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# Deactivation of palladium catalyst in catalytic combustion of methane

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## Abstract

Catalytic combustion of natural gas, for applications such as gas turbines, can reduce $NO_x$ emissions. Palladium-on-stabilised alumina has been found to be the most efficient catalyst for the complete oxidation of methane to carbon dioxide and water. However, its poor durability is considered to be an obstruction for the development of catalytic combustion. This work was aimed at identifying the origin of this deactivation: metal sintering, support sintering, transformation $PdO \rightarrow Pd + \frac{1}{2}O_2$ or coking.

Catalytic combustion of methane was studied in a 15 mm i.d. and 50 mm length lab reactor and in a 25 mm i.d. pilot test rig on monolithic honeycomb substrates. Experiments were performed at GHSV of 50 000 $h^{-1}$ in lab test and 500 000 $h^{-1}$ in pilot test. The catalysts used were palladium on different supports on cordierite substrate. The catalysts were characterised by XRD, STEM, ATG and XPS.

In steady-state conditions, deactivation has been found to be dependent on the air/methane ratio, the palladium content on the washcoat and the amount of washcoat on the substrate. An oscillating behaviour of the methane conversion was even observed under specific conditions, due to the reducibility of palladium oxide PdO to Pd. The influence of the nature of the support on the catalyst deactivation was also investigated. It has been shown that some supports can surprisingly eliminate this oscillating behaviour. However, in pilot test, deactivation was found to be very rapid, even with stabilised alumina supports. Furthermore, successive tests performed on the same catalyst revealed that the activity (light-off temperature, conversion) falls strongly from one test to another.

Then, the stabilised alumina support was calcined at 1230°C for 16 h prior to its impregnation by palladium, in order to rule out its sintering. Experiments carried out on precalcined catalysts point out that deactivation is mostly correlated to the metal transformation under reaction conditions: activity decreases gradually as PdO sinters, but it dropped much more steeply in relation to appearance of metallic palladium.

*Keywords:* Catalytic combustion; Methane oxidation; Palladium catalyst; Deactivation

## 1. Introduction

Catalytic combustion of natural gas, for applications such as gas turbines, is one of the measures for reducing $NO_x$ emissions [1,2]. Three catalytic reactors concepts have received most attention [3,4]: the multi-monoliths combustor [5], the hybrid combustor [6] and the partial catalytic combustor [7,8]. Catalyst formulations can be divided in two groups which correspond to the different segments of the catalytic section [8,9]. Firstly, the low-temperature catalysts, which are used in the front stage to initiate combustion and to raise the temperature high enough to initiate flame combustion. Active supported palladium cata-

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lysts are used in these stages. Secondly, the high-temperature catalysts which are used in the multi-monolith reactor (substituted hexaaluminates: BaMn-$Al_{11}O_{19}$) [5]) and optionally in the partial catalytic combustor (perovskites: $LaCrO_3$, $LaMnO_3$ [10] or palladium combined with rare earth: $Pr_4PdO_7$ [11]). Whatever the type of catalytic combustor, one of the main issues is to develop active supported palladium catalysts which are able to work at 400–900°C over thousands of hours. The temperature range for the stability of these catalysts is crucial for the design flexibility of the catalytic combustor. Our study has been focused on deactivation of palladium catalysts supported on alumina. It was aimed at an identifying classification of the main modes of deactivation which are known [12,13]:$\gamma$-$Al_2O_3$ sintering [14], deactivation due to spinel formation [15], PdO or Pd sintering [16], or transformation of PdO$\rightarrow$Pd [17] and to assess the impact of excessive temperatures on catalyst activity.

## 2. Experimental

### 2.1. Catalyst preparation

Catalysts were prepared on a cordierite monolith having 62 cells/cm$^2$. Monolithic substrates were coated with stabilised or promoted aluminas. Stabilised aluminas: 3 wt% $La_2O_3$–$Al_2O_3$ and 3 wt% BaO–$Al_2O_3$ were prepared by nitrate impregnation on $\gamma$-$Al_2O_3$ and 4 wt% $SiO_2$–$Al_2O_3$ was prepared by impregnation with $Si(OEt)_4$ as described in [36]. Promoted aluminas: $ZrO_2$–$Al_2O_3$, $La_2O_3$–$Al_2O_3$ and $CeO_2$–$Al_2O_3$ were prepared by nitrate impregnation. Monolith samples were dipped into a slurry prepared with these supports and the excess slurry removed. This procedure was repeated until the desired wash-coat loading was obtained. After drying and calcining, palladium was deposited by impregnation of $Pd(NO_3)_2$, dried and calcined at 600°C for 2 h.

