Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 107–108 (2005) 487–492

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Effect of the reduction temperature on the catalytic activity of Pd-supported catalysts☆

Victor Ferrer [a], Alexander Moronta [a], Jorge Sánchez [a], Roger Solano [a],
Serafín Bernal [b], Dora Finol [a,*]

[a] Instituto de Superficies y Catálisis, Facultad de Ingeniería, La Universidad del Zulia, P.O. Box 15251, Maracaibo 4003A, Venezuela
[b] Departamento de Ciencias de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cádiz, Spain

Abstract

Four catalysts (0.58%Pd/Al_2O_3, 2.1%Pd/CeO_2, 7%Pd/Al_2O_3 and 7%Pd/$Ce_{0.8}Tb_{0.2}O_x$/La_2O_3-Al_2O_3) were prepared by the incipient wetness impregnation method using aqueous solutions of $Pd(NH_3)_4(NO_3)_2$ and $Pd(NO_3)_2$. In all cases, the metallic loading was referred to as 100 g of support. The catalysts were characterized by XRD, temperature-programmed reduction (TPR) and surface area. The catalytic activity was measured using the methane combustion at 300 °C. The presence of large PdO particles was verified by the diffraction peak observed at 33.8° in the catalysts. TPR results for the 2.1%Pd/CeO_2 catalyst showed that the decoration effect of Pd by the support increased with the reduction temperature. The catalytic activity results revealed that the nature of the PdO_x active phase strongly depended on both the reduction treatment and the oxygen partial pressure. The conversions for catalysts 2.1%Pd/CeO_2 (71%), 7%Pd/Al_2O_3 (79%) and 7%Pd/$Ce_{0.8}Tb_{0.2}O_x$/La_2O_3-Al_2O_3 (80%) were higher than that of catalyst 0.58%Pd/Al_2O_3 (14%).

Keywords: Methane combustion; PdO; Pd catalysts; TPR

1. Introduction

Recently, catalysts for environmental protection have had an accelerated growth, because the pollution problem is progressively more severe. Exhaust gases coming from the internal combustion of automobile engines are a main cause of atmospheric contamination, particularly, in urban areas. These gases contain toxic substances as hydrocarbons, CO and NO_x, generated by incomplete combustion [1,2]. Nowadays, catalytic control systems allow the reduction of the pollutant concentration to desirable values in a narrow range of stoichiometric air/fuel (A/F) ratios. This kind of unit is called "three way catalyst" (TWC) whose name is derived from the functions that it displays, i.e. promoting complete combustion of CO and non-burnt hydrocarbons to CO_2 and H_2O, as well as reducing NO_x to N_2.

The classic formulation of these catalysts includes a support of high surface area (typically, γ-alumina), a redox promoter (classically, CeO_2) and combinations of transition metals (Pt, Pd and Rh) that constitute the active phase. The study of the catalytic combustion of CH_4 is particularly relevant, because it is the most stable hydrocarbon [3,4] and mainly because there is a worldwide agreement of using natural gas as an alternative source of energy [5,6]. The use of Pd as an active phase is related to the well-known application of Pd in reactions of total combustion of light hydrocarbons, particularly, CH_4. Additionally, Pd has economic advantages in comparison with Pt and Rh [7–9]. The cerium oxide is widely used, because of its high capacity to store oxygen, giving oxygen under reduction conditions and taking it under oxidation conditions [10,11], however, CeO_2 presents a poor thermal stability [12].

☆ Paper presented at the "XIX Iberoamerican Symposium on Catalysis", Mérida-México, 2004.

* Corresponding author. Tel.: +58 261 7598797; fax: +58 261 7598797.
E-mail address: dfinol20@hotmail.com (D. Finol).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.07.059

Bernal et al. [13] showed that a new mixed oxide based on cerium could be an alternative for the classic TWC components. The temperature-programmed reduction (TPR) and desorption studies on $CeTbO_x$ mixed oxide revealed that the redox behavior is less affected than that of cerium oxide in successive reduction–oxidation cycles at high temperatures. The incorporation of lanthanide ions to the CeO_2 network is an innovation in the TWC synthesis and the modification of the alumina by La_2O_3 is also a new method for support preparation [14].

