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Catalytic combustion of methane over cerium-doped palladium catalysts

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Abstract

Various Pd-supported catalysts have been prepared using three different types of alumina as support material: (a) γ-alumina, (b) Ba-stabilized alumina, and (c) La-stabilized alumina. The presence of La and Ba negatively affects the catalytic activity of the supported palladium particles, despite improving the thermal stability of alumina. The previously mentioned supports have then been doped by addition of cerium, prior to impregnation with Pd. In the case of the La–alumina support, Ce was deposited by incipient wetness (IW) or specific adsorption (SA). The palladium catalysts were prepared by the incipient wetness technique in order to attain a noble metal loading of 2.5 wt%. The catalyst powders, calcined at 1000 °C in air for 4 h, have been coated onto a mullite tube in order to test their activity for the combustion of methane in a single annular channel reactor. Specific attention was given to the intensity and temperature of the PdO–Pd transition, which directly affects the combustion of methane. The presence of Ce enhances the thermal stability of alumina but entails a decrease in combustion activity. Considering the La–Al_2O_3 and Ba–Al_2O_3 supported catalysts, the presence of Ce results in an increased combustion activity. In addition, the reoxidation of Pd into PdO occurs at higher temperature than in the case of Ce-free samples. The mode of preparation of the Ce-doped support plays an important role, and the use of specific adsorption results in a catalyst with a higher combustion activity, as well as an improved thermal stability when compared to Al_2O_3.

Keywords: Catalytic combustion; Methane; Palladium; Cerium; Stabilized alumina; Lanthanum; Barium; TPO; XRD; XPS

1. Introduction

Catalytically stabilized combustion has been demonstrated as one of the most attractive alternatives for performing environmentally friendly combustion of gaseous fuels [1]. This technology has largely been developed during the past decades and is now close to commercialization. Nevertheless, there are still some remaining problems that need to be solved, among them the low-temperature ignition of the fuel. This particular problem is of great importance when methane or natural gas is considered as a fuel. Because of their low reactivity when compared to other fuels, pilot flames are required to preheat the catalyst up to its working temperature. The use of these pilot flames entails the formation of significant amounts of nitrogen oxides.

The use of palladium is therefore mandatory as PdO has been demonstrated to be the most active species for the complete oxidation of methane under lean conditions [2]. The use of palladium presents some typical characteristics when considering the combustion of methane. PdO, which is reported as being the active species at low temperatures, decomposes into a less active metallic form, Pd^0, resulting in a decrease in combustion activity, at about 750 °C [3]. This intrinsic property of palladium has been used in some catalytic combustor designs to self-regulate the catalyst temperature and avoid over-heating of the catalyst [4].

The doping of alumina supports has been widely reported in the literature [5,6]. Most of the attention has focused on their application in three-way catalysts. In this case, cerium dioxide acts as an O_2 reservoir [7]. The presence of Ce enables the retention of oxygen under lean conditions. This oxygen is then released when operating under a

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rich atmosphere to perform the oxidation of CO and HC. Furthermore, it has been claimed that the presence of cerium dioxide inhibits the sintering of alumina and enhances the dispersion of noble metals. In catalytic combustion, the main purpose for the use of cerium is slightly different as the oxidation of methane takes place under lean conditions.

Its role is therefore to stabilize Pd in a high oxidation state and enhance the reoxidation of Pd into PdO under cooling conditions. In a previous work performed at our laboratory [8], we noticed that the presence of La or Ba has a strong influence on the combustion activity of supported Pd particles. The purpose of the present work is to investigate the possibility of combining a thermally resistant support material and a catalyst with a high oxidation activity. The focus of the present study is to examine the influence of the addition of CeO_2 to Al_2O_3 and La- and Ba-stabilized Al_2O_3 supports with respect to the catalytic activity in complete oxidation of methane. Various techniques for impregnation of Ce will be described and compared.

2. Experimental

2.1. Catalyst preparation

Supports with the following chemical composition have been employed: Al_2O_3 (Condea, Puralox HP 14-150, 144 m^2/g), Ba-Al_2O_3 (Condea, Puralox SCFa-140 B3, 143 m^2/g), and La-Al_2O_3 (Condea, Puralox SCFa-140 L3, 142 m^2/g). The content of Ba and La, respectively, was 3 wt% for both supports. Cerium has been added to the three different support materials by two different techniques, incipient wetness and specific adsorption [9], in order to reach a final Ce loading of 5 wt%.

2.1.1. Incipient wetness method

In the case of the incipient wetness technique, a solution containing the Ce precursor has been impregnated on the three different supports. The volume of the solution is equal to the total pore volume of the support considered. Cerium nitrate (Novakemi AB, $Ce(NO_3)_2 \cdot 6H_2O$, 99.9%) has been used as a Ce precursor. The support materials are dried overnight at 120 °C prior to calcination at 500 °C for 4 h in air.

2.1.2. Specific adsorption

The specific adsorption is based on the IEP (isoelectric point) of the support material. Previous investigations [9] show that the IEP values for different types of alumina are in the range 7–9.

In order to adsorb the negatively charged $[Ce(EDTA)]^-$ complex, the pH of the solution is set to 5. The complex of cerium and ethylenediaminetetraacetic (EDTA) acid, $[Ce(EDTA)]^-$, was prepared using the procedure described by Tijburg et al. [9]. The adequate amount of EDTA (KEBO AB, $C_{10}H_{16}N_2O_8$, 99.9%) was dissolved in deionized water by raising the pH from 3 to 5. An equimolar amount of cerium nitrate was dissolved into 10 cm^3 of deionized water and added dropwise to the EDTA solution. The pH was kept above 4 by addition of dilute ammonia in order to prevent precipitation of Ce(EDTA). In another beaker, 30 g of alumina was suspended in 1125 ml of deionized water by vigorous stirring. The pH was adjusted at 5.0 by addition of dilute HNO_3. The $[Ce(EDTA)]^-$ solution was added dropwise to the stirred alumina suspension. As previously described, under these conditions the complex adsorbs on the surface of the solid. After filtration, the material was dried at 120 °C overnight and then calcined at 1000 °C for 4 h, in order to decompose the EDTA complex and obtain CeO_2 on the surface of the alumina. The Ce-impregnated powders were then dried at 120 °C and calcined at 500 °C for 4 h.

