Oxidation and reduction effects of propane–oxygen on Pd–chlorine/alumina catalysts

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Pd–chloride precursor salt was used to prepare Pd/Al_2O_3 catalysts. TPSR measurements showed three distinct reactions for the oxidation of propane on palladium surface under excess of hydrocarbon: complete oxidation, steam reforming and propane hydrogenolysis. Propane oxidation on palladium catalysts was related to the Pd^{2+} sites observed on Pd/Al_2O_3 through infrared of adsorbed carbon monoxide. In fresh catalysts reduced by H_2, the IR spectra showed the linear and bridge adsorbed CO species on the Pd^0 surface. After propane reaction, a new band at 2130 cm^{-1} related to CO adsorption on Pd^{2+} species was noted. Carbon monoxide species adsorbed on Pd^0 were also observed in all samples after reaction. Our results suggest surface ratios of Pd^0/PdO during the propane oxidation. On the other hand, time on stream conversions of the complete oxidation of propane were affected by either the water generated during the reaction or added as a reactant at 10 vol%. The water generated by the reaction helped to eliminate chlorine residues in the form of oxychloride species leading to an increasing of the activity. However, the presence of water into the reaction mixture caused a strong decreasing of the activity. The inhibition mechanism of propane oxidation in the presence of water consisted in the dissociative adsorption of water on palladium sites with the possible formation of palladium hydroxide (Pd–OH) at the surface, diminishing the number of active surface sites. Dynamic fluctuations into the reaction conditions supported the idea that a pseudo-equilibrium adsorption–desorption of water was reached. After water removal or increasing in the reaction temperature the equilibrium was shifted to the direction of OH–Pd decomposition. This behavior suggests that the inhibitory effect of water is a reversible phenomenon, being a function of the amount of water and the reaction temperature.

Keywords: oxidation, reduction of palladium catalysts, chlorine effects

1. Introduction

Catalytic oxidation of hydrocarbons, volatile organic compounds and carbon monoxide has been studied in order to protect the atmospheric environment. Noble metal catalysts are the most active systems, even at low and high reaction temperatures. For combustion of light hydrocarbons, several works have pointed out palladium as the best catalyst [1–3].

However, questions remain yet open about the chemical state of palladium under reaction conditions. Palladium oxide (PdO) has been described as the active phase, but the presence of metallic palladium or even anionic vacancies on the PdO surface structure has contributed to increase the catalytic activity [4], once that Pd^0 is more effective than PdO for hydrocarbons activation. A surface with a metallic character seems to be necessary to allow the first hydrogen abstraction from the hydrocarbon molecule, which is an important step, frequently the rate-determining step for light hydrocarbon combustion [5]. Moreover, the nature of the palladium surface is subject to the reaction conditions, the Pd sites properties being a function of the partial pressure of the reactants and reaction temperature [6–8].

Another very important factor to be considered in the complete oxidation of hydrocarbons is the role of the products generated during the reaction, namely, water and carbon dioxide. It is well known that water inhibits the activity of Pd-based catalysts. The formation of inactive $Pd(OH)_2$ species has been postulated [9], but such species have not yet been characterized and their existence as stable compounds seems unlikely. On the other hand, the inhibition by carbon dioxide only plays a role at concentrations higher than 3–5 mol% and well above the water molar concentration [3].

The aim of this work is to study the oxidation and reduction effects of propane on Pd–chlorine/alumina catalysts during hydrocarbon oxidation. For this purpose, propane oxidation was performed under either excess of oxygen, hydrocarbon or stoichiometric conditions. These systems were characterized by CO chemisorption and an *in situ* dynamic analysis of propane oxidation was done through temperature-programmed surface reaction (TPSR). The palladium surface was also investigated by using infrared of adsorbed CO before and after C_3H_8 reaction.