The TWC catalysts based on CeO_2 treated at high temperatures in a reductive environment cause the formation of perovskites-type mixed phases, $CeAlO_3$ [15]. These phases stabilize the Ce^{3+} ions allowing irreversible loss of CeO_2 and thus producing the catalyst deactivation. When La_2O_3 is added to alumina, a surface phase ($LaAlO_3$) is formed, which is very similar crystallographically to that of $CeAlO_3$. This phase acts as a barrier, limiting the Ce^{3+} stabilization and therefore, avoiding the deactivation of the mixed oxide.

Previous researches have demonstrated that during the catalytic combustion of methane, the Pd metallic surface structure changes to a more active solid (PdO_x) due to metal–support interactions, particle sizes, heating and cooling cycles and the oxidation and reduction treatments [16,17]. However, there is no agreement about what is the most active state of the catalyst for methane oxidation. Lyubousky and Pfefferle [18] and Oh and Mitchell [19] have argued that the reduced Pd form is more active, while Burch et al. [3,20] considered that it is less active for methane transformation. Although, the particle sizes can change during the reaction, they increase due to particle sintering or decrease because of the break up of the particles [21]. These changes produce variations in the effective Pd surface area and the number of active sites during the reaction.

In this research, the catalytic behavior of Pd supported on cerium–terbium mixed oxide on alumina modified with lanthanum oxide ($Pd/Ce_{0.8}Tb_{0.2}O_x/La_2O_3\text{-}Al_2O_3$) is studied. This catalyst has similar characteristics to those currently used in purifying the pollutant emissions generated by automobile engines, when it is exposed to oxidation–reduction treatments.

2. Experimental

2.1. Preparation of catalysts

The following catalysts $Pd/Ce_{0.8}Tb_{0.2}O_x/La_2O_3\text{-}Al_2O_3$ (Pd/CeTb/La-Al), Pd/Al_2O_3 and Pd/CeO_2 were prepared by wet impregnation of aqueous solutions of $Pd(NH_3)_4(NO_3)_2$ (pH 9) and $Pd(NO_3)_2$ (pH 1). The Pd content in the catalysts was: 7% for Pd/CeTb/La-Al ($S_{BET} = 79\ m^2/g$); 0.58 and 7% for Pd/Al_2O_3 ($S_{BET} = 122\ m^2/g$) and 2.1% for Pd/CeO_2 ($S_{BET} = 64\ m^2/g$). The catalysts prepared using $Pd(NH_3)_4(NO_3)_2$ are henceforth identified with an asterisk.

2.2. Techniques

The surface area of the catalysts was measured by N_2 adsorption at −196 °C, using a Micromeritics GEMINI 2375 porosimeter. The samples were outgassed at 150 °C for 2 h before the measurements in a Micromeritics Flowprep 060. The surface area (S_{BET}) was calculated using BET method.

The TPR measurements were carried out in a stainless steel line coupled to a TCD detector. One hundred milligrams of the fresh catalyst sample was cooled down in Ar at a flow rate of 30 ml/min (99.9999%) up to −80 °C in a cold trap. Then, the flow rate was changed to 30 ml/min of H_2 (5.225%)/Ar and the cold trap was removed. The temperature was increased from −80 to 25 °C, afterwards the catalyst was heated up to 900 °C using a heating program of 10 °C/min. After carrying out the methane oxidation reaction at 300 °C, TPR experiments were performed for the used catalysts. These catalysts were previously subjected to a cleaning treatment at 550 °C in O_2 (5.13%)/He at a flow rate of 30 ml/min for 1 h and then cooled down to room temperature. The reduction was carried out in H_2 (5%)/He at a flow rate of 60 ml/min for 1 h at 500, 600 or 700 °C.

The X-ray powder diffraction patterns of the catalysts were recorded on a Philips PW1150 diffractometer, operating at 40 kV and 20 mA at a 2θ scan rate of 2°/min, using a Cu Kα radiation ($\lambda = 1.5418$ Å).

The palladium dispersion was calculated using a CO:Pd stoichiometry of 1 [8] and assuming that all CO was adsorbed on the exposed Pd atoms. CO adsorption on Pd was measured by a pulse method. One hundred milligrams of the catalyst was treated with 5%O_2 in He at a heating rate of 10 °C/min up to 550 °C for 1 h. Then, the catalyst was reduced in H_2 at 500 °C for 1 h. Afterwards, 1.88 μmol of CO was injected repeatedly until no adsorption was detected.

