$, $\text{Pd}(\text{C}_5\text{H}_7\text{OO})_2$ and PdCl_2 . The samples prepared from palladium chloride and nitrate were obtained by alumina impregnation with aqueous solutions of these salts. The sample prepared from palladium acetylacetonate was obtained by alumina wetness impregnation with a toluene solution of this precursor. After impregnation the materials were dried at 110°C for 12 h and calcined at 1000°C for 5 h under air flow (50 mL min^{-1}). The samples obtained from palladium chloride, nitrate and acetylacetonate were labeled PAC, PAN and PAA, respectively.

PdO/ CeO_2 / Al_2O_3 catalysts with nominal Pd loading near 3% (w/w) were prepared from CeO_2 / Al_2O_3 impregnation with solutions of those precursors. CeO_2 / Al_2O_3 support was obtained by alumina impregnation with aqueous solution of $\text{Ce}(\text{NO}_3)_3$, followed by drying at 110°C and calcination at 1000°C for 5 h. After CeO_2 / Al_2O_3 impregnation with the solutions of palladium precursors mentioned above, the materials were dried at 110°C for 12 h and calcined at 1000°C for 5 h under air flow. The samples were labeled PAC-Ce, PAN-Ce and PAA-Ce. Table 1 shows the chemical analysis data for all the prepared catalysts.

Table 1
Chemical analysis data.

| Sample | Pd (%) | CeO_2 (%) |
|--|--------|--------------------|
| PAC-1 | 3.0 | – |
| PAN-1 | 2.8 | – |
| PAA-1 | 2.7 | – |
| PAC-Ce | 2.5 | 10.1 |
| PAN-Ce | 2.8 | 10.1 |
| PAA-Ce | 2.6 | 10.1 |
| CeO_2 / Al_2O_3 | – | 10.1 |

2.1.2. Characterization

The X-ray diffraction (XRD) measurements were carried out on a Shimadzu apparatus (XRD-6000). The Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and the following experimental conditions were used: 2θ range = 10 – 80° , step size = 0.02° and time per step = 4.80 s . The powder samples were analyzed without further treatment.

The palladium and cerium content on the samples were obtained by X-ray fluorescence on a Shimadzu WDS apparatus (XRF-1800).

Specific area measurements were carried out through N_2 adsorption on an ASAP 2000 using the BET method.

PdO thermal stability was studied using temperature programmed oxidation (TPO) in a flow system. 100 mg of the catalyst was loaded into a quartz reactor and heated in a $5\% \text{ O}_2/\text{He}$ flow (30 mL min^{-1}) at a rate of 5°C min^{-1} from room temperature to 1000°C . The samples were cooled to room temperature under the same O_2/He flow. Oxygen in the reactor outlet was detected by using a quadrupole mass spectrometer, Balzers QMS-200. The mass-to-charge ratio (m/e) = 32 was used to monitor the oxygen concentration.

TEM measurements were carried out with a JEOL 100CXII operating at 100 kV . The powder was ultrasonically dispersed in ethanol and the suspension was deposited on a copper grid coated with a porous carbon film.

XPS experiments were recorded on a Vacuum generators Escalab VG MK1 spectrometer operating at constant pass energy (50 eV) with an unmonochromated Mg $K\alpha$ source (200 W) under 10^{-8} mbar . After the pretreatments, the samples were placed in an inert gas atmosphere and rapidly transferred into the spectrometer. The binding energy was referenced to the C 1s binding energy of 285.0 eV .

2.1.3. Temperature programmed catalytic activity tests

Transient flow microreactor experiments were performed in a quartz tubular fixed bed microreactor loaded with 100 mg of catalyst diluted with 100 mg of quartz granules. The reactor was inserted into an electric furnace driven by a proportional-integral-derivative temperature controller/programmer. The temperature of the catalyst was measured and controlled by means of a K-type thermocouple sliding in a quartz compartment beside the catalyst bed. The samples were heated to 1000°C at a rate of $10^\circ\text{C min}^{-1}$, under a flow of 100 mL min^{-1} of a mixture $0.5\% \text{ CH}_4$, $2\% \text{ O}_2$ and $97.5\% \text{ N}_2$. The reactant gases were fed into the reactor by means of an electronic mass flow meter controller MKS 247 and the reactor operated at $\text{GHSV} = 60,000 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$. The effluent gases were detected by using a quadrupole mass spectrometer, Balzers QMS-200, connected at the reactor outlet. The following mass-to-charge ratios (m/e) were used to monitor the concentrations of products and reactants: 15 and 16 (CH_4), 18 (H_2O), 28 (CO), 32 (O_2), 44 (CO_2).

3. Results and discussion

The identification of the palladium phases in the catalysts was carried out by X-ray diffraction. The XRD patterns of the catalysts are shown in Fig. 1. The catalysts without CeO_2 revealed the presence of characteristic peaks of $\gamma\text{-Al}_2\text{O}_3$ and $\delta\text{-Al}_2\text{O}_3$. Regarding palladium, the predominant phase in these samples is the tetragonal form of PdO (peaks at $2\theta = 34^\circ$, 42° , 55° and 61°). Cubic metallic palladium was also detected (peaks at $2\theta = 39.9^\circ$, 46.4° and 67.8°). The XRD patterns of the cerium-containing samples indicate the presence of $\gamma\text{-Al}_2\text{O}_3$, $\delta\text{-Al}_2\text{O}_3$, Pd and PdO phases, characterized by the peaks at 2θ values previously mentioned. The CeO_2 phase, in a hexagonal fluorite structure, was also identified. Characteristic peaks of this phase can be observed at $2\theta = 28.5^\circ$, 33.1° , 47.5° , 56.3° , among others.

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