

Investigation of Parameters Influencing the Activation of a Pd/ γ -Alumina Catalyst during Methane Combustion

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The progressive activation of a Pd(2 wt %)/ γ -alumina catalyst under the reaction conditions of catalytic combustion of methane (CCM) was studied. The reasons of this activation were investigated by XPS, CO-chemisorption, and HR-TEM. The removal of carbon from the surface cannot explain the observed activation process. Sintering of the palladium particles was detected but this parameter alone does not fully explain the activation process of the catalyst. HR-TEM imaging evidences (i) that PdO is present both in the fresh and the active catalyst and (ii) that the PdO nanoparticles sinter and restructure (surface roughening) during the reaction. Development of preferential faces was not observed. It is suggested that this restructuring may be responsible for the activation process by facilitating the formation of an active oxygen layer on the PdO surface. CCM on Pd/ γ -Al₂O₃ depends on the thermal history of the catalyst and is a structure-sensitive reaction.

1. Introduction

Energy production faces two major challenges: fossil fuel resources decrease, and authorized emission levels of noxious gases are continuously lowered. Thus, it is necessary to develop new ways of energy production ensuring higher yields with lower pollutants gases emissions and, if possible, at lower costs. One way to encounter these objectives is to use catalytic combustion (CC) instead of thermal combustion (CT). Indeed, the use of a heterogeneous catalyst leads to operating temperatures lower than thermal NO_x formation temperatures and, thus, strongly decreases the NO_x emissions levels if compared with CT.^{1–12} Moreover, CC also ensures the complete combustion of fuels and allows stable combustion at fuel concentrations much lower (leaner mixtures) than in CT, preventing soot formation, ensuring high energetic yields, and diminishing fuel consumption.^{5–12} However, many problems still have to be solved in order to allow a more widespread use of such an energy production means. In particular, a better activity of the catalyst at low temperature and the improvement of its stability at high temperature are of prime importance.^{2,10,11,13,14} Moreover, more fundamental issues like the nature of the active oxygen species, the nature of the active palladium phase, and the elucidation of the combustion mechanism are still debated and have to be solved for an optimal combustor design.^{11,14–18} Given that natural gas is essentially composed of methane,^{4,7,19,20} the catalyst must be designed for CH₄ since the first major applications will be on natural gas fuelled engines.^{4,21} Actually, two kinds of catalysts are generally distinguished: the active low-temperature (up to ~800 °C) catalyst and the stable high-temperature catalyst (800–1600 °C). For catalytic combustion of methane (CCM) at low temperature, the Pd-supported catalyst is recognized as being a very efficient system.^{1,3,4,6,11–13,15–36} One peculiarity of such a catalytic system is that it can

progressively activate under reaction conditions: its activity increases with time-on-stream.^{7,15,24,29,30,34,36–41} The origin of the increase in activity is still debated, even if reconstruction of the catalyst surface certainly occurs during that period.¹⁵ It is proposed that changes in catalyst activity are correlated with corresponding changes in the catalyst oxidation state, particle size, and morphology.³⁷ The point is that more active catalysts could be designed if these phenomena could be clarified.¹⁵ This requires a complete structural and compositional analysis that could only be possible by combining XPS and HR-TEM data (in addition to other characterization techniques) in order to get new insights into this issue. In a previous study, it was found that a Pd (2 wt %)/ γ -Al₂O₃ catalyst activates under reaction conditions with time on steam.⁴² In particular, a sintering of the palladium phase occurs during the first heating of the catalyst, which seems to be beneficial for the catalytic activity for CCM.⁴² It is indeed reported that the differences in combustion rates and particle morphology of bulk PdO are related to the size of the palladium crystallites.²⁹ The assessment of the palladium dispersion and, a fortiori, its relationship with the catalytic activity of the Pd-supported catalyst for CCM is a debated issue.^{16,24,27,43} We have recently shown that the palladium is in a highly oxidized phase under reaction conditions.⁴⁴ The problem is that chemisorption techniques involve reducing treatments, and this may alter or erase modifications of the palladium particles if compared with their properties under reaction conditions.^{24,27,43} Indeed, the prereduction treatment can cause substantial changes in the dispersion of palladium oxide, e.g., from a two-dimensional layer to a three-dimensional particle.²⁴ As a consequence, dispersion values measured by chemisorption titrations on catalysts reduced at low temperatures may not accurately reflect the surface area of the PdO crystallites present during methane oxidation in excess oxygen.²⁷ It is therefore difficult to establish a correlation between the activity, measured on oxidized palladium, and the average dispersion as determined by chemisorption measurements on reduced palladium.¹⁶ In addition, H₂–O₂ titration and CO-chemisorption

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cannot detect changes in PdO_x surface structure or oxygen content because these reactions are insensitive to the morphology of metal particles, whereas the rate of oxidation could be very structure sensitive.^{16,27} Thus, it is necessary to investigate new ways of determining the dispersion of Pd oxide particles.²⁴ In that sense, this work is concerned with the application of two particular physicochemical techniques. As a “nondestructive” technique, we used X-ray photoelectron spectroscopy (XPS or ESCA), a very sensitive surface spectroscopy technique, to assess variations in the palladium dispersion via the surface Pd/Al ratio. Indeed, we have previously reported a good correlation between the XPS surface Pd/Al ratio and the Pd dispersion, assessed by means of CO-chemisorption.⁴⁵ As a second technique, we used high-resolution transmission electron microscopy (HR-TEM) to carefully examine the dispersion and the microstructure of active (PdO) catalysts. One should note, however, that no exact quantitative information on the phases can be obtained this way and that rather trends are monitored.

2. Experimental Section

2.1. Catalyst Preparation. The Pd(2 wt %)/ γ -Al₂O₃ (65 m² g⁻¹) catalyst was prepared by the wet impregnation technique. To prepare 1 g of sample, 980 mg of γ -alumina (ALFA-AESAR 39812) and 50 mg of Pd(NH₃)₄Cl₂·H₂O (Aldrich 32343-8) are both dipped into 350 mL of distilled water, and the pH of the impregnation solution is raised 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 to 400 °C under O₂ (INDUGAS 99.995%, 60 mL min⁻¹) and kept 1 h at this temperature. O₂ was evacuated under a flow of N₂ (INDUGAS 99.996%, 60 mL min⁻¹) for 30 min, and palladium was reduced by means of a gaseous treatment under H₂ (5 vol %)/N₂ (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. Such a sample is denoted as “fresh” catalyst.

