The effect of precursors salts on surface state of Pd/Al$_2$O$_3$ and Pd/CeO$_2$/Al$_2$O$_3$ catalysts

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ABSTRACT

The influence of the precursors on the promoting effect of ceria on Pd/Al$_2$O$_3$ catalyst, when ceria is coated over alumina was studied. The reaction of propane oxidation proceeded under different feed conditions and the surface active sites were characterized by X-ray photoelectron spectroscopy (XPS) and in situ diffuse reflectance spectroscopy (DRS).

XPS and DRS results show that PdO/Pd^0 interface are the active sites independent of the precursor, while the catalysts containing CeO$_2$ showed formation of palladium species in the highest oxidation state, probably PdO$_2$ (338 eV) after the oxidation of propane. Besides, the O/Al and O/Ce ratios evidenced the increase of oxygen storage in the presence of CeO$_2$. In addition, the precursor acetylacetonate favors the oxygen storage in the lattice.

Key words: Palladium, cerium oxide, precursors, characterization.

INTRODUCTION

Investigations on oxidation of light hydrocarbons such as the partial oxidation of light hydrocarbons are nowadays significant for hydrogen generation in fuel cells. However, there are questions as how to enhance the hydrogen production with minor CO formation. The choice of the catalyst is very important.

Palladium active sites are influenced by several factors, such as the particle mean size, the support interaction, and the nature of precursor salts. The particle size plays an important role for structure-sensitive reactions since, either the site coordination, such as kink, step, and terrace atoms, or the crystal orientation affect the catalytic reactivity (Somorjai 1994). The metal-support interaction also contributes to change in Pd sites, especially when they are supported on reducible transition metal oxides.

Restructuring of catalytic sites at the interface, electronic transfer or encapsulation of metal particles by reduced support species are some of the explanations that are found in literature to define metal-support interaction nature (Alexandrou and Nix 1994, Bernal et al. 1999).

Some authors (Ribeiro et al. 1994, Marécot et al. 1994, Salasc et al. 1999) have studied the influence of the different precursor salts for the prepara-

tion of catalysts. The nature of palladium precursors and their interaction with CeO_2 affected the metallic dispersion and the site morphologies. Highly dispersed metal particles ($d > 50\%$) were obtained by using palladium chloride and acetylacetonate precursors on Pd/Al_2O_3 catalysts. In the presence of ceria, the Pd dispersion was a function of the way in which each Pd precursor interacted with CeO_2. The metallic redispersion may be the result of the occupancy of ceria oxygen vacancies by the palladium crystallites (Appel et al. 1998).

Previous results evidenced that the presence of CeO_2 affected the propane oxidation, inhibiting the reaction as well as the reforming in the first domain. But the combination of both was beneficial in terms of higher H_2 production. XPS results showed that in catalysts containing CeO_2, palladium species in the highest oxidation state, probably PdO_2 (338 eV) were formed after the oxidation of propane. Moreover, the Cl/Al ratio showed a drastic reduction in residual chlorine. From these results, it was suggested that during the reaction the Pd^0 and PdO could be transformed into PdO_2, favoring the selective oxidation for reforming and high production of hydrogen (Guimarães et al. 2003).

The present study focus attention on the influence of the precursors of palladium salts and the effect on CeO_2/Al_2O_3 samples, for the oxidation of propane. XPS and DRS in situ reaction characterization are used for identification of the surface sites.

EXPERIMENTAL

PREPARATION OF THE CATALYSTS

Gama alumina (Harshaw) with a surface area of 208 m^2/g was used as support. Samples were prepared with 1% of palladium, using the impregnation method and different precursor salts. The catalyst was prepared in two steps. First, impregnation of cerium oxide over the alumina support was carried out, using a cerium acetylacetonate solution with a concentration of 17% of cerium oxide, corresponding to a theoretical monolayer, as described elsewhere (Monteiro et al. 2001) and then calcined with

flowing air at 773 K for 4 h. The BET area was 193 m^2/g and pore volume 0.40 cm^3/g. This system was well characterized as reported previously (Monteiro et al. 2001). Then, Pd was similarly impregnated with 1% metallic palladium. The Pd precursors were $PdCl_2$ (Aldrich, 99.999%) and $Pd(acac)_2$ (Aldrich, 99%). A hydrochloric acid solution was used to dissolve the $PdCl_2$, followed by heating in order to evaporate chloride residues. The solution volume for incipient wetness impregnation was the same as the pore volume of the support. Toluene (Vetec, 99%) was used to dissolve $Pd(acac)_2$ and wet impregnation was carried out at room temperature for 24 hrs, followed by filtration. After impregnation the catalysts were dried in a muffle at 393 K for 18 hrs, followed by calcination in an aerated muffle furnace at 773 K for 4 hrs. Pd-X or PdCe-X (X means Cl or acac) was used to denote Pd/Al_2O_3 or $Pd/CeO_2/Al_2O_3$ catalysts prepared using chloride and acetylacetonate precursors (Table I).

