



Thermal stability, structural properties and catalytic activity of Pd catalysts supported on Al₂O₃–CeO₂–BaO mixed oxides prepared by sol–gel method

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Dedicated to Professor Renato Ugo in occasion of his 65th birthday

Abstract

Al₂O₃–CeO₂–BaO oxides with constant Al/Ba mass ratio and increasing cerium content were prepared, using the sol–gel procedure, and calcined at 1000 °C for 5 h. The influence of barium oxide on the thermal stability and on the morphological and structural properties of the corresponding supports, in terms of increasing surface area of alumina and ceria dispersion, was studied. The corresponding Pd (1 wt.%) catalysts were prepared by a stepwise impregnation method with a solution of palladium acetylacetonate in benzene. Palladium was introduced in two sequential steps by impregnation 0.5 wt.% of Pd each time. The structural and textural properties of the materials were studied by X-ray diffraction (XRD) analysis, BET surface area and pore size distribution measurements. The effect of ceria on structural properties and methane combustion activity of the Pd-based catalysts was investigated. The light-off temperatures of low-ceria loaded catalysts are both shifted 60–90 °C, respectively, below the corresponding temperature observed on high-ceria loaded samples.

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1. Introduction

Several catalytic processes with environmental application require temperatures of the order 1000–1200 °C and therefore thermally stable catalysts. Among these reactions we can cite the catalytic combustion for application in gas turbines, whose mayor purpose is to minimize the formation of nitrogen oxides [1,2]. One of the most important problems

related to the use of catalysts in this application is the decrease in their activity after thermal exposure to the exhaust gas. Research on the sintering mechanism of supported metal catalysts has been the subject of intense study during the last 20 years [3]. It is well known that the catalyst thermal deactivation is related to the sintering of active components. Alumina, which is one of the most common catalyst carrier, may exist in several transition forms, depending on the temperature and processing conditions [4]. Therefore, the stabilization of transition aluminas, at high temperature, is necessary in order to improve the catalyst durability. To prevent or delay the alumina

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transformations the addition of dopant elements has been extensively used [5,6]. Among these, the most frequently cited are lanthanum [7] and the alkaline earth metals (more often barium) [8]. Alumina–baria doped nano-composites show excellent thermal stability above 1200 °C when a surface layer of BaAl₂O₄ on the alumina crystals is formed. It is also known that ceria can act as phase-stabilizer for γ -alumina, although the stabilization is negligible at temperatures higher than 1100 °C under oxidizing conditions [9]. Ceria is a well known promoter in noble metal-based combustion catalysts [10]. Tests in CH₄ combustion under lean conditions showed that the addition of ceria to Pd supported catalysts strongly improves the catalytic combustion at high temperature [11]. Studies on properties of ceria and related materials have been recently reviewed by Trovarelli [12], however much less work has been done to investigate the influence of catalysts preparation method on the nature of palladium–ceria interactions. Up to now the mechanism by which ceria has a synergistic effect on the noble metal is not yet completely clear, nevertheless has been reported that the effectiveness of the ceria depends on the interaction with the noble metal particles and increases as the ceria particle size decreases [13]. Recently we have studied the effect of baria and ceria addition to Pd-alumina catalysts for hydrocarbons combustion [14]. A good thermal stabilization of the alumina was found, depending on the nature of additives and their weight contents. A synergism between ceria and palladium leading to a better activity in the ethene combustion was also observed.

However, considering that the extent of such beneficial effects depends on several factors, including loading, synthesis procedure, particle size dispersion, we considered of interest to deepen the study of thermal stability and structural properties of Pd catalysts supported on alumina–ceria–baria mixed oxides, by synthesizing a new series of supports. In the present study we have prepared a series of mixed oxides by an improved sol–gel method, with increasing Ce content percentage and constant Al/Ba mass ratio. With the aim to synthesize alumina supports with high specific surface area and good homogeneity, ethyl acetoacetate (etac) for aluminum sec-butoxide complexation, was used in order to control the hydrolysis and gelation processes.

For comparison two binary supports, ceria–alumina and baria–alumina, have been also prepared. The syntheses were performed by sol–gel method which takes advantages of good reproducibility and possibility to introduce the dopant element (Ce, Ba) at different stage of preparation procedure.