2.3. Methane oxidation

The methane reaction over the Pd catalysts was performed from room temperature up to 750 °C. One hundred milligrams of the catalyst was cleaned and then reduced at 500, 600 or 700 °C ($\beta = 10$ °C/min). The reactor was fed with a gas mixture using a flow (60 ml/min) of methane (99.99%), oxygen (99.6%) and helium (99.9999%), in stoichiometric proportions ($CH_4/O_2 = 0.5$) or in oxygen excess ($CH_4/O_2 = 0.25$). The methane composition was analyzed at the reactor exit with a FID gas chromatograph equipped with a Molecular Sieve 5A column of 2.5 m.

Catalysts regeneration tests consisted of three successive treatments: (I) after cleaning treatment, the catalyst was reduced at 700 °C before reaction; (II) the previous used catalyst was treated for cleaning, reduced at 500 °C and the reaction was carried out again; (III) the catalyst resulting from treatment II was oxidized at 700 °C for 1 h in O_2 (5%)/

He at a flow rate of 30 ml/min, then, reduced at 500 °C and the reaction was carried out afterwards.

3. Results and discussion

3.1. Characterization of the catalysts

Fig. 1 shows the X-ray diffractograms of the prepared catalysts after calcination at 500 °C for 2 h. The XRD diagram of catalyst 2.1%Pd/CeO_2 (Fig. 1a) presents three sharp peaks, one at 28.9°, which is attributed to the 1 1 1 plane of fluorite structure of CeO_2 and the other two centered at 33.4° and 47.6° correspond to high order reflections of CeO_2 [22,23]. The diffractogram of 7%Pd/Al_2O_3 catalyst (Fig. 1b) shows a peak at 33.8°, assigned to the tetragonal phase of palladium oxide; the other two peaks observed at 13.0° and 45.9° have been attributed to γ-Al_2O_3 phase [14,24]. Finally, the XRD pattern of 7%Pd/CeTb/La-Al catalyst (Fig. 1c) has the characteristic diffraction peaks of cerium oxide (28.9°, 33.4° and 47.6°), alumina (13.0° and 45.9°) and PdO in tetragonal phase (33.8°) [23,24].

Fig. 2 shows the TPR diagrams obtained for 2.1%Pd/CeO_2 catalyst after methane oxidation at 300 °C. Fig. 2a corresponds to the TPR for the fresh catalyst previously cleaned. The peak observed at 34 °C is attributed to the presence of large PdO particles. Lieske and Volter [25] observed the reduction of two different species of Pd: the first one at 5 °C was attributed to the reduction of crystalline PdO and the second one, more stable and reducible at higher temperature (300 °C), was assigned to the reduction of PdO that strongly interacts with the support. The negative peak observed at 86 °C is ascribed to the decomposition of β-hydride palladium phase. This fact is well documented in the literature; it has shown that palladium, at room temperature and above 15 Torr, adsorbs hydrogen due to a superficial process and is also capable to absorb H_2 inducing the formation of massive PdH_x phases, whose formation is favored by the existence of large palladium particles [25–27]. The peak at 846 °C corresponds to the reduction of massive CeO_2, which starts to reduce at 400 °C [28]. Finol et al. [29] reported that the reduction of Ce/Tb mixed oxide starts at 100 °C, reaching two maxima at 500 and 830 °C, attributing the former to the reduction of superficial Ce^{4+} ions and the latter to the reduction of massive Ce^{4+} ions.