TABLE I
Metal contents and dispersions.

Sample	Pd metal content	Dispersion (%)
Pd-Cl	0.99	51
Pd-acac	0.94	51
PdCe-Cl	0.91	25
PdCe-acac	0.93	50

Both materials were pretreated differently, as reported previously (Guimarães et al. 2003). While the Pd/Al_2O_3 catalyst was submitted to a He flow at 423 K for 30 min, the $Pd/CeO_2/Al_2O_3$ was first calcined with $5\%O_2/He$ at 673 K for 60 min, followed by He flow at 50 ml/min, at 773 K for 90 min. The reduction was similar, first with pure H_2, at 773 K for 60 min, then purging with He at the same temperature.

CHARACTERIZATIONS AND REACTIONS

Characterization techniques were used with measurements in situ, in particular spectroscopic XPS and DRS.

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was performed in a Perkin Elmer instrument using radiation source Al Kα, with energy of 1486.6 eV and 12 kV. The pass time was 0.2 s and scanning of 20, 100, 50, 30 and 10 for elements Ce 3d, Cl 2p, Al 2p, C 1s and O 1s, respectively. For palladium (Pd 3d), 30 and 200 scanning were used in order to observe if photoreduction of palladium might occur after exposure to the X-ray beams. The correction for charging effects was made with the C 1s peak at 284.6 eV. Analyses were performed recording spectra of Pd 3d, Ce 3d, Cl 2p, Al 2p, C 1s and O 1s, for the Pd/Al$_2$O$_3$ and Pd/CeO$_2$/Al$_2$O$_3$ systems. Samples were pretreated with hydrogen and propane oxidation in the presence or absence of water under stoichiometric reaction condition in a pre-chamber. After evacuation and cool down, samples were introduced in the UHV chamber and spectra were obtained as described elsewhere (Guimarães et al. 2003). Aiming to identify the oxidation state of palladium and cerium during the oxidation of propane, the samples were submitted separately to 1% C$_3$H$_8$/He with 5% O$_2$/He, and 1% C$_3$H$_8$/He, 5% O$_2$/He with 5% H$_2$O, both under stoichiometric conditions (R=5.0), at 150 ml/min and at 673 K for 60 min. These experiments were performed ex-situ and the samples were transferred to the pretreatment chamber.

Diffuse Reflectance Spectroscopy (DRS)

Diffuse Reflectance Spectroscopy (DRS) was carried out in a Cary 2000 spectrophotometer equipped with a Harrick System cell and measurements were obtained in situ under similar reaction conditions, as described above. Spectra were taken after treatment at the reaction temperature and cooled to room temperature, in the range of 800-200 nm.

Reaction

The catalytic reaction test was carried out in a micro reactor, using 25 mg of the catalyst diluted in 250 mg of glass. Reaction was performed flowing a mixture of 150 ml/min of 1000 ppm C$_3$H$_8$/He and different O$_2$/C$_3$H$_8$ ratios (R) with balance He. The reaction temperature was 673 K. The reaction of propane oxidation was performed under different O$_2$/C$_3$H$_8$ ratios (reduction R=2.5; stoichiometric R=5 and excess of oxygen R=7.5 and 10). The reaction was stable after 20 h of time on stream. In addition, water was introduced through a saturator under controlled temperature, such as the concentration of water was around 3%. Conversions were calculated by measuring the exit gas composition on a GC chromatograph.