Palladium was then deposited onto the Ce-doped support by incipient-wetness impregnation, as described above. For comparison purposes, Pd was deposited onto the three Ce-free supports as well. In all cases, a $Pd(NO_3)_2$ solution (Alfa Aesar, 8.41 wt%) was used as the metal precursor. The volume of the impregnation solution was adjusted in order to achieve a final washcoat with a precious metal loading of 2.5 wt%. The Pd-impregnated powders were then dried at 120 °C and calcined at 1000 °C for 4 h. Following this thermal pretreatment, part of the powder is then coated onto the ceramic sticks for activity testing. The remaining dry powders are used for further material characterization (BET, XRD, TPO, XPS).

2.2. Catalyst characterization

The catalyst powders were characterized by XRD to examine the catalyst properties with respect to crystal phase as well as oxidation state and particle size. BET analysis provided information concerning the specific surface area. Furthermore, temperature-programmed oxidation (TPO) experiments were performed to investigate the Pd–PdO transition (decomposition and reoxidation).

2.2.1. BET surface area

The surface areas have been evaluated from N_2 adsorption isotherms (at the liquid nitrogen temperature), with the BET method, using a Micromeritics ASAP 2000. Prior to adsorption measurements, the samples were degassed under vacuum for at least 12 h at 200 °C.

2.2.2. X-ray powder diffraction

The phase composition of the various samples was determined by means of X-ray powder diffraction, using a Siemens Diffraktometer 5000. The operating parameters were: monochromatic Cu-K_α radiation, Ni filter, 30 mA, 40 kV, 2θ scanning from 20 to 80°, scan step size of 0.02. Phase identification was carried out using the reference database (JCPDS-files) supplied with the equipment.

2.2.3. Temperature-programmed oxidation (TPO)

The redox properties of the samples were measured by means of temperature-programmed oxidation (TPO) experiments on a Micromeritics AutoChem 2910 equipped with a thermal conductivity detector (TCD). Approximately 100 mg of calcined powder was used for each measurement. Prior to TPO experiments, the samples were calcined in a stream of 5.0% O_2/He at a flow rate of 10 $cm^3\,min^{-1}$, increasing the temperature from 300 to 950 °C at a rate of 10 °C min^{-1}. The cooling rate has been controlled at 10 °C min^{-1} in the same atmosphere. Subsequently, TPO experiments were performed under conditions similar as the above mentioned pretreatment.

2.2.4. X-ray photoelectron spectroscopy (XPS)

Photoelectron spectra were recorded on a VG Escalab 200R electron spectrometer equipped with a hemispherical electron analyzer and an Mg-K_α ($h\nu = 1253.6$ eV, 1 eV = 1.603×10^{-19} J) X-ray source. A computer provided with the Eclipse software was used to record and analyze the spectra. All samples were mounted on a manipulator, which allows transfer from the preparation chamber to the analysis chamber. All samples were then outgassed at 393 K for 1 h prior to being moved to the analysis chamber. During data acquisition, residual pressure was kept below 3×10^{-9} mbar. Each spectral region of the photoelectrons of interest was scanned a number of times at a pass energy of 20 eV to obtain a good signal-to-noise ratio. Peak intensities were estimated by calculating the integral of each peak and fitting it to a combination of Lorentzian/Gaussian lines (10% G–90% L). Although surface charging was observed on all the samples, accurate binding energies (BE) (±0.1 eV) could be determined by charge referencing with the Al2p peak at 74.5 eV or with adventitious carbon at a BE of C1s at 284.9 eV. For each catalyst sample, Al2p, Pd3d, and Ce3d (and Ba3$d_{5/2}$ or La3$d_{5/2}$ peaks, if present) were recorded.

2.3. Experimental set-up and combustion test procedure

The combustion experiments have been performed in an annular reactor described elsewhere [10]. The design of this annular reactor was first proposed by McCarty [3] and its use has since been widely reported in the literature [11,12]. It consists of a quartz reactor with a mullite (or dense alumina) thermocouple pocket in it. A thin layer of catalyst (20 mg) is coated onto the outer surface of the thermocouple pocket. The reactant gases (1.0 vol% CH_4 in air) are passed through this narrow annular space of 0.1–0.3 mm. The total gas flow rate was 0.94 $dm^3\,min^{-1}$, resulting in a linear gas velocity of 1.0 m s^{-1}. A K-type thermocouple is inserted into the ceramic tube to measure the catalyst temperature under reaction conditions. For the transient experiments, the temperature of the furnace is raised from 250 °C up to 950 °C with a heating rate of 3 °C min^{-1}. The composition of the combustion products is analyzed by on-line gas chromatography (GC Varian 3800) equipped with a thermal conductivity detector. The conversion is calculated by using the concentration of methane and confirmed by the yields of CO_2 and CO.

3. Results

3.1. Specific surface area

The results of the BET surface area measurements, following calcination at 1000 °C for 4 h in air, are reported in Table 1. As described in a previous study [8], the presence of La or Ba strongly enhances the resistance of the alumina-based catalyst to sintering, for the Ce-free samples. The PdA catalyst exhibits a BET surface area of about 85 $m^2\,g^{-1}$ after the above-described thermal treatment. In contrast, the samples containing 3 wt% of La and Ba exhibit surface areas of 114 and 107 $m^2\,g^{-1}$, respectively, after equivalent thermal treatment.