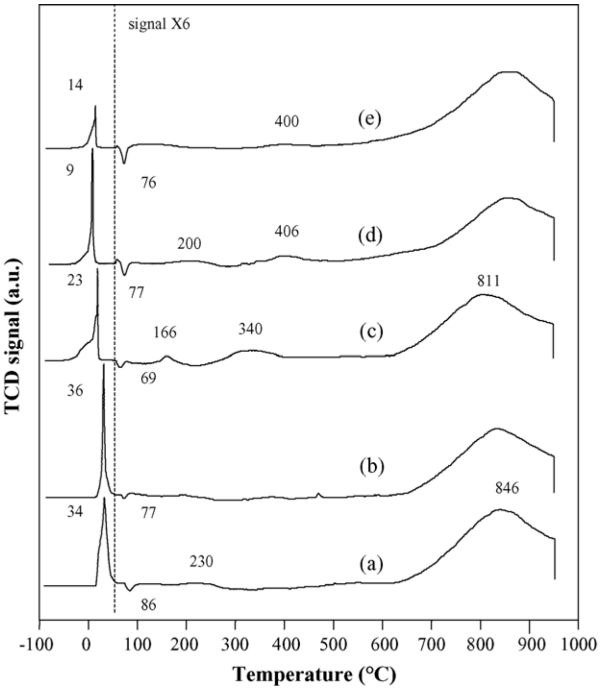

Fig. 2. H_2 consumption for 2.1%Pd/CeO_2 catalyst after reaction at stoichiometric conditions ($CH_4/O_2 = 0.5$): (a) fresh catalyst; (b) after cleaning treatment; (c) reduction at 500 °C; (d) reduction at 600 °C; (e) reduction at 700 °C.

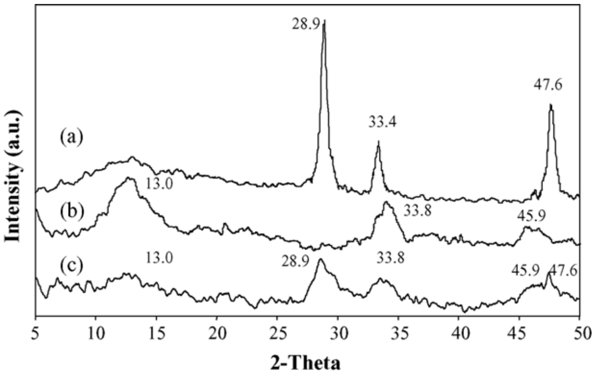

Fig. 1. X-ray diffraction patterns for catalysts: (a) 2.1%Pd/CeO_2; (b) 7%Pd/Al_2O_3; (c) 7%Pd/CeTb/La-Al.

The TPR diagram in Fig. 2b was obtained after reaction at 300 °C, using a catalyst that was only cleaned. The peaks observed were similar to those reported in Fig. 2a, which indicate that the reaction, under operating conditions used did not modify significantly the Pd phase. The TPR diagram of Fig. 2c shows peaks at 23, 69 and 811 °C similar to those observed in Fig. 2a and b, which, respectively, correspond to the reduction of crystalline PdO particles, decomposition of β-hydride palladium phase and reduction of massive CeO_2.

It is worth noticing that H_2 consumption peaks appeared at 166 and 340 °C, which were not observed in Fig. 2a and b. Lieske and Volter [25] and Baldwin and Burch [20] have attributed the peak at 166 °C to the reduction of small Pd particles interacting with the support, while the peak at 340 °C is assigned to the reduction of superficial CeO_2 [8,22]. This suggests that Pd particles are redispersed after being in contact with the reaction mixture at 300 °C. Fig. 2d shows the TPR diagram of 2.1%Pd/CeO_2 catalyst after cleaning and reduction treatments at 600 °C, followed by methane oxidation under stoichiometric conditions. The peaks are similar to those reported in Fig. 2c, discussed previously. Fig. 2e presents a decrease in peak intensity at 14 °C, which perhaps suggests that the active phase loss

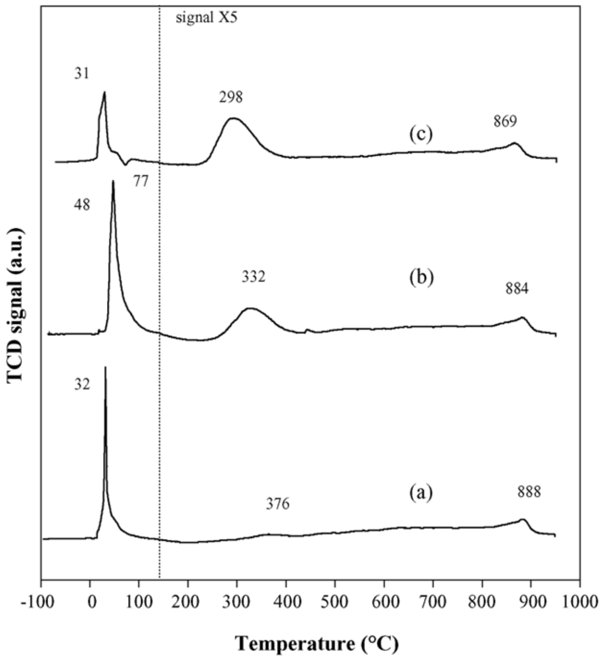

Fig. 3. H_2 consumption for 7%Pd/CeTb/La-Al catalyst after reaction at stoichiometric conditions ($CH_4/O_2 = 0.5$): (a) fresh catalyst; (b) after cleaning treatment; (c) reduction at 500 °C.

could be due to an encapsulation of Pd by the support [30,31].