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2. Experimental

2.1. Catalyst preparation

An γ-Al_2O_3 (Degussa) was used as support. Al_2O_3 was previously calcined in air at 823 K for 16 h (BET area = 180 m^2/g). Pd/Al_2O_3 samples were obtained by incipient-wetness impregnation of Al_2O_3 with a hydrochloric solution of $PdCl_2$. Then, the samples were dried at 373 K for 16 h followed by calcination under air flow at 773 K for 2 h. The metal loading was 1% (wt/wt).

2.2. CO chemisorption

The chemisorption uptakes were measured in an ASAP (Micrometrics) apparatus. Before the reduction, the catalysts were dehydrated at 423 K for 0.5 h under vacuum. Then, the catalysts were reduced at 773 K (5 K/min) in flowing H_2 (30 cm^3/min). Following reduction, the samples were evacuated for 1 h at 773 K and cooled to room temperature under vacuum. Irreversible CO uptakes were determined from dual isotherms using the method of Benson et al. [10].

2.3. Temperature-programmed surface reaction under excess of propane (TPSR)

The oxidation of propane was performed in a flow microreactor at atmospheric pressure. The catalyst (ca. 50 mg) was mixed with quartz as diluent (500 mg) and then dried with flowing nitrogen at 393 K before reduction with hydrogen at 773 K. The reaction mixture consisted of 2.2% O_2/0.55% C_3H_8/97.25% N_2 (reduction condition), flowed at 135 ml/min through the catalyst. In addition, measurements with He instead of N_2 were obtained in order to detect the mass spectra of CO ($m/e = 28$). The reactor was linearly heated (5 K/min) from room temperature up to 773 K. Similar conditions were used in the FTIR measurements. The effluent gas composition was monitored on-line by a quadrupole mass spectrometer (Dycor MA100M, Ametek).

2.4. CO infrared

Samples in the form of self-supporting disks and weighing around 25 mg were used. The cell consisted of a quartz tube with calcium fluoride windows. Viton o-rings provided a gas-tight seal between removable parts of the cell. The analyses were carried out with a Perkin–Elmer model 2000 FTIR and the resolution was 2 cm^{-1}. The catalyst was first dried, reduced and evacuated, as described above. CO uptakes were taken at 298 K, following evacuation at 10^{-5} Torr. Then, oxidation of propane was performed under similar conditions of TPSR measurements, using a reaction mixture of 2.2% O_2/0.55% C_3H_8/97.25% N_2 (flow rate = 135 ml/min) for reduction conditions. Under oxygen excess, a reaction mixture of 1% C_3H_8/N_2 at 90 ml/min and 21% O_2/N_2 at 60 ml/min was used. Finally, after evacuation and cooling, the CO uptakes were obtained at 298 K in order to investigate the palladium surface after reaction. The absorbance spectra were obtained by using the interferograms of reduced samples as background references.

2.5. Propane oxidation under stoichiometric condition

The oxidation of propane was performed in a microflow reactor at atmospheric pressure. The catalyst (ca. 50 mg) was mixed with quartz as diluent (500 mg), dried with flowing nitrogen at 393 K, and then reduced with hydrogen at 773 K for 2 h. After reduction, the reaction was carried out stepwise varying the temperature from 473 to 773 K in intervals of 20 K. The reaction mixture consisted of 2% O_2/0.4% C_3H_8/97.6% N_2 (flow rate = 300 ml/min). Analyses were obtained by on-line gas chromatography with a Haysep D column (6 m, carrier gas H_2). Propane conversions were calculated from the molar balance.

2.6. Propane oxidation under excess of oxygen and in the presence of water

The oxidation mixture in excess of oxygen (molar ratio $O_2/C_3H_8 = 14$) was 1% C_3H_8/N_2 at 90 ml/min and 21% O_2/N_2 at 60 ml/min. The TOS run was performed at 673 K up to 40 h. The reaction in the presence of water was performed under similar conditions by introducing 10% of water in the reaction mixture at 15 ml/min and the products were analyzed similarly. These samples were then analyzed by FTIR under similar conditions, described above. The dynamic fluctuation experiment was performed under similar conditions, except that mass of the catalyst in the reactor was reduced to 12.5 mg and mixed with quartz as diluent (125 mg).

