Applied Catalysis B: Environmental 132–133 (2013) 80–89

Contents lists available at SciVerse ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

# Enhanced electropromotion of methane combustion on palladium catalysts deposited on highly porous supports

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ARTICLE INFO

*Article history:*
Received 15 June 2012
Received in revised form 25 October 2012
Accepted 1 November 2012
Available online 29 November 2012

*Keywords:*
Methane oxidation
Electrochemical promotion
NEMCA
Pd catalyst-electrode
Porous YSZ

ABSTRACT

The aim of the present study was to explore the potential to electrochemically promote the methane oxidation reaction over palladium catalyst-electrodes deposited on a combination of porous-dense $Y_2O_3$-stabilized-$ZrO_2$ (YSZ), an oxygen ion conductor. We have prepared for the first time an electro-active palladium catalyst on a highly porous support, which was successfully used to enhance the catalytic activity by electrochemical promotion (NEMCA effect or EPOC). The wet impregnation technique has been used over highly porous YSZ disks to achieve very active catalyst-electrodes, with a metal catalyst dispersion of 27% (up to 4.5 times higher than that obtained for catalysts supported on dense YSZ), and susceptible to be electropromoted, despite its relatively high in-plane electrical resistance. The sample impregnated on porous YSZ turned to be much more active in methane combustion than the sample prepared by impregnation on dense YSZ, reaching, under similar working conditions, one order of magnitude higher $CO_2$ formation rates. The catalyst supported on porous YSZ was characterized by XRD, XPS, SEM and TEM techniques, while galvanostatic transients and electrochemical current–potential curves were recorded in order to assess the electropromotion of the catalytic reaction in a temperature range from 350 to 430 °C under reducing, stoichiometric and oxidizing conditions.

## 1. Introduction

Methane is a greenhouse gas estimated to have a 20-year global warming potential 35 times larger than that of carbon dioxide at equivalent emission rates. Therefore, it is important to reduce the amounts emitted into the atmosphere to mitigate in the short term the global warming. Catalytic combustion of methane, which is the main component of natural gas, is of actual interest both as a means for generating power with minimal formation of $NO_x$, and as a means for removing small amounts of methane from emissions of methane-burning engines [1,2]. Thus, on one hand, catalytic combustion of natural gas is being vigorously explored as a route to production of heat and energy in view of its capability to achieve effective combustion at much lower temperatures than in conventional flame combustion, hence allowing lower emissions [3,4]. On the other hand, lean burn natural gas vehicles (NGVs) are now commercially available in service vehicles as a viable approach to meet particulate and gaseous emission standards in urban environment in United States and Europe. However, methane is the main hydrocarbon species emitted by these vehicles, so development of efficient catalysts is needed to approach methane emissions control from NGVs [5,6].

Several effective combustion catalysts have been developed so far. They can be divided in two main categories: mixed metal oxides, and noble metals. Higher catalytic activity per site and greater resistance to sulfur poisoning are the main advantages of noble metal catalysts over metal-oxide catalysts [7]. Among the noble metal catalysts, supported Pd has been widely reported as the catalyst of choice for methane combustion applications [8–10]. It has been reported that the catalytic activity for the methane combustion depends strongly on the chemical state of palladium. It is commonly accepted that at low temperature the active phase is crystalline PdO, which may exist in more than one form depending on the oxidized particles size and on the nature of the support, but at high temperature metallic Pd is the active phase for methane oxidation [11–15].

Since the active phase, in the case of noble metals, is quite expensive, it is rather advantageous to prepare catalysts with high dispersions. This can be usually accomplished by the preparation of the catalyst as well as the calcination process. The support has

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http://dx.doi.org/10.1016/j.apcatb.2012.11.011

an important role in the metal dispersion since the maximization of the surface area could provide a large area over which it may be spread, thus providing larger active surface. Additionally, the support may act as a stabilizer of the active phase and, in some cases even, may be involved in the catalytic reaction [16].

Alumina and zirconia are the most studied supports for palladium catalysts in the methane oxidation reaction, but other supports have also been observed to improve the catalytic performance. For the Pd/alumina system, Baldwin and Burch [17] observed that the catalysts supported on δ-alumina were significantly more active than catalysts supported on γ-alumina. However, instead of attributing this to a support effect, the authors related the effect to the difference in morphology of Pd on different supports. Cullis and Willat [18] tested titania, thoria, and tin oxide, and found that Pd on these supports was less active for methane oxidation than when supported on alumina. Ribeiro et al. [19] demonstrated that Pd/$ZrO_2$ leads to a higher reaction rate than Pd/$Al_2O_3$. Sekizawa et al. [20] showed that Pd-supported on monoclinic $ZrO_2$ was more active than that on tetragonal $ZrO_2$. Interestingly, Escandón et al. [21] demonstrated that zirconia-based supports present high stability, especially in the case of the yttrium-doped support. Furthermore, many investigators have shown that the oxidation/reduction behavior of supported Pd catalysts can be strongly affected by metal–support interactions [9,16,22]. In brief, it has been demonstrated that the choice of the support can clearly affect the Pd—PdO transformations that are important for methane combustion since the catalytic activity strongly depends on the palladium oxidation state.