Fig. 3 shows TPR diagrams for 7%Pd/CeTb/La-Al catalyst. Fig. 3a, representing the fresh catalyst, shows three peaks of H_2 consumption at 32, 376 and 888 °C, which are, respectively, attributed to large PdO particles [8], reduction of the support via spillover and reduction of massive CeO_2 [29]. Fig. 3b also shows three peaks, but at 48, 332 and 884 °C. Comparing Fig. 3a and b, it is necessary to point out that there are differences in the peaks intensity at 48 and 332 °C and to those observed at 32 and 376 °C. These differences in the peaks intensity are due to changes in the nature of PdO_x phases caused by the oxygen partial pressure (p_O) [32]. Fig. 3c presents a negative peak at 77 °C, which is assigned to the decomposition of β-hydride palladium phase indicating a dispersion decrease [25,26,33]. This result is consistent with the low dispersion values for all the studied catalysts reported in Table 1.

Fig. 4 shows TPR diagrams for 7%Pd/Al_2O_3 catalyst. In Fig. 4a, two H_2 peaks at 21 and 291 °C are observed, which correspond to both the reduction of crystalline PdO and reduction of PdO particles that strongly interact with the support [20,25]. Fig. 4b clearly presents four peaks at 17, 76, 281 and 385 °C. The first three are in line with those reported for the fresh catalyst (Fig. 3a). However, the last peak could indicate some changes in the interaction of Pd with the support as a consequence of cleaning and reaction treatments. When comparing Fig. 4c and d with Fig. 4b, non-appreciable changes caused by the reduction temperature were noticed. This could indicate that the catalyst surface was affected by the contact with the reaction mixture, but not by the reduction treatment at 500 °C. The nature of the peaks in Fig. 4d is similar to that of the peaks reported in Fig. 4c. The change in p_O could influence the resulting PdO_x phase on the catalyst.

Table 1
Palladium dispersion in the prepared catalysts

Catalyst	Dispersion (%)
0.58%Pd/Al_2O_3	9.3
7%Pd/Al_2O_3	6.6
2.1%Pd/CeO_2	6.0
7%Pd/CeTb/La-Al	7.3

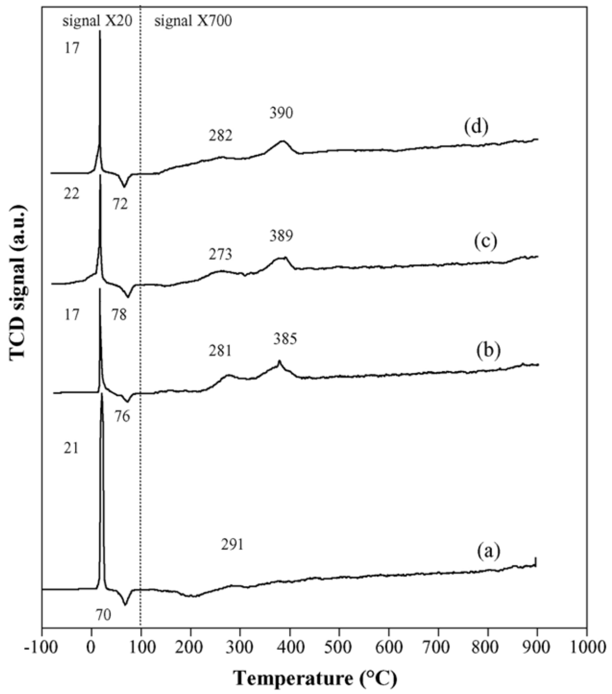

Fig. 4. H_2 consumption for 7%Pd/Al_2O_3 catalyst after reaction: (a) fresh catalyst; (b) cleaning treatment; (c) reduction at 500 °C; (d) reduction at 500 °C in O_2 excess. The reaction conditions for catalyst in (b) and (c) were stoichiometric.

