Surface Sites of Pd/CeO$_2$/Al$_2$O$_3$ Catalysts in the Partial Oxidation of Propane

A. L. Guimarães, L. C. Dieguez, and M. Schmal*

NUCAT/PEQ/COPPE, Federal University of Rio de Janeiro, C.P. 68502, CEP 21945-970,
Rio de Janeiro, Brazil

Propane oxidation was studied on a Pd-supported Al$_2$O$_3$ catalyst promoted by ceria, when this ceria was first grafted as a monolayer over alumina. The reaction proceeded under different feed conditions, and the surface sites were identified by X-ray photoelectron spectroscopy (XPS) in a pretreatment chamber and then compared to temperature-programmed desorption, temperature-programmed surface reaction (TPSR), and catalytic results, in the presence and absence of water. Stable catalyst performance was achieved in experiments after 20 h with time on stream, to get reliable data for further interpretation. This observation is true for all reaction conditions, with reducing, stoichiometric, or excess oxygen content in the reaction feed. The Pd/CeO$_2$/Al$_2$O$_3$ catalyst is less active for oxidation at low temperatures but suddenly becomes very active at high temperatures. However, in the case of the latter, large quantities of H$_2$ were released, which suggests a drastic change in selectivity. TPSR results showed that the presence of CeO$_2$ affected the oxidation, inhibiting the reaction as well as the re-forming in the first domain. But the combination of both was beneficial in terms of higher H$_2$ production. XPS results showed that the catalysts containing CeO$_2$ form the highest oxidation state palladium species, probably PdO$_2$ (338 eV), after the oxidation of propane. From these results it is suggested that besides the Pd^0/PdO interface, which are active sites for propane oxidation, the Pd^0/PdO$_2$ sites also favor the selective oxidation toward re-forming.

Introduction

The investigation of oxidation of light hydrocarbons has been successful, and there are many papers discussing the problems concerning this reaction. In particular, the catalysts are very susceptible to poisoning due to the presence of compounds and/or products of reaction, which deactivate the catalysts very quickly. Besides the total oxidation, which is important for environmental reasons, several authors pointed out that the partial oxidation of light hydrocarbons is nowadays significant for hydrogen generation in fuel cells. However, there are questions as to how to increase hydrogen and produce less CO. In this case the choice of catalyst is very important. Important questions, such as the presence of water, can affect the active sites for catalysis.

The influence of products and subproducts, such as CO, CO$_2$, and H$_2$O, and the different precursor salts for the preparation of catalysts have been studied by Ribeiro et al.,[1] Marécot et al.,[2] and Salasc et al.[3] Their catalysts, when prepared with precursors containing chlorine, were inferior, inhibiting the reactions under oxidative conditions. However, some specific additional effects were observed when the chlorine content was very low and under reductive conditions, improving the activity of these catalysts.

The literature contains strong evidence for the main role of the active sites of these catalysts in the oxidation reaction. Burch et al.[4] suggested that interfaces such as Pd^0/PdO are the active sites for propane oxidation. In our previous work, we agreed with this suggestion. Besides, when in the presence of water, these active sites are deactivated, because of the formation of palladium hydroxides. However, the process is reversible.[5]

Cerium oxide has been suggested to promote catalysis of oxidation reactions, due to its oxi-reduction potential and mainly due to the high capability of oxygen storage. Indeed, the easy transition between oxidation states Ce^{3+}−Ce^{4+} is essential to promote catalysis, especially in oxidation reactions. However, ceria causes several additional problems. On one hand, it stabilizes the catalyst, but on the other, it also creates side reactions, which causes changes at the surface sites. The main questions are what happens during the reaction and what kinds of surface active sites are formed or changed.

The present study seeks to focus on these questions in the oxidation of propane and test the promoting effect of ceria on the Pd/Al$_2$O$_3$ catalyst, prepared by coating the alumina with ceria and then spreading Pd over both. The reaction was studied under different feed conditions, and the surface active sites were characterized by X-ray photoelectron spectroscopy (XPS) in situ and then compared to the tempperature-programmed desorption (TPD), temperature-programmed surface reaction (TPSR), and catalytic results, to yield an explanation of the surface active phenomena in the presence and absence of water.

Experimental Section

Preparation of the Catalysts. γ-Alumina (Harshaw) was used as support, with a surface area of 208 m^2/g. One sample was prepared with 1% of palladium, using the conventional incipient wetness method and palladium chloride as precursor. A hydrochloric acid solution (1:1) was used for dissolution of PdCl$_2$, followed by heating to eliminate residual chlorine. The second catalyst was prepared in two steps. First, Cerium oxide was added to the surface of alumina support, using a cerium acetylacetonate solution whose concentration corresponded to 17% of the cerium oxide present in a theoretical monolayer formation, as described elsewhere.[6] The BET area was 193 m^2/g

* To whom correspondence may be addressed. E-mail: schmal@peq.coppe.ufrj.br.

and pore volume was 0.40 cm^3/g. This system has been well characterized, as previously shown.[7] After calcination with a flux of air at 773 K for 4 h, Pd was similarly impregnated, so that the final Pd content was held at around 1% of that of metallic palladium. After impregnation, these samples were dried in a muffle furnace at 393 K for 18 h, followed by calcination in flux of air at 773 K for 4 h. Pd−Cl and PdCe−Cl were used as references for Pd/Al$_2$O$_3$ and Pd/CeO$_2$/Al$_2$O$_3$, respectively.

The samples were pretreated differently; while the Pd/Al$_2$O$_3$ catalyst was submitted to a flow of He at 423 K for 30 min, the Pd/CeO$_2$/Al$_2$O$_3$ catalyst was first calcined with 5% O$_2$/He at 673 K for 60 min, followed by a 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, and then purged with He at the same temperature. The metallic surface area was measured by H$_2$ chemisorption. The calculated dispersions were 51% and 25% for Pd−Cl and PdCe−Cl, respectively, as reported previously.[7]

Characterization and Reactions. The principal characterization techniques were chosen in order to make measurements on these samples in situ. Specifically, XPS, TPSR, and TPD were used. A quadrupole mass spectrometer was used to record the signal intensity of different masses (*m/e* 2, 16, 18, 28, 32, and 44) during TPSR and TPD. Quantification was done through calibration of each component and expressed in mole fraction.

TPD and TPSR measurements were carried out in a multipurpose unit, equipped with mass flow meters for blending gases and coupled to a quadrupole mass spectrometer. A heating system was adapted to raise the temperature to desired settings. TPD was obtained by pulse adsorption of a mixture of 1% C$_3$H$_8$/He at room temperature and desorbed with He flow at a heating rate of 10 K/min, up to 773 K. TPSR was performed by using a flux of the reaction mixture under reducing conditions (150 mL/min of 1% C$_3$H$_8$/He and 2.5% O$_2$ balanced with He), at a high heating rate of 20 K/min up to 823 K, to avoid readsorption during heating. Different reaction conditions were selected, to study the reaction under reduction conditions ($R =$ 2.5), with or without water in the feed, and under selective reforming ($R = 0$, $S = 3$), where R is the molar ratio O$_2$/C$_3$H$_8$ and S the molar ratio H$_2$O/C$_3$H$_8$ in the main stream feed.