The addition of Ce to the Ba–Al_2O_3 and La–Al_2O_3 supports does not significantly affect the thermal stability. There is not much of a difference between the PdLa and PdBa catalysts and their Ce-doped counterparts. PdBa and PdBaCe present similar BET surface areas, 114 $m^2\,g^{-1}$ and 116 $m^2\,g^{-1}$, respectively. Similar observations can be made for PdLa, PdLaCe, and PdLaCe-SA. In addition, considering the La–Al_2O_3 supported catalyst, the method used for the deposition of Ce does not affect the thermal stability.

The stabilization of γ-Al_2O_3 by Ce is on the same order of magnitude as that when using La or Ba as a stabilizing agent. Moreover, the addition of Ce does not further improve the thermal stability of La- and Ba-containing samples, regardless of the mode of impregnation of cerium.

3.2. Crystal structure determination

The presence of La and Ba inhibits the transformation of alumina into the low-surface-area α-phase. The supports containing La or Ba have a predominantly δ-phase structure, whereas the neat alumina tends to sinter and undergoes phase transformation during thermal treatment at 1000 °C. These results have already been reported in a previous study

Table 1
Denomination and surface area of the various catalysts following calcination in air at 1000 °C for 4 h

Name	Composition	BET surface area ($m^2\,g^{-1}$)
PdA	Pd/Al_2O_3	85
PdBa	$Pd/Ba–Al_2O_3$	114
PdLa	$Pd/La–Al_2O_3$	107
PdACe	$Pd/CeO_2/Al_2O_3$	102
PdBaCe	$Pd/CeO_2/Ba–Al_2O_3$	116
PdLaCe	$Pd/CeO_2/La–Al_2O_3$	102
PdLaCe-SA	$Pd/CeO_2/La–Al_2O_3$	100

SA refers to the catalyst where Ce was impregnated by specific adsorption.

performed at our laboratory [8]. The purpose of the present investigation is to examine the role and influence of Ce, with or without the presence of La or Ba, with respect to both the thermal stability of the support material and the combustion activity of lean mixtures of methane in air. The present X-ray diffraction evaluation focuses on the Ce-doped samples only since XRD results for the Ce-free samples have recently been reported in a previous study [8]. However, the XRD pattern of PdA is included and will be used as a reference.

The diffraction patterns of the different catalysts are represented in Fig. 1. Concerning the identification of crystalline structures of Pd, the focus of attention was the oxide form, PdO, as it is the most active species for the complete oxidation of methane, when operating in an excess of oxygen. Specific attention was given to the Ce-doped catalyst in order to evaluate the influence of Ce with respect to the oxidation state and crystalline nature of the palladium particles. The chemical nature of the support will be taken into account as well. The reflections at $2\theta = 33.889°$ and $2\theta = 40.115°$ are used for the identification of the tetragonal (PdO) and the cubic (Pd^0) form of Pd, respectively. Other major PdO reflections at $2\theta = 41.948°$ and 60.207° cannot be applied due to overlapping by alumina peaks. Similar comments are valid for the Pd^0 reflection at $2\theta = 46.682°$. The presence of CeO_2 was identified by the reflection at $2\theta = 28.55°$. The CeO_2 reflection at $2\theta = 33.08°$ is overlapped by alumina peaks and can therefore not be utilized for identification.

The reflection attributed to CeO_2 at $2\theta = 28.55°$ is noticeable in all doped catalysts, PdACe, PdBaCe, PdLaCe, and PdLaCe-SA. The presence of La and Ba has a strong effect with respect to the thermal stability of alumina and avoids the formation of α-Al_2O_3. Similar observations can be made with respect to Ce. The presence of α-Al_2O_3 can be detected in PdA with a reflection at $2\theta = 35.13°$. The addition of Ce prevents the transition into the low-surface-area α-Al_2O_3, as seen in PdACe. In addition, the θ-Al_2O_3 reflection, observable in PdA at $2\theta = 31.43°$, is not present in the Ce-containing samples. In contrast, the addition of Ce to La-Al_2O_3 and Ba-Al_2O_3 does not further improve the thermal stability of the support. When the pure alumina is compared with the other supports containing La or Ba, the presence of La and Ba, respectively, was sufficient to stabilize the alumina in its δ-phase. The addition of Ce does not show any significant influence with respect to the crystal structure of the support material.

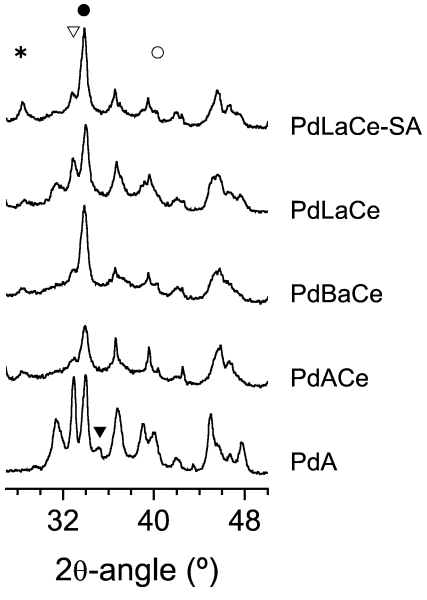

Fig. 1. X-ray diffractograms of PdA, PdACe, PdBaCe, PdLaCe, and PdLaCe-SA. Reflections of (∗) CeO_2, (●) PdO, (○) Pd^0, (▼) α-Al_2O_3, and (▽) θ-Al_2O_3.

3.3. Temperature-programmed oxidation (TPO)

The results from the TPO experiments are depicted in Fig. 2. The positive peaks represent oxygen release due to the decomposition of PdO into metallic Pd and occur during the heating process. The oxidation of Pd is characterized by negative peaks due to O_2 consumption which takes place during cooling. The purpose of the present TPO experiments was to investigate the influence of cerium addition on the PdO–Pd transformation during the heating and cooling process.