3. Results

The dispersion for Pd/Al_2O_3 was 32% and the average particle size was 3.4 nm (CO uptake 30.1 μmol s/g_{cat}).

Figure 1 presents the conversion of propane as a function of the reaction temperature (light-off curves) for the Pd/Al_2O_3 catalyst under stoichiometric and oxidative conditions. The behavior of these profiles is as expected very common for hydrocarbon combustion, exhibiting low activity at temperatures lower than the light-off temperature, but once it is reached, the reaction rate increases exponentially, which means at this point the heat of combustion generated is greater than heat transferred [11].

Oxidation under excess of oxygen ($O_2/C_3H_8 = 14$) showed a decreasing of the light-off temperature around 100 K when compared to the stoichiometric conditions. Table 1 presents the rates and TOF values under kinetic conditions at lower conversions, and shows that the activity increased by a factor of 3.0 when reaction was performed under oxidation condition at low temperatures 390

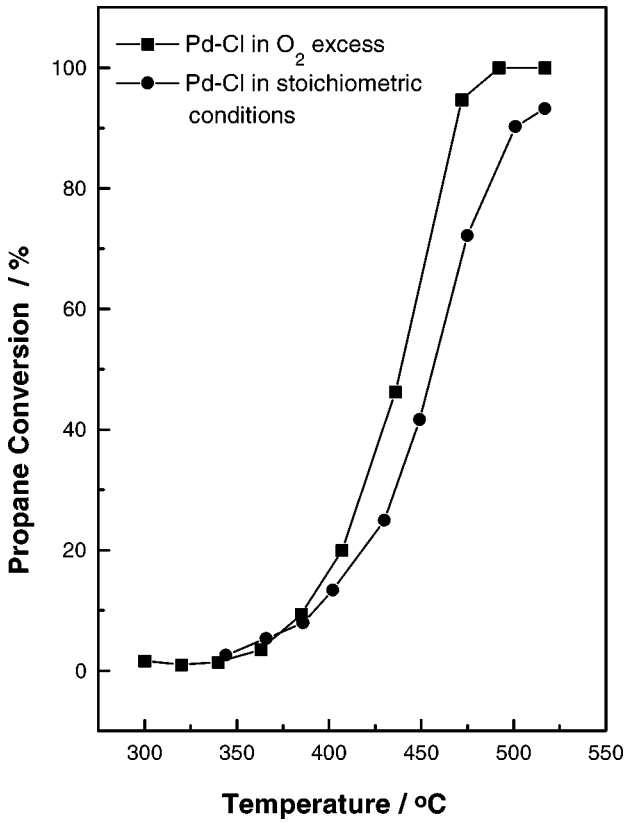


Figure 1. Propane activity under stoichiometric and oxygen excess conditions.

Table 1
Rates and TOF values under stoichiometric and oxidative conditions.

T	Stoichiometric			Oxygen excess		
(°C)	Conversion (%)	Rate[a]	TOF[b]	Conversion (%)	Rate[a]	TOF[b]
390	9.4	1.12	1.8	11.6	3.11	5.2
400	12.5	1.50	2.5	16.6	4.45	7.4

[a] Rate of reaction (10^6 mol/s g_{cat}).
[b] Turnover frequency (10^2 s^{-1}).

and 400 K. Indeed, the greater efficiency of propane combustion under lean conditions is an expected behavior and that result may be attributed to the faster oxidation of palladium. The formation of palladium oxide is required for a better activity and its formation depends on the oxygen partial pressure and the temperature [12–14].

Figure 2 presents the profiles of TPSR measurements of the Pd/Al_2O_3 catalyst (excess of hydrocarbon). Oxidation started at 520 K on 1% Pd/Al_2O_3. After complete oxygen consumption, a secondary reaction attributed to steam reforming took place. At this point one can see the start of the hydrogen formation and a clear transition in the CO_2 curve. Methane was also observed after the beginning of steam reforming and this is related to hydrogenolysis of the hydrocarbon. The hydrogen produced *in situ* reacted with the propane chemisorbed on the palladium surface. Notice that CO was not observed during the TPSR measurement.