For some experiments, the reduced sample was calcined at 600 °C for varying durations, namely 1, 3, and 24 h, to obtain catalysts with different palladium dispersions.

2.2. Catalytic Tests. Catalytic tests were performed in a conventional fixed-bed microreactor operated at atmospheric pressure. The reactor was made of a stainless steel tube with an internal diameter of 8 mm into which the catalyst was introduced and covered with glass beads (diameter > 800 μ m), checked to be inactive under the conditions of reaction used. The amount of catalyst was 320 mg. The catalyst was used as powder with a granulometry comprised between 100 and 315 μ m. The reactor was inserted in a furnace which, in turn, was enclosed in a heated box which ensured the heating of all the reacting system, comprising lines and valves, at a temperature of 150 °C. The reactants mixture was composed of 1 vol % CH₄ (INDUGAS 99.95%), 10 vol % O₂ (INDUGAS 99.995%), and 89 vol % He (INDUGAS 99.996%), and the total flow rate was set at 100 mL min⁻¹. These conditions are defined as standard conditions, and various tests, detailed below, were performed under such conditions:

Evolution with Time-on-Stream at 400 °C. The catalyst was fed with the reactant mixture (standard conditions) at 400 °C, and the evolution of the CH₄ conversion was recorded for the next 72 h at 400 °C.

Test of Reference (TR). The reaction was run under standard conditions between 200 and 550 °C, and the CH₄ conversion was measured every 50 °C in a stepwise way, staying 90 min at each temperature.

Temperature Cycle. The catalyst was heated to 550 °C under standard conditions (TR), held for 90 min or 16 h at 550 °C, and cooled to RT under standard conditions in a 50 °C stepwise way.

TEM Samples Conditioning. In one case, the catalyst was heated under standard conditions up to 550 °C and then rapidly cooled to RT under He. This sample is called “heated”. In the other case, the sample underwent a temperature cycle procedure with a staying time of 90 min at 550 °C. This sample is denoted “cycled”.

TR after an in Situ Reducing Pretreatment. The reactor containing the catalyst was heated to 400 °C (10 °C min⁻¹) under H₂ (10 vol %)/He (INDUGAS, 60 mL min⁻¹), was kept 2 h at 400 °C under these conditions, and was cooled to room temperature (RT) under He (60 mL min⁻¹). A TR under standard conditions was then directly run.

Analysis of reactants and products was performed by on-line gas chromatography (Varian CP-3800) during the whole catalytic test. Two chromatography columns were used for this purpose: a CP-PoraPLOT Q 25 m \times 0.53 mm allows to separate H₂, O₂, CO, and CH₄ (forming one gross peak) from CO₂ and H₂O; then, H₂, O₂, CH₄, and CO are resolved in a CP-Molsieve 5A 25 m \times 0.53 m. The detection and quantification of compounds were performed using TCD's. Reproducibility was checked by performing the same test with fresh samples coming from the same batch, and conversion curves were similar, nearly superimposed. To compare experiments, the results will sometimes be expressed in terms of T_{50} values, which are the reaction temperatures necessary to ensure 50% of methane conversion. To assess the extent of the gap of hysteresis of activity during temperature cycles, ΔT_{50} values are used which are defined as $T_{50 \text{ rise}} - T_{50 \text{ fall}}$, where $T_{50 \text{ rise}}$ and $T_{50 \text{ fall}}$ are the T_{50} values recorded respectively at the increase and at the decrease of temperature under standard conditions.

2.3. Characterization. The 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.

CO-chemisorption experiments were performed on a Micromeritics Pulse Chemisorb 2700 apparatus. Samples were pre-treated under H₂ (28 mL min⁻¹, 10 °C min⁻¹) at 400 °C for 3 h. After that, a He flow (28 mL min⁻¹) was passed for 1 h. After cooling to room temperature, CO pulses (72 μ L) were performed. On the basis of these dispersion (D) data, the crystallite size can be estimated from the expression d (nm) = $112/D$ (%), assuming spherical particles and a Pd surface atom density of 1.27×10^{19} atoms m⁻².^{24,43,46}

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 homemade ceramic carousel (MACOR, Switzerland) 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.⁴⁷ 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 ~ 1.4 mm², and the pass energy was set at 150 eV. In these conditions, the resolution determined

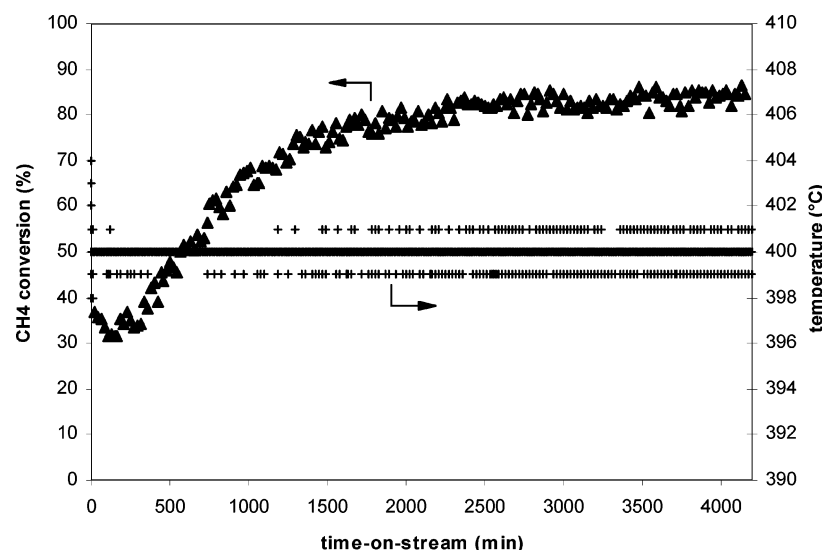


Figure 1. Evolution of CH₄ conversion (▲) and temperature (+) of a Pd(2 wt %)/ γ -Al₂O₃ catalyst with time-on-stream at 400 °C.