Considering the Ce-free samples, i.e., PdA, PdLa, and PdBa, the decomposition of PdO takes place in two steps with maximum intensity at 740 and 785 °C, regardless of the nature of the support. The relative intensity between the two decomposition peaks is affected by the nature of the support. The reoxidation into PdO, upon cooling, takes place in a single step. The reoxidation temperature is shifted toward

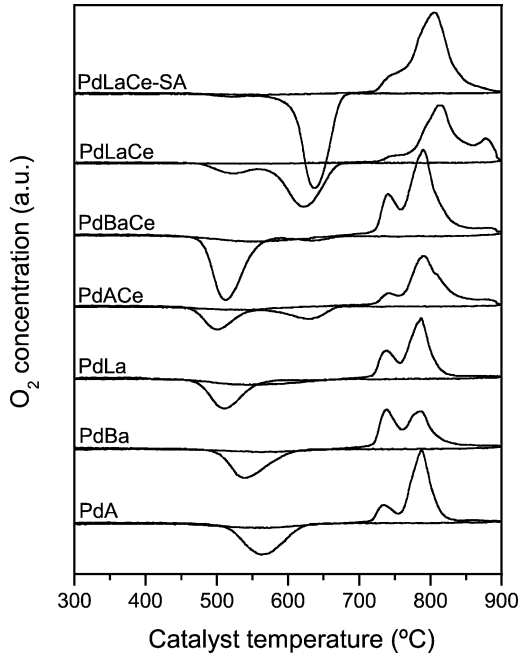

Fig. 2. Temperature-programmed oxidation of PdA, PdBa, PdLa, PdACe, PdBaCe, PdLaCe, and PdLaCe-SA upon ramped heating and cooling.

lower temperature when the support is changed from Al_2O_3 to La–Al_2O_3 and Ba–Al_2O_3. There is a difference of about 60 °C between the reoxidation of PdA and PdBa.

For the Ce-doped samples, the decomposition takes place in two or three steps, depending on the nature of the support. The intensity of the first decomposition peak at 740 °C is rather weak for all Ce-doped samples except PdBaCe. Considering the second decomposition peak, we notice some slight discrepancy with respect to the temperature at which it is observed. In the case of PdACe and PdBaCe, the second decomposition temperature is 790 °C, whereas PdLaCe and PdLaCe-SA exhibit a second decomposition step at ca. 810 °C. The presence of a third decomposition peak is clearly observed on PdLaCe and to some lesser extent on PdACe and PdBaCe. It is almost absent from the TPO profile of PdLaCe-SA.

The major discrepancy concerning the TPO profiles of the catalysts modified by addition of Ce is observed during the cooling process. The Ce-doped catalysts present two separate peaks of O_2 consumption with varied relative intensity depending on the nature of the support and Ce deposition method. The temperature at which these two reoxidation steps take place is identical for all Ce-impregnated samples. The reoxidation can be characterized by a first step at about 625–630 °C (high-temperature reoxidation) followed by a second step at about 510 °C (low-temperature reoxidation).

The relative reoxidation intensity between these two steps has been determined by integration of the resulting oxygen consumption peaks during the cooling ramp. The reoxidation coefficient ρ is the ratio (O_2 release/O_2 uptake) based on the areas of the concerned peaks.

In addition, it has been evaluated by integration of the peaks for oxygen uptake and release, respectively. If $\rho > 1$, the decomposition is more important than the reoxidation and the catalyst exhibits both the oxidic and reduced forms of palladium. If $\rho = 1$, the catalyst is fully reoxidized, whereas $\rho \gg 1$ corresponds to a catalyst in a fully metallic state. The ρ values for the different catalysts are reported in Table 2.

Concerning the samples doped with cerium, the reoxidation during the cooling cycle starts at a much higher temperature than in the case of the Ce-free catalysts. This reoxidation step at high temperature is more important in the case of PdLaCe, especially when Ce has been deposited by specific adsorption.

Furthermore, the addition of Ce entails reoxidation closer to completion than in the case of the Ce-free samples. For PdLaCe and PdLaCe-SA, ρ is equal to 1.08 and 1.1, respectively, reflecting intense reoxidation during the cooling process. A similar trend is noticed for the alumina-supported materials. In contrast, for PdBa ($\rho = 1.31$), large amounts of metallic palladium are present in the samples at the end of one TPO cycle. The PdO–Pd transition of the Ba–Al_2O_3-supported catalyst is affected by the presence of cerium as well, but to a much lesser extent. The Ce-free and Ce-doped samples show small differences with respect to the temperature at which the reoxidation takes place, but have an equal ρ value of 1.31. Finally, since all ρ values in Table 2 are above 1, the catalyst is not completely reoxidized following a TPO cycle and metallic palladium is assumed to be present.

Table 2
Relative reoxidation intensity and reoxidation coefficient (ρ) for each Ce-free and Ce-doped catalyst

Sample	Low-temperature reoxidation[a] (%)	High-temperature reoxidation[a] (%)	ρ[b]
PdA	100	0	1.31
PdBa	100	0	1.31
PdLa	100	0	1.56
PdACe	61	39	1.16
PdBaCe	96	4	1.31
PdLaCe	12	88	1.08
PdLaCe-SA	2	98	1.10

[a] The calculation of the relative reoxidation intensity is made by integration of the respective areas of the reoxidation peaks. Low-temperature range: 500–570 °C. High-temperature range: 625–630 °C.

[b] The reoxidation coefficient, ρ, is equal to (area of the decomposition peaks)/(area of the reoxidation peaks), measured from the corresponding TPO profiles.

3.4. X-ray photoelectron spectroscopy

The Ce3*d* and Pd3*d* spectra measured from PdACe, PdLaCe, PdLaCe-SA, and PdBaCe are represented in Figs. 3 and 4, respectively. In addition, the binding energy of the principal elements and the surface atomic ratio are reported in Table 3.

