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High stability and activity of solution combustion synthesized Pd-based catalysts for methane combustion in presence of water



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ABSTRACT

Pd-ceria and Pd-ceria-zirconia catalysts were prepared by solution combustion synthesis (SCS) and tested for methane oxidation in presence of 10 vol% H₂O. Their behavior was compared with that of traditional incipient wetness impregnated catalysts (IW). Both SCS samples showed better stability and complete recovery of catalytic activity after prolonged time-on-stream at 723 K in cycling wet/dry atmosphere compared to IW ones. During transient light-off experiments, the increase in the temperature to achieve 30% methane conversion was of only 34 K for Pd/Ce_{0.75}Zr_{0.25}O₂ SCS. The better performance of SCS samples has been attributed to their strong Pd-ceria interaction and to their higher oxygen exchange capability, as measured by Temperature Programmed Reduction experiments and oxygen storage capacity measurements. For Pd/Ce_{0.75}Zr_{0.25}O₂ SCS, CO chemisorption, DRIFT and TEM characterization revealed the presence of very small Pd nanoparticles also after the aging cycle, indicating that on this sample palladium is present in a finely dispersed form that remains stable during cycling wet/dry atmosphere.

1. Introduction

The number of natural gas fueled vehicles (NGVs) is increasing worldwide, raising serious concern about the emissions at the tailpipe of unburned methane. Methane is known to be a greenhouse gas with a global warming potential about 30 times that of CO_2 on a 100-year horizon [1]. Palladium-based catalysts are recognized as the most active for the catalytic oxidation of methane, and in recent years several studies addressed the issues related to their application for exhaust methane abatement [2–8]. In particular, the presence of 10–15 vol% of water in the exhausts represents one of the main challenges for the catalytic system that controls the emissions of NGVs.

Keeping in mind that a catalyst very active at low temperature and with enhanced stability in presence of water would be a significant advancement towards more efficient methane abatement systems, many authors investigated the strong impact of water on the catalytic performance of Pd-based materials, especially at low temperatures [9–13]. In the literature different mechanisms have been proposed to explain the deactivation observed when water is added in the feed gas. From a kinetic point of view, the reaction rate for methane oxidation (1) is of order -1 with respect to water concentration [14,15]; the presence of additional water slows down the reaction by inhibiting the desorption of water (reaction product) from catalyst surface.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
 (1)

Beside this aspect, some authors indicated the formation of inactive Pd(OH)₂ as the main responsible for the activity loss, due to blockage of PdO active sites [11,16]. Palladium hydroxyls are formed preferentially in presence of PdO with respect to metallic Pd, but hydroxyls accumulation has been observed also on the support and at the metal-support interface [9,17]. In any case, the maximum OH coverage and water adsorption has been reported in presence of PdO with respect to bare supports [17,18]. The mechanism involving the formation of Pd(OH)₂ seems to be valid at relatively low temperatures (< 450 °C) due to the reversibility of the reaction $PdO + H_2O \rightarrow Pd(OH)_2$, in agreement with the total or partial recovery of catalytic activity observed on these systems after water removal [11,19,20]. At higher temperatures, the sintering of Pd/PdO particles in presence of water has been reported, giving rise to permanent deactivation [11]. Also a stronger effect of water on large palladium crystallites with respect to smaller ones has been observed [21], suggesting a sort of structure sensitivity for the inhibition induced by water.

Starting from the evidence of OH accumulation on Pd-based catalysts after the addition of water, another mechanism accounting for the activity loss has been suggested. Firstly, Ciuparu et al. reported that water inhibits the re-oxidation of the surface with oxygen from the gas phase [22], and in a subsequent work they observed that supports

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having high oxygen mobility show lower hydroxyl coverage and a higher rate of surface dehydroxylation [17]. In more recent works, it has been proposed that the hydroxyl accumulation blocks the oxygen exchange between the oxide support and the active phase, recognized as a key step in the catalytic methane oxidation [9,12]. This is consistent with the previous reports, in which it was observed that supports with high oxygen mobility are effective towards water induced inhibition. Also the acidity/basicity [23] and hydrophobicity [24] of the supports were investigated to check their impact on catalytic activity. Apparently, lower acidity suppresses the formation of Pd(OH)₂ during hydrothermal aging, while interestingly the hydrophobicity does not seem to affect the activity in presence of water.