Infrared of adsorbed carbon monoxide was used to investigate the palladium surfaces before and after propane

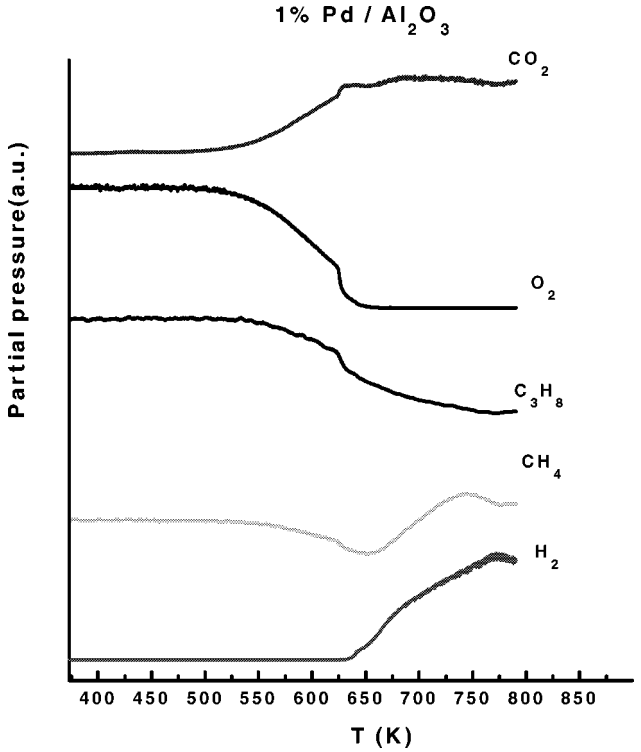


Figure 2. TPSR profiles of propane oxidation for hydrocarbon excess.

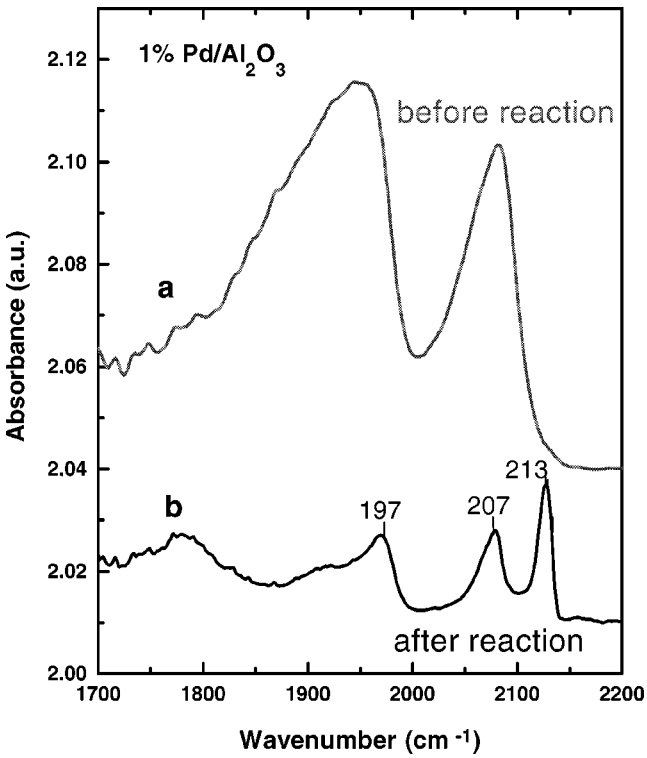


Figure 3. FTIR spectra of adsorbed CO on Pd/Al_2O_3 catalyst before and after propane oxidation under reduction conditions.

reaction. In the fresh catalyst reduced by H_2, the spectrum in figure 3 shows the linear (2073–2079 cm^{-1}) and bridged (1973–1977 cm^{-1}) adsorbed CO species on Pd^0 surface.