Pd (1 wt.%) catalysts were prepared by impregnation, with palladium acetylacetonate, of the resulting oxides calcined at 1000 °C for 5 h. The effects of barium oxide as stabilizing CeO₂–Al₂O₃ surface area and ceria crystallites dispersion were investigated. The study of ceria–palladium interaction on the methane combustion activity was also addressed.

2. Experimental

2.1. Catalyst preparation

The supports were synthesized by sol–gel method, in order to obtain reproducible, homogeneous and thermally resistant materials [15]. The Al₂O₃–CeO₂–BaO supports were synthesized by modifying a described procedure leading to xerogels resistant to high-temperature calcination treatments [16,17]. Indeed, the cerium was added after the gelation step of the alumina–baria pseudo-boehmite hydrated.

A typical preparation of an alumina–ceria–baria oxide is described below: 15 g of aluminum tri-sec-butoxide, Al[O–C₂H₅CH(CH₃)₃] were dissolved in 50 ml of sec-butanol in Ar, under stirring, and added of etac (6.32 ml) for complexation. Calculated amount of barium acetylacetonate hydrate, Ba(CH₃COCHCOCH₃)₂·xH₂O in ethanol was added to this solution and the resulting mixture was stirred for 3 h at 100 °C. The hydrolysis was performed by adding dropwise a water solution (in stoichiometric amount with respect to the aluminum alkoxide) containing NH₄OH, at pH 10. As water was added to the solution, immediately, a fine pseudo-gel was obtained. The resulting suspension was maintained at 100 °C for 16 h to complete the gelation process. Then, the cerium dopant was added as solution of cerium acetylacetonate hydrate, Ce(CH₃COCHCOCH₃)₃·xH₂O in ethanol and the gel was aged at 100 °C for 18 h. After evaporation to dryness, the resulting powder was heated at 250 °C for 3 h, in order to remove physically

Table 1

Chemical composition and main morphological and structural parameters of alumina–ceria–baria mixed oxides, after calcination at 1000 °C for 5 h

Support	Ce (wt.%)	Ba (wt.%)	Al (wt.%)	Ba/Ce (mass ratio)	BET (m ² /g)	<i>d</i> _{CeO₂} by XRD (Å)
Al ₂ O ₃	0.0	0.0	100.0	–	70.0	–
CeO ₂ –Al ₂ O ₃	4.0	0.0	96.0	–	95.0	260.0
BaO–Al ₂ O ₃	0.0	7.4	92.6	–	150.0	–
AlCeBa ₁	4.0	7.4	88.6	1.85	180.0	170.0
AlCeBa ₂	8.0	7.0	85.0	0.87	170.0	185.0
AlCeBa ₃	12.0	6.75	81.0	0.56	148.0	195.0
AlCeBa ₄	16.0	6.45	77.5	0.40	136.0	211.0

adsorbed water, then was calcined in flowing O₂ at different temperatures (rate 10 °C/min), in the range 450–1000 °C to convert the pseudo-boehmite structure to γ -alumina [18]. All the supports with their chemical composition and structural properties after calcination at 1000 °C for 5 h, are listed in Table 1. The oxides were labeled as AlCeBa_{*x*} (*x* = 1–4) as increasing the Ce wt.% content. For reason of comparison a sample of Al₂O₃ and two selected supports CeO₂–Al₂O₃ and BaO–Al₂O₃ were also reported. The chemical composition of the samples, as determined by atomic absorption spectroscopy (AAS) is very close to the theoretical one. On the supports calcined at 1000 °C for 5 h, the Pd (1 wt.%) catalysts were prepared by a stepwise impregnation method using a solution of Pd acetylacetonate, Pd(CH₃COCHCOCH₃)₂ in benzene and stirred at 70 °C for 5 h. In order to control the metal dispersion and to achieve a homogeneous particle size distribution, palladium was introduced in two sequential steps by impregnation (0.5 wt.% of Pd each time). The resulting catalysts were dried in rotavapor, calcined in O₂ (5% in He) at 350 °C for 8 h and reduced in H₂ (5% in Ar) at 350 °C for 6 h, (heating rate 2 °C/min). In Table 2 a list of the structural parameters of Pd (1 wt.%) catalysts along with

the Ce weight content in the corresponding support, is reported.

2.2. Characterization

2.2.1. Surface area and pore size volume determination

Surface area and pore size measurements were performed by using a Sorptomatic 1900 Carlo Erba Instrument. Surface areas were determined by physical adsorption of N₂ at the liquid nitrogen temperature, using the BET equation [19].