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 program (CASA Software, Ltd., UK); 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 nonlinear baseline.⁴⁸ Molar fractions were calculated using peak areas normalized on the basis of acquisition parameters and sensitivity factors provided by the manufacturer.

Structural characterization of the pure alumina support and various catalysts (i.e., fresh, heated and cycled) was carried out by high-resolution transmission electron microscopy (HR-TEM) and transmission electron diffraction (TED), using a JEOL 200 EX microscope operated at 200 kV. Calibration of the magnification and camera constant was performed using (metallic) Pd particles supported on carbon films as reference. The catalyst samples were removed from the reactor as described in section 3.5 and stored in airtight containers until TEM inspection. The TEM samples were prepared by dipping TEM Cu grids covered with holey carbon films into the powders.

3. Results

3.1. Influence of Time-on-Stream. The evolution of both the CH₄ conversion and the temperature of the Pd(2 wt %)/ γ -Al₂O₃ catalyst is displayed in Figure 1. An activation phenomenon of the catalyst clearly occurs between 200 and 2000 min of time-on-stream at 400 °C. The CH₄ conversion increases from about 30 to about 80% in 30 h, and then it remains constant for the next 36 h while the temperature was very stable throughout the whole experiment, as shown in Figure 1. The XPS analysis results of the sample before and after the test are given in Table 1. The overall oxidation state of the palladium phase, as determined by the binding energy (BE) value of the Pd 3d_{5/2} peak, is not affected by the prolonged exposure to the reactant mixture and indicates that PdO is the predominate phase present. However, a sintering of the palladium phase occurs, evidenced by a decrease of the XPS Pd/Al atomic ratio (from 122 $\times 10^{-4}$ to 90 $\times 10^{-4}$). Finally, there is no coke deposition or removal

TABLE 1: XPS Analysis of a Pd(2 wt %)/ γ -Al₂O₃ Catalyst before and after 72 h under Reaction Conditions (CH₄/O₂/He = 1/10/89 Vol)

sample	BE Pd 3d _{5/2} (eV)	Pd/Al ($\times 10^{-4}$)	C (%)	Cl (%)
fresh	335.9	122	10.1	0.24
after 72 h at 400 °C	336.2	90	10.0	0.08

TABLE 2: BE of Pd 3d_{5/2} (XPS), Surface Pd/Al Atomic Ratio (XPS), Pd Dispersion (CO-Chemisorption), and Derived Particle Size of a Pd(2 wt %)/ γ -Al₂O₃ Catalyst Calcined at 600 °C for 1, 3, and 24 h

calcination duration (h)	BE Pd 3d _{5/2} (eV)	Pd/Al ($\times 10^{-4}$)	Pd dispersion (%)	particle size ^a (nm)
1	336.3	141	19.7	5.7
3	336.3	130	16.3	6.9
24	336.4	99	12.5	9.0

^a Deduced from the expression d (nm) = 112/ D (%).^{24,43,46}

from the surface during the reaction, while the amount of surface chlorine seems to decrease during the reaction but some chlorine is still present on the surface, even after the activating procedure. One has to note that the uncertainty on the exact amount of Cl is large due to the very poor signal-to-noise (S/N) ratio of the Cl 2p peak of these samples (about 4/1 and 2/1, respectively). Indeed, the detection sensitivity in XPS is limited by the high background caused by the predominance of energy-degraded electrons in the spectrum.⁴⁹ With most commercial X-ray sources and counting times, elemental detection limits (S/N = 3/1) range between 1.0 and 0.1% of the total composition.⁴⁹ Thus, no quantitative analysis of Cl can be accurately made on our samples, especially when the Cl content is below 0.1%; only qualitative interpretation can be made.

3.2. Influence of Initial Dispersion. After calcination at 600 °C for various durations, namely 1, 3, and 24 h, the catalysts were characterized by XPS and CO-chemisorption techniques. Results are given in Table 2. These samples originate from another catalyst preparation batch. The overall oxidation state of palladium does not seem to be influenced by the duration of the calcination and again points to PdO. On the contrary, the palladium dispersion, determined by both CO-chemisorption measurements and the XPS surface Pd/Al atomic ratio, decreases as the calcination duration increases. These various samples were tested for the CCM reaction, and results are given in Figure 2. It can be seen that samples calcined for 1 h (Pd dispersion = 19.7%) and 3 h (Pd dispersion = 16.3%) display almost the

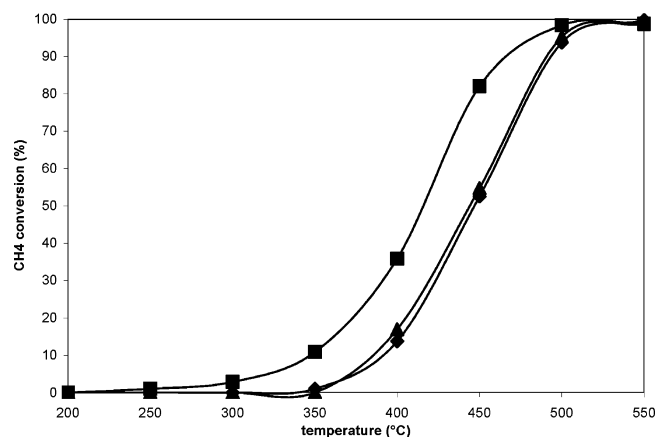


Figure 2. CH₄ conversion as a function of the temperature for a Pd(2 wt %)/ γ -Al₂O₃ catalyst calcined at 600 °C for 1 (◆), 3 (▲) and 24 h (■).