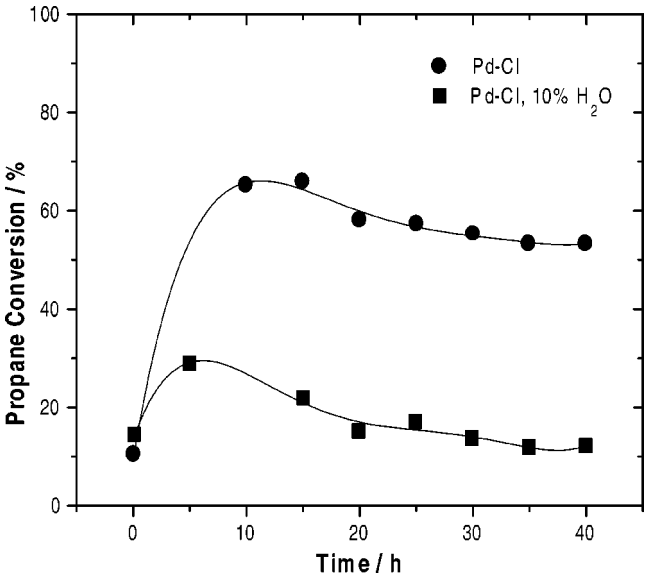


Figure 4. Time on stream profiles during propane oxidation on Pd/Al_2O_3 catalyst.

After reaction, the sample was darker and the absorbance intensity was smaller than over the clean catalyst. Moreover, propane conversion produced different sites on the catalyst surface. One can see a new band at 2130 cm^{-1} related to CO adsorption on Pd^{2+} species [4]. This oxide site is the most intense on Pd/Al_2O_3. Carbon monoxide species adsorbed on Pd^0 were also observed in the sample.

Figure 4 shows the time on stream conversion of propane after running the reaction at 673 K for 40 h. In the absence of water in the reaction medium, the activity increased markedly in the first 10 h, reaching a maximum value, and then stabilizes after approximately 40 h with TOS. The increasing activity is associated to the removal of chlorine species present on the catalyst surface by water generated during the reaction. Such species interacting with metallic clusters caused reaction inhibition due to the formation of inactive oxychlorides species whose elimination would restore the active sites for propane oxidation. The maximum conversion was observed around 10 h with TOS and may be attributed to the transition point between the beneficial effect of water (chlorine removal) and the inception of water inhibition.

In fact, the addition of 10 vol% of water in the reactant flow led to a remarkable decrease of the activity, as can be also seen in figure 4. This behavior is expected according to Cullis and Willatt [14], since water inhibits the reaction, depending on the water content. It is evident that without water the activity was relatively high at 673 K and, hence, the formation of water was responsible for the elimination of residual chlorine. However, in the presence of water at higher temperature (723 K) the initial activity was higher during the first 5 h, decreasing drastically as an effect of the water inhibition. From these results one can conclude that temperature and water play an important role in the inhibitory effect of chlorine, where a combination of both

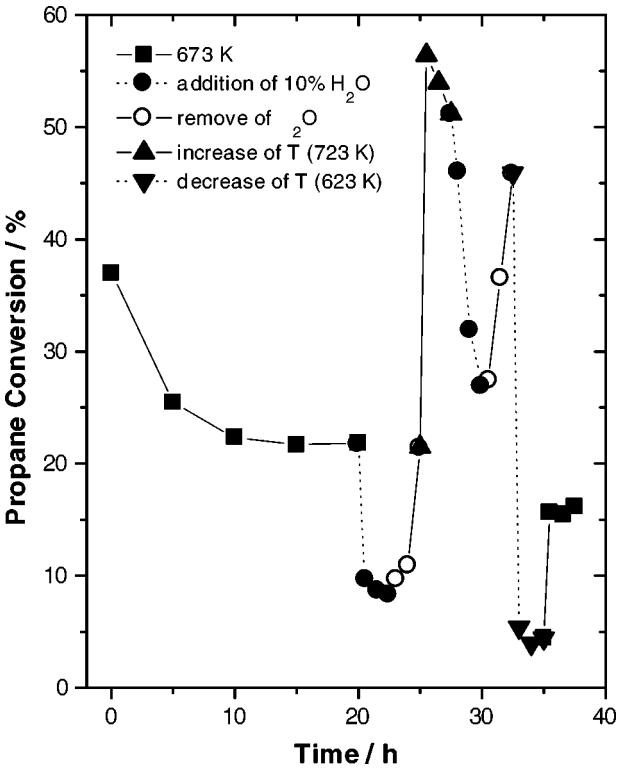


Figure 5. Dynamic behavior of propane oxidation in the presence of water.

parameters would enhance the activity of catalysts prepared from chloride precursors.

