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The activation of a Pd/γ-alumina catalyst during methane combustion: investigation of the phenomenon and of potential causes

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Activation phenomena of a Pd/γ-Al_2O_3 catalyst under methane combustion reaction conditions were studied. The activation of the catalyst with time-on-stream is not due to Cl removal from the surface but seems to be related to sintering of the palladium particles. This could induce structural changes in the palladium particle, which would favor the activation of O_2 on the surface of PdO.

KEY WORDS: catalytic combustion; methane oxidation; palladium; activation.

1. Introduction

Catalytic combustion of methane (CCM) is a promising way in order to produce energy at lower costs, higher yields and in a more environmental friendly way than thermal combustion [1–7]. Actually, this technology emerged in the beginning of the 1970s [2,8], but its large-scale application is still limited by some problems that have to be solved like a better activity of the catalyst at low temperature and the improvement of its stability at high temperature [5,6,9,10]. For CCM at low temperature, Pd-supported catalysts are largely recognized as the best catalytic systems [2–5,9,11,12].

In this work, we focus our attention towards the activation phenomena occurring when a Pd/γ-Al_2O_3 catalyst is under reaction conditions and the related changes from a physico-chemical properties point of view. The evolution of activity of Pd-supported catalysts during CCM is a controversial and contradictory issue. Some authors reported activation of the catalyst with time-on-stream [7,13–23], whereas other researchers mentioned deactivation phenomena [24,25], while some others observed varying behaviors [4,11,12,26–29] depending on the reaction conditions and/or on the catalyst characteristics. In this paper, we study the catalytic combustion of methane on a palladium alumina-supported catalyst (Pd/γ-Al_2O_3) as function of the temperature and the time on stream. Temperature was increased and decreased in order to study stability of solid state, hysteresis phenomena in the activity and in particular any modification of the catalyst which could be interpreted as an activation process. A characterization of the catalysts, principally with XPS as a very sensitive surface technique, was also performed.

2. Experimental

2.1. Catalyst preparation

Pd(2 wt%)/γ-Al_2O_3 (65 $m^2\ g^{-1}$) catalyst was prepared by the wet impregnation technique. In order to prepare 1 g of sample, 980 mg of γ-alumina (*Alfa-Aesar* 39,812) and 50 mg $Pd(NH_3)_4Cl_2 \cdot H_2O$ (*Aldrich* 32,343-8) were both dipped into 350 mL distilled water and the pH of the impregnation solution was raised up to 10.6 by addition of a solution of ammonia 25 vol% (*Merck* 1.05432). After stirring for 1 h, water was evaporated under reduced atmosphere in a rotavapor (45 °C) and dried overnight in an oven at 110 °C. Then, the sample was heated up to 400 °C under O_2 (*Indugas* 99.995%, 60 mL min^{-1}) and kept 1 h at this temperature. O_2 was evacuated under a flow of N_2 (*Indugas* 99.996%, 60 mL min^{-1}) for 30 min and palladium was reduced by means of a gaseous treatment under H_2 5 vol%/N_2 (*Indugas* 60 mL min^{-1}) for 3 h at 400 °C. Finally, the reduced catalyst was calcined for 3 h at 600 °C under air in a muffle furnace.

2.2. Catalytic tests

Catalytic tests were performed in a conventional fixed-bed micro-reactor operated at atmospheric pressure. About 320 mg of powdered catalyst (granulometry: 100–315 μm) were introduced into a U-shape quartz reactor (internal diameter: 8 mm) and were covered with glass beads (diameter >800 μm) checked to be inactive under the conditions of reaction used. The reactor was inserted in a furnace and the reaction was run between room temperature (RT) and 550 °C. Methane conversion was measured every 50 °C in a stepwise way with a staying time of 90 min at each temperature, and was then plotted as a function of the temperature. Temperature cycles (between RT and 550 °C) with varying

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durations of the stay at 550 °C (2, 4, 16 and 65 h) were performed under reaction conditions.