The catalytic reaction test was carried out in a microreactor at atmospheric pressure, using 25 mg of the catalyst diluted in 250 mg of glass, under different ratios (2.5, 5, and 10) and at flow rates of 150 mL/min of 1% C$_3$H$_8$/He and y% O$_2$ balanced with He. The reaction temperature was 673 K, and the total time of the reaction was 40 h. Conversions were calculated by measuring the exit gas composition on a GC chromatograph.

X-ray photoelectron spectra were obtained on a Perkin-Elmer model no. 1257 instrument using Al Kα as the radiation source, with energy of 1486.6 eV and 12 kV. The pass time was 0.2 s with scanning of 20, 100, 50, 30, and 10 for elements Ce (3d), Cl (2p), Al (2p), C (1s), and O (1s), respectively. For Pd (3d), 30 and 200 scannings were used in order to observe if photoreduction of Pd might occur after exposition to the X-ray beam. Correction of the charge effect 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 then propane oxidation was performed in the presence or absence of water under stoichiometric reaction conditions in a prechamber. After evacuation and cool down, samples were introduced into the ultrahigh vacuum (UHV) chamber and spectra were obtained. To identify the oxidation states of palladium and cerium during the oxidation of propane, the samples were submitted separately to 1% C$_3$H$_8$/He with 5%
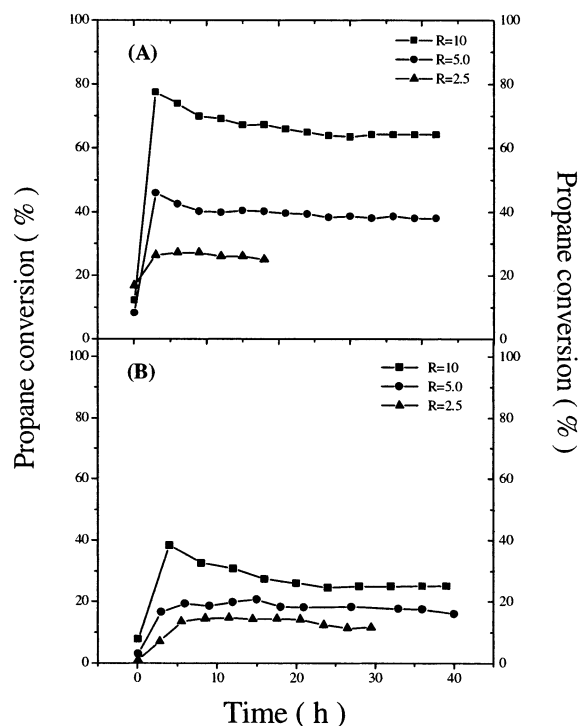

Figure 1. Effect of O$_2$/C$_3$H$_8$ ratio (R) on propane conversion for the catalysts: Pd−Cl (A) and PdCe−Cl (B): $T = 673$ K and WSHV = 230 s^{-1}.

O$_2$/He and 1% C$_3$H$_8$/He with 5% O$_2$/He and 5% H$_2$O, both under stoichiometric conditions ($R = 5.0$), at 150 mL/min and at 673 K for 60 min. Water was introduced through a saturator under controlled temperature, such that the concentration of water remained around 5%. These experiments were performed ex situ and transferred to the pretreatment chamber.

Results

It is widely known that pretreatment of catalysts with cerium oxide is important, as is verification of residual chlorine due to the precursor. Carbon dioxide is easily adsorbed on CeO$_2$, and therefore, it was eliminated, as far as possible. MS quadrupole spectrometry showed a great amount of H$_2$O and CO$_2$ above 423 K, up until 673 K. The PdCe−Cl sample, after oxidative pretreatment, showed an increase in hydroxyls around the latter temperature. These were desorbed only above 723 K; however CO$_2$ was not desorbed in this temperature range. It is worthwhile to point out that the elimination of CO$_2$, which is one of the products of this reaction, is very important. Therefore, it would appear that the above cited pretreatment was correct to study this reaction.

Stability. The reaction of propane oxidation was performed using different R ratios (reducing/2.5, stoichiometric/5, and excess of oxygen/10) at 673 K. These results are displayed in Figure 1, which allows one to make some important observations. First, there is an initial activation period of around 5 h for the catalyst, and then the conversion decays slowly, becoming stable with time on stream (TOS) after 20 h. This implies that the active sites attain stabilization after a long time, remaining stable for more than 40 h on stream. The Pd/CeO$_2$/Al$_2$O$_3$ catalyst is less active than the Pd/Al$_2$O$_3$ under similar conditions. In conclusion, for stable catalyst performance, it is important to setup the experiments after 20 h with TOS, to get reliable data for further interpretation. In addition, this observation is true for all other reaction conditions, under reduction,
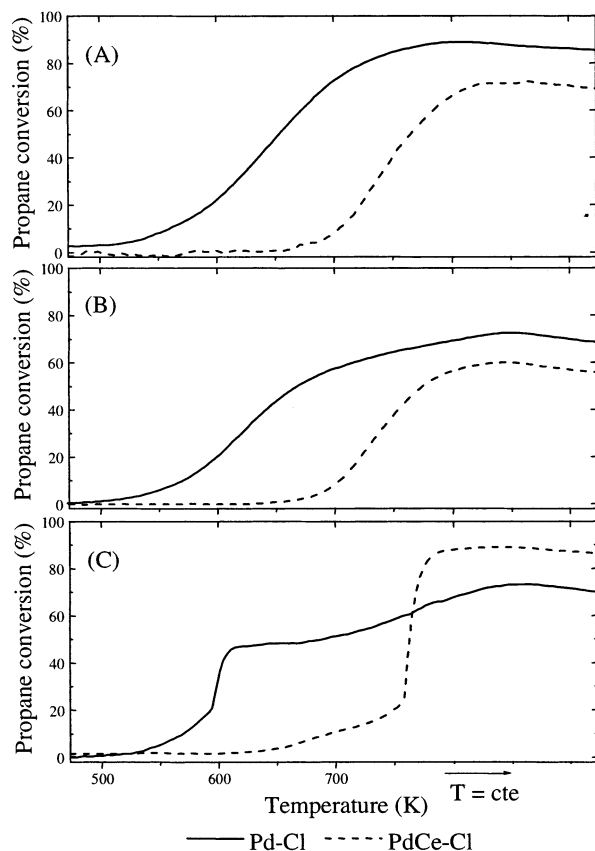
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Figure 2. Propane oxidation profiles for $R = 10$ (A), $R = 5$ (B), and $R = 2.5$ (C) and WSHV $= 230$ s^{-1}.