Pore size distributions were obtained from the desorption curve of the isotherm, by using the procedure developed by Dollimore and Heal [20].

2.2.2. X-ray analysis

X-ray diffraction patterns were obtained with a Philips diffractometer. Nickel-filtered Cu K α radiation was employed and a proportional counter and a 0.05° step size in 2 θ were used. Crystalline phases were identified by comparison with ICDD reference files [21]. Mean crystallite sizes *d* (Å) of Pd and CeO₂ were estimated using the Scherrer equation [22]. The obtained particle diameters of Pd were converted into

Table 2

Palladium particles size (by H₂ chemisorption and XRD measurements) and calculated Pd dispersion percentage of the Pd–AlCeBa_{*x*} catalysts

Catalyst	Ce (wt.%)	Support mean pore size distribution (Å)	Cumulative pore volume (cm ³ /g)	<i>d</i> (Å) Pd by H ₂ chemisorption	<i>d</i> Pd by XRD (Å)	<i>D</i> _{XRD} (%)
Pd–AlCeBa ₁	4.0	40.0	0.48	30.0	25.0	45.0
Pd–AlCeBa ₂	8.0	50.0	0.47	40.0	30.0	37.0
Pd–AlCeBa ₃	12.0	90.0	0.34	150.0	112.0	10.0
Pd–AlCeBa ₄	16.0	80.0	0.32	100.0	93.0	12.0

Cerium weight content (wt.%) and mean porosity of the corresponding supports are also reported.

the percentage of exposed metallic atoms, $D_x(\%)$, as previously published [23].

2.2.3. H_2 chemisorption measurements

The determination of chemisorbed H_2 allowed to measure the accessible Pd surface of the samples after being calcined “in situ” using O_2 (5% in He) at $350^\circ C$ for 1 h, and reduced with H_2 (5% in Ar), at atmospheric pressure, at $350^\circ C$ for 1 h. The chemisorption measurements were carried out at $70^\circ C$ in order to avoid β -hydride formation, in a pulse flow system equipped with QMS and thermal conductivity detector (TCD). Pulses of H_2 (5% in Ar, loop 0.5 ml) were injected onto the Ar stream flowing on the above reduced sample (250 mg), until the break-through point was attained. Successive injections of H_2 pulses produced, in the TCD signal, peaks of different area. The catalyst metal surface was considered saturated when two consecutive peaks exhibit the same area.

2.2.4. Catalytic reactions

The steady-state activity in methane combustion was studied in a plug-flow reactor equipped with a Balzers Thermostar, mass-quadrupole detector. In a typical experiment, the gas mixture consisting of 1000 ppm of methane and 2.5 vol.% O_2 (He to balance) was led over the catalyst (100 mg diluted with

inert SiC to avoid thermal gradient) at a total flow rate of 50 ml/min, equivalent to a weight hourly space velocity (WHSV) of 30.000 h^{-1} .

Combustion tests were carried out in the temperature range $100\text{--}600^\circ C$, waiting for each temperature that the conversion reaches a constant value, usually within 15–20 min. A thermocouple in contact with the catalytic bed allowed the control of the temperature inside the catalyst. After reaching steady-state conditions, effluent gases were analyzed in real time by mass quadrupole, taking into account for mass overlapping. The CH_4 conversion well corresponds to the CO_2 yield, in any case no CO formation was observed.

3. Results and discussion

The sol-gel synthesis involves the hydrolysis and polycondensation of oxides precursors, as alkoxide or acetylacetonates, producing a transparent gel, that by calcination in flowing O_2 until $1000^\circ C$ turns into a vitreous material. The gel \rightarrow glass transition occurs with considerable modifications in the structural properties of the materials. Fig. 1 shows the X-ray diffraction patterns of a selected sample $AlCeBa_4$, after calcination at $250^\circ C$ (3 h), $450^\circ C$ (4 h), $650^\circ C$ (4 h) and $1000^\circ C$ (5 h), respectively.