The reactants mixture was composed of 1 vol% CH_4 (*Indugas* 99.95%), 10 vol% O_2 (*Indugas* 99.995%) and 89 vol% He (*Indugas* 99.996%) and the total flow rate was set at 100 ml min^{-1}. Analysis of reactants and products was performed by on-line gas chromatography (*Delsi Di200*) during the whole catalytic test. The detection and quantification of compounds were performed using a TCD.

2.3. Characterization

BET specific surface was determined using a *Micromeritics FlowSorb II 2300* instrument by adsorption of nitrogen at −196 °C. A mass of 200 mg of sample, previously degassed at 150 °C overnight under a flow of a 70/30 vol% mixture of helium and nitrogen (*Indugas*), was used for the measurement.

XRD was performed on a Siemens D5000 diffractometer using the K_α radiation of Cu ($\lambda = 1.5418$ Å). The 2θ range was scanned between 10° and 90° by steps of 0.02° with an acquisition time of 2 s at each step. Identification of the phases was carried out using the ICDD-JCPDS database.

XPS analyses were performed on a SSX 100/206 photoelectron spectrometer from *Surface Science Instruments* equipped with a monochromatized microfocus Al X-ray source (powered at 20 mA and 10 kV), a 30° solid angle acceptance lens, a hemispherical analyzer and a position sensitive detector. The powder samples pressed in small stainless steel troughs of 4 mm diameter were placed on an insulating home made ceramic carousel (*Macor*) in order to avoid differential charging effect. Moreover, a flood gun set at 8 eV and a Ni grid placed 3 mm above the sample surface and grounded to the carousel support were used for charge stabilization [30]. The pressure in the analysis chamber was around 10^{-6} Pa. The angle between the surface normal and the axis of the analyzer lens was 55°. The analyzed area was approximately 1.4 mm^2 and the pass energy was set at 150 eV. In these conditions, the resolution determined by the full width at half maximum (FWHM) of the Au $4f_{7/2}$ peak was around 1.6 eV. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, Al 2p, Pd 3d, Cl 2p and C 1s again, to check the absence of sample degradation and/or the constancy of charge stabilization with time. The binding energies were calculated with respect to the C-(C,H) component of the C 1s peak fixed at 284.8 eV. Data treatment was performed with the *CasaXPS* software, the spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function and after subtraction of a non-linear baseline [31]. Molar fractions were calculated using peak areas normalized on the basis of acquisition parameters and sensitivity factors provided by the manufacturer.

3. Results and discussion

Results obtained during temperature cycles with various durations of the stay at 550 °C are given in figure 1. A hysteresis of activity can clearly be seen when the temperature is decreased from 550 °C down to RT. Moreover, the longer the duration of the stay at 550 °C, the wider the hysteresis gap. However, after 16 h of time-on-steam at 550 °C, the catalyst does not seem to further activate since the activity recorded during the temperature decrease is the same after 16 or 65 h of time-on-stream. The BET surface area did not change after test (65 ± 3 m^2 g^{-1}) and no differences were observed on the XRD patterns. XPS analyses were performed in order to investigate relationships between this activation phenomenon and some physico-chemical properties of the catalysts. Results are given in table 1. The carbon content is very stable among the various samples implying that there is no coke deposition on the surface of the catalyst during the reaction. On the other hand, there is a sintering of the palladium phase under reaction conditions, as evidenced by the decrease of the Pd/Al ratio. However, this sintering of the metallic phase seems to occur mainly during the heating period and its extent is independent of the duration of the stay at 550 °C under reaction conditions. More precisely, the sintering remains constant whatever the duration of the stay at 550 °C under reaction conditions. The same comment is also valid for the oxidation state of palladium: the palladium phase is in an oxidized form (PdO) in every case. The assignment of BE values observed to the overall surface oxidation state of palladium is based on literature data [32,33]. These combined data mean that the palladium phase is always oxidized and sinters under reaction conditions, which seems to be beneficial for the