Figure 3. TPD profiles of propane for the Pd−Cl (A) and PdCe−Cl (B) catalysts

stoichiometric, or with excess oxygen content in the reaction feed. For the Pd−Cl the conversion is higher when $R = 10$, starting from approximately 10% to 80% after almost 5 h and stabilizing around 70%, after 20 h. For reducing condition, the maximum conversion was around 23%, while, under stoichiometric feed, it reaches 40%. The second conclusion is that feed conditions are very important to establish the desired final performance of the catalyst.

Activity. The activity of the catalysts for different reaction conditions (R) is displayed in Figure 2, showing the conversion with the temperature. Marked differences in the activity were observed for Pd/Al$_2$O$_3$ and Pd/CeO$_2$/Al$_2$O$_3$ catalysts. While the Pd/Al$_2$O$_3$ exhibits increasing conversion with temperature up to 723 K and reaches 90% for $R = 10$, the activity of the Pd/CeO$_2$/Al$_2$O$_3$ catalyst is retarded in approximately 150 K. It increases sharply above 673 K and reaches only 70% conversion at 773 K. The behavior is similar under stoichiometric conditions ($R = 5$), but the maximum conversions are lower, around 70 and 55%, respectively, for Pd−Cl and PdCe−Cl. However, for the reduction condition ($R = 2.5$), the conversion for Pd/Al$_2$O$_3$ increases sharply up to 50%, in the interval of 60 K, and began at 573 K. This increase changed smoothly during the next 100 K and reached a maximum conversion of 70% at 773 K. The line shape changed drastically for the Pd/CeO$_2$/Al$_2$O$_3$ catalyst. It is much less active at the beginning, retarding also the ignition temperature around 150 K. At 623 K the activity increases smoothly until 723 K, but then, instantaneously, the conversion increases sharply, surpassing the conversion of the Pd/Al$_2$O$_3$ catalyst. The conversion reaches 90% in an interval of temperature of 20 K. Although the Pd/CeO$_2$/Al$_2$O$_3$ catalyst is less active for oxidation at low temperature, suddenly it becomes very active above 723 K.
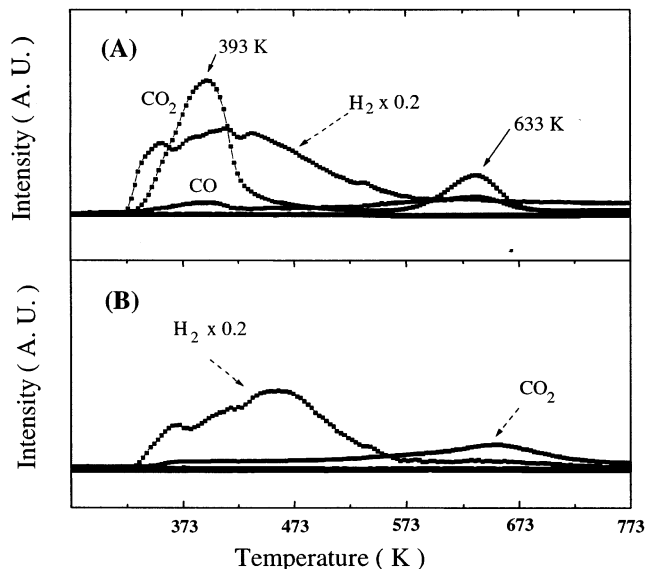
Thermodesorption (TPD). Thermodesorption of propane for both catalysts is displayed in Figure 3. First, notice that propane is not desorbed at all. However, for the Pd−Cl catalyst, CO$_2$ and CO are desorbed at 393 and 633 K, together with a great amount of H$_2$ and CO$_2$ in the whole temperature range. According to Creazer et al.,[8] propane dissociates on Pd sites, releasing H$_2$ and forming CO$_x$. On the other hand, on the PdCe−Cl catalyst, CO and propane are not desorbed, but only a small amount of CO$_2$ and a huge amount of H$_2$ were released at high temperature, which suggest a drastic change in the selectivity.

Temperature-Programmed Surface Reaction (TPSR). The most interesting case was observed when the reaction was done under reducing condition, $R = 2.5$, without or in the presence of water ($S = 0$ or $S = 3$). These results are shown in Figure 4. Comparing the results of Pd and Pd−Ce catalysts for $R = 2.5$ and $S = 0$, it is very clear that Ce retards the ignition temperature by approximately 200 K. As propane is consumed by oxygen, only CO$_2$ was formed, but when O$_2$ was totally consumed, beside CO$_2$ formation, large amounts of CO and H$_2$ were released. The main difference is the retarding temperature on PdCe−Cl catalyst. Moreover, when the reaction was performed in the presence of water ($S = 3$), a drastic change was also observed on both catalysts, concerning the amounts of H$_2$ released. Indeed, this can be attributed to the re-forming of propane, due to the formation of water in the first reaction step. To prove it, the reaction was performed separately under re-forming conditions, without oxygen but with water ($R = 0$, $S = 3$), as shown in Figure 5. Indeed, without oxygen, propane was only transformed into CO and H$_2$ for the Pd−Cl catalyst. But for the PdCe−Cl, besides CO$_2$ formation, a greater amount of H$_2$ was observed above 573 K, compared to the Pd−Cl catalyst itself, which indeed, corresponds to the re-forming reaction in the partial oxidation of propane.