To provide for a presintered support, a 4 wt% $SiO_2$–$Al_2O_3$ was calcined at 1230°C for 16 h in air. Then, palladium was deposited. Before testing, samples were precalcined at 600°C, 900°C, 1000°C, 1100°C and 1200°C for 4 h in air. In this case, the furnace regulation was switched off and the temperature of the samples decreased slowly to ambient. A fraction of each slurry was set aside, and dried and calcined in the same way as the monolith, for ageing tests and characterisation.

### 2.2. Catalysts characterisation

XRD was carried out using a PHILIPS PW182O diffractometer to determine the crystalline phases of palladium species. Surface area was determined by nitrogen adsorption using a $\Phi$-Sorb (Vinci Technologies). Transmission electronic microscopy was performed using a TEM JEOL 2010.

### 2.3. Activity measurement

The catalytic performances were determined in lab test for cylindrical samples (diameter 15 mm, height 50 mm) in a flow reactor unit. They were conducted at atmospheric pressure. Methane and air were fed to the reactor using mass gas flowmeters. Experiments were performed with GHSV of 50 000 h$^{-1}$.

Catalytic activity was measured by conducting a "light-off" experiment. A steady feed stream of the desired gas composition was prepared at 200°C. Then, the temperature was ramped at 5°C/min up to 900°C while the exiting gases were analysed by on-line analysers. Flame ionisation was used to measure methane conversion. The conversion of methane was followed as a function of gas inlet temperature.

In lab test, catalyst life studies were carried out at GHSV of 50 000 h$^{-1}$ and an inlet temperature of 500°C. The methane conversion was followed as a function of time on stream, which ranged from 10 to 50 h.

The pilot test rig was designed to work at a pressure up to 5 bars with 1 in. diameter substrates. An electric air heater was used to preheat up to 800°C. Typical air mass flows are in a range 20–60 kg/h, which corresponds to linear velocities between 5 and 50 m/s depending on the pressure and temperature. The maximum length of the catalytic section was 25 cm but variable configurations were allowed. Before entering the catalytic section, fuel was mixed with air by a multi-injection pipe located at the throat of a venturi.

Substrate temperature was measured at the inlet and outlet of the catalytic section with platinum thermocouples. Radiative effects due to the high temperatures downstream the catalytic section could not be neglected. So, the gas temperature was measured with a suction pyrometer in which the thermocouple was protected from radiations by a ceramic screen. The high gas velocity in the probe brought about a high convective heat exchange between the gases and the thermocouple. The combustion gases composition and all the parameters were recorded continuously by a microcomputer data acquisition system.

In order to be representative of the catalytic combustion gas turbine chamber, the pilot test experiments have been performed at a space velocity of 500 000 $h^{-1}$. Two 400 cpsi cordierite monoliths of 5 cm length spaced with a 3 mm length alumina ring have been used for the catalytic section. The tests were realised both at atmospheric pressure and under 4 bars.

## 3. Results and discussion

### 3.1. Laboratory durability test on fresh palladium catalyst

Durability tests were performed with GHSV of 50 000 $h^{-1}$ and an inlet gas temperature of 500°C.