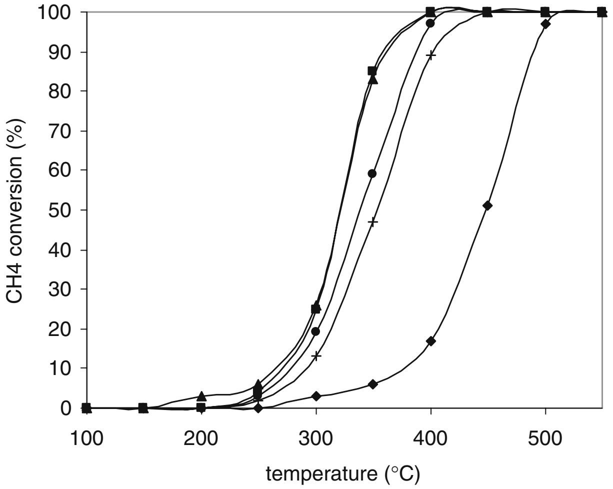

Figure 1. Catalytic combustion of methane. CH_4 conversion as a function of the temperature and of the duration of a stay at 550 °C under reaction conditions ($CH_4/O_2/He = 1/10/89$ vol.). Conversion during heating (RT-550 °C) (◆) and during cooling (550 °C-RT) after 2 h (+), 4 h (●), 16 h (▲) and 65 h (■) at 550 °C.

Table 1
XPS analysis results

Duration at 550 °C	C (%)	Pd/Al ($\times 10^{-4}$)	BE Pd $3d_{5/2}$ (eV)
Fresh catalyst	13.3	107	336.0
0 h	13.7	81	336.1
2 h	13.7	73	336.3
4 h	16.5	75	336.0
16 h	15.0	62	336.3
65 h	14.9	69	336.4

Carbon content (C), surface atomic Pd/Al ratio and binding energy (BE) of the Pd $3d_{5/2}$ peak of the surface of the Pd/γ-Al_2O_3 catalyst after various time durations (0, 2, 4, 16 and 64 h) at 550 °C under reaction conditions.

activity in methane combustion of the Pd/γ-alumina catalyst. The sole sintering phenomenon does not explain the full activation process since it does not vary with time-on-stream at 550 °C whereas the catalytic activity does. The increase of activity with the size of the palladium particles has already been reported and would reflect some structure sensitivity of the CCM reaction on Pd-supported catalysts [3,4,7,12,14,15,19,28,29,34]. However, other researchers came to opposite conclusions, claiming that there is no correlation between the activity and the particle size of the Pd-supported catalyst [17,20,35]. The fact that the temperature did not exceed 550 °C seems to allow us to rule out the hypothesis of decomposition of PdO being responsible of the catalyst activation, as suggested in [26]. Indeed, thermodynamics predicts that, at 550 °C, the equilibrium constant is 1.526×10^{-4} for the PdO decomposition to metallic Pd [36]. Furthermore, activation observed even at higher temperature (675 °C) was reported not to be due to decomposition of Pd process [37], while the decomposition is favored when increasing temperature. Some researchers also suggested that the activation phenomenon could be explained by some carbon deposition [18,21], whereas others report that carbon deposition, which occurs during the reaction, has almost no effect on the catalytic activity [38]. Our results are at variance with both views since no carbon deposition was observed on any of our samples. *A fortiori*, carbon deposition cannot explain the activating effect observed.

