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Effect of water vapor on the activity of Pt-Pd/Al_2O_3 catalysts for methane combustion

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Abstract

A study on the deactivation phenomena affecting the catalysts of small-scale natural gas catalytic combustors was undertaken in this work. The influence of simulated aging pretreatments on the activity of Pt-Pd catalysts supported over gamma alumina for the catalytic combustion of CH_4 was assessed under atmospheric conditions and in the 50–950 °C temperature range. Accelerated deactivation tests consisted of steaming at temperatures between 500–800 °C.

The results showed that the activity of the deactivated catalysts depended on two opposite phenomena. An enhancement of the activity was encountered for low aging temperatures and was addressed to chlorine (Cl) elimination (as detected by chemical analysis). Conversely, at higher temperatures the accelerated aging treatment produced a decrease in the activity, and this was allegedly linked to a decrease in the available metal surface area produced by sintering. During the catalyst lifespan and under real operation conditions, a first period is therefore expected where the catalytic activity improves due to the Cl elimination by the water (H_2O) produced during combustion. Afterwards, the activity would decrease because of the sintering of the metal phase. Both processes, Cl elimination and sintering, occur simultaneously.

Five different catalyst formulations with variable Pt and Pd contents were tried and 0.4%Pt-0.8%Pd was found to be the most active. The results found are discussed in terms of the activity of the monometallic catalysts, the degree of interaction of the Pt and Pd phases and the previously mentioned phenomena of sintering and Cl elimination.

Keywords: Catalytic combustion; Pt-Pd; Methane; Deactivation; Sintering

1. Introduction

Catalytic combustion has lately emerged as an alternative to conventional thermal combustion. Research efforts have been boosted by the need to control the issue of pollutants during the combustion in industrial facilities and the need to make an efficient use of fuels, both at industrial and house heating scale. The main advantages of catalytic combustion can be summarized in two points [1]: (i) catalytic combustion can be performed over a wide range of fuel to air ratios and at low temperatures; (ii) low temperatures result in low levels of emission of NO_x.

In non-catalytic combustion, a non-negligible amount of hydrocarbons is not completely reacted and also toxic gases (CO) are either formed or unreacted hydrocarbons are issued among the exhaust gases. CH_4 is especially environmentally aggressive because it has a "greenhouse" effect 21 times greater than CO_2 [2,3]. Though currently there is no legislation regulating the issue of unreacted hydrocarbons, it is possible that in the near future there will be. In order to solve this problem and in the case of the residential

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heating sector, stoves and catalytic heaters are already reaching the market. Most of them operate on the diffusive catalytic combustion principle. The catalyst is a perforated low-density mat made of quartz fibers or porous alumina fibers on which noble metals like Pt, Pd or Rh are impregnated. Metal precursors are usually chlorides or other inorganic salts.

The reduction in the issue of NO_x on catalytic combustors is mainly related to the relatively high activation energy for the formation of nitric oxides. Catalytic combustion in small-scale applications (e.g. residential heating) is performed at low temperatures (400–500 °C). Normal non-catalytic combustion is usually performed at 850 °C and higher temperatures. When the temperature of combustion is reduced, the formation of NO_x is inhibited because these compounds are formed in non-negligible amounts only at temperatures higher than 1500 °C [4].

Catalysts capable of promoting the reaction of combustion can be divided into two groups: (i) noble metals, over which the reaction begins at very low temperatures (as low as ambient temperature); (ii) oxides of transition metals, which are less efficient but more resistant at high temperatures. Among the catalysts of the first group, one of the most commonly used ones is the Pt-Pd bimetallic, because of its combined features of high activity and sulfur tolerance [5–7].

Catalytic combustion is a complex reaction and the literature on catalytic combustion is abundant in seemingly contradictory results. The nature of some basic phenomena still remains controversial. For example, in the case of methane combustion over supported metal catalysts, many researchers report opposite conclusions on the "structure-sensitiveness" of the reaction [8–13]. Hicks et al. [9] reported that the reaction was structure-sensitive in the case of supported Pt and Pd and that the number of turnovers decreased proportionally with metal dispersion. On the contrary, Baldwin and Burch [11,12] did not find any correlation between the activity and the crystal size. After working with catalysts prepared in different ways Dalla Betta and co-workers [13] concluded that the reaction was structure-insensitive. Structure sensitivity is a especially important issue in the case of systems suffering from metal particle growth and it will be discussed in this work.

From a practical point of view, one of the critical properties for catalytic combustion is stability because deactivation may lead to incomplete combustion and formation of toxic gases (CO by incomplete combustion, unreacted hydrocarbons). Part of the activity drop is related to a decrease in the specific surface of the support. Alumina is widely used as a support though it sinterizes to a great extent during the transition of its metastable phases into the stable α phase, at temperatures higher than 1000 °C [14]. In most cases, sintering of the metal phase has been identified as the main cause of deactivation.