The influence of methane concentration on catalytic durability was studied first with 1% Pd on stabilised alumina: 3 wt% $La_2O_3$–$Al_2O_3$. Fig. 1 represents the conversion-versus-time on stream at three different air/methane ratios. Three concentrations were studied: 2, 2.75 and 3.5 vol%. High initial methane conversion was observed for each concentration. For a concentration of 2.75 vol%, the hydrocarbon conversion decreased gradually to levels of 80% after 15 h. At 3.5 vol%., the conversion decreased while oscillating. Conversion oscillates from 40% to 80% after 3 h. Such an oscillating behaviour of activity was already observed by Furuya et al. [18] during atmospheric pressure combustion testing. These authors feel that this phenomenon is due to oxygen release from PdO in bulk, resulting from the transformation PdO→Pd [19]. This conversion self-oscillation is related to the catalyst temperature, which varied with the methane content. An oxidised form of palladium is considered to be the most active phase of palladium [9]. As soon as the temperature of the catalyst exceeds 800–900°C, active PdO transforms into Pd which is less active. Hydrocarbon conversion falls, leading to a catalyst temperature decrease. Using thermogravimetric analysis, Farrauto et al. [17] have studied the combustion of methane on 4% PdO supported on $\gamma$-$Al_2O_3$ within a temperature range. They have shown that palladium reoxidation [17] occurs around 650°C and palladium acquires a coating of palladium oxide, followed by an increase of methane conversion. On cooling, hydrocarbon conversion thus increases again, as a result of this palladium reoxidation, causing hydrocarbon conversion self-oscillation. Thus, the skin of oxide on the palladium core may be responsible for the oscillations, due to its instability.

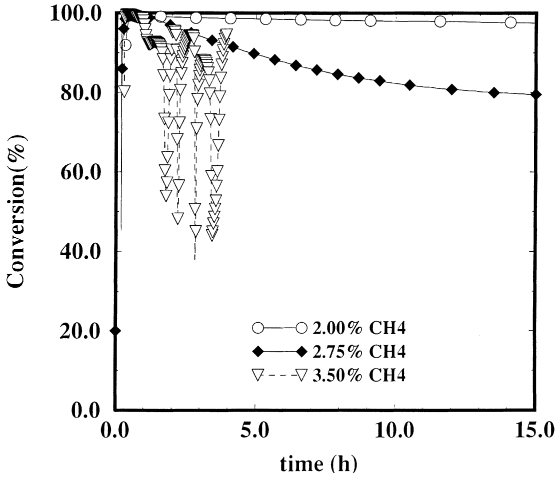

Fig. 1. Influence of methane/air ratio on catalyst durability – catalyst: Pd/3 wt% $La_2O_3$–$Al_2O_3$.

The influence of the palladium content deposited on stabilised alumina (4 wt% $SiO_2$–$Al_2O_3$) on the catalytic durability was then investigated at a fixed methane concentration: of 3.5%. Fig. 2 represents methane conversion-versus-time plots for three palladium loadings, viz., 1, 3, 10 wt% on 4 wt% $SiO_2{\cdot}Al_2O_3$.

At the palladium content of 3 wt%., methane conversion declined without oscillating to levels of 85% after 10 h. At the higher loading of 10 wt%., the conversion remained higher than 95% during 30 h but began to oscillate weakly after around 30–35 h. Then, the amplitude of self-oscillation increased gradually. Finally, conversion oscillated from 50% to 95% between 60 and 70 h. This figure indicates that stabilisation against PdO decomposition increases with the palladium content. But, the apparition of

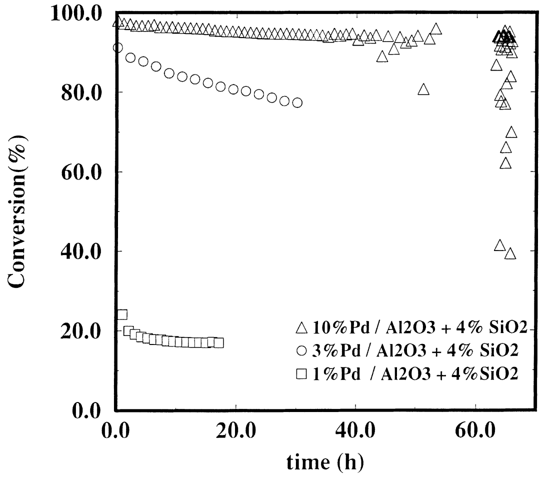

Fig. 2. Influence of palladium concentration on catalyst durability – methane/air ratio=3.5%.