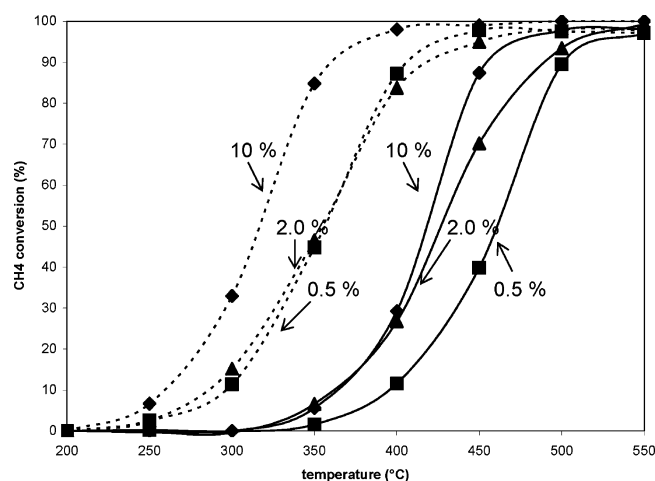


Figure 3. CH₄ conversion as a function of the temperature for a Pd(10 wt %)/ γ -Al₂O₃ (◆), a Pd(2 wt %)/ γ -Al₂O₃ (▲), and a Pd(0.5 wt %)/ γ -Al₂O₃ (■) catalysts during a temperature rise (solid lines) and a temperature fall (dotted lines), after 16 h of time-on-stream at 550 °C. The loading percentage of metallic palladium is indicated in the figure.

same behavior toward methane oxidation. However, the 24 h-calcined catalyst (Pd dispersion = 12.5%) has a much higher activity than the two other samples. Thus, the longer the calcination time, the lower the dispersion, and the higher the activity.

3.3. Influence of the Pd Loading and of the Duration of the Time Period at 550 °C. Three different loadings of palladium, i.e., 0.5, 2, and 10 wt % Pd, were tested in temperature cycles experiments under reaction conditions. Figure 3 displays the CH₄ conversion curves obtained during the heating ramp and during the temperature decrease after a 16 h stay at 550 °C under reaction conditions. Obviously, the higher the loading, the more active the catalyst. However, a hysteresis of activity is observed in every case during the temperature decrease under reaction conditions. To evaluate the extent of this activation phenomenon, ΔT_{50} values were calculated and are reported in Table 3. It can be seen that the extent of the gap of the hysteresis is not influenced by the Pd loading since ΔT_{50} is 105 °C for both the 0.5 and 10 wt % Pd samples. On this table, it can also be observed that the gap increases with the duration of the time period at 550 °C: ΔT_{50} is higher for 16 h than for 1.5 h at 550 °C for every sample. However, the gain of activation does not depend on the Pd loading; indeed, the $\Delta(\Delta T_{50})$ values are similar for all the three loadings. XPS and CO-chemisorption results of the various samples are reported

TABLE 3: ΔT_{50} Values of a Pd(0.5 wt %)/ γ -Al₂O₃, a Pd(2 wt %)/ γ -Al₂O₃, and a Pd(10 wt %)/ γ -Al₂O₃ Catalysts during Temperature Cycles between RT and 550 °C under Reaction Conditions (CH₄/O₂/He = 1/10/89 Vol)^a

Pd loading (wt %)	time period at 550 °C (h)	ΔT_{50} (°C)	$\Delta(\Delta T_{50})$ (°C)
0.5	1.5	75	
0.5	16	105	30
2	1.5	45	
2	16	70	25
10	1.5	85	
10	16	105	20

^a The system was maintained at 550 °C for 1.5 and 16 h and the difference of gap of activity hysteresis between both experiments is expressed as $\Delta(\Delta T_{50})$.

in Table 4. The overall oxidation state of palladium (oxidized form) is influenced neither by the Pd loading nor by the reaction conditions. The same observation is made concerning the C content of the catalyst surface. As mentioned above (3.1), the poor S/N ratio of the Cl 2p signal does not allow making an accurate quantitative analysis of the evolution of the Cl content, at least for both the 0.5 and 2.0 wt % loaded catalysts. Concerning the 10 wt % loaded sample, the S/N ratio is higher (5/1 on the fresh catalyst), and a decrease of the surface Cl content seems to effectively occur during the reaction. The XPS Pd/Al atomic ratio increases with the Pd loading: 52, 102, and 442×10^{-4} Pd/Al for 0.5, 2, and 10 wt % Pd, respectively. On the contrary, the Pd dispersion dramatically decreases when the Pd loading increases: 41.1, 12.0, and 4.3% for 0.5, 2, and 10 wt % Pd, respectively. In every case, the XPS Pd/Al atomic ratio decreases during the test, in agreement with the Pd dispersion values measured by CO-chemisorption, essentially for the initially highly dispersed samples.

3.4. Influence of Initial Oxidation State of Palladium.

Catalytic tests were performed on the Pd(2 wt %)/ γ -Al₂O₃ catalyst as (i) TR and as (ii) TR after an in situ reducing pretreatment. Results are given in Figure 4. Obviously, the application of a reducing pretreatment does not significantly influence the catalytic behavior of a Pd(2 wt %)/ γ -Al₂O₃ catalyst. The T_{50} values are very close, indeed ($\Delta T_{50} < 5$ °C). Nonetheless, some discrepancy can be noticed at lower conversion, evidencing that a reducing pretreatment allows the reaction to start at lower temperature. On the basis of reproducibility experiments, these differences of CH₄ conversion values at low temperature can be considered as significant. The various samples were characterized by XPS as fresh, after the reduction pretreatment and after both kinds of catalytic tests. The characterization results can be found in Table 5. It is observed that the fresh catalyst is in an oxidized state (336.3 eV), typical of PdO, but is severely reduced after the pretreatment (334.4 eV), evidencing the presence of metallic Pd. However, both samples are in a highly oxidized state after test (336.5 eV), independently of the pretreatment. These oxidation state assignments are made on the basis of literature data.^{49,50} The XPS Pd/Al atomic ratio is severely decreased by the reducing pretreatment (85 vs 130×10^{-4}). The sintering of the palladium phase is even stronger after test but is of the same extent with and without reducing pretreatment (65 vs 64×10^{-4}). Finally, all treatments do not induce any change of the surface C content.