Whatever the deactivation mechanism proposed, all studies agree on a strong effect of the support. The comparison between catalysts prepared by the same groups and in the same experimental conditions evidence that the worst performances are recorded for Pd supported on Al_2O_3 , while in general CeO₂-ZrO₂ solid solution and ZrO₂ show less deactivation [11]. Taking into account all these studies, it seems then possible to try to overcome water inhibition by tuning opportunely the metal-support interaction and the oxygen exchange capability of the support.

In this work we addressed this issue by preparing highly active Pdceria systems using solution combustion synthesis. The method was applied successfully in our group for Pd/CeO₂ catalysts [25–27], giving rise to materials with very high catalytic activity for methane oxidation in dry conditions. Their remarkable performance was attributed to the inclusion of Pd ions into ceria lattice, and subsequent formation of oxygen vacancies and highly reactive undercoordinated oxygen atoms. Following the previous literature suggestions, we synthesized Pd/CeO₂ and Pd/Ce_{0.75}Zr_{0.25}O₂ samples to test their activity for methane oxidation in transient and steady state conditions, both in dry and wet atmosphere. Catalysts of same composition were prepared also by traditional incipient wetness impregnation, in order to evaluate the effect of the solution combustion synthesis method on the overall catalytic performances.

2. Experimental

2.1. Catalysts preparation

Catalysts with 1 wt% of Pd supported on ceria and ceria-zirconia (75 mol. % CeO₂ and 25 mol.% ZrO₂, Ce_{0.75}Zr_{0.25}O₂) were prepared by solution combustion synthesis (SCS) following a well-established protocol [25]. Pd(NO₃)₂ precursor salt (Johnson Matthey) was dissolved in a little amount of deionized water to which a suitable amount of cerium or cerium-zirconium was added in the form of ceric ammonium nitrate (NH₄)₂Ce(NO₃)₆ (Treibacher Industrie AG) and zirconyl nitrate ZrO (NO₃)₂ (Treibacher Industrie AG). The liquid mixture was stirred for a few minutes until a clear solution was obtained. Oxalyl dihydrazide (C₂H₆N₄O₂) was used as the fuel, or reducing agent, and poured into the solution in suitable amount. Then the solution was transferred in a furnace heated at 623 K where the combustion took place with complete evaporation of water. The catalyst so obtained was then crushed with a pestle in its final powder form.

Catalysts with the same composition were prepared also by traditional incipient wetness impregnation (IW). The oxide supports (CeO₂ and Ce_{0.75}Zr_{0.25}O₂) were synthesized by precipitation or co-precipitation in presence of H₂O₂. In detail, a suitable amount of zirconyl nitrate solution (ZrO(NO₃)₂ 0.4 M, Treibacher Industrie AG) and/or cerium nitrate (Ce(NO₃)₂6H₂O, Treibacher Industrie AG) were dissolved in distilled water and kept under stirring. Hydrogen peroxide (H₂O₂, Aldrich 30%) was added to the solution with a molar ratio of H₂O₂:Ce-Zr = 3:1. After about 45 min ammonium hydroxide solution (NH₄OH, Aldrich 30%) was introduced till the pH reached a value of 10.5, causing the precipitation of the oxide powder. The slurry so obtained was filtered, washed with distilled water and dried overnight at 373 K. The solid powders were then calcined at 1173 K in a muffle in circulating air. On these supports Pd was impregnated by using palladium nitrate solution $(Pd(NO_3)_2 \ 10 \text{ wt\%} \ in \ 10 \text{ wt\%} \ HNO_3$, Sigma Aldrich). The impregnated samples were dried at 373 K overnight and then calcined at 1173 K for 3 h. Actual Pd loading was determined on all samples by elemental ICP analysis.