For a better understanding of temperature and the water addition effects during the propane oxidation, dynamic fluctuations in the reaction conditions were done, as shown in figure 5. Starting at 673 K and running the reaction for 20 h the catalyst reached the steady state in the absence of water, and its behavior agreed with a previous test (figure 4), which allowed the elimination of chloride due to the water generated from the reaction itself. Then, water was added for a short time, which promoted drastic decay of activity. Furthermore, removing water it immediately returned to the former steady-state conversion at 673 K. Following the reaction at 723 K the conversion increased significantly, but the water generated at such high conversions speeded up the reaction inhibition. Water addition led again to a decreasing activity, so once it is removed the activity was practically recovered. Finally, decreasing the temperature to 623 K the activity fell drastically but reached easily its initial steady-state condition after returning to the initial condition at 673 K.

4. Discussion

Several authors have reported hydrocarbon oxidation on palladium catalysts and the present scenery evidences that the catalytic combustion is influenced by several factors such as the nature of Pd sites, the reaction environment, products and so on. Indeed, there is still some uncertainty in general knowledge of the oxidation mechanism.

TPSR results showed that after running out with oxygen, secondary reactions were observed with formation of hydrogen and a visible transition in the CO_2 curve. Methane was also observed after starting the steam reforming. In fact, steam reforming and hydrogenolysis were observed on the Pd/Al_2O_3 catalyst.

Possible explanations for these results are given in sections 4.1–4.4.

4.1. Sintering

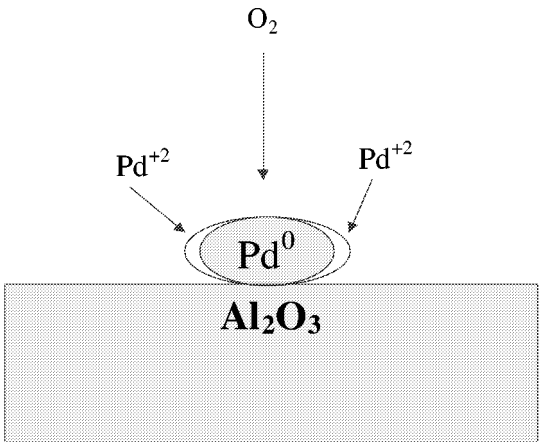
Hicks et al. [15] showed that the turnover frequency of methane oxidation on the dispersed Pd was lower than on large palladium particles. Anomalous large enhancements in activity with time on stream have been associated to sintering of the metallic phase [16]. This was confirmed by *in situ* electron microscopy at 623 K by Rodriguez et al. [17]. At elevated temperatures, the support can also suffer sintering and the activity decays. Muto et al. [18] suggested the importance of choosing an appropriate support in order to resist sintering which weakly interact with the loaded metal or metal oxide. It has also been shown that palladium presented high activity under weaker interaction conditions with the support such as Pd/SiO_2–Al_2O_3 [18,19].

4.2. The nature of surface site

It is important to stress the nature of the active sites of palladium for the hydrocarbon oxidation. Burch [2] showed that the oxidized Pd form is considered the most active state. They have done kinetic experiments by measuring the rate of oxygen uptake as a function of time over a pre-reduced 4% Pd/Al_2O_3 catalyst at 573 K, and the corresponding change in the activity for the combustion of methane at the same temperature. Indeed, at this temperature, Pd metal is not very active for oxygen chemisorption but the most active phase corresponds to a "skin" of PdO over Pd, as proposed elsewhere [20]. Garbowski and Primet [21] claimed that the total oxidation of Pd is not a requirement for an active catalyst. They proposed a redox mechanism involving surface Pd^0 and surface PdO.