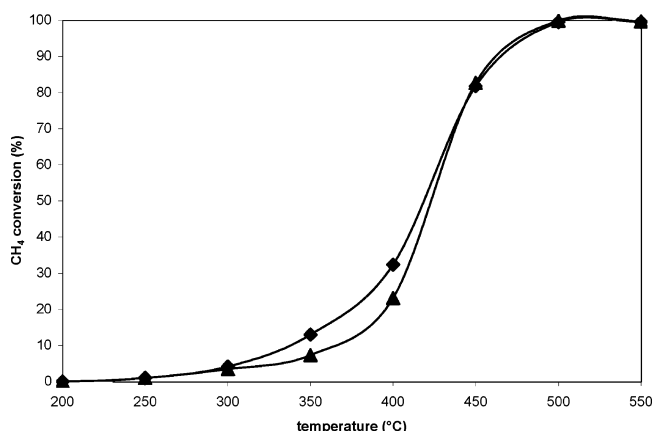
3.5. Electron Microscopy (HR-TEM) Characterization.

Figure 5 compares electron micrographs of the pure γ -alumina support, a “fresh” Pd(2 wt %)/ γ -Al₂O₃ catalyst, a “heated” catalyst (up to 550 °C under reaction conditions, then rapidly cooled under He), and a “cycled” catalyst (heated to 550 °C under reaction conditions, kept for 90 min at 550 °C, then 50

TABLE 4: Characterization Results (XPS and CO-Chemisorption) of a Pd(0.5 wt %)/ γ -Al₂O₃, a Pd(2 wt %)/ γ -Al₂O₃, and a Pd(10 wt %)/ γ -Al₂O₃ Catalysts during Temperature Cycles between RT and 550 °C under Reaction Conditions (CH₄/O₂/He = 1/10/89 Vol)

sample	Pd loading (wt %)	BE Pd 3d _{5/2} (eV)	Pd/Al ($\times 10^{-4}$)	C (%)	Cl (%)	Pd dispersion (%)	particle size ^a (nm)
fresh	0.5	335.7	52	9.8	0.13	41.1	2.7
after heating	0.5	336.2	27	11.5	0.09	20.0	5.6
1.5 h at 550 °C	0.5	335.7	30	10.8	0.05	12.9	8.7
16 h at 550 °C	0.5	336.4	23	10.3	0.00	18.0	6.2
fresh	2.0	335.9	102	11.1	0.09	12.0	9.3
after heating	2.0	336.1	85	11.3	0.10	6.4	17.5
1.5 h at 550 °C	2.0	335.9	80	10.4	0.08	6.4	17.5
16 h at 550 °C	2.0	336.1	76	9.3	0.06	6.0	18.7
fresh	10	336.5	442	9.6	0.32	4.3	26.0
after heating	10	336.1	377	10.4	0.22	3.8	29.5
1.5 h at 550 °C	10	335.9	345	9.7	0.12	3.4	32.9
16 h at 550 °C	10	336.2	331	10.2	0.14	4.0	28.0

^a Deduced from the expression d (nm) = 112/ D (%).^{24,43,46}

**Figure 4.** CH₄ conversion as a function of the temperature on a Pd(2 wt %)/ γ -Al₂O₃ catalyst between 200 and 550 °C for both a TR (\blacktriangle) and a TR after a reducing pretreatment (\blacklozenge) in a microreactor.**TABLE 5: XPS Analysis. Binding Energy (BE) Values of Pd 3d_{5/2}, Surface Pd/Al Atomic Ratio and C Content of a Pd(2 wt %)/ γ -Al₂O₃ Catalyst as Fresh, after an in Situ Reducing Pretreatment, after a TR and after a TR Following an in Situ Reducing Pretreatment**

sample	BE Pd 3d _{5/2} (eV)	Pd/Al ($\times 10^{-4}$)	C (%)
fresh	336.3	130	12.6
after 2 h at 400 °C, H ₂	334.4	85	13.2
after TR	336.5	64	13.5
after H ₂ pretreat. + TR	336.5	65	13.5

°C stepwise cooled under reaction conditions). These samples are similar to those of the 2 wt % catalyst series in Table 4. The alumina support consists of sheets \sim 50 nm in size and typically shows low contrast at thin edge areas (Figure 5a). After the whole catalyst preparation procedure (“fresh” catalyst), particles with a size of about 8–10 nm can be identified (Figure 5b). The particles often exhibit straight edges pointing to the presence of low-index facets, but the corners are typically truncated leading to a “rounded” appearance (typical of higher-index (stepped) surfaces). After the heating process under reaction conditions up to 550 °C (“heated” catalyst), the mean particle size of the Pd(2 wt %)/ γ -Al₂O₃ catalyst has increased to \sim 13–16 nm. After a whole temperature cycle under reaction conditions (“cycled” sample), the particles appear even larger (13–18 nm). The sintering behavior is in agreement with the XPS and chemisorption values presented in Table 4. It is worth noting that a very good correlation is found between the mean particle size measured by TEM and that deduced from the CO-chemisorption measurements (8–10 vs 9.3 nm for the “fresh” sample, 13–16 vs 17.5 for the “heated” sample, and 13–18 vs

17.5 nm for the “cycled” sample). High-resolution lattice images of single particles are shown as insets. Typically, interplanar distances of \sim 0.26 nm were observed, which are characteristic of PdO(101) planes. This observation further confirms that the palladium particles are oxidized to a considerable extent during the reaction. Thus, both XPS and HR-TEM strongly suggest PdO as active phase, in agreement with previous results.^{44,51} After long reaction times the fraction of “polycrystalline” particles, i.e., particles composed of crystalline subunits connected by twin or grain boundaries, seems to be increased. This is probably the result of a continuous oxidation/reduction of the particles in the course of the CCM reaction. Such restructuring was also previously observed, e.g., for oxidation/reduction treatments of supported Rh nanoparticles.^{52,53} Transmission electron diffraction was employed for further structure analysis, but here TED is somewhat limited because the interplanar distances of alumina (i.e., 0.228 nm (222), 0.198 nm (400), or 0.140 nm (440)) overlap with the lattice parameters of Pd (0.225 nm (111), 0.195 nm (200), 0.138 nm (220)). Nevertheless, typical interplanar distances of PdO (0.264 nm (101)) could be identified for the fresh catalyst as well as for the “used” catalysts. Consequently, TED corroborates the presence of PdO but a simultaneous presence of metallic Pd, for instance as surface patches or as core, cannot be excluded.