Cerium has a very complicated 3*d* spectrum, as with several satellites. The binding energy for Ce3$d_{5/2}$ is 882.8–

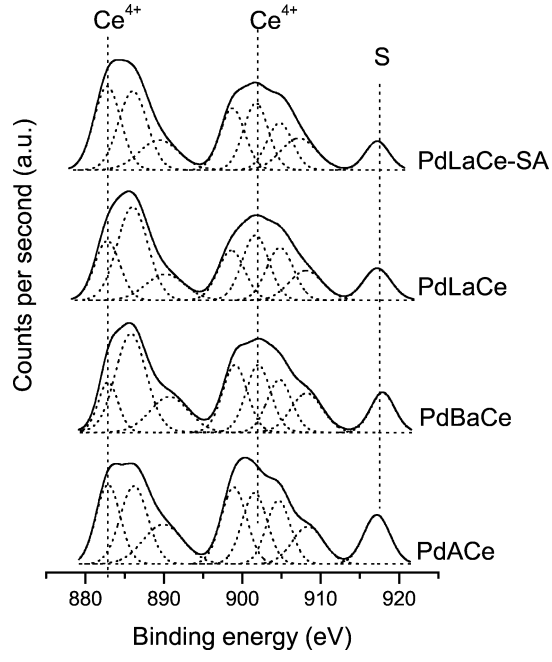

Fig. 3. Ce3*d* XPS lines of PdACe, PdBaCe, PdLaCe, and PdLaCe-SA.

Table 3
Binding energy (BE) in (eV) of core electrons of the Ce-doped catalysts and surface atomic ratio

Sample	Binding energy (eV)				Surface atomic ratio	
	Ce3$d_{5/2}$	Pd3$d_{5/2}$	La3$d_{5/2}$	Ba3$d_{5/2}$	Ce/Al	Pd/Al
PdACe	882.8	335.6 (18)	–	–	0.0016	0.0012
	917.3 (8)	335.7 (82)				
PdBaCe	882.9	335.6 (45)	–	780.7	0.0010	0.0014
	917.5 (8)	337.5 (55)				
PdLaCe	882.9	335.7 (62)	n.m.	–	0.0010	0.0009
	917.3 (9)	337.5 (38)				
PdLaCe-SA	882.8	335.5 (61)	835.7	–	0.0012	0.0009
	917.2 (6)	337.6 (39)				

All BEs referenced to Al2p = 74.5 eV. n.m.: nonmeasured.

883.9 eV. The literature values for CeO_2 are 881.8–882.4 eV [13]. The spectra (cf. Fig. 3) present another two satellites (marked as S) which are characteristic of Ce^{3+} species. The presence of an important fraction of Ce^{3+} species is also confirmed by the low intensity of one of the satellites, which appears at a BE energy close to 917.4 eV and is characteristic of Ce^{4+}. If all the Ce is in the Ce^{4+} oxidation state, the ratio of the intensities of the satellite at 917.4 eV and the total intensity of Ce3d peaks is about 0.14. Conversely, if all the Ce is present as Ce^{3+}, no satellite at 917.4 eV should be observed. Because of the rather elevated calcination temperature (1000 °C), both Ce^{3+} and Ce^{4+} are present in the catalysts. Nevertheless, because of interaction between the Ce particles and the support, a small variation in the ratio Ce^{3+}/Ce^{4+} can be observed.

The binding energy of the other additives, La and Ba was also measured (when they were present in the samples). The binding energy for La and Ba are 835.7 eV and 780.7 eV, respectively. The BE value for the 3$d_{5/2}$ peak of Ba in BaO is reported to be 779.1–799.9 eV [13]. Moreover, the BE value measured for La is characteristic for well-dispersed La particles, as previously reported by Haack and co-workers [14]. They report a value of 835.0 eV, when the surface atomic ratio of La/Al is in the range 0.05–0.15.

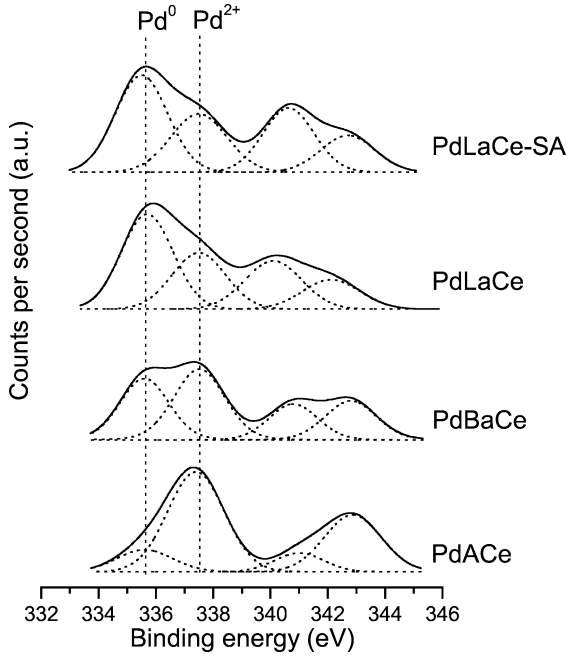

Fig. 4. Pd3d XPS lines of PdACe, PdBaCe, PdLaCe, and PdLaCe-SA.

The most intense component of the Pd3d doublet (Pd3$d_{5/2}$) presents two peaks, one at 335.6 ± 0.1 eV and one at 337.6 ± 0.1 eV. The BE of 335.6 corresponds to that of Pd^0. The second BE, measured at about 337.6, corresponds to Pd^{2+} species. These results are in agreement with the literature [15,16]. The BE value attributed to PdO is ca. 0.5 eV higher than for bulk PdO, which probably corresponds to a dispersed state. The presence of La and Ba in the supports clearly enhances the reduction of PdO into Pd (cf. Fig. 4). In PdLaCe and PdLaCe-SA, palladium is more than 60% in the metallic form, whereas PdACe presents mostly an oxide form with 82% of PdO. When analyzing the Pd/PdO ratio based on the value reported in Table 3, we noticed that the PdACe catalysts has a Pd/PdO ratio of about 4.55, whereas PdBaCe, PdLaCe, and PdLaCe-SA have Pd/PdO ratios of 1.22, 0.61, and 0.64, respectively. PdO_2, if present, would have been characterized by a peak at 338.3 eV [17].