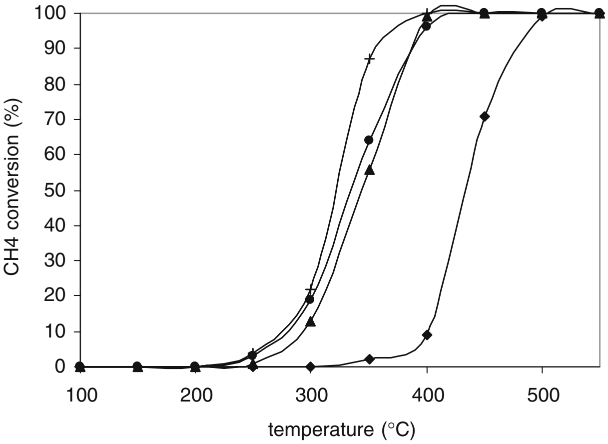

Figure 2. Catalytic combustion of methane. CH_4 conversion as a function of the temperature under reaction conditions ($CH_4/O_2/He = 1/10/89$ vol.) between RT and 550 °C and between 550 °C and RT. Conversion during first heating (◆), first cooling (+), second heating (●) and second cooling (▲).

Table 2
XPS analysis results

Sample	C (%)	Cl (%)	Pd/Al ($\times 10^{-4}$)	BE Pd $3d_{5/2}$ (eV)
Fresh catalyst	14.8	0.09	100	336.3
After heating (RT-550 °C-He)	15.8	0.10	60	336.5
After 1 cycle (RT-550 °C-RT)	12.9	0.07	62	336.3
After 2 cycles (RT-550 °C-RT-550 °C-RT)	14.3	0.07	60	336.4

Carbon content (C), chlorine content (Cl), surface atomic Pd/Al ratio and BE of the Pd $3d_{5/2}$ peak of the surface of the Pd/γ-Al_2O_3 catalyst after various thermal treatments between RT and 550 °C under reaction conditions.

Additional experiments were performed in order to see if (i) the hysteresis of activity is still present during a second temperature cycle under reaction conditions and (ii) if the removal of chlorine from the surface of the catalyst could be responsible for the activation phenomenon. Indeed, another explanation for the activating effect could be the removal of chlorine, coming from the palladium precursor, under reaction conditions, as suggested by some authors [11,16,24,28,39,40]. Results of these experiments are shown in figure 2 and table 2. Obviously, the activity hysteresis is suppressed when a second temperature cycle is performed under reaction conditions. The methane conversion observed during a second heating is almost identical to that recorded during the first temperature decrease. Such an 'activity preservation' during a second cycle performed under reaction conditions was also observed by Ciuparu and Pfefferle [37]. The physico-chemical data indicate again that the C content on the palladium surface does not vary even after 2 cycles under reaction conditions, while the amount of surface Cl does not significantly change, either. The palladium phase sinters during the first heating ramp but, then, is no longer influenced by subsequent temperature variations under reaction conditions. Finally, the oxidation state of palladium does not change under reaction conditions: the palladium phase always remains in a highly oxidized state (surface PdO). The fact that the Cl content does not significantly vary under reaction conditions clearly shows that the activation phenomenon observed can surely not be fully explained by the chlorine removal from the catalyst surface during the reaction. This is not in line with the above-mentioned expectations, based on literature data [11,16,24,28,39,40], but some other researchers came to conclusions similar to ours concerning the effective influence of residual chlorine [18,20,41].

These are strong experimental arguments to suggest that the activation of the Pd/γ-alumina catalyst with time-on-stream during the combustion of methane is mainly related to an *in situ* solid state reconstruction of the PdO catalyst. This emphasizes the fact that dynamic phenomena occurring during the reaction have to be taken into account in order to explain catalytic performances. It has been clearly observed that a sintering phenomenon of the PdO on the surface of the alumina occurs (XPS). The sintering could lead to a more active configuration of palladium particles for methane oxidation. Evidences of such particle reconstruction have been reported by Garbowski *et al.* on a Pd(1.95 wt%)/Al_2O_3 catalyst [7]. They have shown that such surface phase transformations occur under the influence of the reactants (present simultaneously) but also of the support which epitaxially guides the development of (200) planes of the metallic palladium particles. Given that it is much easier to form PdO on a (200) plane than on a (111) plane, which is predominant on the fresh catalyst, this would explain the activation process observed with the time-on-stream. Indeed, the reversible transition from surface Pd to surface PdO can then occur without drastic changes of the lattice parameters [7]. These authors notice that the gaseous atmosphere (oxidizing or reducing) has no influence on such phase transformations. Hicks *et al.* and Baldwin and Burch suggest that the structure sensitivity is caused by the different reactivities of adsorbed oxygen on the surfaces of palladium particles [4,20,28].