4. Discussion

4.1. Palladium Sintering Phenomena. As expected, the increase of the calcination duration favors a reduction of the dispersion of the palladium phase (Table 2). It is worth noting that the length of the calcination process does not influence the PdO \rightarrow Pd phase transformation since, at the temperature used (600 °C), thermodynamics strongly favors the PdO phase ($K = 1.081 \times 10^{-3}$).⁵⁴ Moreover, literature data confirm that at such a temperature the PdO phase is by far the main species present.^{24,37,55,56} Our XPS data indeed evidence the predominance of the oxidized state of palladium after the calcination process, independently of its duration. Given that catalytic tests experiments were performed below 600 °C, the PdO \rightarrow Pd phase transformation can be ruled out to affect our data. In addition, under conditions very similar to ours, Zhang et al. showed by means of an in situ XRD study at 1 atm that the PdO phase was stable up to 800 °C under a CH₄/O₂/N₂ = 1/10/89 volume mixture.⁵⁶ These authors also reported that the PdO phase did not decompose to Pd even after 20 h of time-on-stream at 700 °C.⁵⁶ Furthermore, both our XPS and TEM results confirm that PdO is the predominant phase identified on the samples after tests. In the data presented here, sintering of the palladium phase is always observed after test under reaction conditions, for all

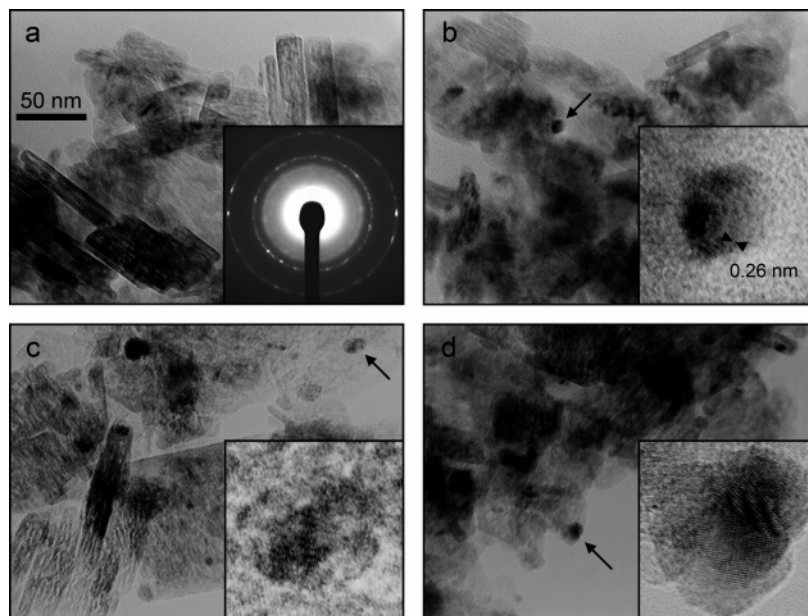


Figure 5. Transmission electron micrographs of the pure γ - Al_2O_3 support (a), of a "fresh" Pd(2 wt %)/ γ - Al_2O_3 catalyst (b), a "heated" catalyst (up to 550 °C under reaction conditions, then rapidly cooled under He) (c), and a "cycled" catalyst (up to 550 °C under reaction conditions, held for 90 min at 550 °C and subsequently cooled in 50 °C steps under reaction conditions). High-resolution lattice images of single particles and an electron diffraction pattern are shown as insets.

types of experiments. This phenomenon is revealed by a decrease of both the XPS Pd/Al atomic ratio and the Pd dispersion assessed by CO-chemisorption. TEM micrographs confirm this trend and, furthermore, validate the use of the XPS Pd/Al atomic ratio as a probe of the dispersion of the palladium phase on the alumina support. It is observed, in Table 4, that the palladium dispersion also decreases as the Pd loading increases, as expected.³⁰ A reducing pretreatment also induces sintering of the palladium phase but not as much as a test under reaction conditions up to 550 °C. It is worth noting that the reducing pretreatment does not influence the final XPS Pd/Al atomic ratio, which is identical after a test with or without pretreatment. Indeed, if the sintering of palladium is observed in a H_2 -containing atmosphere,^{57,58} other factors can also influence the palladium dispersion, for instance a modification of its oxidation state, a temperature increase, and/or the presence of water coming from the combustion process.^{6,16,22,23,37,59,60} This may explain why the extent of the sintering of the palladium phase is governed by the exposure to reaction conditions at high temperature and not by the initial reducing pretreatment. On the basis of the various experiments, it seems that sintering of the palladium particles is involved in the activation process of the Pd/ γ - Al_2O_3 catalyst under CCM conditions. This is indicated by the catalytic test made with similar catalysts calcined at the same temperature but for various durations: the longer the calcination time, the more sintering, and the more active the catalyst. We can therefore suggest that larger palladium particles lead to higher catalytic activity. Other researchers also reached the conclusion that large palladium crystallites catalyze the CCM reaction more effectively than highly dispersed palladium particles.^{3,7,26–29,37,43,61,62} For instance, Lyubovsky et al. report that the formation of large, highly reactive faceted crystallites of palladium under reaction conditions is correlated to an increase of activity.³⁷ Such a correlation between the increase of the particle size and of the catalytic activity has also been reported in the case of platinum for the oxidation of methane (CCM)⁶³ or of other hydrocarbons.^{64,65} On the contrary, other authors did not find any relationship between the particle size of palladium-supported catalysts and their activity for methane

oxidation,^{24,30,32} in agreement with similar statements made for toluene oxidation.^{66,67}