The objective of this work was to elucidate the role of different processes that contribute to the total deactivation rate of supported noble metal catalysts used for the low temperature small-scale combustion of natural gas (e.g. fiber mat catalytic heaters). For these catalytic burners, the interplay of different processes that might lead to deactivation, like metal sintering, support sintering and loss of adsorbed anions is far from clear. We have specifically concentrated our attention on Pt-Pd catalysts supported over γ alumina and prepared from chloride salts. Combustion was studied at atmospheric pressure and in the 50–950 °C range, a temperature interval that corresponds to that used by home heating appliances. Different Pt:Pd ratios were used in the formulation of the catalysts in order to find an optimum in the resistance to deactivation. Deactivation, which is a slow process under real combustion conditions, was emulated and accelerated by the direct steaming of the samples. Apart from the combustion reaction itself, the catalysts were further characterized by the test reaction of cyclohexane dehydrogenation and TPR.

2. Experimental

2.1. Catalysts preparation

The catalysts were prepared by coimpregnating Pt and Pd salt precursors over a γ alumina support (Keitjen CK-300, 188 m^2/g). Instead of using alumina in the form of fibers, as in home catalytic heaters, and for the sake of simplicity, the catalysts were prepared and tested in the form of ground porous particles. Before the impregnation step, the γ alumina support was ground and sieved to 35–80 meshes. The particles were then immersed in a solution of HCl 0.2 M. The objective of the addition of acid was to produce an homogeneous distribution of the metal phase by means of the competitive adsorption of chlorine (Cl) [15]. After the addition of the salts of Pt and Pd, the samples were dried slowly until a dry powder was obtained. Then they were further dried in a stove at 120 °C for 12 h. Finally, they were activated by calcination at 500 °C for 4 h in a stream of dry air. $PdCl_2$ and $Pt[(NH_3)_4]_2Cl_2$ (Aldrich) were used as noble metal precursors. The Pt content of all samples was adjusted to 0.4%. The Pd content was varied between 0.0 and 0.8% (0.0, 0.2, 0.4 and 0.8%).

In order to clearly assess the influence of the Cl content, a catalyst with a slightly different preparation procedure was also prepared. A 0.4%Pt-0.8%Pd content catalyst was prepared using $Pt(NH_3)_4(NO_3)_2$ and $Pd(NO_3)_2$ as noble metal salts. The addition of HCl as adsorption competitor was also eliminated. The catalyst thus prepared contained no Cl.

2.2. Combustion of methane

The catalytic combustion of methane was chosen as test reaction because methane is the most refractory hydrocarbon for combustion [16,17] and is the most abundant in natural gas (96%). The reaction was performed in a fixed bed quartz reactor and the temperature was varied linearly from room temperature up to 900 °C with a heating rate of 5 °C min^{-1}. The feed consisted of a mixture of methane (1.1 vol.%), oxygen (2.7 vol.%) and nitrogen (96.2 vol.%), and it was injected at a flow rate of 20 ml min^{-1}. A low concentration of methane was used in order to have an adequate control of the temperature of reaction, because the combustion of methane is highly exothermic. The proportion of oxygen in the mixture was 25% higher than that stoichiometrically needed for total combustion. The results were analyzed in terms of $T_{1/2}$, so-called mean temperature of combustion, defined in this work as the temperature at which a 50% conversion of methane is achieved.

2.3. Dehydrogenation

Dehydrogenation properties of the noble metal phase were measured by the reaction test of cyclohexane hydrogenation. The reactant (pure cyclohexane, Merck, 99.9%) was injected in a stream of hydrogen flowing through a quartz tube reactor containing the catalyst. Reaction conditions were: $T = 300\,^{\circ}C$; WHSV $= 10\,h^{-1}$; H_2:HC (molar ratio) = 30; catalyst mass = 30 mg; pressure = 1 atm. Prior to the reaction, the metal function was reduced in hydrogen (1 h, 500 °C, 80 $cm^3\,min^{-1}$).

2.4. Accelerated deactivation

It was performed in a quartz fixed bed reactor. A constant flow of water (H_2O) (0.356 $cm^3\,h^{-1}$) was injected with a syringe pump into an air stream (60 $cm^3\,min^{-1}$) for 4 h at the desired temperature (500, 600, 700 and 800 °C). The latter is to be referred as “deactivation temperature” throughout the article. The steaming emulated the deactivation of the catalysts produced by the formation of H_2O during combustion. This deactivation was performed in a cumulative fashion. A first treatment was performed at 500 °C. The following steaming treatments were performed over the same catalyst at successively higher temperatures until the final temperature of 800 °C was reached.

2.5. Temperature programmed reduction

TPR assays were performed in an Ohkura TP-2002S equipment. All samples were previously oxidized at 600 °C (with a 2%O_2 in argon mixture). The gas of reduction used was hydrogen (4.8% in argon) and the heating rate was 10 °C min^{-1}.

2.6. Metal dispersion

Only the Pt/Al_2O_3 catalyst was characterized with this technique. Metal accessibility was determined by selective chemisorption of H_2 (at room temperature) and with the use of the double isotherm method. The amount of adsorbed hydrogen was measured in a static volumetric equipment (Micromeritics Accusorb 2100, vacuum level = 10^{-5} mm Hg). Degassing and reduction with hydrogen before the test were performed at 500 °C.