3.2. Catalytic activity

Fig. 5 illustrates the curves of conversion versus temperature for 2.1%Pd/CeO_2, 7%Pd/Al_2O_3 and 7%Pd/CeTb/La-Al catalysts. These curves describe the behavior of the oxidized form in the catalysts obtained after cleaning treatment. The 7%Pd/Al_2O_3 catalyst presented a 33% conversion at 300 °C, followed by 24% for 7%Pd/CeTb/La-Al, 22% for *7%Pd/CeTb/La-Al and 13% for 2.1%Pd/CeO_2. For temperatures higher than 400 °C, methane conversions were >90% for all catalysts. Excepting the 2.1%Pd/CeO_2 catalyst, the other three did not present significant differences in their conversions at 300 °C, thus, giving evidence that the cerium–terbium mixed oxide promoter does not play a key role in the activity. The fact that these three catalysts do not show remarkable differences

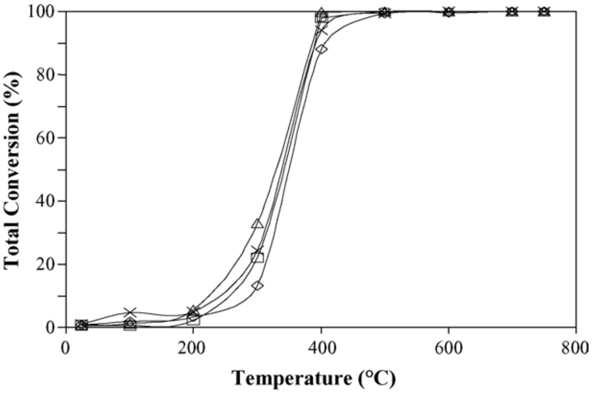

Fig. 5. Conversion vs. temperature curves for methane oxidation at stoichiometric conditions ($CH_4/O_2 = 0.5$) after cleaning treatment for catalysts (◇) 2.1%Pd/CeO_2; (△) 7%Pd/Al_2O_3; (×) 7%Pd/CeTb/La-Al; (□) *7%Pd/CeTb/La-Al.

could be explained by both the similarity in nature of the PdO_x phase on the catalysts after cleaning treatment and the contact with the reaction mixture. The low activity of 2.1%Pd/CeO_2 catalyst could be due to the effect of the support, which has a poor thermal stability [12,31].

Regarding the effect of the Pd precursors, non-significant differences were observed in the activity for samples prepared with $Pd(NH_3)_4(NO_3)_2$ or $Pd(NO_3)_2$, which confirms that the pH of the Pd solution does not influence the activity.

Table 2 reports methane conversion results obtained under stoichiometric conditions. After reducing the catalysts at 500 °C, an increase in the activity was noted, indicating that the treatment caused a change in the nature of the PdO_x phase. The p_O was 5.1 kPa (5%O_2/He) during cleaning treatment and approximately, 6.7 kPa during the reaction. Salomonsson et al. [32] have stated that the nature of the PdO_x phase resulting from the oxidation of Pd^0 is a function of the oxygen partial pressure. Ciuparu and Pfefferle [34] have suggested that the reduction process generates a more active catalytic surface for the methane oxidation.

The 2.1%Pd/CeO_2 catalyst was seriously affected by the reaction treatments. Bernal et al. [30] proposed that for reduction temperatures > 500 °C, a partial deactivation is observed as a consequence of electronic metal–support interactions. The conversion difference between 7%Pd/Al_2O_3 and 7%Pd/CeTb/La-Al catalysts could be explained in terms of the presence of a high Ce content (80%Ce–20%Tb), that probably causes encapsulation of Pd by the support.

Table 2
Methane conversion at 300 °C for 2.1%Pd/CeO_2, 0.58%Pd/Al_2O_3, 7%Pd/Al_2O_3, 7%Pd/CeTbO/La-Al and *7%Pd/CeTbO/La-Al catalysts in stoichiometric reaction conditions ($CH_4/O_2 = 0.5$)

Catalysts	Oxidation (550 °C)	Reduction (500 °C)	Reduction (600 °C)	Reduction (700 °C)
2.1%Pd/CeO_2	13	71	42	18
0.58%Pd/Al_2O_3[a]	9	14	–	–
7%Pd/Al_2O_3	33	79	73	93
7%Pd/Ce_8Tb/La-Al	24	80	88	88
7%Pd/CeTb/La-Al[a]	22	82	–	74

[a] Catalysts impregnated using $Pd(NO_3)_2$ solution.