RESULTS

Reaction Kinetics and the Influence of the R ratio ([O$_2$]/[C$_3$H$_8$]) on the Precursor

Figure 1 shows the conversion of propane for different precursors after 20 h with time on stream as function of the oxygen/propane ratio, and at a constant temperature (673 K). The conversion increases with the R ratio but presents a different behavior for the acetylacetonate precursor, indicating a minimum around R=5.
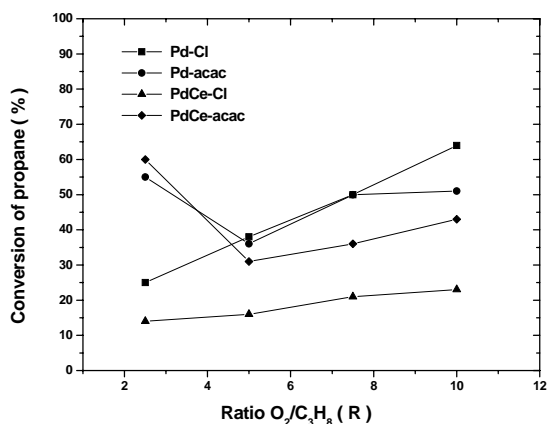

Fig. 1 – Conversion of propane – the effect of the ratio oxygen/propane and the precursor.

The reaction rate was determined using the general power rate law according to

$$Rate_{C_3H_8} = k(C_{C_3H_8})^{\alpha} (C_{O_2})^{\beta} (C_{H_2O})^{\gamma}$$

where k = reaction constant; α, β and γ = reaction orders.

These parameters were calculated from the experimental data. Table II and III present the values with or without water addition. Results show an inhibiting effect of water and dependence of the feed conditions. In these cases, the α and γ values are negative for all catalysts.

TABLE II

Influence of partial pressure on the reaction order in the presence of water.

Catalyst	Reaction order		
	C_3H_8 (α)	O_2 (β)	H_2O (γ)
Pd-Cl	–	–0.7	–0.6
Pd-acac	–0.4	–1.0	–0.6
PdCe-Cl	–	0	–0.6
PdCe-acac	–0.7	0	–0.6

TABLE III

Influence of propane and oxygen partial pressures on the reaction rate in the absence of water.

Catalyst	Reaction order	
	C_3H_8 (α)	O_2 (β)
Pd-Cl	0.3	0.6
Pd-acac	0.3	0.6
PdCe-Cl	0.3	0.9
PdCe-acac	0.3	1.0

The effect of the partial pressure of oxygen, as presented in Table II and III, indicates strong influence of the CeO_2. The chloride and acetylacetonate precursors (Pd-Cl and Pd-acac) exhibited negative values, $\beta = -0.7$ and -1.0, respectively. We observed, as described in the discussion, re-dispersion of Pd after introducing water in the reactants, which means that these reactants are strongly adsorbed provoking negative orders, as indicated in Table II. The effect of the precursor on the reaction rate is indeed noticed in Table II. The reaction orders of oxygen are different for chlorine and acetylacetonate precursors in the presence of water. The more negative order of oxygen for the acetylacetonate precursor decreases the reaction rate with increasing oxygen until saturation (R=5), as shown in Figure 1. On the other hand,

it seems that ceria affected the interaction of oxygen with the palladium sites during the reaction, because the reaction order was $\beta = 0$ for both cases, PdCe-Cl and PdCe-acac. However, in the absence of water (Table III) the effect of propane partial pressure on the reaction rate was relatively small, because $\alpha \cong 0.3$ in the range of $5 \leq R \leq 10$. On the other hand, the value of β varies from 0.6 to 1.0 without water for all catalysts, suggesting that the reaction rate increases with oxygen partial pressure.

DIFFUSION REFLECTANCE SPECTROSCOPY IN SITU (DRS)

The DRS spectra of the Pd/Al_2O_3 and $Pd/CeO_2/Al_2O_3$ catalysts, after successive cycles of treatment, are presented in Figure 2 and 3, respectively. The Pd-Cl and Pd-acac catalysts exhibit ionic palladium species, even after reduction, as shown in bands A and B. The oxide samples present besides the band A (300 nm) the band D (400 nm), which is attributed to the transition band d-d of palladium, according to the literature (Tessier et al. 1992, Rakai et al. 1992). After treatment of the reduced samples with inert gas and oxygen, both in the presence of water, there are two new bands appearing at C (370-380 nm) and E (450-460 nm). According to Tessier et al. (1992) these bands are associated to the formation of two types of complexes in the coordination sphere of palladium, such as $Pd(H_2O)_4^{+2}$ and PdO_2, respectively.