Enough evidence has been accumulated supporting the idea that the active sites for combustion of noble metal supported catalysts are of the $M/M_{\delta+}$ type. Also, the shape of the combustion curves (% conversion as a function of temperature) is the same (sigmoidal) for any noble metal system, Pd, $Pd_{\delta+}$ or PdO/support. For different catalysts, the differences in catalytic activity for combustion are only detected as shifts in the temperature corresponding to a given conversion value [18]. As the activity patterns are similar for all the catalytic species, either metallic or oxidized, in this work the oxidized state was chosen as the base state for the catalysts under study. The catalysts were therefore not reduced before the catalytic test of methane combustion.

3. Results and discussion

In order to assess the importance of the presence of the catalyst in the following combustion tests, we should first indicate that the mean temperature of combustion without catalyst is 825 °C. This result was obtained by performing the combustion of methane in an empty quartz reactor (blank, not shown). At this temperature, methane gas burned in a homogenous chain reaction in the gas phase, self-sustained by highly reactive radical intermediates.

Fig. 1 shows the curves of the catalytic combustion of CH_4 corresponding to the fresh catalysts without deactivation. In comparison with the catalyst-free system, it can be seen that the temperature at which combustion begins is substantially reduced. Combustion begins at 300 °C on most catalysts and it reaches total conversion in a fairly small temperature interval. Conversion is complete at 600 °C for practically all catalysts.

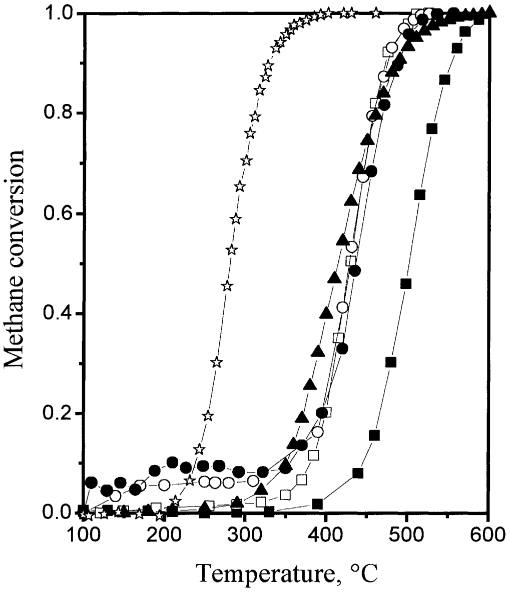

Fig. 1. Conversion of CH_4 as a function of the reaction temperature(fresh catalysts), (■) 0.4%Pt, (□) 0.8%Pd, (▲) 0.4%Pt-0.8%Pd, (○) 0.4%Pt-0.4%Pd, (●) 0.4%Pt-0.2%Pd. (☆) 0.4%Pt-0.8%Pd (Cl-free).

The Cl-free Pt-Pd catalyst had the highest activity in catalytic combustion. Combustion began on this catalyst at a temperature as low as 200 °C and conversion was greater than 40% at 300 °C. At 400 °C, combustion was complete.

For the other catalysts containing Cl, the activity in combustion was lower. The Pd monometallic catalyst had a higher activity than the monometallic Pt one. This result was in agreement with the results reported by Hicks et al. [9] and Kooh et al. [10]. Bimetallic catalysts were always the most active ones, especially at temperatures lower than 400 °C. At higher temperatures, the activity of (0.4%Pt-0.4%Pd), (0.4%Pt-0.2%Pd) and monometallic Pd was similar and we can see that in the entire temperature range the catalyst (0.4%Pt-0.8%Pd) had the best performance of the Cl-containing catalysts.

Fig. 2 shows a plot of the mean combustion temperature, $T_{1/2}$, as a function of the deactivation temperature. It can be seen that with the exception of the Cl-free catalyst prepared from nitrate salts, the activity of all the catalysts tested followed a common pattern. The mean combustion temperature for the non-steamed catalyst laid between 400–500 °C. After deactivating the catalysts, an increase in activity was produced and the mean combustion temperature decreased at least by 50 °C and more than 200 °C in some cases. This phenomenon was, however, reversed when the accelerated deactivation was performed at temperatures higher than 600 °C. In this case, the mean combustion temperature was again shifted to high temperatures.

In the case of the Cl-free catalyst, the variation of the conversion level was smoother. For the fresh catalyst $T_{1/2}$ was 275 °C. For the deactivated ones, $T_{1/2}$ was about 310–325 °C at intermediate temperatures of deactivation, and 336 °C at the highest temperature of deactivation (800 °C).