During the last years, the possibility of enhancing the catalytic activity by applying small currents or potentials between a catalyst (which serves also as the working electrode) supported on a solid electrolyte, and a counter electrode also supported on the same electrolyte, has been investigated. This phenomenon, introduced first by the group of Prof. Vayenas in the early 1980s [23,24], is called electrochemical promotion of catalysis (EPOC) or non-Faradaic electrochemical modification of catalytic activity (NEMCA) and originates from the controlled migration of promoting species from the electrolyte support to the catalytic metal/gas interface during polarization. These backspillover ionic species form an overall neutral double layer at the metal/gas interface and affect catalytic rates by modifying the catalyst work function, i.e. the binding energy of chemisorbed reactants and intermediates primarily via lateral electrostatic interactions [25,26]. Thus, it was shown conclusively that electrochemical promotion is an electrically controlled metal–support interaction and at least certain types of metal–support interactions are induced by reverse spillover of promoter species from the solid electrolyte onto the surface of the catalyst-electrode [27].

This phenomenon has been studied for a wide variety of catalytic reactions including methane oxidation on Rh [28,29], Pt [30] and Pd catalyst-electrodes [31–34]. In these systems dense pellets of $Y_2O_3$-stabilized-$ZrO_2$ (YSZ), with $O^{2-}$ conductivity have been used as the solid electrolyte. In the majority of these studies, porous pasted catalytic films were used [25]. However, recently, it has been demonstrated that the wet-impregnation procedure is a suitable and simple technique for preparing thin catalyst-electrode films [35–37]. Besides, in the last years, there have also been reported new routes to improve the metal–support interactions and to increase the dispersion of the metal particles in NEMCA electrodes. For instance, it has been investigated the use of an interlayer between the catalytic film and the YSZ dense electrolyte support such as $CeO_2$ [38,39] or $TiO_2$ [40]. It was found that the enhancement in the catalytic activity was due to the increase in metal dispersion, and the improvement in the magnitude of the electrochemical promotion was mainly influenced by the mixed ionic-electronic conductivity of the interlayer. Moreover, Jiménez et al. [41] prepared composite electrodes based on Ni or Ru impregnated CNF (carbon nanofibers) with dispersions of up to 7% that were successfully applied for electropromoting the $CO_2$ hydrogenation reaction. Also, De Lucas-Consuegra et al. [42] found that the addition of some YSZ powder to the platinum paste ink led to the decrease of the metal particle size, thus stabilizing higher dispersion.

The aim of this work was to prepare Pd catalytic films interfaced with either highly porous or dense YSZ and to comparatively investigate their electrochemical promotion for methane oxidation under reducing, stoichiometric and oxidizing conditions. The catalytic experiments were complemented with different characterization techniques, which provided useful insights in the intimate mechanisms governing the performance of these types of catalytic systems.

## 2. Experimental

The catalyst-electrodes used in this work consisted of a palladium film deposited on either dense or porous solid electrolyte pellets, i.e. 8 mol% $Y_2O_3$-stabilized $ZrO_2$ (YSZ). Fully dense YSZ disks (19 mm diameter and 1 mm thickness) were prepared after pressing commercial YSZ powders (Pi-KEM) at 1 ton and sintering at 1500 °C for 24 h. As prepared dense disk were used to prepare the catalysts used as the reference material for the dense catalyst in one experimental run.

For the preparation of the Pd catalyst on porous YSZ, a porous YSZ interlayer was deposited on a dense YSZ disk, prepared as described above. The porous layer was prepared by mixing YSZ powder with an organic binder (Decoflux, Zschwimmer and Schwartz) in a 1:1 (w/w) ratio and spin-coating on one side of the dense electrolyte. The assembly was dried at 100 °C for 1 h in an oven and then calcined at 1000 °C for 6 h to ensure good adherence.

The solid electrolyte disk was covered by three electrodes: working, counter and reference. Inert gold counter and reference electrodes were deposited on the dense side of the solid electrolyte by application of thin coatings of gold paste (Metalor, A1118) followed by calcination in air for 30 min at 450 °C and for 60 min at 650 °C.

The Pd catalytic film, serving as the working electrode, was deposited on the porous side of the disk, opposite to the counter electrode. The Pd film was prepared by an impregnation technique consisting of successive steps of deposition and thermal decomposition of the aqueous solution of 0.1 M $[Pd(NH_3)_4](NO_3)_2$ Pd precursor. Initially, 20 $\mu$l of precursor solution were deposited on the YSZ substrate using a plastic circular mask in order to obtain a 2.01 $cm^2$ geometric surface area of the catalytic film. Then, evaporation of the solvent took place at 70 °C for 10 min, followed by drying of the sample at 120 °C overnight and then calcination at 450 °C for 2 h. Several successive steps of this deposition procedure followed by drying and heating were repeated until a final metal loading of 0.85 mg Pd was obtained. The active area of the catalyst-electrode film was determined by the electrochemical technique developed by Ladas et al. [43] and it was found to be 64 $cm^2$ for the Pd catalyst supported on dense YSZ, and 345 $cm^2$ for the Pd catalyst supported on porous YSZ. Considering the atomic density of PdO (1 0 1), $2.75 \times 10^{-20}\ m^2\ atom^{-1}$ [44], the resulting dispersions are 4.9 and 27% for the catalyst supported on dense, and porous YSZ, respectively.

The structure and morphology characterization of the fresh catalytic layers were carried out by scanning electron microscopy (SEM) using a JEOL JSM-6300 microscope. Fresh Pd films were also imaged by transmission electron microscopy (TEM) using a JEOL 2100 microscope. The crystalline phases of the palladium catalysts supported on the porous electrolyte were examined by X-ray powder diffraction (XRD) performed using a PANalytical diffractometer