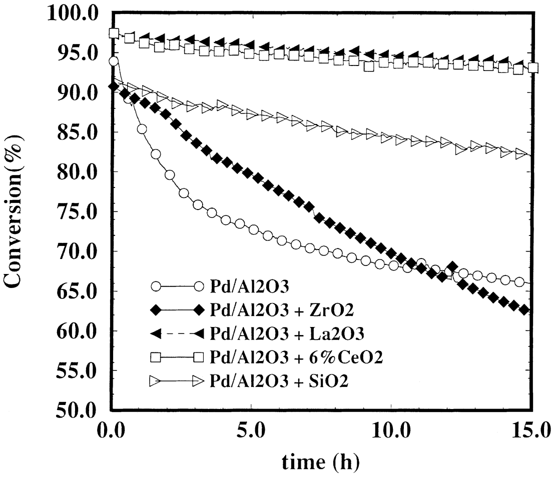

Fig. 3. Influence of promoters on catalyst durability – conversion-versus-time on stream.

self-oscillation after several hours on stream emphasises that PdO transforms progressively into metallic palladium. XRD analysis of samples confirms this transformation: PdO intensity peak declines, whereas Pd intensity peak increases. Thus, the palladium content is a parameter which can improve the design flexibility of the catalytic combustor. Nevertheless, the effect of palladium seems insufficient to inhibit consumption of structural O from bulk PdO during the catalytic oxidation of methane.

We have investigated the influence of several promoters ($ZrO_2$, $La_2O_3$, $CeO_2$, $SiO_2$). As shown by Fig. 3, which displays the evolution of the hydrocarbon conversion-versus-time for $Al_2O_3$+$ZrO_2$, $Al_2O_3$+6% $CeO_2$, $Al_2O_3$+$La_2O_3$, $Al_2O_3$+$SiO_2$, the promotion of alumina by ceria or lanthana is advantageous in maintaining a high conversion of hydrocarbon. Finally, we are interested in mixed oxides supported on γ-$Al_2O_3$ [25].

Fig. 4 shows the evolution of methane conversion for γ-$Al_2O_3$ promoted with a mixed oxide and for γ-$Al_2O_3$ promoted with 6% and 20% $CeO_2$. The palladium content was fixed at the same loading. No significative difference was observed between formulations promoted by ceria at 6% and 20% loadings. Moreover, the combination of mixed oxides seems to have a synergetic effect on the stability of PdO. The methane conversion remains higher than 95% after 40 h on stream. This effect is very interesting, since it gives to the palladium catalyst a larger range of stability.

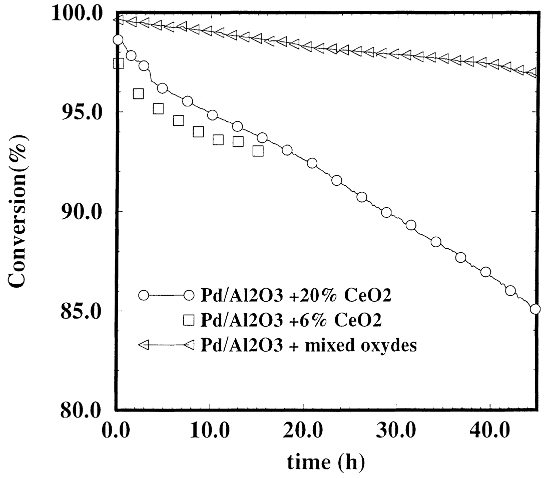

Fig. 4. Influence of promoters on catalyst durability – conversion-versus-time on stream.

Kosanovich [23] mentioned that addition of cerium improves the palladium resistance to sintering [20]. On the other hand, Kato et al. [21] indicated that some cations ($Mg^{2+}$, $Ni^{2+}$) whose ionic radii are smaller than the $Pd^{2+}$ radius (0.80 Å) are able to migrate into the PdO structure to form with Pd a solid solution, which is responsible for the inhibition of sintering.

Recently, Farrauto et al. [22] have indicated that the addition of 10% rare earth to palladium oxide can increase the PdO decomposition temperature to over 900°C [22] and proposed that rare earth provides structural O to palladium. Such an effect on the transformation of PdO→Pd was evidenced by ATG [23]. The PdO decomposition temperature shifts upwardly with addition of rare earth. In the same way, Furuya et al. [24] have found that Ni is an activity promoter. $CeO_2$ can therefore either act as an activity promoter giving structural O to Pd in order to slow down the transformation of PdO→ Pd or improve the PdO resistance to sintering. Our results are in agreement with these studies and suggest also that the role of $CeO_2$ against palladium decomposition is to act as an activity promoter of methane oxidation.