3.5. Catalytic activity

The performance of the various catalysts during the complete oxidation of methane under lean conditions is reported in Figs. 5–7.

Fig. 5 shows methane conversion over PdA and PdACe catalysts. During the heating ramp, the conversion of methane starts at about 350 °C for PdA. PdACe presents lower activity and only starts to oxidize methane when the temperature exceeds 400 °C. The conversion reaches a maximum at about 800 °C for both catalysts. Nevertheless, PdA presents a conversion of about 73%, against 49% for PdACe. Above the temperature corresponding to this value, the conversion decreases to reach a minimum slightly below 900 °C and eventually increases again. Upon cooling, methane conversion decreases, passing through a minimum at 760 °C for PdACe and 720 °C for PdA; both catalysts show a conversion of about 9%. The conversion then increases, passes through a maximum, and eventually decreases. This behav-

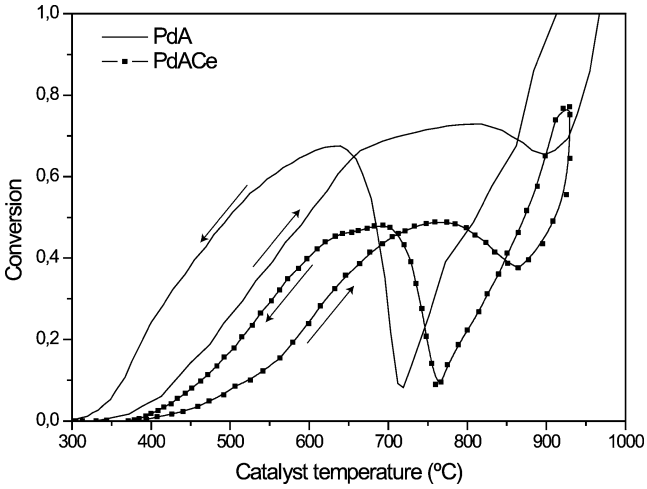

Fig. 5. Catalytic combustion of 1 vol% CH_4 in air over PdA and PdACe catalysts.

ior is typical for the oxidation of methane over palladium in an excess of oxygen and has been attributed to the transition between the active species PdO and a less active Pd^0 [18]. The main feature to be noticed with respect to the comparison of PdA and PdACe is that PdACe presents a lower activity than the Ce-free PdA. In addition, upon cooling, PdACe starts to recover its activity at a temperature of about 40 °C higher than PdA.

Comparing PdBa and PdBaCe in Fig. 6, the conversion of methane takes place in a similar manner. The main difference is that the Ce-doped catalyst presents a higher combustion activity than PdBa. During the heating ramp, the conversion of methane starts at about 400 °C over PdBaCe and 470 °C over PdBa. During the cooling ramp, PdBa recover its activity when the temperature is below 700 °C, instead of 750 °C in the case of PdBaCe. The presence of Ce, in this case, considerably enhances the combustion activity and entails a reoxidation that is initiated at higher temperature.

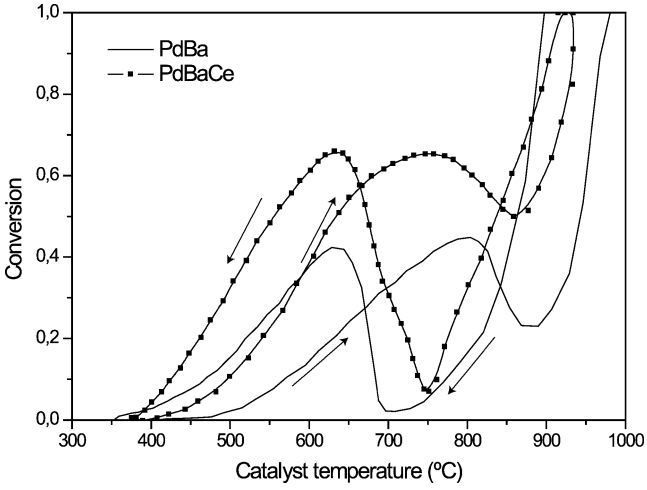

Fig. 6. Catalytic combustion of 1 vol% CH_4 in air over PdBa and PdBaCe catalysts.

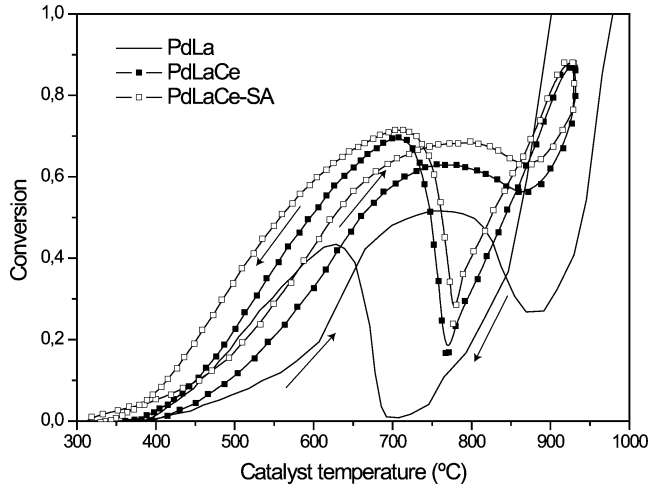

Fig. 7. Catalytic combustion of 1 vol% CH_4 in air over PdLa, PdLaCe, and PdLaCe-SA catalysts.

The effect of Ce addition on PdLa catalyst is reported in Fig. 7. PdLaCe presents a higher conversion than PdLa. During the heating ramp, both catalysts present a decrease in activity at about 775 °C. There is a difference of about 10% with respect to the conversion of methane at this temperature.