Effect of Pretreatment on the Catalyst. The surface state of the catalysts in the propane oxidation could be nicely observed through TPSR experiments, when the catalyst are submitted to different pretreatment and reaction conditions (Figure 6). When the catalyst was first reduced, and the reaction was performed under reduction conditions ($R = 2.5$), the reaction started below 573 K and increased quickly up to 50%. Then, the conversion changed smoothly with increasing tem-
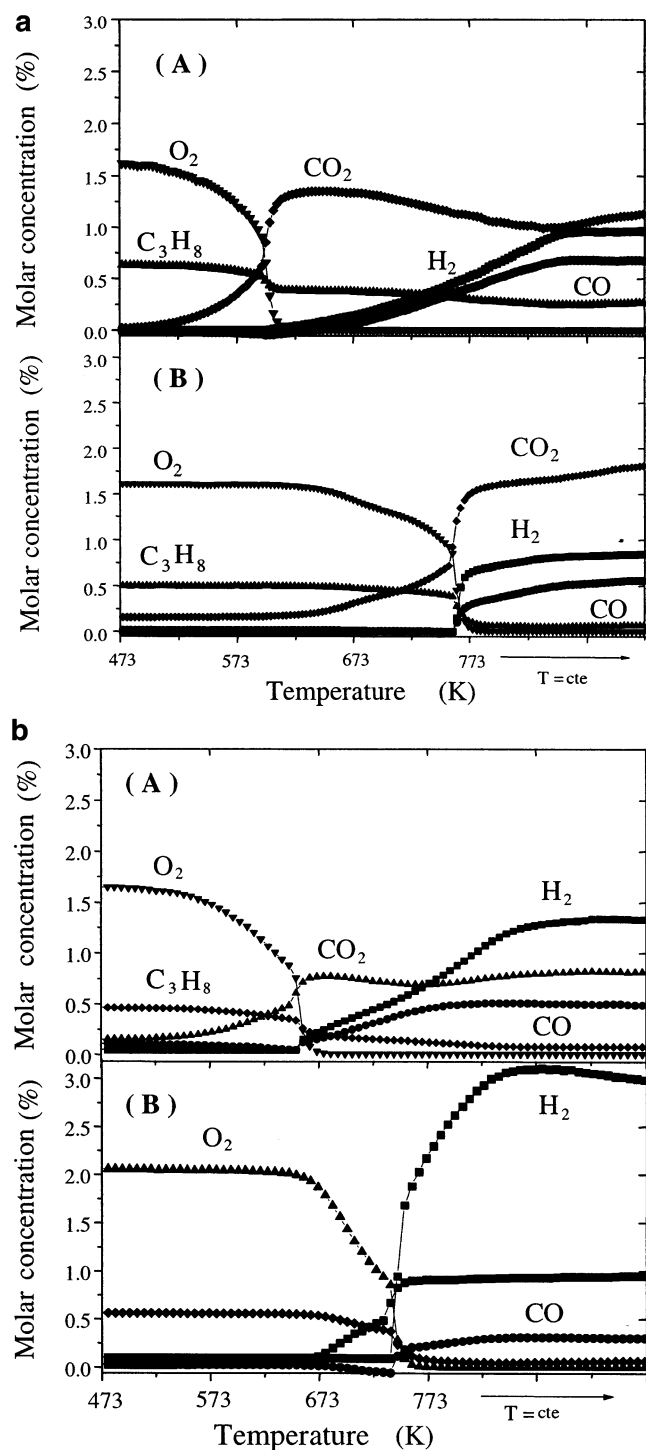
a

b

Figure 4. (a) Reactant and product yields in propane oxidation for $R = 2.5$ and $S = 0$ on Pd–Cl (A) and PdCe–Cl (B) catalysts. (b) Reactant and product yields in propane oxidation for $R = 2.5$ and $S = 3.0$ on Pd–Cl (A) and PdCe–Cl (B) catalysts.

perature. When the catalyst was not priori reduced, under similar reaction conditions, the temperature start up was retarded by almost 100 K and then it behaves likely. In the presence of water (SRO), the behavior was almost similar but the conversion was shifted to higher temperatures. The maximum conversion was obtained around 700 K for all reaction and pretreatment conditions. Unlikely are the results for the PdCe–Cl catalyst, exhibiting a retarded effect for all reaction and pretreatment conditions. The conversion increases sharply around 773 K in a range of 20 K and reaches approximately 90% or more.
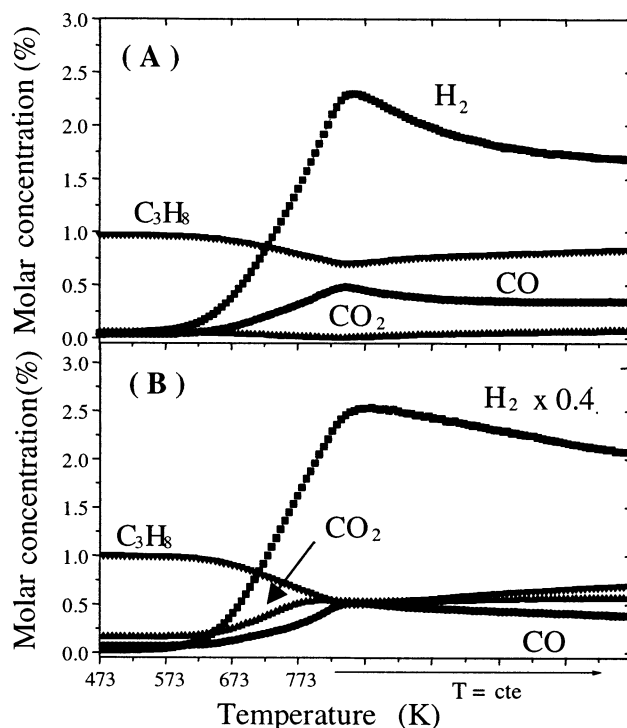

Figure 5. Reactant and product yields in steam re-forming of propane ($R = 0$, $S = 3$) on Pd–Cl (A) and PdCe–Cl (B) catalysts

XPS Results. The Pd 3d spectrum region was analyzed using 30 and 200 scans, to verify whether photoreduction of palladium with prolonged exposition to X-ray beam exists. Comparing the spectra of 30 and 200 scans, it is impossible to observe any shift in the binding energy of Pd 3d for all samples. These results allow us to rely on the analyses for any Pd modification during different pretreatments and reduction or oxidation reaction conditions.

XPS results for Pd $3d_{5/2}$ on Pd/Al$_2$O$_3$ are displayed in Figure 7a, showing that the binding energy changed after successive cycles of treatment. The binding energy of Pd for the reduced Pd–Cl catalyst was 335.2 eV, in agreement with the value reported in the literature for metallic palladium;[9] however, after oxidation of propane (O$_2$/C$_3$H$_8$ = 5.0 at 673 K), there is a band shift toward 337.2 eV. The effect of water was analyzed by comparing the XPS line shapes with and without water in the reaction mixture. No sensible differences were observed for the Pd $3d_{5/2}$ binding energy, but only a little shift to 336.9 eV for the reaction with water mixture. According to Brun et al.,[9] this value corresponds to a higher oxidation state of palladium than PdO (336.3 eV).

Concerning the PdCe–Cl, in Figure 7b, the line shape for Pd $3d_{5/2}$ is similar to the reduced Pd–Cl, giving evidence for the presence of Pd^0 (335.4 eV). However, after oxidation of propane and with addition of water, the band shift of Pd was greater than 2.0 eV. The binding energies for Pd $3d_{5/2}$ are also similar, 337.8 and 337.6 eV, respectively. According to Suhonen et al.,[10] this corresponds to a higher oxidation state, probably PdO$_2$ (338 eV).

Table 1 presents the bulk atomic and surface element ratios for the reduced catalysts. The bulk atomic ratios were calculated from its chemical composition (wt %), which are 1Pd and 99Al$_2$O$_3$ for Pd/Al$_2$O$_3$ and 1Pd, 17CeO$_2$, and 82Al$_2$O$_3$ for Pd/CeO$_2$/Al$_2$O$_3$. Tables 2 and 3 present the binding energy of Pd $3d_{5/2}$ and the surface atomic ratios for Pd/Al$_2$O$_3$ and Pd/CeO$_2$/Al$_2$O$_3$ catalysts, respectively, after different treatments.