For the catalysts prepared from Cl salts, in all cases, an improvement in catalytic activity was achieved upon steaming. The mean combustion temperature

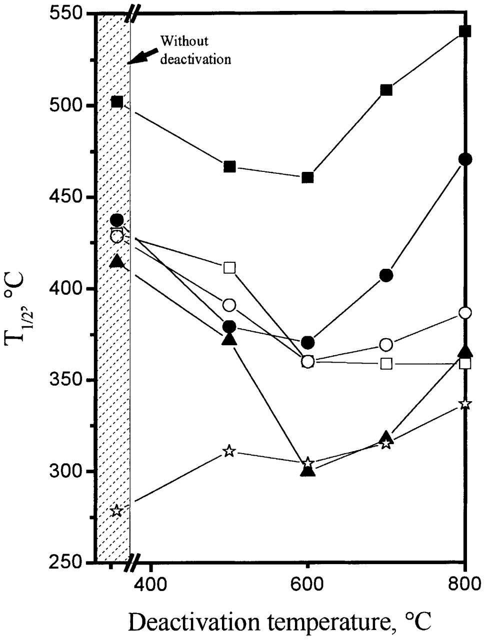

Fig. 2. Mean temperature of combustion as a function of the temperature of deactivation (symbols as in Fig. 1).

($T_{1/2}$) decreased when the catalyst was deactivated at temperatures equal or lower than 600 °C. At higher temperatures of deactivation, the catalytic activity decreased. In the case of the catalysts with a major presence of Pt, the improvement was reversed upon aging at 700–800 °C and an optimum in activity can be clearly seen at 600 °C. In the case of the Pd monometallic catalyst, the activity after steaming at 600, 700 and 800 °C was practically the same. Catalytic combustion over this metal was then not adversely affected by deactivation and the conversion was always improved by the steaming pretreatment.

It is worth to note that in the case of the 0.4%Pt-0.8%Pd catalysts, both Cl-containing and Cl-free, there is a coincidence in the value of $T_{1/2}$ at the temperatures of deactivation of 600 and 700 °C. This result might indicate that both catalysts are equal in most aspects and that the only difference is posed by the Cl content. This difference is removed when Cl is desorbed after deactivating the catalyst with H_2O vapor at 600 °C.

All Cl-containing catalysts pretreated with H_2O had a better activity for combustion of methane than the fresh ones, for deactivation temperatures lower than, or equal to 600 °C. The improvement was lost upon further aging at higher temperatures. This activity pattern must be due to the concurrence of two or several opposing phenomena. These phenomena could be: (i) loss of metal area (active sites of the active phase); (ii) sintering of the support; (iii) change in the Cl content; (iv) a phase change of the supported metal element.

A decrease in the number of active sites (metal phase, hypotheses (i)) could be thought of being related to the volatilization of metal atoms (net loss of Pt and Pd) and/or the sintering of the metal particles (decrease of the fraction of exposed metal atoms). In the case of (iv), the factor that should be taken into account is the transformation of PdO into Pd^0, which takes place in an H_2O/air atmosphere at high temperatures, as reported by Lyubousky and Ferfferle [19]. The phase change produces a drop in the activity for combustion. The effect has been ascribed to the inability of Pd^0 for adsorbing oxygen from the gas phase [19–22].

In order to discard option (i), chemical analyses were performed on the samples deactivated at different temperatures. The results indicated that the Pt and Pd contents remain unaltered. For this reason, a change in the catalytic activity due to a net loss of active phase must be discarded. If the amount of metal phase remains the same, the number of active sites should vary in response to another process, e.g. sintering.

Fig. 3 shows values of conversion as a function of the temperature of deactivation, for the reaction of dehydrogenation of cyclohexane. This is a structure-insensitive reaction and the conversion is proportional to the number of surface atoms [23,24]. Therefore, the conversion can be taken as an indirect measure of the metal dispersion. In can be seen that in the case of the fresh catalysts the monometallic Pt catalyst was more active than monometallic Pd. In turn, bimetallic catalysts had an intermediate activity. This activity followed the order: Pt $>$ 0.4%Pt-0.2%Pd $>$ 0.4%Pt-0.4%Pt $\approx$ 0.4%Pt-0.8%Pd (Cl-free) $>$ 0.4%Pt-0.8%Pd $>$ Pd. These results are in agreement with others previously reported [25].

With respect to the deactivated catalysts, it can be seen that Pt is more affected than Pd by pre-deactivation. This is true for the monometallic catalyst and for the bimetallic ones. When the percentage of Pd increases, the stability of the catalyst at

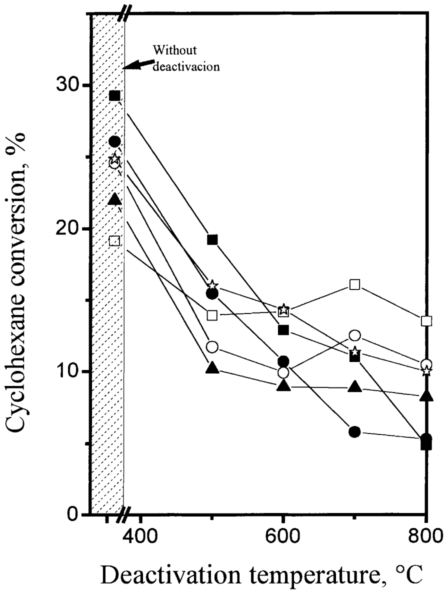

Fig. 3. Conversion of cyclohexane as a function of the temperature of deactivation (symbols as in Fig. 1).