Upon cooling, the Ce-free catalyst, PdLa, presents a minimum at 700 °C, with a conversion of about 1%. When the temperature is further reduced, the conversion rises to reach a maximum at 640 °C. Concerning PdLa, the minimum in conversion observed during the cooling ramp takes place at a much higher temperature, 770 °C, and exhibits a conversion of 18%. Comparing PdLaCe and PdLaCe-SA, both catalysts exhibit a parallel profile with respect to their catalytic activity for the combustion of methane. Nevertheless, PdLaCe-SA presents a slightly higher combustion activity than PdLaCe. The PdLaCe-SA exhibits a conversion 10% higher than PdLaCe for a similar catalyst temperature. The decrease and recovery of combustion activity occur at an identical temperature regardless of the method used for the deposition of cerium.

4. Discussion

The effect of La and Ba in PdLa and PdBa, respectively, has been reported in a previous study preformed in our laboratories [8]. The presence of foreign ions such as lanthanum and barium strongly improved the thermal stability of alumina. One of the major drawbacks of the addition of La or Ba is the negative effect with respect to the combustion activity of the palladium particles. We showed that the presence of La or Ba within the alumina structure results in lower catalytic activity for the complete oxidation of methane. In the present study, we focus on the effect of Ce addition on the above-named catalysts. Specific attention has been given to the thermal stability of the catalyst as well as to the effect on the PdO–Pd transition.

4.1. Thermal stability of alumina

Considering the thermal stability of the Ce-doped catalysts, different behaviors are observed. For PdA, the stability of the support is strongly enhanced by the addition of cerium. The BET results show that PdACe exhibits a surface area of 102 $m^2\,g^{-1}$ instead of 87 $m^2\,g^{-1}$ for PdA calcination at 1000 °C for 4 h. This result is corroborated by the XRD analysis. The decrease in surface area observed when alumina sinters is usually accompanied by a modification of the crystal structure. The γ-alumina undergoes changes in crystal phase when submitted to temperatures above 850 °C and α or θ phase are often present following calcination at 1000 °C. No α-Al_2O_3 phase is detected in the X-ray diffractogram of PdACe and the intensity of the θ-Al_2O_3 is significantly diminished when compared to the Ce-free samples where the α-phase can be clearly detected and the θ-reflection is rather intense. The effect of Ce is probably similar to that of La and Ba when the thermal stability of PdBa and PdLa are compared with that of PdA.

When Ba- and La-containing catalysts are investigated, the addition of Ce does not further improve the thermal stability. PdBa and PdBaCe exhibit a BET surface area ($m^2\,g^{-1}$) of 114 and 116, respectively. Similar remarks can be made for PdLa, PdLaCe, and PdLaCe-SA, which have a specific surface area ($m^2\,g^{-1}$) of 107, 102, and 100, respectively. The crystal structure of PdLa and PdLaCe, on the one hand, and PdBa and PdBaCe, on the other hand, are similar and do not present any variation with respect to the observed crystal phases and their intensity.

4.2. PdO–Pd transformation

The PdO–Pd transformation is an important feature of the palladium-based catalysts used for the complete oxidation of methane as it directly affects the combustion activity. It has been evaluated by means of temperature-programmed oxidation (TPO) and examination of the activity profile during combustion experiments. Specific attention is given to the effect of Ce, the deposition technique of Ce, and the nature of the support.

The addition of Ce has various effects with respect to the PdO–Pd transition. The major effect of Ce is to shift the reoxidation of Pd toward higher temperature in the temperature range 600–700 °C. The TPO profiles of the Ce-free catalysts present a single reoxidation peak in the temperature window 500–600 °C. PdACe, PdLaCe, and PdLaCe-SA are all reoxidized in two steps during the cooling ramp, with the first step in the range 600–700 °C and the second step in the range 500–600 °C.

The relative intensity between these two steps strongly varies from one sample to another. In the case of the PdBaCe system, the reoxidation takes place mostly in the low temperature region. In the case of PdACe, the reoxidation starts in the high temperature region, but is completed in the low temperature window. The most noteworthy effect is observed on the PdLaCe and PdLaCe-SA. As seen in Table 2, about 88% of the reoxidation of PdLaCe takes place in the high-temperature region. When Ce has been deposited by specific adsorption this value is even higher and reaches 98%. Besides affecting the temperature at which the reoxidation occurs, we noticed that the presence of Ce results in a higher reoxidation coefficient. The Ce-free samples present a reoxidation coefficient of 1.31–1.56, whereas the Ce-doped catalyst are more oxidized following the cooling step and present a reoxidation coefficient of 1.08–1.31.

This entails that part of the palladium is remaining in the metallic state. This result is in line with the XRD analysis which reported on the presence of small amounts of metallic Pd. Most of the Pd detected by XRD is present as PdO with a reflection at the characteristic value of $2\theta = 33.889°$. When considering the XPS spectra of palladium, PdLa, PdLaCe-SA, and PdBaCe exhibit a large amount of Pd^0, with comparison to the amount of palladium oxide. This result is in contradiction to TPO, XRD, and combustion tests as well. Only PdA presents a Pd^0/PdO ratio which is in agreement with the results obtained suggested by the above-mentioned techniques. XPS analysis takes place under ultrahigh vacuum and due to the small amounts of metal several scans were required in order to obtain a satisfactory signal-to-noise ratio. It has been previously reported that long exposure under ultrahigh vacuum, combined with the photoelectron beam, may result in a substantial "apparent reduction" of the sample due to a charging effect [19]. Kobayashi et al. [20] reported a similar behavior of Pd–Ba/alumina catalysts, in which the BE value for the Pd3$d_{5/2}$ was shifted to a lower value (between PdO and Pd^0). Klingstedt et al. [21] attributed this phenomenon to a strong charge transfer from the BaO, which is a base oxide (electron pair donor), to the Pd^{2+} species at the surface, resulting in a negatively charged PdO. It then appears as metallic Pd^0. The presence of CeO_2 on the support seems to strongly enhance the intensity of this electron transfer. A similar effect is attributed to the apparent reduction of PdO during XPS analysis in the PdLaCe and PdLaCe-SA samples. During XPS analysis of the Ce-free PdA, PdLa, and PdBa, no significant reduction of the samples could be detected.