### 3.2. *Experiments within the pilot scale test ring*

In order to be representative of the conditions in a catalytic gas turbine combustor, the pilot test experiments have been performed with GHSV of 500 000 $h^{-1}$. A first experiment was made at equivalence ratio $\Phi=0.33$ (3.54% $CH_4$) on a 5 wt% Pd/$La_2O_3$–$Al_2O_3$ catalyst. After a heating ramp at a rate of 5°C/mn, the inlet temperature was stabilised at 550°C during 4 h. Two 400 cpsi cordierite monoliths of 5 cm length spaced with a 3 mm length alumina ring have been used for the catalytic section.

In this configuration, a simple calculation done by assuming that fuel conversion is limited by mass transfer phenomena predicts a conversion rate of 80%. It was expected that this conversion rate was sufficient to heat the gases up to the auto-ignition temperature in order to achieve complete conversion. This level was not reached in steady-state conditions. Catalyst ignition occurs at 350°C and after a transient heating phase, the oscillating behaviour characteristic of the transformation of PdO into metallic palladium was observed for outlet temperatures beyond 750°C. The measurement of CO (1000 ppm) characteristic of low-temperature homogeneous combustion during the oscillating phase of the test showed that a fraction of the natural gas burnt in homogeneous gas phase. After 1 h running, steady-state behaviour was observed. The outlet catalyst temperature stabilised at 780°C (Fig. 5) and the conversion at 45%. An equilibrium between PdO and Pd is reached. During this stabilised phase, outlet catalyst temperature and gas temperature measured 10 cm downstream the catalyst section were equal (Fig. 5) showing that the fuel was completely burnt inside the catalytic section.

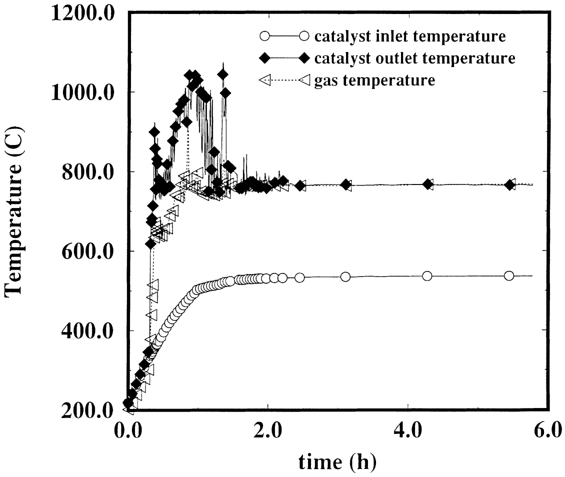

Fig. 5. Temperatures of the fresh catalysts-versus-time – self-catalyst temperature regulation.

Catalyst stability is a critical parameter for use in gas turbine applications in which durabilities targets are over thousands of hours. So, in order to get a first indication of the catalyst evolution in time, the previous test has been repeated three times

The curves of fuel conversion-versus-temperature are plotted in Fig. 6. The oscillating behaviour of the catalyst has not been observed after the first ramp. This phenomena can be explained by a partial reoxidation of Pd in PdO between the temperature ramps. During steady-state conditions, a conversion of 45% was obtained for each test. But the examination of Fig. 6 shows that the catalyst deactivation is pursuing, in particular between ramps 2 and 3.

The previous experiment was realised under severe conditions for which catalyst deactivation occurs immediately. In order to establish precisely the range of catalyst temperatures allowed to avoid deactivation, the following experiments were realised.