Indeed, our TPSR and FTIR results before and after reaction indicated the formation of PdO during the reaction that have promoted a faster start up of the propane oxidation. Noteworthy is that the Pd/Al_2O_3 catalyst was very active and seems to have a great amount of PdO after the reaction, although surface Pd^0 is present as also shown by FTIR. Burch [2] proposed that the most important parameter to get high activity in hydrocarbon oxidation is the PdO surface. In that way, morphological, poisoning or support effects seem to have a secondary role. Our results confirmed this statement, since the intensity of PdO/Pd^0 surface ratio could explain the start up in the catalytic propane oxidation. These results agree with the redox mechanism, as proposed elsewhere [21], which is shown in scheme 1.

Pd/Al_2O_3 Model during Reaction



Scheme 1.

Table 2
XPS results of Cl/Al surface ratios after calcination (C) and after calcination and reduction (R).

Catalyst	Cl/Al
Pd/Al_2O_3 (C)	0.03
Pd/Al_2O_3 (R)	0.007

4.3. Effects of chlorine and particle size

Particle size seems not to be a very important parameter in the redox environment. On the contrary, in the excess of oxygen most palladium particles are in the form of Pd^{2+} species, and according to the literature they exhibit low dispersions and are considered the most actives [15–17].

Figure 4 shows an increasing initial activity passing through a maximum value after 10 h, which would explain this mechanism. Besides this parameter the literature has claimed the poisoning effect of chlorine or water [3,22]. On the other hand, the increasing activity with time on stream would also suggest chlorine removal during the reaction. Indeed, XPS measurements showed the presence of residual chlorine in the Pd–Cl catalyst. According to table 2 the XPS results of Cl/Al surface ratios were of the order of 0.03 after calcination and 0.007 after calcination and reduction with hydrogen at 773 K [23]. Therefore, the increasing activity with time, as shown in figure 4, would justify that water generated during the reaction itself was responsible for the elimination of residual chlorine, confirming XPS results.

Water is adsorbed dissociatively on palladium leading to the formation of H^* and OH^* species, which are recombined very quickly only when water is present in the reaction environment. Otherwise, H* should also recombine with chlorine that interacts with the metallic surface releasing HCl, as follows:

$$Cl\text{–}Pd^* + H\text{–}Pd^* \rightarrow HCl + Pd^*$$

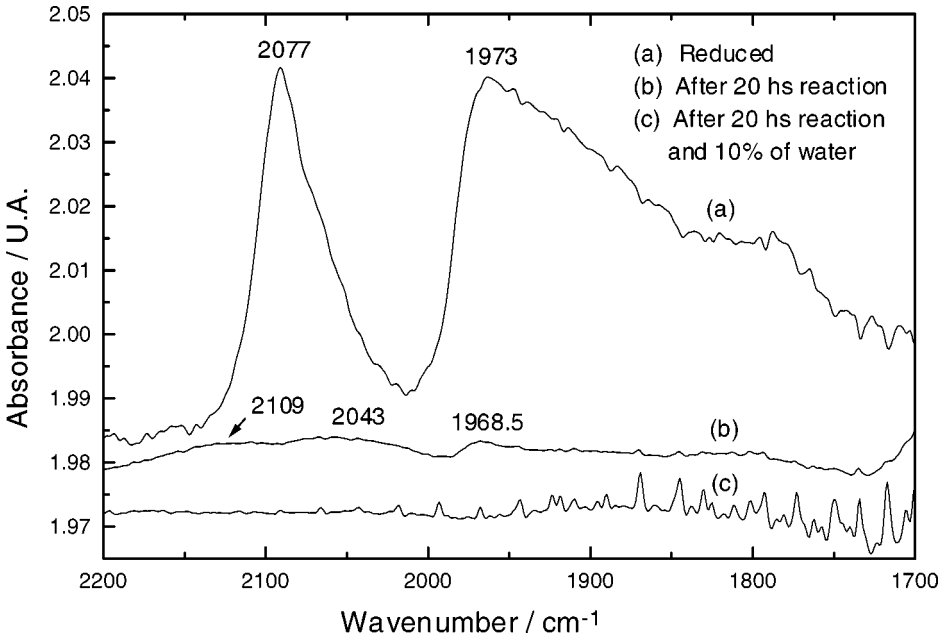


Figure 6. FTIR spectra of adsorbed CO on Pd/Al_2O_3 catalyst before and after propane oxidation with oxygen excess and presence of water.

