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Synthesis and Characterisation of Bimetallic Pd–Rh/Alumina Combustion Catalysts

Mohamed Rassoul,[1] François Gaillard,[2] Edouard Garbowski, and Michel Primet

Laboratoire d'Application de la Chimie à l'Environnement (LACE), UMR 5634 CNRS, Université Claude Bernard Lyon 1, 69622 Villeurbanne Cedex, France

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This paper reports the possibility of associating Pd with another noble metal (rhodium) which is able to form a thermally stable oxide to extend toward higher temperatures the stability range of PdO. Bimetallic Pd–Rh/alumina catalysts were prepared and compared to reference Pd/alumina and Rh/alumina solids. The synthesis of the bimetallic catalysts was carried out by either co-impregnation or stepwise impregnation of alumina from solutions of $RhCl_3$ and H_2PdCl_4. When submitted to TPO/TPD cycles, $Pd_{0.75}Rh_{0.25}$/alumina catalysts obtained by the co-impregnation method exhibited oxidation and decomposition peaks at the same temperatures as those for reference Pd/alumina samples. The amounts of oxygen involved at each step were also comparable for the two solids and lower than the expected stoichiometric atomic ratio O/Pd = 1. Conversely, $Pd_{0.75}Rh_{0.25}$/alumina catalysts obtained by the stepwise impregnation method exhibited improved stability of the PdO oxide, the maximal decomposition temperature being increased from 730 to 800°C. In addition, the amounts of oxygen involved at each step were also increased and exceeded the value O/Pd = 1. As shown by TPR, Rh_2O_3 and PdO particles on the surface of catalysts obtained by the co-impregnation technique behave like the respective monometallic catalysts. When the catalyst was elaborated by stepwise impregnation, some Rh_2O_3 and PdO oxide particles were in strong interaction and were simultaneously reduced at room temperature in a H_2/He medium. © 2001 Academic Press

Key Words: **combustion catalyst; palladium; rhodium; bimetallic; alumina; TPD; TPO.**

INTRODUCTION

The catalytic combustion of hydrocarbons, compared to the combustion in a flame, presents several advantages, such as (i) a lower combustion temperature, avoiding any NO_x formation and allowing easier CO oxidation, (ii) accurate control of the combustion reaction within a wide range of fuel/air ratios, provided oxygen is in excess, and (iii) a lower amount of unburned fuel (1–3). The catalysts employed for such a purpose are selected for their ability to initiate the reaction at a temperature as low as possible, for their selectivity toward CO_2 production and for their thermal stability. These catalysts can be either supported precious metals or mixed oxides, such as perovskites (4), hexa-aluminates (5, 6), or spinels (7).

The main applications of such catalytic systems are infrared emitters, gas turbines, and boilers. Concerning this last application, the domestic use of catalytic burners is possible. Such burners can work according to both the catalytic and flame routes, the first one at low power (householding, for example) and the second one at high power (hot water for sanitary purposes, for example). Under these conditions, the catalyst must be able to initiate the reaction at a temperature as low as possible but also to withstand the high temperatures involved at full power, i.e., 1000–1100°C or more.

As far as precious metals are concerned, supported palladium catalysts demonstrated excellent activity for total combustion of natural gas (8, 9) which made them suitable for commercial applications (10, 11). Supported palladium catalysts exhibit better durability than their platinum counterparts due to the superior activity of the PdO oxide, even in the form of large particles resulting from sintering at high temperatures (12, 13). However, PdO decomposes at temperatures of about 750°C, even in oxygen-containing atmospheres, and this leads to the formation of supported metallic Pd particles, which are less active for methane combustion. This phenomenon is at the origin of the large hysteresis in methane combustion during heating and cooling cycles, as shown by Farrauto *et al.* (14). The nature of the phase supporting Pd is obviously important with respect to activity for methane oxidation (15–17) but also for PdO thermal stability. Narui *et al.* (18) found that the drop of catalytic activity due to the decomposition of PdO in the 700–900°C range was suppressed by using a ZrO_2 support,

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[1] Present address: Laboratoire de Valorisation des Coupes Pétrolières, Institut de Chimie, Université Houari-Boumediene, BP 131 El Alia, Alger, Algeria.