Previously, we have shown that high performances in methane combustion of a Pd/γ-Al_2O_3 catalyst are related to the presence of an external layer of highly active oxygen species on the surface of the PdO particles [42]. The development of such a layer would ensure an optimal activity to the Pd/γ-Al_2O_3 catalyst, as detailed elsewhere (Demoulin *et al.*, submitted).

It could be suggested that the activation phenomena observed in this work actually reflect the tiny reconstruction in the solid state of the palladium structure allowing PdO to operate with a high efficiency. This reconstruction would allow a more favorable structure of the PdO particles for the development of such a surface layer of active oxygen species. Such a configuration of the palladium particles would lead to a more easy and rapid replenishment of the external oxygen layer which is continuously consumed by the reductant molecules (CH_4). This rapid process is realized efficiently when the reconstruction of the palladium particles enables the easy activation of the O_2 molecules and/or allows the easy diffusion of oxygen from the bulk to the surface. This implies that the high efficiency of Pd-based catalysts is related to their ability to dissociate the O_2 molecules in ions, forming an oxide layer on the top of PdO. Combustion is realized by the reaction between CH_4 and these very active oxygen species composing the external layer of the palladium particles. However, we cannot rule out the hypothesis that particular faces, where the activation of O_2 is more favored, can be developed during the reaction. The hypothesis of an activation of the catalyst related to structural changes of the palladium particles is shared by many other authors [4,11,13,14,17,19,20]. Some literature results strongly support our explanation. Fujimoto *et al.* suggest that the initial activation period is related to the presence of oxygen-deficient PdO_x crystallites, which contain stronger Pd–O bonds and increase their oxygen content during steady-state combustion reaction [12]. The strength of the Pd–O bond decreases as the PdO_x crystallite size increases or as crystallites become less oxygen-deficient, which enhances the catalytic activity. The correlation between the restructuring (involving sintering) of the palladium particles and the weaker Pd–O bond, inducing a higher activity, had already been proposed by Briot and Primet [19]. Mc Carty proposes that the hysteresis in methane combustion activity stems for the formation of a relatively stable saturated layer of chemisorbed oxygen [22]. The extent of formation of surface complexes is determined by the morphology of underlying bulk Pd metal and oxide phases which is, in turn, influenced by the thermal history of the catalyst [22]. Based on our previous data [42], we agree with that view and suggest that this activation phenomenon reflects structural changes, which allow the progressive covering of the palladium particles with highly reactive oxygen species, coming from the dissociative adsorption of O_2. This process could be favored by the development of preferential planes onto which such species are more easily produced and/or stabilized, but it would principally result from the formation of a more flexible structure where the lattice oxygen can migrate (by diffusion) more easily. The experimental fact that the activity hysteresis disappears when a second temperature cycle is performed under reaction conditions is strongly in favor of such a hypothesis.

4. Conclusions

Activation phenomena occur during the catalytic combustion of methane on Pd/γ-alumina catalysts. The activity for methane combustion increases with time-on-stream when a temperature cycle is performed. However, the hysteresis of activity disappears when a second temperature cycle is performed under reaction conditions. This activation phenomenon cannot be explained by chlorine removal from the surface of the catalyst but seems to be related to some sintering of the palladium phase on the alumina surface. This sintering would induce structural changes in the palladium particles, leading to more efficient catalysts thanks to the easier activation of the O_2 molecules.

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