Catalyst Surface Sites

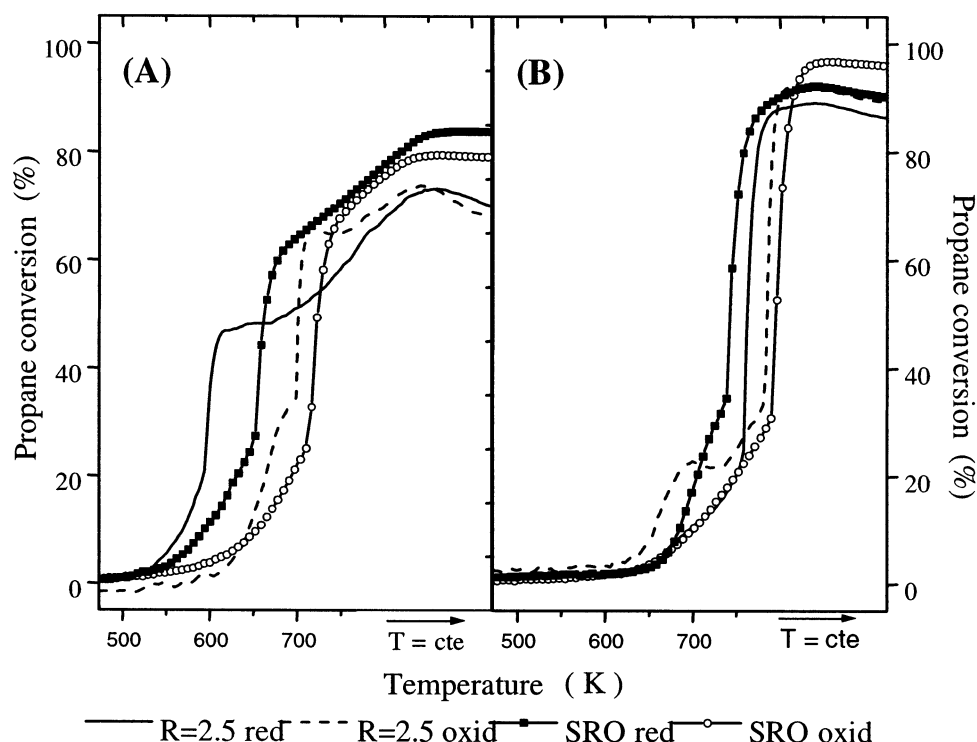*J. Phys. Chem. B, Vol. 107, No. 18, 2003* **4315**

Figure 6. Influence of pretreatment atmosphere in propane oxidation under reducing condition ($R = 2.5$) and with water into reaction mixture (SRO → $R = 2.5$, $S = 3$) for the catalysts: Pd−Cl (A) and PdCe−Cl (B). red and oxid refer to reduced and oxidized samples, respectively.
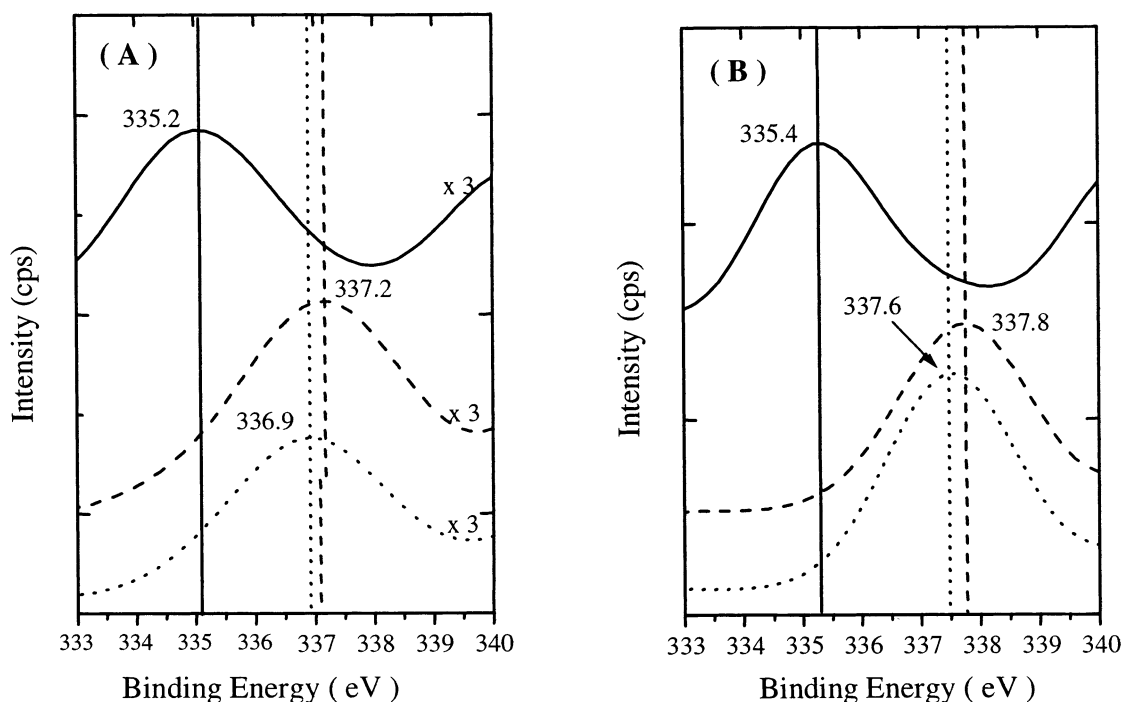

Figure 7. XPS analyses of Pd−Cl (a) and PdCe−Cl (b) after different treatments: (—) reduced; (- - -) reduced + O_2/C_3H_8 ($R = 5.0$) at 673 K; (· · ·) reduced + O_2/C_3H_8 ($R = 5.0$) and 5% H_2O at 673 K.

Table 1 shows that for Pd/Al_2O_3, the Pd/Al ratio is lower at the surface than in the bulk phase, 0.0024 and 0.0048, respectively. This result is in principle not expected and can be explained through the aggregation of Pd particles during the reduction step, since in the calcined form this ratio is 0.0043, in accordance with previous results.[11] Table 2 shows also that this low Pd/Al ratio remains after reaction with C_3H_8, O_2, and H_2O. By contrast, the Pd/Al ratio is higher at the surface of PdCe−Cl compared to the bulk value (Table 1). Notice that if

the alumina surface is partially covered by cerium and rating to Ce + Al, then the surface ratio Pd/(Al + Ce) is 0.023 and the bulk ratio is 0.0055 (4-fold). However, in both cases the surface ratio on the PdCe−Cl sample in the reduced form is greater than that in the bulk phase. Probably, this behavior can be associated to the preparation method of the CeO_2/Al_2O_3 system, made by grafting, which facilitates the reaction between the cerium acetylacetonate and alumina surface hydroxyl groups, favoring the dispersion of Ce species at the surface and

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TABLE 1: Bulk Atomic Ratios of the Elements and XPS Analyses for Pd/Al$_2$O$_3$ and Pd/CeO$_2$/Al$_2$O$_3$ Catalysts, after Reduction Treatment

| | bulk atomic ratios | | | XPS atomic ratios[a] | | |
catalyst	Pd/Al $\times 10^2$	O/Al	Ce/Al $\times 10^2$	Pd/Al $\times 10^2$	O/Al	Ce/Al
Pd—Cl	0.48	1.50		0.24	2.07	
PdCe—Cl	0.58	1.62	6.14	5.0	3.70	1.19

[a] Atomic ratios calculated using the intensities (corrected with the sensibility factors) of the lines Pd 3d, Al 2p, O 1s, and Ce 3d.