Table 3
Methane conversion at 300 °C for 2.1%Pd/CeO_2, 7%Pd/Al_2O_3 and 7%Pd/CeTbO/La-Al catalysts in oxygen excess ($CH_4/O_2 = 0.25$)

Catalysts	Oxidation (550 °C)	Reduction (500 °C)	Reduction (600 °C)	Reduction (700 °C)
2.1%Pd/CeO_2	9	59	31	20
7%Pd/Al_2O_3	41	94	94	95
7%Pd/CeTb/La-Al	10	87	70	77

Table 3 reports the methane conversion under oxygen excess conditions. Conversions of 9, 41 and 10% were obtained for 2.1%Pd/CeO_2, 7%Pd/Al_2O_3 and 7%Pd/CeTb/La-Al catalysts, respectively. The differences among the activities could be explained by the formation of a new PdO_x phase, produced by changes in the p_O. For oxygen excess conditions at low temperature, the partial pressure of oxygen is 13.5 kPa, which is twice the pressure at stoichiometric conditions. An increase in the reduction temperature produces similar results to those obtained under stoichiometric conditions.

Despite the 7%Pd/CeTb/La-Al catalyst was treated under severe reduction treatments at 600 and 700 °C, high conversions were obtained (70–77%). However, they were not as high as the conversion detected for 7%Pd/Al_2O_3 catalyst, which showed conversions of 94% at different reduction treatments. Finol et al. [29] carried out temperature-programmed desorption of H_2 on 7%Pd/CeTb/La-Al and 7%Pd/Al_2O_3 catalysts reduced at 700 °C, finding that 7%Pd/Al_2O_3 catalyst did not have any desorption peak of H_2 from the Pd, while 7%Pd/CeTb/La-Al catalyst presented a peak at 100 °C attributed to H_2 coming from the metal. These observations suggest that 7%Pd/CeTb/La-Al catalyst has a better dispersion of the Pd phase than that in 7%Pd/Al_2O_3, which could allow a higher H_2 adsorption. The relative higher dispersion (Table 1) indicates that a less amount of large particles of PdO exists and therefore, the methane oxidation would be less favored.

Catalyst 7%Pd/Al_2O_3 under oxygen excess conditions presented a high activity at all reduction temperatures. The high activity is because of the PdO phase that is thermodynamically stable at both low temperatures and high partial pressures of oxygen. Since Pd/CeO_2 catalyst was the most affected by reduction treatments, the regeneration of the catalyst was obtained by the reduction at 700 °C, carrying out treatment I. After the reduction specified in treatment II, a complete regeneration of the catalyst was obtained due to the high conversion achieved (82%), which is comparable to that obtained for the reduced catalyst at 500 °C (71%). Bernal et al. [35] pointed out that the regeneration of a reoxidized catalyst at 500 °C and reduced at 500 °C showed that deactivation effects are related to electronic perturbations induced on Pd by the reduction of the support. A conversion of 82% was obtained from the reoxidation at 700 °C and reduction at 500 °C (treatment III), which means that reoxidation temperature used did not produce sintering phenomena that causes a catalytic activity loss.

4. Conclusions

Methane oxidation activity is strongly influenced by reduction treatments. The nature of the PdO_x phase is modified by the p_O. The presence of large particles of palladium oxide improves the activity because of high loadings of Pd. CeO_2 was the support more affected by reduction treatments. The use of a strongly acidic Pd precursor does not alter the catalytic properties of the resulting materials. The total regeneration of 2.1%Pd/CeO_2 catalyst confirms that reduction temperatures lower than 700 °C do not produce sintering.

Acknowledgements

This research was partially supported by the Consejo de Desarrollo Científico y Humanístico of La Universidad del Zulia (CONDES). We wish to thank Jackeline Quiñones of Laboratorio de Rayos X of the Universidad Central de Venezuela for XRD analysis and to professors Marlene Castro and Milagros Alburgues for English assistance.