Two catalysts containing, respectively, 5% and 10% of palladium were tested under 4 bars at GHSV of 500 000 $h^{-1}$. The inlet temperature was set at 420°C and 520°C and during 4 h the equivalence ratio $\Phi$ was increased from 0.06 to 0.36. Figs. 7 and 8 represent

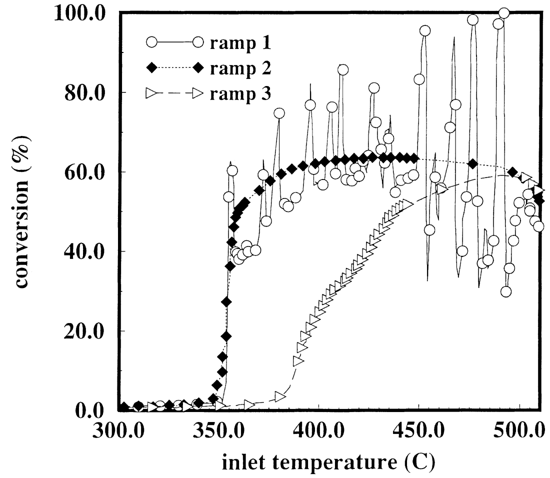

Fig. 6. Effect of aging on catalyst activity – running time: 4 h between the temperature ramps; equivalence ratio=0.33.

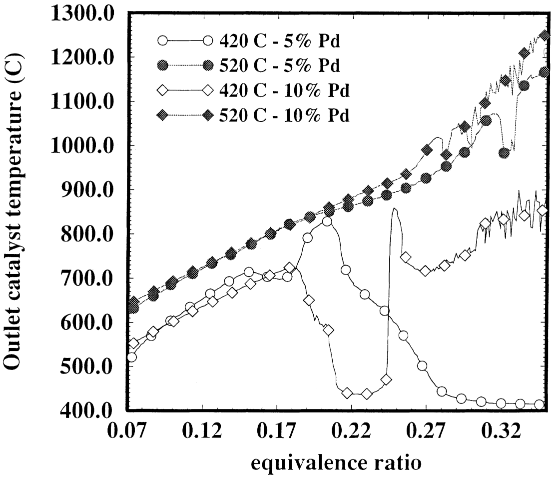

Fig. 8. Effect of equivalence ratio on catalyst temperature: $P$=4 bars; GHSV=50 000 $h^{-1}$.

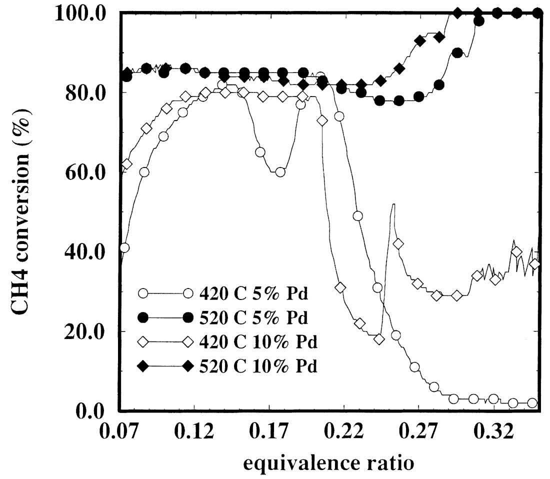

Fig. 7. Effect of equivalence ratio on catalyst activity: $P$=4 bars; GHSV=500 000 $h^{-1}$.

the fuel conversion and the outlet catalyst temperature-versus-equivalence ratio, respectively.

At an inlet temperature of 420°C the first effect of deactivation appears for outlet catalyst temperature above 700°C, with both catalysts. After a short oscillating period characteristic of the transformation of $Pd + \frac{1}{2}O_2 \longleftrightarrow PdO$, the catalyst activity continuously decreases to zero for catalyst A (5% Pd), which seems to indicate that the catalyst remains for the main part in the form Pd. With catalyst B 10% Pd, the conversion level is high enough to reach the methane ignition temperature and then, to burn all the fuel, showing the remaining PdO content is higher than with catalyst A. By increasing the inlet temperature from 420°C to 520°C, a different catalyst behaviour was observed. It can be first noticed that the curves corresponding to catalyst A and B are very similar. The conversion is first stabilised at 80% (value predicted by supposing that the conversion is limited by mass transfer phenomena). The first sign of deactivation appears for outlet temperatures above 850°C, but the Pd activity is high enough to heat the gases to the auto-ignition temperature with catalysts A and B. A complete conversion is observed for equivalence ratio above 0.3.