TABLE 2: XPS Analyses for Pd/Al$_2$O$_3$ Catalyst

| | | | surface atomic ratio[b] | | |
catalyst	treatment	binding energy[a] (eV)	Pd/Al $\times 10^2$	Cl/Al $\times 10^2$	O/Al
Pd—Cl	calcined sample	336.9	0.43	1.91	1.90
	reduction	335.2	0.24	0.40	2.07
	C$_3$H$_8$/O$_2$	337.2	0.22	1.50	2.15
	C$_3$H$_8$/O$_2$/H$_2$O	336.9	0.19	1.15	2.20

[a] Pd 3d$_{5/2}$. [b] Atomic ratios calculated using the intensities (corrected with the sensibility factors) of the lines Pd 3d, Al 2p, Cl 2p, and O 1s.

TABLE 3: XPS Analyses for Pd/CeO$_2$/Al$_2$O$_3$ Catalyst

| | | binding energy[a] | surface atomic ratio[b] | | | |
catalyst	treatment	(eV)	Pd/Al	Cl/Al	O/Al	Ce/Al
PdCe—Cl	calcined sample	337.7	0.14	0.11	3.87	0.67
	reduction	335.4	0.05	0.29	3.70	1.19
	C$_3$H$_8$/O$_2$	337.8	0.22	0.18	5.60	1.70
	C$_3$H$_8$/O$_2$/H$_2$O	337.6	0.23	0.12	6.60	1.61

[a] Pd 3d$_{5/2}$. [b] Atomic ratios calculated using the intensities (corrected with the sensibility factors) of the lines Pd 3d, Al 2p, Cl 2p, O 1s, and Ce 3d.

consequently the dispersion of Pd.[7] After treatment under different reaction conditions, the surface ratio of Pd/Al increased 4-fold in comparison to the reduced sample (Table 3). If the Pd/(Ce + Al) ratio is used, although the values are much lower, it shows the same tendency. After reaction, this ratio increased 4-fold from 0.023 to 0.082 with C$_3$H$_8$ and O$_2$ and to 0.088 with H$_2$O, which is almost the same value of the calcined sample (0.084). Therefore, the presence of ceria modifies markedly the dispersion of Pd during the reaction, which is not the case of the Pd/Al$_2$O$_3$ catalyst.

The results also show a high increase of the surface Ce/Al ratio in relation to the bulk. This ratio increases almost three times (1.70) at the surface after reaction, compared to the calcined sample (0.67), but was not much affected in relation to reduced treatment (1.19).

On the other hand, the O/Al ratio is higher at the surface than in the bulk for both catalysts (Table 1). While for Pd/Al$_2$O$_3$ catalyst, the O/Al did not change after the reaction, for the Pd/CeO$_2$/Al$_2$O$_3$ it increases (Tables 2 and 3). The same tendency was observed for the Ce + Al rating bases. The calculated O/(Al + Ce) ratio (Table 3), increases after the reaction, from 1.69 after reduction to 2.53 after reaction in the presence of water. Therefore, both the increasing O/Al ratio and Pd binding energy after the reaction, for the Pd/CeO$_2$/Al$_2$O$_3$, reveal the incorporation of oxygen in the palladium, suggesting a higher oxidation state of Pd, probably PdO$_2$.
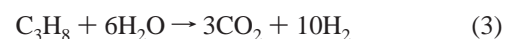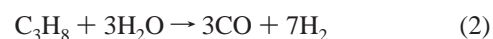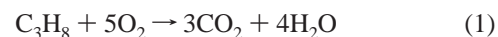
Table 2 shows residual chlorine because the Cl/Al ratio is still 0.004 after calcination and reduction. The key point is that the interaction of chlorine with palladium sites is different for both cases. While on the reduced Pd—Cl, the Cl/Pd ratio is

1.67; with ceria this value increases to 5.8 (Tables 2 and 3). Marked changes were also observed during the reaction. So, for Pd/Al$_2$O$_3$, the Cl/Pd ratio increases from 1.67, after reduction, to 6.8 after oxidation of propane (around 4-fold). By contrast, for Pd/CeO$_2$/Al$_2$O$_3$, the Cl/Pd decreases around 7-fold, from 5.8 to 0.82.

Discussion

TPD results of the PdCe—Cl catalyst showed the influence of the pretreatment conditions, because CO$_2$ is easily adsorbed on CeO$_2$, as seen previously on CeO$_2$/Al$_2$O$_3$ systems.[12] In particular, FTIR results confirmed CO$_2$ adsorption and identified surface carbonate species, such as mono- and bidentate or carboxylic ions, which are stable at low temperatures. These compounds can be eliminated as CO$_2$ under oxidative thermal treatment. Binet et al.[13] observed similar results investigating Lewis sites on CeO$_2$. Carbonate compounds are easily formed on CeO$_2$. It is understandable, since the cerium oxide can be transformed into the highest oxidation state (Ce^{3+} → Ce^{4+}), promoting the formation of carbonates in the presence of CO$_2$, which are then decomposed in CO$_2$ and eliminated from the surface under thermal treatment.
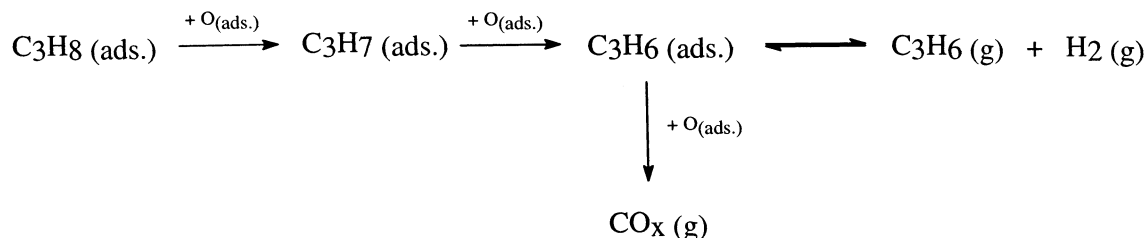
TPSR results provide evidence of two distinct regions under reducing feed. In the first region, only oxidation of propane occurs, with the formation of a large amount of CO$_2$, while in the second region, when oxygen is totally consumed, there are, besides releasing of CO$_2$, CO and H$_2$, which depend on the catalyst. Figure 4 presents the product distribution of propane oxidation under reduction conditions ($R = 2.5$). According to Maillet et al.,[14,15] and Barbier et al.,[16] there are two discrete domains. The first one corresponds to the complete oxidation (reaction 1), while the second follows the residual propane reaction with water formation during the first step, corresponding to the re-forming of propane with steam (SR), according to reactions 2 and 3:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \quad (1)$$

$$C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2 \quad (2)$$

$$C_3H_8 + 6H_2O \rightarrow 3CO_2 + 10H_2 \quad (3)$$

Creaser et al.[8] investigated the kinetics and mechanism of the propane oxidative dehydrogenation reaction and suggested that propane is first adsorbed on metallic sites, followed by the abstraction of H from the C—H bond, which is the limiting step in this process. Then, the abstraction of a second H is very fast for C$_3$H$_6$ formation, which is then adsorbed and reaches equilibrium in the gas phase, as shown in Scheme 1.