References

[1] C. Satterfield, Heterogeneous Catalysis in Practice, Mc Graw Hill, 1980,, p. 224.
[2] R. Heck, R. Farrauto, Appl. Catal. A 221 (2001) 443.
[3] R. Burch, F.J. Urbano, Appl. Catal. A 124 (1995) 121.
[4] F.H. Ribeiro, M. Chow, R.A. Dalla Beta, J. Catal. 146 (1994) 573.
[5] E. Garbowski, C. Feuni-Jantou, N. Mouaddib, M. Primet, Appl. Catal. A 109 (1994) 227.
[6] A.M. De Groote, G.F. Froment, Appl. Catal. A 138 (1996) 245.
[7] K. Muto, N. Katada, M. Niwa, Appl. Catal. A 134 (1996) 203.
[8] M.F. Luo, X.M. Zheng, Appl. Catal. A 189 (1999) 15.
[9] P. Fornasiero, J. Kaspar, V. Sergo, M. Graziani, J. Catal. 182 (1999) 56.
[10] S. Matsumoto, N. Miyoshi, T. Karazawa, M. Kimura, Toyota Motor Corp., Toyota Aichi. 471 (1991) 335.
[11] A.F. Diwell, R.R. Rajaram, H.A. Chaw, T.J. Truex, in: A. Crucq (Ed.), Catalysis and Automotive Pollution Control II, Elsevier Science Publishers B.V., Amsterdam, 1991, p. 139.
[12] S. Bernal, F.J. Botana, J.J. Calvino, M.A. Cauqui, G.A. Cifredo, A. Jobacho, J.M. Pintado, J.M. Rodríguez-Izquierdo, J. Phys. Chem. 97 (1993) 4118.
[13] S. Bernal, G. Blanco, M.A. Cauqui, P. Corchado, J.M. Pintado, J.M. Rodríguez-Izquierdo, Fourth International Congress on Catalysis and Automotive Pollution Control, CaPoC4, vol. 2, Brussels, 1997, p. 293.
[14] S. Bernal, J. Calvino, G. Cifredo, D. Finol, J. Gatica, C. Kiely, C. López-Cartes, J. Zheng, H. Vidal, Chem. Mater. 14 (2002) 1405.
[15] G. Graham, P. Schmitz, R. Usmen, R. McCabes, Catal. Lett. 17 (1993) 175.
[16] C.A. Müller, M. Maciejewski, R. Koeppel, A. Baiker, J. Catal. 166 (1997) 36.
[17] G. Groppi, C. Cristiani, L. Lietti, C. Parella, M. Valentini, P. Forzatti, Catal. Today 50 (1999) 399.
[18] M. Lyubousky, L. Pfefferle, Catal. Today 47 (1999) 29.
[19] S.H. Oh, P.J. Mitchell, Appl. Catal. B 5 (1994) 165.
[20] T.R. Baldwin, R. Burch, Appl. Catal. 66 (1990) 337.
[21] E. Ruckenstein, J.J. Che, J. Phys. Chem. 85 (1981) 1606.
[22] R. Sasikala, N.M. Gupta, S.K. Kulshreshtha, Catal. Lett. 71 (2001) 69.
[23] D.H. Kim, S.I. Woo, J.M. Lee, O. Yang, Catal. Lett. 70 (2000) 35.
[24] D.H. Kim, S.I. Woo, J. Noh, O.B. Yang, Appl. Catal. A 207 (2001) 69.
[25] H. Lieske, J. Volter, J. Phys. Chem. 89 (1985) 1841.
[26] M. Boudart, H.S. Hwang, J. Catal. 39 (1975) 44.
[27] J. Benson, H. Hwang, M.K. Boudart, J. Catal. 30 (1973) 146.
[28] H.C. Yao, Y.F. Yao, J. Catal. 86 (1984) 254.
[29] D. Finol, A. Moncada, J. Méndez, J. Sánchez, H. Vidal, Rev. Téc. Ing. 25 (2002) 149.
[30] S. Bernal, J. Calvino, M. Cauqui, J. Gatica, C. Larese, J. Pérez-Omil, J. Pintado, Catal. Today 50 (1999) 175.
[31] L. Kepinski, M. Wolcyrz, Appl. Catal. A 150 (1997) 197.
[32] P. Salomonsson, S. Johansson, B. Kasemo, Catal. Lett. 33 (1995) 1.
[33] P. Aben, J. Catal. 10 (1968) 224.
[34] D. Ciuparu, L. Pfefferle, Appl. Catal. A 218 (2001) 197.
[35] S. Bernal, G. Blanco, J. Calvino, C. López-Cartes, J. Pérez-Omil, J. Gatica, O. Stephen, C. Colliex, Catal. Lett. 76 (2001) 131.