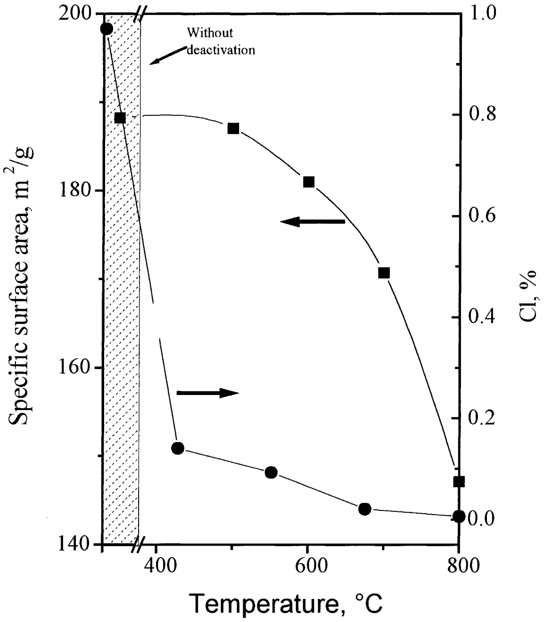

Fig. 4. Percentage of Cl and specific surface area as a function of the temperature of deactivation.

high temperatures (600–800 °C) is improved. These findings are in contradiction with some results of Narui et al. [26] who reported a stabilization of Pd after the addition of Pt. These seemingly contradictory results are surely due to the different reaction conditions and materials. In the case of the experiments in [26], they were performed at 350 °C and in the absence of H_2O, and the support was α alumina.

The bimetallic catalysts suffered a drastic decrease of their dehydrogenating activity when they were deactivated at 500 °C but further treatments at higher temperatures did not substantially modify the activity level. There was a similar behavior between the catalysts (0.4%Pt-0.2%Pd)-(0.4%Pt/Al_2O_3) and between the catalysts (0.4%Pt-0.8%Pd)-(0.4%Pt-0.4%Pd)-(0.4%Pd/Al_2O_3). The first group had the lowest amount of Pd and was more affected by deactivation. In the second group, the fraction of Pd was equal or greater than 50% and the catalysts were less affected by deactivation. It seems that in the first group, the influence of Pt prevailed while in the second group, the same happened with Pd. In summary, when a metal was in higher proportion in any system its individual properties seemed to dominate.

The results of the H_2 chemisorption experiments for the Pt/Al_2O_3 catalyst (results not shown) confirmed a direct relation between the activity in the dehydrogenation of cyclohexane and the metal dispersion, i.e. as the deactivation temperature increased, there was also an increase in the sintering rate of the metal phase.

Fig. 4 shows the variation of the specific surface area and the Cl content as a function of the temperature of deactivation. Both a decrease in chlorine and specific surface area can be seen as the temperature increases. The surface decreases monotonically while the Cl content drops sharply at 500 °C and then continues decreasing much more slowly at higher temperatures. The results agree well with the expected stability of the chloride ion in the presence of H_2O. Much evidence has been accumulated regarding the equilibrium concentration of surface Cl in the presence of H_2O at different temperatures, since the Cl level is crucial in regulating the acidity of reforming catalysts [27–29]. The equilibrium concentration of Cl over reforming catalysts during redispersion of the metal depends on the amount of Cl and H_2O of the feed. Bishara et al. [30] found that the activation energy for Cl desorption was 6 kcal mol^{-1} during calcination in dry air and 2.6 kcal mol^{-1} when reducing in hydrogen. They also reported that the presence of moisture in the feed greatly enhanced the loss of Cl. Reforming catalysts need a minimum acidity level in order to sustain acid catalyzed reactions like isomerization and ring expansion. For a given level of moisture content in the feed, a proper amount of Cl must be added in order to maintain the surface Cl content, e.g. 20 ppm Cl for 100 ppm H_2O. Parera and co-workers [31,32] have found that in typical reforming catalysts, the saturation level of Cl is 0.9–1.0% for a gamma alumina of 200 m^2/g in the presence of a Cl:H_2O mixture of concentration (1:20). The Cl intake-loss is an equilibrium reaction of the type

$$\text{Al–OH} + \text{HCl} \rightleftarrows \text{Al–Cl} + H_2O. \qquad (1)$$

The Cl saturation value for the above considered H_2O:Cl ratio in the feed corresponds roughly to a surface density of 1 Cl/nm^2 and to a 1/10th coverage of the entirely available surface Al. In the presence of Cl-free wet air (4700 ppm H_2O) at 500 °C, the equilibrium value should be zero but the rate of dechlorination is slow and decreases monotonically so that total dechlorination becomes asymptotic. Under these conditions, sufficiently small Cl content values are obtained only after 100 h of treatment [30]. Total removal is also perturbed by the migration of trapped chloride ions from the bulk to the surface, an activated process that only proceeds at a non-negligible rate in conditions of high ionic diffusion, usually coinciding with the temperatures at which sintering is important.

In our case, it can be seen that the first deactivation pretreatment at 500 °C eliminates most of the Cl (80%) and that total removal is only achieved at 800 °C. The low efficiency of the Cl removal process must be related both to the slow kinetics of dechlorination at low and medium temperatures (200–500 °C), and to the migration of Cl from the bulk at higher temperatures (600–800 °C).