Thus, Pd* would be regenerated to promote the propane oxidation [24]. On the other hand, water is also a strong inhibitor for this reaction and the degree of inhibition increases with higher amounts of water in the reaction mixture [25].

It is important to stress that the activity increases up to 10 h with TOS, which characterizes the transition state of the beneficial effects (elimination of chlorine) and the inhibiting effect of water. On the other hand, the literature attributed this effect to the support, which can be better related to the promotion of water desorption or hydroxyl affinity, than to the metal–support interaction or the particle size change [18,19].

4.4. Effect of water addition

Effect of water addition or removal in the reactant mixture and of increasing temperature with time on stream is displayed in figure 5. It shows a great inhibiting effect of water, which can be attributed to a pseudo-equilibrium adsorption–desorption of water, according to the reaction

$$2\text{OH–Pd}^* \rightleftharpoons \text{H}_2\text{O}_{(g)} + \text{O–Pd}^* + \text{Pd}^*$$

where Pd^* is the active site as suggested by Fujimoto et al. [5]. Increasing the amount of water, the equilibrium is shifted to the reverse direction, where OH^- species titration occurred either on Pd and PdO sites, inhibiting the reaction activity. Indeed, Ribeiro et al. [3] showed an inverse dependence of first order for the oxidation of methane in the presence of water on supported palladium catalysts. Thus, the inhibition mechanism of propane oxidation in the presence of water consists in the dissociative adsorption of water on palladium sites with the formation of palladium hydroxide (Pd–OH) at the surface, diminishing the number of active surface sites.

Figures 3 and 6 show the FTIR spectra of the reduced catalyst before and after the reaction under reduction and oxidation conditions, respectively. The linear (2073–2079 cm^{-1}) and bridged (1973–1977 cm^{-1}) adsorbed CO species appeared on the Pd^0 surface just after reduction and after reaction under reduction conditions. After the reaction one can see a new band at 2130 cm^{-1}, which is related to the CO adsorption on Pd^{2+} species. This oxidized site is the most intense band on Pd/Al_2O_3. Carbon monoxide species adsorbed on Pd^0 were also observed in this sample. However, after 20 h of reaction under oxidation conditions the linear and bridged CO bands decreased drastically with the appearance of a linear band on Pd^{2+} (2110 cm^{-1}) and a bridged band on Pd^0 (1968 cm^{-1}). When water was added these bands disappeared completely. Therefore, it supports the idea that after removing water or increasing the reaction temperature the equilibrium is shifted towards the formation of Pd* sites, thus favoring the reaction and increasing the conversion of propane. This behavior suggests that the inhibiting effect of water in the reaction mixture is reversible and depends on the amount of water and on the temperature of reaction.

5. Conclusions

Propane oxidation under O_2/C_3H_8 ratio = 4 induced a redox behavior of palladium particles. On Pd/Al_2O_3 catalyst, Pd^{2+} species prevail during the propane reaction and these particles are more active for combustion.

Our results confirmed the statement that the Pd^0/Pd^{2+} surface ratio is determinant for the activity of hydrocarbon oxidation. In that way, morphological, poisoning or support effects seem to have a secondary role.

The inhibition mechanism of propane oxidation in the presence of water consists in the dissociative adsorption of water on palladium sites with the formation of palladium hydroxide (Pd–OH) at the surface, diminishing the number of active surface sites. This behavior suggests that the inhibiting effect of water in the reaction mixture is reversible and depends on the amount of water.

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