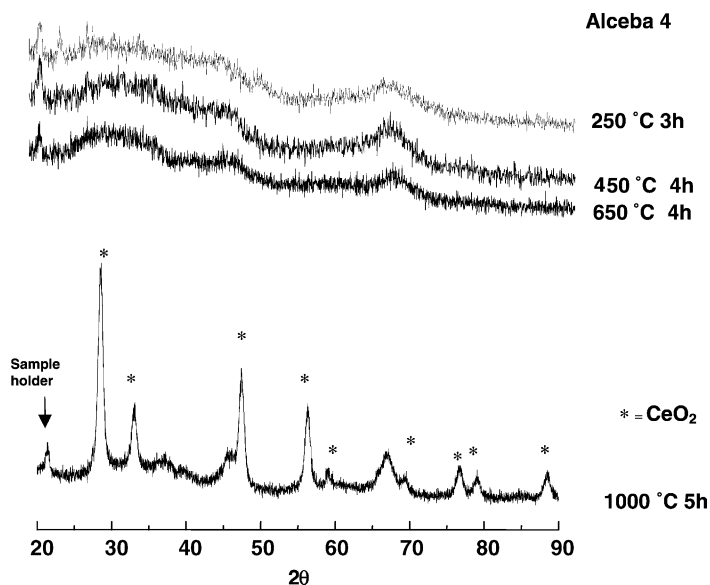


Fig. 1. XRD patterns of the sample $AlCeBa_4$ after calcination treatments at different temperatures (250, 450, 650, $1000^\circ C$).

The pattern of the support calcined up to 650 °C is amorphous, after calcination to 1000 °C characteristic reflections of CeO₂ (2θ values of 28.55°, 33.08°, 47.47°, 56.33°, 59.09°, 69.40°, 76.70°, 79.07°, 88.41°) [ICDD 340394] were observed, whereas, the alumina showed a gradual modification from γ [ICDD 290063] to δ phase [ICDD 160394]. No barium–aluminate features were detected or α -alumina phases. In Table 1 the BET surface area values of the supports AlCeBa_{1–4} are listed along with those of pure Al₂O₃ and two samples CeO₂–Al₂O₃ and BaO–Al₂O₃, synthesized for comparison. A perusal of this table evidences the influence of baria and ceria on the thermal stability and morphology of the alumina supports.

The addition of barium and cerium oxides to alumina results in an enhanced thermal stability of the support, which maintains large surface area after calcination at 1000 °C for 5 h. However, the degree of stabilization strongly depends on the nature of additives and on their weight contents. As comparing ceria–baria doped aluminas with ceria–alumina, baria–alumina and pure alumina, it appears that the presence of a few percent of ceria is sufficient to produce an increase of specific area of the baria–alumina support. For higher ceria loading a decrease of sur-

face area is evidenced, that could be ascribed to the formation of ceria phase well crystallized (see Fig. 1) that induces a sintering of the support. On the other hand, barium is more effective in the alumina structure stabilization. In Table 1 the BET surface area along with the Ba/Ce (mass ratio) are listed for all the synthesized supports, after calcination at 1000 °C for 5 h. The relative surface areas appear to increase as a function of the Ba/Ce mass/ratio. A promoting effect of barium on ceria dispersion was also detected, as shown in Fig. 2, where the relationship between the crystallite size d (Å) of CeO₂ and the Ba/Ce mass ratio is reported.

Ceria is known to disperse and stabilize the metal in a more active form, due to strong metal support interaction (SMSI) effects [12,24,25]. A perusal of Table 2 indicates that Pd catalysts with a low-ceria content (4–8 wt.%) are better dispersed than the corresponding high-ceria (12–16 wt.%) samples. This finding suggests that the presence of cerium in the support, up to a certain amount stabilizes the corresponding Pd catalyst. Accordingly, other authors reported the beneficial effect of cerium in Pt metal particles dispersion [26]. Pd diameters were also determined by H₂ chemisorption measurements, Table 2. The average particle sizes found by chemisorption are