### 3.3. *Catalytic combustion of methane over presintered palladium catalyst*

We have studied firstly the stability of the alumina support. Fig. 9 displays the evolution of surface area of 3 wt% $La_2O_3$–$Al_2O_3$, 3 wt% $BaO$–$Al_2O_3$ and 4 wt% $SiO_2$–$Al_2O_3$ versus calcining time. Aging above 1200°C can discriminate the inhibiting effect of lanthana or baria from silica. At 1230°C, silica was more efficient than Ba and La in inhibiting the sintering of alumina towards α-alumina. δ- and θ-alumina were already detected by XRD analysis after 60 h. While the 3 wt% $La_2O_3$–$Al_2O_3$ was transformed into

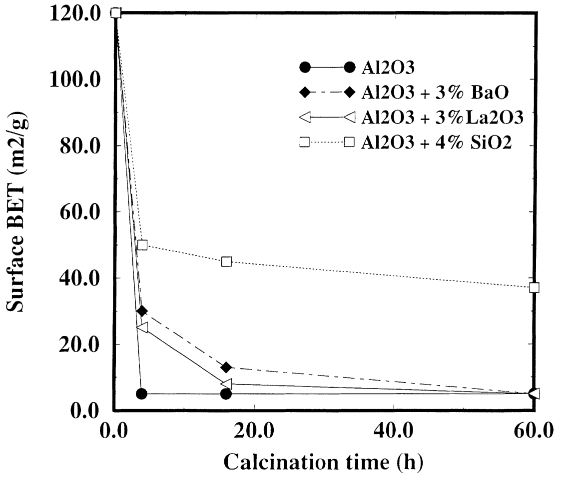

Fig. 9. Influence of dopants on alumina support stability. Surface area-versus-calcination time.

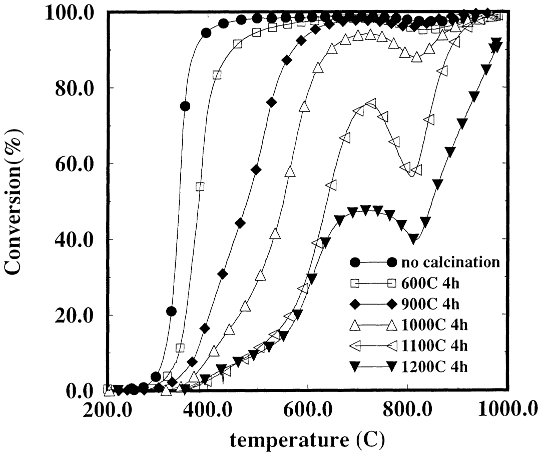

Fig. 10. Catalytic activity of palladium over presintered supports.

$\alpha$-$Al_2O_3$ and traces of $LaAl_{11}O_{18}$ or $LaAlO_3$ were detected and the 3 wt% BaO–$Al_2O_3$ was transformed into $\alpha$-$Al_2O_3$ and $BaAl_{12}O_{19}$.

The evolution of $\gamma$-$Al_2O_3$ towards $\alpha$-$Al_2O_3$ has been widely investigated [15,26]. This mechanism is governed by the structure of boehmite and its mechanism of dehydration [27]. The thermal stabilisation of $\gamma$-$Al_2O_3$ by rare earth or barium is well known [28–31]. Burtin et al. [32,33] show that additives with both high charge and large ionic radius are more effective to reduce the rate of formation of $\alpha$-$Al_2O_3$. Trimm et al. [34] confirmed that an increase in ion size accounts for the effectiveness of barium and lanthanum as stabilisers. Nevertheless, $Si^{4+}$ whose radius is lower (0.41 Å) is more effective than barium and lanthanum under severe conditions. Beguin et al. [35] proposed that formation of perovskite $LaAlO_3$ on the surface of transition aluminas is responsible for the stabilising effect. On calcination at higher temperatures (>1200°C), the surface loss was shown (by XRD) to coincide with the appearance of mixed oxides such as $BaAl_{12}O_{19}$ and/or $BaAl_2O_4$ for Ba, $LaAl_{11}O_{18}$ and/or $LaAlO_3$ for La. Sintering of these mixed oxides leading to a decrease of the surface coverage by lanthana or baria may explain the loss of stabilising effect. As for silica, the formation at low temperature of dispersed silica–alumina moieties is promoted by impregnation with $Si(OEt)_4$ [36]. These moieties transformed at intermediate temperature to oxides, such as $Al_2SiO_5$, which are dispersed and strongly bonded at the surface of alumina. $Al_2SiO_5$, which is detected by XRD after extensive calcination at 1300°C, may be more resistant to sintering than $LaAlO_3$.