Curves corresponding to the tests of temperature-programmed reduction (TPR) of the monometallic catalysts and the bimetallic catalysts of best performance (0.4%Pt-0.8%Pd, Cl-containing and Cl-free), have been included in Fig. 5a. All undeactivated catalysts had a single peak of reduction at 150 °C. In the case of the bimetallic system, this result indicates that Pt and Pd were both simultaneously reduced, probably because Pd catalyzed the reduction of Pt. A similar phenomenon has been reported for Pt and Re in naphtha reforming catalysts [33,34]. From one point of view, this result would indicate that the metals were alloyed or had a high degree of interaction.

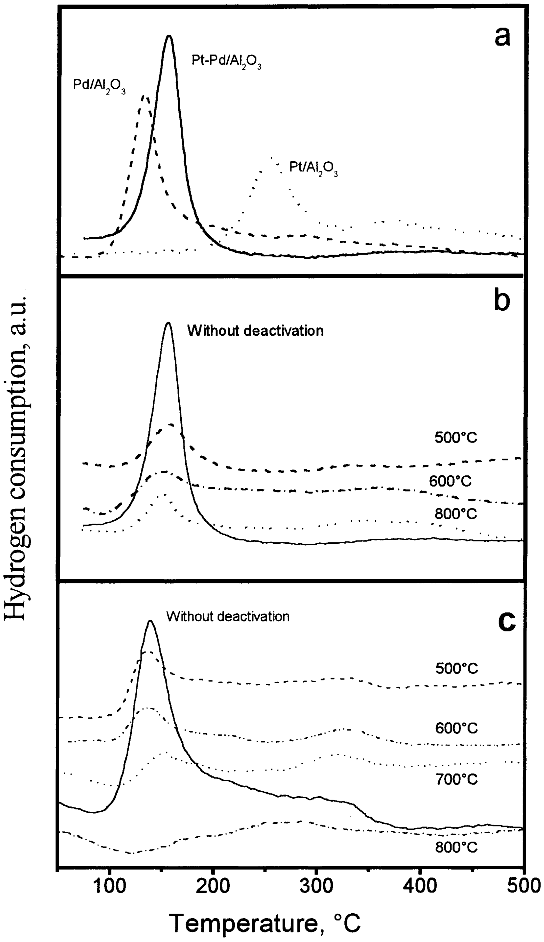

Fig. 5. (a) TPR test of monometallic fresh catalysts; (b) TPR tests of the (0.4%Pt-0.8%Pd/Al_2O_3) catalyst, fresh and deactivated at 500, 600, 700 and 800 °C; (c) TPR tests of the (0.4%Pt-0.8%Pd/Al_2O_3) Cl-free catalyst, fresh and deactivated at 500, 600, 700 and 800 °C.

Fig. 5b contains the TPR plots corresponding to the (0.4%Pt-0.8%Pd) catalyst, in the fresh and deactivated state (for different deactivation temperatures). The other catalysts had a similar behavior upon deactivation (not shown). It can again be seen that in all cases only one peak of reduction is present, corresponding to the simultaneous reduction of Pt and Pd.

Upon aging, a decrease in the intensity of the peak of reduction occurred. The reduction of the TPR area is already important at 500 °C and diminishes slowly at higher temperatures. The results suggest that a process of sintering of the metal phase occurred during deactivation. The big sintered particles with neglegible metal area practically did not consume hydrogen. It is important to note that although the area of the TPR peak decreases, there is no peak splitting. This would indicate that the interaction between Pt and Pd was almost the same after the thermal treatment. It must also be remarked that the decrease observed in the area of the TPR peaks cannot be ascribed to a reduction of PdO to the metal state during the treatment with H_2O at high temperature. Pd^0 would have been completely oxidized during the oxidation step previous to the TPR experiment (see Section 2).

Fig. 5c contains the results corresponding to the TPR of the Cl-free catalyst. The comparison of fresh and deactivated catalysts yields the same pattern of Fig. 5b. A big broad peak at about 145 °C corresponds to highly dispersed Pt-Pd. As only one peak is observed, it is assumed that both metals had a very good interaction. When the Cl-free catalyst was steamed at a temperature as low as 500 °C most of the dispersion must have been lost because the size of the first TPR peak was decreased to about 20% of its original size. As the temperature of deactivation was increased the size of the TPR peak at about 150 °C was further decreased indicating that more sintering of metal particles occurred. For a deactivation temperature of 800 °C, the reduction peak was completely lost, indicating that the metal phase was completely sintered.