TPD results indicate, according to this scheme, that the presence of hydroxyls on the support would be very significant, aging as oxidant for the reaction, which promoted the formation of CO and H$_2$, this later one by dissociation over the palladium sites. However, TPD results from the Pd catalyst containing CeO$_2$ exhibited lower CO$_2$ amounts and the absence of CO in a wide range of temperatures (Figure 3). Since CeO$_2$ is gafted on alumina, the hydroxyl groups were mostly eliminated or have interacted with the CeO$_2$ during the preparation method.[7] This also explains the retarding effect of the temperature in the Pd/CeO$_2$/Al$_2$O$_3$ system.

The Influence of Water in the Oxidation and Re-forming of Propane. Under reduction conditions ($R = 2.5$) the conversion of propane exhibits two clear discrete domains of reactions in good agreement with Maillet et al.[14,15] They observed, besides oxidation, steam re-forming and also deactivation of the catalyst,
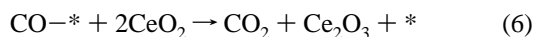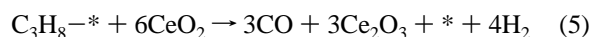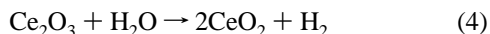
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SCHEME 1: Oxidative Dehydrogenation of Propane

$$C_3H_8 \text{ (ads.)} \xrightarrow{+ O_{(ads.)}} C_3H_7 \text{ (ads.)} \xrightarrow{+ O_{(ads.)}} C_3H_6 \text{ (ads.)} \rightleftharpoons C_3H_6 \text{ (g)} + H_2 \text{ (g)}$$

$$\downarrow {+ O_{(ads.)}}$$

$$CO_x \text{ (g)}$$

due to the reduction of the PdO_x sites in Pd^0, which is less active for the oxidation of propane. The presence of water prevents this effect and inhibits the oxidation process. Indeed, water is one of the crucial problems in the oxidation process. Exhaust gases, which contain 10% water,[17] in general, inhibit the kinetics under oxidation conditions. However, under reduction conditions, the reactions follow different pathways. Barbier et al.[16] also observed re-forming of propane with rhodium catalysts, when feed conditions were $[O_2]/[C_3H_8] < 5$, which is in good agreement with these results. Moreover, the bimetallic system Pd−Rh was even better. Bart et al.[18] studied the effect of steam (0−10%) in the propane conversion for different feed conditions and observed similar results. Our TPSR results give evidence that the presence of CeO_2 affects the oxidation by inhibiting the reaction, as well as the re-forming in the first domain, but the combination of both was beneficial in terms of higher H_2 production.

Role of CeO_2 in the Selective Re-forming of Propane−Hydrogen Production. The behavior of $Pd/CeO_2/Al_2O_3$ catalysts in the oxidation of hydrocarbons is relatively scarce in the literature, although there are many of them for the TWC system, which in principle stabilizes and activates the catalyst for these coupled oxidation systems. Lee et al.[19] observed an inhibiting effect in the oxidation of light hydrocarbons, increasing the CO formation of Pd/Al_2O_3 catalyst in the presence of promoters such as CeO_2 and K_2O, which induced the re-forming reaction (WGS). This was attributed to the enhancing basicity. Bensalem et al.[20] have shown that the crystalline structure of CeO_2 affected the oxidation reactions, and that ceria, in the reduced state (Ce^{3+}) and in the presence of water, induced a cyclic reaction mechanism. It suggests that, under reduction condition, different reactions may occur, beside the re-forming (Scheme 2), assuming the following:

(1) Water adsorption prevails on the promoter. This is thermodynamically favorable in relation to the oxidation of palladium sites.

(2) Reaction of propane with CeO_2, which, in the presence of water, favors the formation of H_2 and CO_2, reestablishing, thus, the sites for the start up of the process

SCHEME 2: Effect of Water and of the Reaction State of CeO_2 on the Reaction

$$Ce_2O_3 + H_2O \rightarrow 2CeO_2 + H_2 \tag{4}$$

$$C_3H_8-* + 6CeO_2 \rightarrow 3CO + 3Ce_2O_3 + * + 4H_2 \tag{5}$$

$$CO-* + 2CeO_2 \rightarrow CO_2 + Ce_2O_3 + * \tag{6}$$

where asterisks are the sites on palladium.

It turns out that the H_2/CO and H_2/CO_2 molar ratios are quite different as required for the re-forming reaction. The first one is much higher, and the last is lower than the expected stoichiometric value, which supports the above schematic reactions in the catalytic system, although the water gas shift

reaction in the re-forming cannot be disregarded during the re-forming reaction. Noteworthy is the huge amount of H_2, besides the greater CO_2 formation in the ceria promoted Pd catalyst. In contrast, Barbier et al.[16] studied the propane oxidation under reduction conditions and observed that these ratios were close to the thermodynamic values for the water gas shift reaction on $Pt/Rh/Al_2O_3$.

The Surface Site Transformations. The conversion of propane increases markedly during the first hours and then stabilizes (Figure 1). It suggests that the initial activation period provokes drastic transformations of the surface sites during the oxidation process. According to the literature, several authors have attributed the existence of initial activation periods to the presence of oxygen-deficient PdO_x crystallites, which increases their oxygen content during the oxidation reactions. If this is true, the same behavior would occur with other Pd precursors. However, the catalyst prepared with palladium acetylacetonate showed that the initial conversion was very high, decreasing quickly until steady-state conditions, the opposite of the catalysts with chloride precursor.[21] Therefore, the initial activation period should be affected by the presence of chlorine and water formation as reaction proceeds, affecting the surface sites. The formation of water during the oxidation of propane can be responsible for the elimination of residual chlorine. The activity growth is attributed either to the presence of oxi-chloride species at the surface or to the interaction of residual chlorine with metallic sites. Due to the dissociation of adsorbed water on Pd^0, the H^* and OH^* species can easily recombine, but in the presence of chlorine, H^* recombines with Cl at the metallic interface and releases HCl, regenerating sites, according reaction

$$Cl-Pd* + H-Pd* \rightarrow HCl_{(g)} + Pd*$$
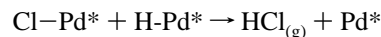
where asterisks represent the metallic site.