The DRS spectra of the PdCe-Cl and PdCe-acac, in Figure 3, exhibit significant modifications. Besides the small intensity band relative to the palladium, the band C (370-380 nm) disappeared and a new band appeared at C' (480 nm), which is attributed to the formation of palladium oxide as bulk oxide, and therefore, an oxide which is less susceptible to the support. In addition, notice the absence of band A' (420-430 nm), which is attributed to the transfer charge of palladium.

With CeO_2 the transition d-d bands are shifted toward higher wavelengths, D' (500 nm) and E' (530 nm). Worth noticing is the great intensity and broadband of the reduced palladium when compared to the oxide catalyst. According to Tessier et al.
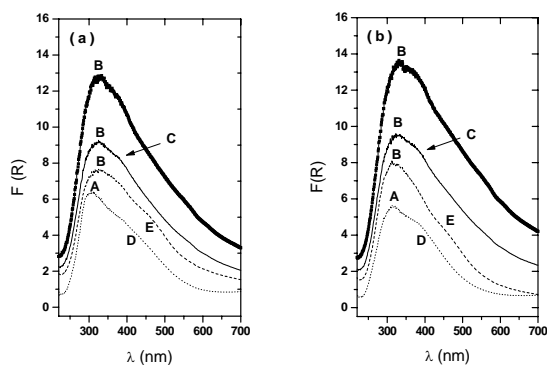
Fig. 2 – DRS spectra after successive treatment cycles; (· · ··) oxidation, (━━) reduction, (───) reduction +3% H_2O/He at 673K, (- - - -) reduction +3% H_2O/5% O_2/He at 673K. (a) Pd-Cl e (b) Pd-acac.
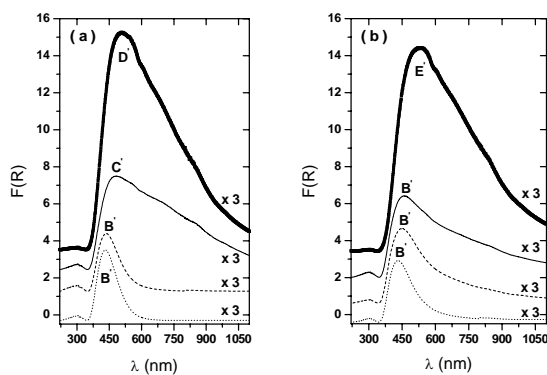

Fig. 3 – DRS spectra after successive treatment cycles; (· · ··) oxidation, (━━) reduction, (───) reduction +3% H_2O/He at 673K, (- - - -) reduction +3% H_2O/5% O_2/He at 673K. (a) PdCe-Cl e (b) PdCe-acac.

(1992) it is probably a superposition of the adsorption bands of the ionic and the reduced species, which cannot be disregarded and probably avoids the formation of surface of palladium complexes with chlorine.

X-ray Photoelectron Spectroscopy (XPS)

XPS results for Pd/Al_2O_3 are displayed in Table IV, showing that the binding energy of Pd $3d_{5/2}$ changed after successive cycles of treatment. The binding energy of Pd after reduction was 335.2 eV, in agreement with the literature for metallic palladium (Brun

et al. 1999). However, after oxidation of propane (O_2/C_3H_8, R=5.0 at 673 K), it is shifted to 337.2 eV for the Pd-Cl catalyst. The Pd-acac shifted similarly to 336.8 eV under similar reaction conditions.

The effect of water is seen comparing the line shapes. No significant difference was observed for the $Pd_{5/2}$ binding energy, which was shifted towards 336.9 eV and 336.6 eV in the presence of water for Pd-Cl and Pd-acac, respectively. This value corresponds to a higher oxidation state of palladium than PdO (336.3 eV), probably Pd^{+x}, according to the literature (Brun et al. 1999).

The XPS results for Pd/CeO_2/Al_2O_3 (Table V) after reduction also evidence the presence of metallic Pd (335.4 eV), similar to the reduced Pd/Al_2O_3. However, after oxidation and with water, the band shift of Pd was greater than 2.0 eV, which also corresponds to a higher oxidation state, probably PdO_2 (338 eV). The binding energy of $Pd_{5/2}$ for the PdCe-acac was 338.0 and 337.6 eV, without and with water, respectively. Similar values were obtained for PdCe-Cl.