4.2. Activation with Time-on-Stream. Results displayed in Figure 1 clearly show that the Pd(2 wt %)/ γ - Al_2O_3 catalyst progressively activates when kept under reaction conditions at a fixed temperature, which was carefully monitored due to the high exothermicity of the reaction. The variation of activity with time-on-stream of palladium-supported catalysts has been investigated by many researchers so far.^{3,7,15,16,18,22,24,25,27–30,34,36–41,43,68} However, their observations and reported conclusions were divergent. Some authors reported activation of the catalyst with time-on-stream,^{7,15,24,29,30,34,36–41} whereas others mentioned deactivation phenomena,^{18,68} while some others observed varying behaviors,^{3,16,22,25,27,28,43} depending on the reaction conditions and/or on the catalyst's characteristics. Nonetheless, there is a general agreement that pretreatment with the reactant mixture leads to catalysts more active than freshly prerduced ones.^{26,28–30,32} This emphasizes the fact that the presence and reaction of both reactants are necessary for the activation to occur.³⁰ The same is also true for deactivation.⁶⁸ The exact reasons for the activation of the Pd-supported catalyst under CCM reaction conditions are strongly debated. According to Lyubovsky and Pfefferle, the particle size and morphology experience a reversible change during reduction/reoxidation cycles at 800 °C, which can at least partially explain the observed change in apparent activation energy.²² For other researchers, the increase in reaction rate is not due to redispersion of the PdO phase during the reaction.^{24,27,30} Instead, it should result from a change in morphology or surface reconstruction of the PdO particles under reaction conditions to yield a more active phase.^{24,29,30,37,40,43} For Briot and Primet, the reason for the increase in activity is a restructuring of the particles (including an increase in average particle size) leading to weaker Pd–O bonds and consequently higher activity.²⁹ Fujimoto et al. also invoke changes in the strength of the Pd–O bonds to explain the activation process.²⁷ However, they suggest that the initial activation period observed during methane oxidation does not reflect structural changes induced by the initial stages of the reaction but are 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 reactions.²⁷ According to Baldwin and Burch, the activation is not due to a simple support effect or to the removal of chlorinated species from the catalyst under reaction conditions but to morphological changes.^{30,40} The effect of the activation is to sinter the palladium and the increase in the catalytic activity results from the changes in the reactivity of adsorbed oxygen, caused by a change in the noble metal particle size.³⁰ On the contrary, Burch and Hayes never observed activation phenomena but report that deactivation with time-on-stream is routinely seen on their Cl-free catalysts. They claim therefore that activation, when observed, is not due to morphological effects but to Cl removal.¹⁸ This point is largely discussed elsewhere (ref 42 and references therein). Our TEM investigations indicate that morphological changes may (at least in part) be responsible for the activation with time-on-stream. Beside the increase in particle size, it seems that the surface of the PdO aggregates restructures and becomes “rougher”, as discussed above. This could change the binding strength of the reactants and thus affect reactivity. The activation process during methane oxidation can be suppressed by increasing the temperature very slowly during the preparation procedure.²⁷ However, prereduction of such samples in H₂ at 773 K led to very low initial methane oxidation rates and to subsequent activation under reaction.²⁷ Activation with time-on-stream on prereduced samples has been reported by other researchers.^{32,34,39,40} This would be due to the fact that prereduced Pd/Al₂O₃ catalyst absorbs oxygen to form PdO_x during the activation period after contact with CH₄/O₂ reactants mixture, and the catalytic activity of PdO_x increases with increasing oxygen content.³⁴ Moreover, the particle size of Pd/Al₂O₃ freshly prepared by reduction in hydrogen is smaller than that of Pd/Al₂O₃ aged at 600 °C in CH₄ and O₂ streams for 14 h before reduction.²⁹ This particle size effect may also have an influence upon the activation process.

4.3. Origin and Causes of the Catalyst Activation. **4.3.1. Deposition or Removal of Contaminants.** As stated above (4.2), the role of residual chlorine in the activation process of the catalyst is a debated issue, which is more specifically addressed in another paper.⁴² Nonetheless, the XPS results seem to show that, taking the poor (S/N) ratio into account, the surface Cl content decreases after test, but no clear relationship could be established between this decrease and the activation of the catalyst. On the basis of these considerations, it is proposed that this parameter alone does not fully explain the activation process of the catalyst. The Cl issue thus remains an open question before a more accurate quantification is available. The present results also show that carbon deposition or removal from the surface cannot be invoked to explain activation phenomena since the C content was very stable in all experiments. Some researchers indeed suggest that the activation of the Pd-supported catalyst could be due to deposition of carbon, resulting in a modification of the active sites or surface reconstruction of the crystallites.^{39,40} On the contrary, other authors claim that carbon deposition effectively occurs during CCM, but it does not influence the catalytic activity,⁶⁹ or that this C deposition inhibits the reaction.⁶⁸ This inhibition can be suppressed by a reducing pretreatment which removes carbon from the surface.⁶⁸ In our experiments, we also applied a reducing pretreatment but no effect on the surface C content could be observed (Table 5).

4.3.2. Sintering of the Palladium Phase. The most obvious modification of the catalyst's properties after a test is the remarkable sintering of the palladium oxide phase. However, given that the extent of the sintering is not influenced by the

duration of the time period at 550 °C (Table 4), this parameter alone surely not fully explains the activation process of the Pd/γ-Al₂O₃ catalyst. Actually, our results show that sintering of the palladium phase is probably a first step involved in the overall activation process of the Pd/γ-Al₂O₃ catalyst because the initially less dispersed catalyst exhibited the best catalytic behavior (Figure 2). This leads us to conclude that CCM on Pd/γ-Al₂O₃ (i) depends on the thermal history of the catalyst, as already proposed by other researchers,^{16,20,21,24,41} and (ii) is a structure-sensitive reaction, in agreement with many authors.^{3,7,20,26–30,37,43,36,40,41,62,70} However, Ribeiro et al. conclude, on the contrary, that the reaction is structure-insensitive.²⁴ The fact that sintering of the palladium particles leads to a higher activity of the catalyst may have to do with a better ability of larger PdO particles to rapidly develop an active surface oxygen layer, as compared to smaller (oxide) particles (see below). This could result from a decrease in the heat of oxygen chemisorption when the particle size increases.²⁶ Moreover, it is well-known that highly dispersed palladium oxide is less active than the bulk oxide.^{3,7,24,28} Another explanation might be that bigger particles develop preferential faces. This would improve the efficiency of the methane oxidation process by promoting, for example, the adsorption of the reactants or the formation of highly reactive oxygen species. However, this last hypothesis is not supported by our TEM studies. They indicate structural changes (roughening) which may allow more rapid oxygen diffusion inside the palladium particle. This oxygen reservoir may act to replenish the surface top layer at a higher rate. Indeed, we have previously shown that the most active configuration of the palladium particles is obtained when this top layer is continuously replenished with oxygen active species.^{44,51} This process could therefore explain the activation phenomena observed.