In the case of the results of temperature-programmed catalytic combustion, a table of activation energy values was also obtained (see Table 1). The experimental curves of methane conversion as a function of temperature were used. The reactor was assumed to operate in the integral mode. Fluid velocity and reactant conversion profiles in the radial coordinate

Table 1
Values of the energy of activation (E_a) for the fresh and deactivated catalysts (prepared from chlorinated precursors)[a]

Catalysts	Pretreatments	E_a ($n = 0$) (kcal mol^{-1})	E_a ($n = 1$) (kcal mol^{-1})
0.4%Pt	Fresh	28.75	42.50
	Deactivated at 500 °C	27.10	36.43
	Deactivated at 600 °C	22.19	30.96
	Deactivated at 700 °C	24.66	27.87
	Deactivated at 800 °C	25.85	33.73
0.8%Pd	Fresh	30.48	38.87
	Deactivated at 500 °C	27.63	39.12
	Deactivated at 600 °C	21.70	29.08
	Deactivated at 700 °C	20.40	28.86
	Deactivated at 800 °C	25.77	39.93
0.4%Pt-0.4%Pd	Fresh	28.57	41.32
	Deactivated at 500 °C	23.53	36.34
	Deactivated at 600 °C	19.79	27.79
	Deactivated at 700 °C	21.74	29.09
	Deactivated at 800 °C	19.48	27.10
0.4%Pt-0.2%Pd	Fresh	22.43	33.81
	Deactivated at 500 °C	18.44	26.46
	Deactivated at 600 °C	16.38	24.74
	Deactivated at 700 °C	20.81	27.48
	Deactivated at 800 °C	23.04	36.97
0.4%Pt-0.8%Pd	Fresh	18.63	26.14
	Deactivated at 500 °C	26.80	30.50
	Deactivated at 600 °C	21.10	38.73
	Deactivated at 700 °C	22.06	31.41
	Deactivated at 800 °C	20.32	30.43

[a] Rate constant, $k = A\exp(-E_a/RT)$. Rate, $d[CH_4]/dt = k[CH_4][O_2]^n$.

were assumed to be flat, i.e. the reactor was assumed to obey to the plug-flow one-dimensional model

$$\frac{W}{F_A} = \int \frac{dX}{r_A}. \quad (2)$$

The reactor was assumed to work under total kinetic control, i.e. that no diffusional effects constrained the mass-transfer inside the catalyst pores or through the gas film surrounding the catalyst pellets. This hypothesis was checked by evaluating the Weisz–Prater modulus at the conditions of reaction

$$\Phi = R^2 \frac{r_v}{CD_{eff}}. \quad (3)$$

R is the particle radius (approximately 0.1 mm), D_{eff} is the effective diffusivity, r_v is the observed reaction rate (per unit volume) and C is the concentration of the reactant (taken here as the concentration of methane for zero conversion). In the temperature interval 200–600 °C and for a conversion of 50%

$$C = 300\,\mu\text{mol/l}, \qquad D_{eff} = 0.05\,\text{cm}^2\ \text{per second},$$

$$r_v = 0.2\,\mu\text{mol per (second } g_{cat}), \qquad \Phi = 0.002 \ll 1.$$

D_{eff} was calculated from the expression for the Knudsen coefficient because the mean Wheeler pore radius (10 nm) was smaller than the mean free path between molecular collisions as calculated by the kinetic theory.

The external resistance to mass-transfer in the gas film surrounding the catalyst particles, was also neglected. Petersen [44] has demonstrated that with realistic values of the mass-transfer and diffusion parameters, external transport limitations will never exist unless internal diffusion limitations are also present. Nevertheless, the neglect of external limitations was verified by calculating the mass-transfer coefficient (k_g) and the Damköhler number (Da). External mass-transfer resistance would be considered negligible if $\eta Da \ll 0.01$ [45] (η = global effectiveness). The mass-transfer coefficient was calculated according to Hougen's correlation for j_D in laminar flow [46]. Properties are calculated at 500 °C.

$$j_D = 1.66 Re^{1/2} \quad (4)$$

$$j_D = \frac{k_g Sc^{2/3}}{u}, \quad k_g = 70\,\text{cm min}^{-1} \quad (5)$$

$$\eta Da = \frac{r_v}{C k_g a} = 10^{-6} \ll 0.01 \quad (6)$$

Sc = Schmidt number of the gas; Re = Reynolds number of the gas stream; d_p = particle diameter; u = gas velocity; a = area per unit of catalyst volume.

Kinetic models for the combustion of hydrocarbons over various transition metal oxides are available in the literature [35,36]. In general, it has been found that the rate of oxidation is not greatly influenced by the oxygen partial pressure, but is inhibited by H_2O vapor and exhibits a first-order dependence on the partial pressure of the hydrocarbon [28,35,37,38]. No terms of adsorption (as in a Langmuir–Hinshelwood reaction rate equation) are usually used and only a simple power law expression is used. Some authors have reported that methane combustion more likely proceeds via a two-step mechanism. Partial oxidation of methane (Eq. (7)) occurs first and the CO formed is afterwards completely oxidized to CO_2 (Eq. (8)).

$$CH_4 + O_2 \rightarrow CO + 2H_2O \quad (7)$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \quad (8)$$

Reaction (8) is very rapid and on most noble metals CO is completely converted to CO_2 at temperatures lower than 200–300 °C [39]. Therefore, it seems correct to approximate the overall reaction scheme by adopting a kinetic expression that depends only on the concentration of methane of the slowest step (Eq. (7)). In agreement with all these reports, the kinetic expression to be used in the reactor model should be

$$r_A = k[CH_4], \qquad k = A \exp\left(-\frac{E_{activ}}{RT}\right). \quad (9)$$

A simple Arrhenius law was adopted for the variation of the constant. Eqs. (2) and (9) were used to fit the experimental data (conversion versus temperature). From the integral conversion data the overall rate of reaction k_{reac} was calculated. Function ln(k) of (1/T) (in Kelvin) was then linearly regressed.