The values of the Pd^0/PdO ratio for PdA [8] and for the present PdACe are identical. We can therefore conclude that the presence of Ce enhances the reduction of the Pd-based catalyst only when it is in combination with La or Ba. There is a synergy between Ce and La or Ba which entails an easier PdO–Pd transformation.

This idea is confirmed by the combustion tests. The activity of PdLaCe and PdBaCe is higher than that of the Ce-free counterparts. In contrast, PdACe exhibits lower combustion activity than PdA. The use of specific adsorption further improves the combustion activity of the Ce-doped catalyst. The use of specific adsorption results in Ce particles which present a stronger interaction with the Pd particles. The reoxidation of palladium into palladium oxide takes

place at higher temperatures because of the presence of cerium, which is in line with previous studies [22]. This effect is increased when cerium particles are deposited by specific adsorption onto the support.

5. Conclusions

The objective of the present paper was to investigate the influence of Ce addition on γ-alumina, Ba-stabilized alumina, and La-stabilized alumina supports. Specific attention was given to the combustion activity of palladium when deposited on the above-mentioned support. The results have been compared with the activity and properties of the Ce-free counterparts.

Considering the thermal stability of the support, the presence of Ce significantly improves the resistance to sintering of the γ-alumina support. On the other hand, the addition of cerium on the La- and Ba-stabilized alumina supports does not further improve the thermal stability. Temperature-programmed oxidation experiments pinpoint the effect of Ce with respect to the reoxidation of Pd into PdO following the thermal decomposition of PdO. The interaction of Ce with Pd particles results in a reoxidation temperature higher than for the Ce-free samples. This is confirmed by combustion experiments where the Ce-doped catalysts recover their activity at higher temperature. The addition of cerium results in a higher oxidation activity for catalysts supported on La- and Ba-stabilized alumina and lower for the catalyst supported on alumina. Improvement of the deposition technique of cerium results in a more intense effect with respect to both the TPO profiles and activity for the combustion of methane under lean conditions.

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References

[1] W.C. Pfefferle, J. Energy 2 (1978) 142.
[2] R.B. Anderson, K.C. Stein, J.J. Feenan, L.J.E. Hofer, Ind. Eng. Chem. 53 (1961) 809.
[3] J.G. McCarty, Catal. Today 26 (1995) 283.
[4] E.M. Johansson, D. Papadias, P.O. Thevenin, A.G. Ersson, R. Gabrielsson, P.G. Menon, P.H. Björnbom, S.G. Järås, in: J.J. Spivey (Ed.), Catalysis—Specialists Periodical Reports, Vol. 14, Royal Society of Chemistry, Cambridge, UK, 1999, p. 183.
[5] M. Shelef, L.P. Haack, R.E. Soltis, J.E. de Vries, E.M. Logothetis, J. Catal. 137 (1992) 114.
[6] G.W. Graham, H.-W. Jen, R.W. McCabe, A.M. Straccia, L.P. Haack, Catal. Lett. 67 (2000) 99.
[7] R. Taha, N. Mouaddib-Moral, D. Duprez, Appl. Catal. A 223 (2002) 287.
[8] P.O. Thevenin, E. Pocoroba, L.J. Pettersson, H. Karhu, I.J. Väyrynen, S.G. Järås, J. Catal. 207 (2002) 139.
[9] I.I.M. Tijburg, J.W. Geus, H.W. Zandbergen, J. Mater. Sci. 26 (1991) 6479.
[10] D. Papadias, U. Würtenberger, L. Edsberg, P. Björnbom, Chem. Eng. Sci. 57 (2002) 749.
[11] G. Groppi, W. Ibashi, E. Tronconi, P. Forzatti, Chem. Eng. J. 82 (2001) 57.
[12] E.M. Johansson, S.G. Järås, Catal. Today 47 (1999) 359.
[13] A. Talo, J. Lahtinen, P. Hautojärvi, Appl. Catal. B 5 (1995) 221.
[14] L.P. Haack, J.E. de Vries, K. Otto, M.S. Chattha, Appl. Catal. A 82 (1992) 199.
[15] J.Z. Shyu, K. Otto, W.L.H. Watkins, G.W. Graham, R.K. Belitz, H.S. Gandhi, J. Catal. 114 (1988) 23.
[16] M. Valden, R.L. Keiski, N. Xiang, J. Pere, J. Aaltonen, M. Pessa, T. Maunula, A. Savimäki, A. Lahti, M. Härkonen, J. Catal. 161 (1996) 614.
[17] K. Otto, L.P. Haack, J.E. de Vries, Appl. Catal. B. 1 (1992) 1.
[18] R.J. Farrauto, M.C. Hobson, T. Kennelly, E.M. Waterman, Appl. Catal. A 81 (1992) 227.
[19] B. Imelik, J.C. Vedrine, Catalyst Characterization—Physical Techniques for Solid Materials, Plenum, New York, 1994.
[20] T. Kobayashi, T. Yamada, K. Kayano, Appl. Catal. B 30 (2001) 287.
[21] F. Klingstedt, A.K. Neyestanaki, R. Byggningsbacka, L.-E. Lindfors, M. Lundén, M. Petersson, P. Tengström, T. Ollonqvist, J. Väyrynen, Appl. Catal. A 209 (2001) 301.
[22] G. Groppi, C. Cristiani, L. Lietti, C. Ramella, M. Valentini, P. Forzatti, Catal. Today 50 (1999) 399.