Hicks et al.[22] and Gaspar et al.[11] observed this effect. XPS results suggest the presence of oxi-chloride species on calcined samples, such as $Pd_xO_yCl_z$, since the binding energy of Pd $3d_{5/2}$ for the Pd−Cl was located between the energy of PdO (336.3 eV) and $PdCl_2$ (337.8 eV).
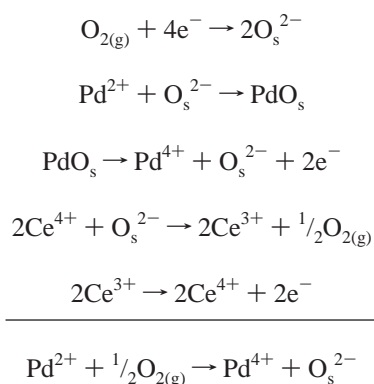
XPS results provide evidence of Pd^0 (335.2 eV) after reduction in situ, but after reaction, there are three possibilities: free PdO, propane associated to Pd sites, such as $Pd-C_3H_7$, and palladium species linked to hydroxyls, due to the water dissociation, probably $(PdO)^{\eta+}(OH)^{\delta-}$.[5] XPS result after the oxidation reaction showed that the binding energy of Pd was shifted to 337.2 eV, which characterizes palladium oxide. These results agree with Hicks et al.[22] for Pd/Al_2O_3 catalyst. Therefore, according to Burch et al.,[23] PdO/Pd^0 interfaces are the active sites. Besides, the catalyst containing CeO_2 showed the same tendency in the XPS results and in addition indicate formation of palladium species in the highest oxidation state, probably PdO_2 (338 eV) after the oxidation of propane.

The Pd/Al ratios at the surface on both catalysts are distinct and suggest the presence of different surface properties. This

ratio decreases on the Pd−Cl catalyst after reduction but is almost the same after oxidation of propane and with addition of water, suggesting that the surface sites remain stable. However, because the Pd/Al ratio of the reduced sample is lower than that of the calcined sample implies strong evidence of sinterization. This is not surprising, since during the activation period the oxi-chloride species present on the calcined samples, such as $Pd_xO_yCl_z$, facilitate the coalescence of particles, favoring the formation of larger particles. According to the literature,[23] the oxidation of propane is favored by larger PdO/Pd^0 interfaces and large particles.

On the other hand, the Pd/Al ratio on the calcined Pd−Ce−Cl catalyst is much greater than that in the previous case, even after reduction. After oxidation and with addition of water, it increases four times. This implies that the dispersion of Pd after reduction is drastically reduced but comparatively still very high in the presence of CeO_2. Therefore, besides migration of Pd particles over CeO_2, there is a migration phenomenon of CeO_2 over Pd particles or sintering during reduction. Opposite to the previous case, after oxidation this ratio surpasses the calcined sample, which gives evidence that no sintering but migration of Pd particles over the CeO_2 layer should occur. When CeO_2 unblocks the Pd particles during the reaction, then the dispersion of Pd over CeO_2 increases, favoring the formation of small particles. Thus, the activity should be lower in this system compared to the Pd/Al_2O_3, independent of the feed conditions, due to a strong Pd−O bond in small crystallites.

Besides, the O/Al ratio provides evidence of increasing oxygen incorporation in the presence of CeO_2, which indeed reveals Pd binding energy and suggests the formation of a higher oxidation state of Pd, probably PdO_2, which is the active site for the selective oxidation of propane, favoring strongly the reforming reaction, prevailing higher production of hydrogen. It seems that the Pd^0/PdO interfaces are the surface sites for the total oxidation reaction; however the presence of Pd^0/PdO_2 interfaces favor the selective oxidation toward re-forming for higher production of hydrogen. The best proof of such interfaces is presented by XPS results after oxidation of propane and enhanced by the addition of water. Schematically it works as follows:

$$O_{2(g)} + 4e^- \rightarrow 2O_s^{2-}$$

$$Pd^{2+} + O_s^{2-} \rightarrow PdO_s$$

$$PdO_s \rightarrow Pd^{4+} + O_s^{2-} + 2e^-$$

$$2Ce^{4+} + O_s^{2-} \rightarrow 2Ce^{3+} + {}^1/_2O_{2(g)}$$

$$2Ce^{3+} \rightarrow 2Ce^{4+} + 2e^-$$

$$\overline{}$$

$$Pd^{2+} + {}^1/_2O_{2(g)} \rightarrow Pd^{4+} + O_s^{2-}$$

XPS results do not provide evidence of the presence of $(PdO)^{\eta+}(OH)^{\delta-}$. Besides with the PdO_2 as active phase, these less active sites are not discarded, acting as inhibitor sites. According to Bunluesin et al.,[24] water can be preferentially adsorbed on CeO_2, which then prevents the formation of such species.

Conclusions

Stabilization of the catalyst performance is important to setup the experiments for oxidation of propane, to get reliable data for further interpretation. This observation is true for all reaction conditions, under reducing, stoichiometric, or excess oxygen content in the reaction feed.

The $Pd/CeO_2/Al_2O_3$ catalyst is less active for oxidation of propane at low temperatures than the Pd/Al_2O_3 but suddenly becomes very active at higher temperatures. On the other hand, CO and propane are not desorbed on the PdCe−Cl catalyst, releasing only a small amount of CO_2 and a huge amount of H_2 at high temperature, which suggests a drastic change in the selectivity during propane oxidation.

TPD results indicate that the presence of hydroxyls in the support would be very significant, aging as oxidants for the reaction. However, TPD results of Pd catalyst containing CeO_2 indicate that CeO_2 grafted over alumina have eliminated hydroxyls groups. Moreover, TPSR results give evidence that the presence of CeO_2 affected the oxidation, inhibiting the reaction as well as the re-forming in the first domain. But the combination of both was beneficial in terms of higher H_2 production.

PdO/Pd^0 interfaces are the active sites, under steady-state condition in agreement with Burch et al.[23] However, an initial activation period is markedly observed, which is attributed to the chlorine present due to the precursor, favoring the migration and formation of larger palladium particles, and besides the oxidation of Pd enhances the activity in the initial period. On the other hand, in the catalysts containing CeO_2, although less active, there is also an initial activation period and, due to the presence of CeO_2, the palladium particles migrate onto the surface of CeO_2, increasing the Pd/Al ratio. In addition, XPS results indicated formation of palladium species in the highest oxidation state, probably PdO_2 (338 eV) after the oxidation of propane, due to the incorporation of oxygen in the presence of CeO_2, as seen from the O/Al ratio. From these results, it may be suggested that besides the Pd^0/PdO interfaces, which are the active sites for the oxidation reaction, the formation of Pd^0/PdO_2 interfaces favors the selective oxidation toward re-forming, with higher production of hydrogen.

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