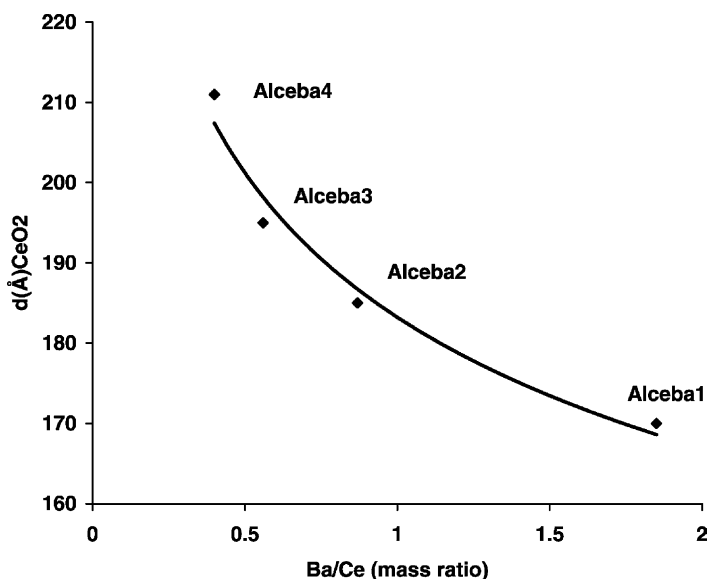


Fig. 2. Dependence of the ceria diameters d (Å), as determined by XRD on the Ba/Ce (mass ratio) for the supports AlCeBa_x ($x = 1–4$), calcined at 1000 °C for 5 h.

systematically higher than the corresponding diameters estimated from XRD data. Nevertheless, the agreement between the two techniques is good and it is confirmed that the low-ceria loaded catalysts are better dispersed than the high-ceria ones.

Some other variables, such as the nature of the support and its morphology were found to have an important effect on the characteristics of the resulting catalysts. A comparison of the Pd particle sizes with supports pore diameters shows that the metal size is always lower or comparable with the pore diameters (see Table 2). It should be noted that the sol-gel procedure allowed the synthesis of alumina-ceria-baria mixed oxides with tailored pore texture and high surface area, after calcination at 1000 °C for 5 h. Moreover, the samples exhibit a better thermal stability, in terms of surface area and pore volume, as compared with our previous results on ceria-alumina based systems [14].

The good correlation reported in Fig. 3 suggests that the support pore sizes can be a determining factor in the extent of metal particles agglomeration. A similar mechanism has been found for the control of PdO particle dimensions [11].

In order to investigate some effect of ceria on the catalytic performances of palladium supported catalysts, activity tests in methane combustion were carried out over the Pd-AlCeBa_x series. In Fig. 4 con-

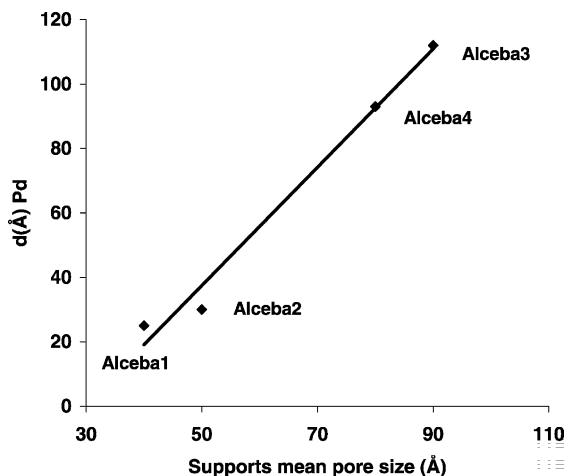


Fig. 3. Dependence of the Pd diameters d (Å), as determined by XRD, on the mean pore size (Å) of the corresponding supports AlCeBa_x ($x = 1-4$).

version curves obtained in steady-state CH₄ combustion experiments are reported. The data evidence that Pd-AlCeBa₁ and Pd-AlCeBa₂ behaved quite similarly and were the most active samples, a decrease of the activity was observed for Pd-AlCeBa₃ and Pd-AlCeBa₄. Thus, it is apparent that the ceria content affects the light-off performances of the corresponding Pd catalysts, being the light-off temperature of low-ceria

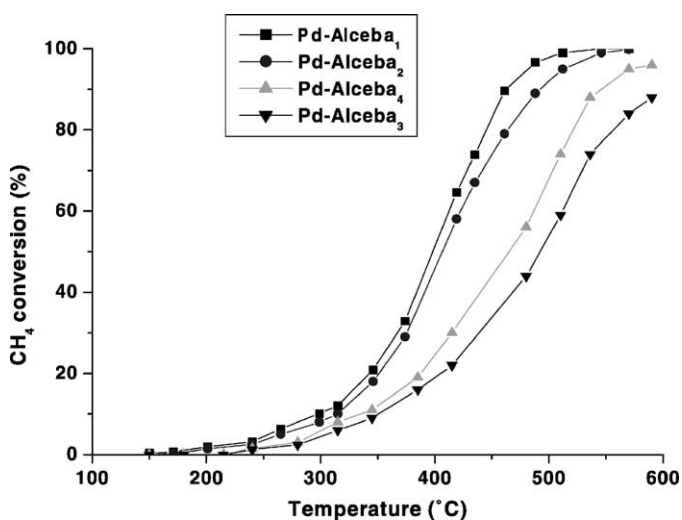


Fig. 4. CH₄ conversion (%) vs. temperature (°C) over Pd-AlCeBa_x ($x = 1-4$) catalysts.