4.3.3. In Situ Reducing Hydrogen Pretreatment. When an in situ reducing pretreatment was performed, the only effect observed, apart from the sintering phenomenon discussed above, was the reduction of PdO to metallic palladium, as intended. However, palladium completely reoxidized during the reaction, as evidenced by the XPS results after test, both with and without pretreatment (Table 5). The conversion values recorded during these experiments (Figure 4) tend to show, as discussed in section 3.4, that a reducing pretreatment allows the reaction to start at slightly lower temperatures. It is indeed often reported that prereduction of supported palladium catalysts enhances performance for CCM.^{16,22,32,35,62,68} One of the effects of the H₂ pretreatment could be to promote the Cl removal by formation of hydrogen chloride,⁷¹ but some structural changes can also be caused by prereduction of PdO,⁶² which induces an enhanced activity compared to unreduced samples. However, in situ reduced catalysts are oxidized upon contact with the reaction atmosphere and bulk oxidation of palladium occurs during the reaction.^{34,35,44,62} Müller et al. concluded that the higher activity of prereduced catalysts cannot be traced back to a higher activity of metallic palladium but rather to altered properties of the palladium oxide phase after reduction.⁶² Moreover, we have recently shown that, under reaction conditions, a Pd(2 wt %)/γ-Al₂O₃ catalyst is always in a highly oxidized state, even after a reducing pretreatment.⁴⁴ Therefore, a more active reduced state cannot be used as an explanation for the lower ignition temperature. On the basis of these considerations, it is likely that a reducing pretreatment produces surfaces that allow the gaseous mixture to ignite at lower temperature. This may be due to an enhanced adsorption and dissociation of O₂, producing an active PdO layer, which is

thought to be the most active configuration of such a catalyst for CCM.^{3,16,20,23} The most active form of the palladium phase for CCM is a largely debated issue in the literature, and we will not repeat this discussion here (for additional information, see for example ref 16 and references therein). Evidence of such particle reconstruction has been reported by Primet et al. for both Pd/Al₂O₃ and Pt/Al₂O₃ catalysts.^{29,36,63} Yet, they state that the activation by aging is much more pronounced on Pd— than on Pt—alumina catalysts.²⁹ Gaseous O₂ could more easily dissociate on the active PdO layer than on metallic palladium, increasing the activity with time-on-stream. However, once the reaction has begun, the difference between the prereduced and the untreated samples does no longer exist ($\Delta T_{50} \sim 0$), probably because, above the light-off temperature, the regime is kinetically limited and the PdO phase is developed, independently of the initial underlying metallic phase. Moreover, the active PdO layer can be very rapidly rebuilt as soon as H₂ is removed, and the palladium-based catalyst is under reaction conditions. This is evidenced by the XPS results which show that palladium is in a highly oxidized state after reaction, with or without a prior reducing pretreatment, whereas it was in a metallic state after the in situ H₂ pretreatment (Table 5). This is in accordance with our previous Raman results showing that an oxide phase of palladium is always present under CCM reaction conditions, even after in situ reduction.⁴⁴

5. Conclusions

1. The Pd(2 wt %)/ γ -Al₂O₃ catalyst progressively activates with time-on-stream. The overall oxidation state of the palladium phase (PdO) is not affected by the prolonged exposure to the reactant mixture but a sintering of the palladium phase occurs.

2. The catalytic activity increases with the Pd loading. A hysteresis of activity is always observed during a temperature cycle under reaction conditions, independent of the Pd loading. The extent of the gap of the hysteresis increases with the duration of the time period at 550 °C, but the gain of activation is the same for every Pd loading studied.

3. Sintering of the palladium phase is always observed after tests under reaction conditions. A reducing pretreatment also induces sintering of the palladium phase but not as much as a test under reaction conditions up to 550 °C. Moreover, the extent of the sintering after test is identical with or without prior reduction pretreatment. Thus, the extent of the sintering of the palladium phase is governed by the exposure to reaction conditions at high temperature and not by the initial reducing pretreatment. After test, samples are in a highly oxidized state independent of the pretreatment.

4. The application of a reducing pretreatment does not significantly influence the catalytic behavior of the Pd(2 wt %)/ γ -Al₂O₃ catalyst but allows the reaction to start at slightly lower temperature. This could be due to the formation of Pd facets that favor the adsorption and dissociation of O₂, producing an active PdO layer. However, once the reaction has begun, the difference between the prereduced and the untreated samples does no longer exist ($\Delta T_{50} \sim 0$), probably because, above the light-off temperature, the regime is kinetically limited and the highly oxidized PdO phase is developed, independently of the initial underlying metallic phase.

5. The increase of the calcination duration leads to a reduction of the dispersion of the palladium phase on the alumina support, inducing a higher activity of the catalyst. This implies that sintering of the palladium oxide particles is involved in the activation process of the Pd/ γ -Al₂O₃ catalyst under CCM conditions: larger particles lead to higher catalytic activity.

However, this parameter alone does not fully explain the activation process of the Pd/ γ -Al₂O₃ catalyst. Sintering of the palladium phase is probably a first step involved in the overall activation process of the Pd/ γ -Al₂O₃ catalyst. This could be explained by a better ability of large particles to develop an active oxygen layer on the PdO surface than smaller particles and/or to favor oxygen migration inside the palladium particle. The development of preferential faces was not observed.

6. HR-TEM imaging confirms that PdO is present in the active catalyst and that the nanoparticles sinter and restructure (roughen) during the reaction, the latter effect being most likely due to repeated surface oxidation/reduction by the reactants.

7. The carbon deposition/removal from the surface cannot explain the observed activation process, while the effective role of residual chlorine remains an open issue.

8. The present results confirm that the surface Pd/Al ratio can be used as an indicator for the dispersion of the palladium phase on the alumina support.

In conclusion, CCM on Pd/ γ -Al₂O₃ depends on the thermal history of the catalyst and is a structure-sensitive reaction.

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