Table IV presents the surface atomic ratio of the elements for the Pd/Al_2O_3 catalysts. The Cl/Al ratio is 0.004 for the catalyst with chloride precursor after reduction. However, after oxidation it increases, evidencing enrichment of chlorine at the surface and with water it decreases to 0.0115. The same occurs with the Pd-acac catalyst, which evidences that the support contains residual chlorine and was practically eliminated after oxidation of propane with water, reducing their content from 0.0060 to 0.0011.

The O/Al ratio on the reduced samples was 2.07, while after reaction it increases to 2.15 and 2.16 for the precursors Pd-Cl and Pd-acac, respectively; thus, above the theoretical value of Al_2O_3 (O/Al ≥ 1.50). After oxidation with water it increases slightly to 2.20 and 2.25, for Pd-Cl and Pd-acac, respectively. However, with the incorporation of CeO_2, these ratios increased drastically, ranging from 3.70 after reduction to 5.60 and 6.80 after oxidation, or 6.60 and 7.20 with water, for the PdCe-Cl and PdCe-acac, respectively. This is approximately 3 times in relation to the precursors without CeO_2.

TABLE IV

Bond energy for Pd 3d$_{5/2}$ and atomic ratios by XPS for Pd/Al$_2$O$_3$.

Sample	Treatment	Bond Energy[1] (eV)	Atomic ratio		
			Pd/Al[2]	Cl/Al[3]	O/Al[4]
Pd-Cl	reduced	335.2	0.0024	0.0040	2.07
	C$_3$H$_8$/O$_2$	337.2	0.0022	0.0150	2.15
	C$_3$H$_8$/O$_2$/H$_2$O	336.9	0.0029	0.0115	2.20
Pc-acac	C$_3$H$_8$/O$_2$	336.8	0.0018	0.0060	2.16
	C$_3$H$_8$/O$_2$/H$_2$O	336.6	0.0016	0.0011	2.25

[1]Pd 3d$_{5/2}$ [2]Al 2p   [3]Cl 2p   [4]O 1s.

TABLE V

Bond Energy for Pd 3d$_{5/2}$ and atomic ratios by XPS for Pd/CeO$_2$/Al$_2$O$_3$.

Sample	Treatment	Bond Energy[1] (eV)	Atomic ratio			
			Pd/Al[2]	Cl/Al[3]	O/Al[4]	O/Ce[5]
PdCe-Cl	reduced	335.4	0.05	0.29	3.70	3.10
	C$_3$H$_8$/O$_2$	337.8	0.22	0.18	5.60	3.30
	C$_3$H$_8$/O$_2$/H$_2$O	337.6	0.23	0.12	6.60	4.10
PdCe-acac	C$_3$H$_8$/O$_2$	338.0	0.11	0.03	6.80	3.60
	C$_3$H$_8$/O$_2$/H$_2$O	337.6	0.12	0.03	7.20	3.80

[1]Pd 3d$_{5/2}$ [2]Al 2p   [3]Cl 2p   [4]O 1s   [5]Ce 3d total.

This big increase of O/Al ratio and the shift of the binding energy of Pd 3d$_{5/2}$ reveal the incorporation of oxygen, suggesting storage of oxygen in the CeO$_2$ lattice and in the palladium after the reaction cycle.

Table IV and V present the Pd/Al ratio for similar conditions of treatments. After reduction the Pd/Al ratio was 0.0024 for Pd-Cl, increasing drastically to 0.05 for the PdCe-Cl. After oxidation, both precursors follow the same trend, evidencing strong modification in the Pd surface with CeO$_2$.

DISCUSSION

The catalysts with different precursors, as shown in Fig. 1, displayed marked differences due to the precursors and the promoter CeO$_2$. Indeed, XPS and

DRS results showed surface modifications after the reduction and oxidation reactions, which affected the nature of sites and the interaction of the palladium with the support, although, the dispersion was approximately equal for all precursors, with the exception of the catalyst PdCe-Cl, as shown in Table I.