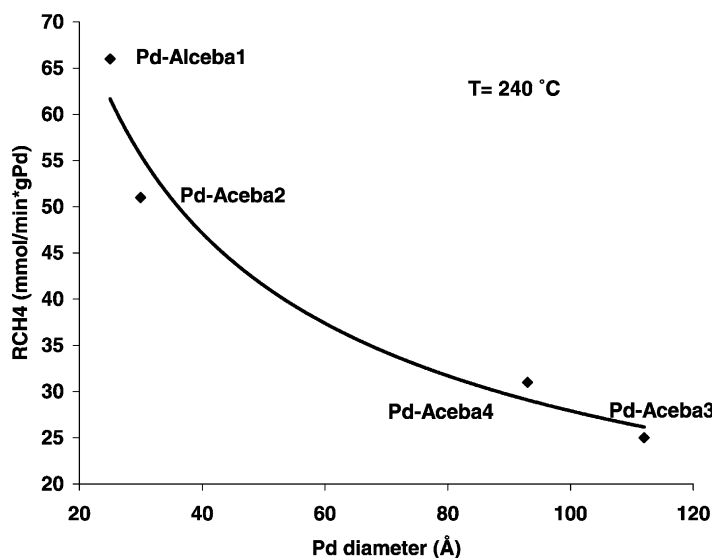


Fig. 5. Rates of CH_4 conversion (r_{CH_4} , $\mu\text{mol}/\text{min g}_{Pd}$) at 240°C vs. Pd diameters (\AA) of the catalysts Pd-AlCeBa $_x$ ($x = 1-4$).

samples shifted $60-90^\circ\text{C}$, respectively, below the corresponding temperature observed on high-ceria loaded samples. The catalytic results, in terms of CH_4 conversion rates (r_{CH_4} , $\mu\text{mol}/\text{min g}_{Pd}$) calculated in differential conditions, at very low conversion are listed in Table 3 along with the turnover frequencies TOF (min^{-1}) arisen from XRD palladium dispersion data. As reported in Fig. 5, the rates of CH_4 conversion decrease with increasing the palladium diameter. This trend might confirm the occurrence of some ceria-Pd interaction, although the influence of samples surface area as well as of surface ceria segregation cannot be excluded.

In summary, according to the literature data [27–29], the results reported so far support the role

of ceria in the stabilization of metallic dispersion that leads to better catalytic performances.

4. Conclusions

The effects of ceria and baria addition to alumina supported palladium catalysts have been investigated through XRD, BET surface area and pore size measurements. The good stability of doped aluminas depends on the synthesis procedure and on the dopant elements. Characterization of the supports has evidenced that barium (about 7 wt.%) is effective in the alumina network stabilization, inhibiting its sintering to α -phase. Cerium can also partially stabilize the surface area of alumina, a few amount (4 wt.%) being sufficient to produce an increase of the surface and an improved thermal stability. For higher loading (>12 wt.%) a decrease of the specific area is evidenced along with sintering of ceria crystallites. The supports porosity is likely responsible for the control of palladium dispersion, although a dependence on the ceria content was also evidenced. Catalytic activity for methane combustion depends on the ceria content which influences the palladium crystallites dispersion. The low-ceria loaded (4–8 wt.%) catalysts were the most active, giving light-off performances at

Table 3

Catalytic results in methane combustion tests, as CH_4 conversion rates ($\mu\text{mol}/\text{min g}_{Pd}$) and turnover frequencies TOF (min^{-1}) calculated from XRD Pd dispersion data

Catalyst	r_{CH_4} ($\mu\text{mol}/\text{min g}_{Pd}$)	TOF (min^{-1})
Pd-AlCeBa $_1$	66.0	0.016
Pd-AlCeBa $_2$	51.0	0.015
Pd-AlCeBa $_3$	25.0	0.026
Pd-AlCeBa $_4$	31.0	0.027

temperature 60–90 °C lower than that observed on high-ceria loaded (12–16 wt.%) samples.

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