2.2. Catalysts characterization

Catalysts were characterized by means of BET surface area measurements, x-ray diffraction analysis, OSC measurements, temperature programmed reduction (TPR) and temperature programmed oxidation (TPO) experiments. CO pulse chemisorption, Transmission Electron Microscopy (TEM) and Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy were used for a deeper characterization of fresh and spent samples. Surface areas were measured in a Micromeritics Tristar porosimeter, after the samples were degassed for 2 h at 423 K under vacuum. X-ray profiles were recorded on a Philips X'Pert diffractometer equipped with an X'Celerator detector, using Ni-filtered Cu K α radiation ($\lambda = 1.542$ Å) and operating at 40 kV and 40 mA, with a step size of 0.02° and 40 counts per step.

Electron micrographs were collected on a Zeiss LIBRA 200FE microscope, equipped with 200 kV FEG source, in-column second-generation omega filter for energy selective spectroscopy (EELS) and imaging (ESI), HAADF-STEM (high angular annular dark field scanning electron microscopy) facility and EDX probe (EDS – Oxford INCA Energy TEM 200) for chemical analysis. Before analysis, the samples were ultrasonically dispersed in isopropyl alcohol and a drop of the suspension was deposited onto a lacey carbon copper grid (300 mesh).

FTIR spectra were collected on a Nicolet iSTM 50 FT-IR Spectrometer equipped with Pike Technologies Diffuse IR^{TM} cell using a DTGS detector. The catalyst powder was placed into the sample holder inside the reaction cell; the IR spectra were collected at room temperature in the range 400–4000 cm⁻¹ recording 32 scans with a resolution of 4 cm⁻¹.

Oxygen storage capacity (OSC) was measured on the bare supports (CeO₂ and Ce_{0.75}Zr_{0.25}O₂) prepared by solution combustion synthesis and co-precipitation in a thermogravimetric analyzer (Q500, TA Instruments). The samples were loaded on a platinum pan, heated up to 573 K at 10 K/min in air and treated for 30 min. Then, the temperature was raised up to 723 K at 10 K/min, introducing 4.5% H₂/N₂ (60 ml/min) and keeping the temperature at 723 K for 150 min, monitoring the weight loss over time.

Temperature programmed reduction (TPR) experiments were carried out in a Micromeritics Autochem apparatus. For each experiment, 50 mg of sample were loaded in a U-shaped quartz reactor supported over a quartz wool bed. Prior to the reduction, the catalyst was pretreated in air at 623 K for 1 h. After cooling to 193 K by using liquid nitrogen and a gaseous N₂ purge for 10 min, the gas was switched to a mixture of 5% H₂ in N₂ (35 ml/min) and the temperature was increased up to 1273 K at a ramp rate of 10 K/min, while monitoring hydrogen consumption with a TCD detector.

CO pulse chemisorption was performed in the same apparatus used for TPR experiments by loading 50–60 mg of sample in a U-shaped quartz reactor. The sample was first reduced at 353 K in a mixture of 5% H₂ in N₂ (50 ml/min). The temperature was chosen according to the reduction profile recorded during TPR as the lowest temperature at which all palladium oxide is reduced and Pd hydrides are decomposed. After cooling to room temperature, the flowing gas was switched to He while dosing 0.5 ml pulses of a mixture containing 5% CO in He. The pulses were repeated until the areas of the eluted peaks were equal. Pd dispersion and particle size were calculated on the basis of chemisorbed CO.

For temperature programmed oxidation (TPO) experiments, 150 mg of catalyst were loaded on a quartz microreactor over a quartz wool bed. The reactor was positioned into a vertical tubular furnace under a

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