Burch et al. (1998) observed the effect of chlorine on the palladium dispersion employing an alumina support. Indeed, during the oxidation of propane the water formation is responsible for the release of residual chlorine, re-dispersing Pd at the surface with the formation of oxy-chloride intermediates (Pd$_x$O$_y$Cl$_z$), as also observed by Schmal et al. (2000) and Gaspar and Dieguez (2000). This phenomenon was associated with the dissociation of water on the palladium sites. Thus, H* and OH*

formed on the catalyst recombine easily with chloride at the interface of the metal, regenerating the metal sites for the propane oxidation. In fact, DRS measurements evidence the presence of $Pd_x(OH)_yCl_z$ and XPS results show oxi-chloride species ($Pd_xO_yCl_z$), as evidenced by the binding energy of Pd $3d_{5/2}$ located between the energy of PdO (336.3 eV) and PdCl2 (337.8 eV).

DRS results showed also the presence of $Pd(H_2O)_4^{+2}$ and PdO_2, respectively. Rakai et al. (1992) assert that palladium is present in square planar coordination, where the formation of a palladium complex is a function of the strength of the bonding molecule, such as O_2, H_2O and NH_3. In addition, DRS results evidence an electronic interaction of the Pd-Ce in the coordination sphere. Similar to the Pd/Al_2O_3 catalysts also ionic species of Pd^{+x} in the reduced catalysts were observed in the presence of the promoter.

On the other hand, the XPS results before and after oxidation in the pre-chamber show a shift of the binding energy of Pd towards 337.2 eV, which is attributed to a higher oxidation state of palladium, according to the literature (Burch et al. 1998, Guimarães et al. 2003). This shift evidences that metallic Pd and PdO/Pd^0 interfaces coexist, which are the active sites for the oxidation reaction (Burch et al. 1998).

XPS results for the catalysts containing CeO_2 showed the same tendency, however, there is an indication of the formation of palladium species in a higher oxidation state, probably PdO_2 (338 eV) after the oxidation of propane. Probably, the presence of PdO_2 is due to oxygen transfer from the promoter to the PdO interface, inducing the formation of new interfacial sites for the oxidation reaction.

We observed another effect of the precursor, based on Figure 1, indicating that during the oxidation the conversion varied with the O_2/C_3H_8 ratio, and differed for each precursor. For reduction conditions, low O_2/C_3H_8 ratio, the effect of the precursor is noteworthy. Searching for an explanation, we observed through XPS analysis, that the oxygen content and in particular the O/Al and O/Ce ratios

before and after oxidation exhibited marked differences with the precursors and with the presence or absence of CeO_2, which evidences excess of oxygen in the lattice. According to Tables IV and V the O/Al ratio increased 3 times with CeO_2 compared to the non-promoted catalysts. After oxidation and with the addition of water this ratio doubled and increased yet more for the PdCe-acac precursor. These results confirm the occurrence of redox processes and oxygen storage in the lattice, depending of the precursor. This oxygen supplies the oxygen needed for the oxidation of propane and the oxygen for the higher oxidation sate of palladium. Moreover, CeO_2 not only is a source of oxygen but also a stabilizer of the catalyst. It also affects the selectivity for hydrogen formation in the partial oxidation, as reported previously (Guimarães et al. 2003).

CONCLUSIONS

XPS results evidence Pd^0 (335.2 eV) in the fresh catalyst. After reaction, results show PdO/Pd^0 interface as the main active sites, independent of the precursor. Catalysts containing CeO_2 showed the same trend, indicating formation of palladium species in the highest oxidation state, probably PdO_2 after the oxidation of propane. Besides, the O/Al and O/Ce ratios evidenced an increase of oxygen storage in the presence of CeO_2, which depends of the precursor. The precursor acetylacetonate favors oxygen storage.

RESUMO

Estudo da influência dos precursores sobre os catalisadores de Pd/Al_2O_3 promovidos com céria ancorado sobre a alumina. A oxidação do propano foi feita sob diferentes condições de alimentação sendo caracterizados os sítios superficiais por Espectroscopia Fotoeletrônica de raios X (XPS) e por Refletância Difusa em ''situ''.

Resultados de XPS e DRS mostraram a formação de interfaces de PdO/Pd^0 como sendo os sítios ativos, independentes do precursor utilizado na preparação, enquanto que os catalisadores contendo CeO_2 mostraram a formação de espécies de paládio com estado de oxidação mais altos, provavelmente PdO_2 (338 eV) após a oxidação do

propano. Além disso, as razões O/Al e O/Ce evidenciaram um aumento de oxigênio armazenado na presença de CeO_2. O precursor acetilacetonato favoreceu o armazenamento de oxigênio na rede.

Palavras-chave: Paládio, Céria, precursores, caracterização.

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