We have also noted that most researchers adopting an order zero in oxygen have worked in conditions of big oxygen excess and that some reports do exist in which a first-order in oxygen has been used [35,40]. In our experiments, there was only a 25% excess over the stoichiometric amount needed. For this reason, also the kinetic Eq. (10) was tried, taking an order one for oxygen.

$$r_A = k[CH_4][O_2], \qquad k = A \exp\left(-\frac{E_{activ}}{RT}\right) \quad (10)$$

The results for both models are included in Table 1 (Cl-containing catalysts). The coefficient of regression was higher than 0.98–0.99 for all the data sets studied if only the points at temperatures higher than 200–300 °C were taken into account. The activation energy, as reported by other authors [35] is about 10–20 kcal mol^{-1} in the case of Pt and Pt-Pd catalysts. The activation energy, as calculated by the model with non-null order in oxygen is too high, and the results must be considered as an artifact introduced by the wrong kinetic model. The results are better in the case of the model with zero-order for oxygen, though the values seem to be fairly high (18–25 kcal mol^{-1}).

For most catalysts, the minimum activation energy was reached at temperatures of deactivation of 600–700 °C. This might indicate that upon removal of most Cl and without extensive sintering, the reaction is energetically favored.

From the results obtained in can be deduced that the change in catalytic activity after the thermal treatment in the presence of H_2O can be due to the concurrence of two phenomena; the elimination of Cl and the sintering of the metal phase. The elimination of Cl produces an increment in the activity [12,41,42]. Farrauto and co-workers [42] studied the influence of Cl on the activity of PdO/Al_2O_3 for the oxidation of methane. They found that high Cl:Al ratios inhibited the activity of these catalysts to a great extent. Cl-free catalysts, prepared from other precursors different from $PdCl_2$, like nitrate, had a lower dispersion but a higher activity. Similar results were recently reported by Sekizawa et al. [43] for Pt catalysts supported on SnO_2. Catalysts prepared from acetate salts yield the best results, in comparison to other catalysts prepared from chlorides.

The negative effect of Cl is reversible and the activity increases upon Cl desorption. Farrauto and co-workers [42] associated the effect of Cl to two factors: (i) the blocking of PdO active sites by chloride ions (decrease in the accessibility of the reactants to the active sites); (ii) chemical interaction between chloride and PdO leading to the formation of surface complexes $Pd_xCl_yO_z$. In our case, it can be thought that these factors appear as a consequence of the addition of chloride ions coming from $PdCl_2$, $Pt[(NH_3)_4]_2Cl_2$ and HCl. The elimination of Cl by steam would produce the unblocking of active sites and the reversible transformation of surface complexes into active PdO sites.

The results of Cl desorption also resemble those reported by Gavalas and co-workers [47,48] for the TiO_2 growth from $TiCl_4$ and H_2O. They reported that the deposition of TiO_2 in porous silica from titanium chloride likely occurred by an agglomeration mechanism that involved intermediate $Ti(OH)_{(4-x)}Cl_x$ ($x = 1$–3). The reaction of $TiCl_4$ and H_2O was believed to proceed by a first fast step of formation of $Ti(OH)_2Cl_2$, followed by a slow further hydrolysis with formation of TiO_2 and HCl. In our case, it is very likely that 2–3 Cl ligands from $PtCl_6H_2$ were first removed during the impregnation step. A slow further hydrolisis of the remaining Cl ligands might have taken place upon steaming at high temperatures and it would be complete after H_2O vapor treatment at 600 °C.

On the other side, there exists a decrease in the reaction rate due to the sintering of the metal phase and also likely due to the reduction of PdO between 700 and 800 °C [22]. There could be a little compensating effect if a higher metal activity per unit exposed metal area were exhibited by these bigger particles. The sintering of the metal phase has indeed been reported sometimes to produce an increase in the specific surface reaction rate (T.O.N.) [9,10]. In our case, this increase, if present, does not compensate the loss of active sites by sintering and as a result the global activity decreases.

4. Conclusions

Real deactivation occurring in small-scale natural gas burners for residential heating, based on Pt-Pd catalysts, prepared from chloride salts and supported over porous alumina, was simulated by accelerated steaming pretreatments. Deactivation was found to depend both on the sintering of the metal phase and on the desorption of the retained Cl.

Bimetallic Pt-Pd catalysts with an atom ratio Pt:Pd = 0.5, either Cl-doped or Cl-free, had the highest catalytic activity and the highest stability in the methane combustion reaction. The activity was much higher for the Cl-free catalyst but after removing Cl by steaming at 600 °C both catalysts displayed a similar conversion level.

The reaction proceeded roughly by first-order kinetics with respect to the hydrocarbon and with a zero-order with respect to oxygen. During the lifespan of the catalyst, a first stage can be defined in which the activity increases due to the removal of Cl by the H_2O produced during combustion. After most Cl has been removed, the activity decreases due to the sintering of the metal phase and the support.

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