Thus, in order to discriminate palladium degradation from alumina sintering, a 4 wt% $SiO_2$–$Al_2O_3$ was calcined at 1230°C for 16 h in air prior to its impregnation by palladium. This temperature was sufficient to reduce the alumina surface to a stable level in the course of tests. Surface area of the support was 47 $m^2$/g (Fig. 9). Fig. 10 shows the catalytic activities of palladium (5 wt%) on presintered 4 wt% $SiO_2$–$Al_2O_3$ support after heat treatment at 600°C, 900°C, 1000°C, 1100°C and 1200°C for 4 h in air. The decrease in catalytic activity can be attributed to metal sintering or to the transformation $PdO \rightarrow Pd + \frac{1}{2}O_2$. Palladium crystallite size and Pd/PdO intensity ratio were estimated from XRD measurement. Fig. 10 shows the evolution of hydrocarbon conversion for these samples. Table 1 plots $T_{10\%}$ and for these samples versus calcination temperature. This table points out that PdO sintering and the transformation of $PdO \rightarrow Pd + \frac{1}{2}O_2$ both contribute to the catalytic activity degradation. $T_{10\%}$ decreases gradually when PdO sinters but it drops in relation to the appearence of the metallic palladium.

The sample aged at 1100°C was analysed by STEM to precise the palladium transformation. STEM

Table 1
Crystallites sizes, peak intensities and 5 wt%/presintered 4 wt% $SiO_2$–$Al_2O_3$

| Calcination temperature (°C) | T(10%) (°C) | Peak intensity *I* (PdO(1 1 0)/(AU)) | Peak Intensity *I* (Pd(1 1 1)/(AU)) | PdO crystallite size (nm) |
|---|---|---|---|---|
| 600 (support non presintered) | 310 | – | – | 6 |
| 600 | 342 | 140 | – | 10.5 |
| 900 | 378 | 155 | 10 | 27 |
| 1000 | 412 | 150 | 10 | 31 |
| 1100 | 496 | 110 | 50 | 45 |
| 1200 | 505 | 90 | 70 | 60 |

reveals an heterogeneous particle size distribution. Crystallites can be divided in two groups: a group composed of very large particles whose size varies from 480 to 2000 Å and a group composed of smaller particles whose sizes vary from 20 to 160 Å. Thus, it appears that some large crystallites fragmented during reoxidation and some of them are redispersed. This observation is in agreement with the work of Ruckeinstein [37] who observed the formation of pits and cavities during oxidation and proposed that this mechanism is induced by stresses on the surface of crystallites.

## 4. Conclusion

It is well known that the most active catalysts for the oxidation of methane are palladium-based catalysts. Their durability is strongly related to the operating conditions and in particular, to catalyst temperature. The palladium degradation has been first investigated on laboratory scale and it has been found that this degradation could be explained by the metal sintering and the transformation of $PdO \rightarrow Pd + \frac{1}{2}O_2$.

In steady-state conditions, deactivation has been found to be dependent of the palladium loading on the washcoat. An oscillating behaviour of the methane conversion was even observed under specific conditions, due to the equilibrium $PdO \rightleftarrows Pd + \frac{1}{2}O_2$. The influence of several promoters has been investigated and some encouraging results have been found with $CeO_2$, which seems to improve the catalyst durability (increasing of PdO resistance to sintering or decreasing of the PdO transformation kinetics into Pd).

However, in pilot tests, deactivation was found to be very rapid, even with promoted stabilised alumina supports. Furthermore, successive tests performed on the same catalyst revealed that the activity fell strongly from one test to another. Variations of the inlet temperature can lead to opposite catalyst behaviours.

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