[2] To whom correspondence should be addressed: LACE, UMR 5634 CNRS, Université Claude Bernard Lyon 1, Bat. Raulin/1, 43 Blvd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France. Fax: +33 4.72.44.81.14. E-mail: Francois.Gaillard@univ-lyon1.fr.

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but Farrauto *et al.* (19) reported that such a support shows the largest hysteresis effect between the temperatures of decomposition and reformation of PdO. Conversely, according to these authors, TiO_2 and CeO_2 supports increase the temperature of reformation of PdO (by about 130°C compared to Al_2O_3 support) and then exhibit a small hysteresis effect. It is also interesting to notice that loading with TiO_2 a Pd catalyst supported on KIT-1 mesoporous material leads to the same beneficial effects and is claimed to suppress the decomposition of PdO up to 820°C (20).

To improve the performances of such Pd-based solids, the synthesis of bimetallic catalysts was also envisaged. For example, the addition of Pt is reported to increase the catalytic activity and to prevent catalyst deactivation (21). Addition of Ru and Rh to Pd/alumina catalysts was also investigated by Ryu *et al.* (22). These authors found a beneficial effect of Ru addition, both in activity and in resistance to sulphur-induced deactivation. This effect was attributed to an improved dispersion of Pd and to the intrinsic resistance of Ru to sulphur poisoning. These authors did not notice any beneficial effect of Rh addition. However, Tochihara and Ozawa, investigating Pt/Pd/alumina catalysts, reported that rhodium addition can change the original rapid weight loss from 750–850°C to a smooth weight loss from about 750 to 1000°C (23). The authors reported that Rh addition, by increasing the stability of PdO, suppressed the high-temperature self-oscillation of methane combustion. Due to contradictory data appearing in the literature, the goal of this paper was to determine the real influence of Rh addition to a Pd/γ alumina catalyst on PdO decomposition and reformation. More particularly, we wanted to elucidate if the presence of the thermally stable Rh_2O_3 species could increase the thermal stability of PdO oxide. The influence of the synthesis route was also investigated, comparing bimetallic catalysts elaborated either by co-impregnation or by stepwise impregnation.

EXPERIMENTAL

2.1. Catalysts Preparation

The support used was a γ-alumina from Rhodia (SPH 569), with a specific surface area of 136 m^2/g. The small grains, about 2 mm in diameter, were crushed and sieved to retain grains of a size lower than 80 μm.

Noble metal salts for preparing solutions of precursors were $PdCl_2$ (Johnson Matthey, Ref. 17 1000) and $RhCl_3$ (Aldrich, Ref. 20,626-1). $RhCl_3$ is water soluble but not $PdCl_2$. Then, a concentrated HCl solution was poured dropwise on this last solid, maintained at 90°C, until a clear solution was obtained, which was later evaporated at 150°C. The so-obtained solid (H_2PdCl_4) was then dissolved in water.

Reference monometallic Pd/alumina and Rh/alumina catalysts. Two monometallic catalysts Pd/alumina and Rh/alumina were prepared using solutions of precursor chosen to obtain a final catalyst with 2 wt% in Pd and 1.5% in Rh. The solution of either H_2PdCl_4 or $RhCl_3$ was added to a suspension of alumina in water at 60°C. Stirring was maintained for 1 h and then water was eliminated under reduced pressure at 60°C. The obtained product was dried in an oven at 120°C overnight. After crushing, the solid was submitted to a calcination in air at 500°C for 6 h. After a purge by nitrogen at 500°C, the catalyst was reduced by hydrogen at the same temperature for 6 h and then purged under nitrogen flow and allowed to cool down to room temperature. The solids obtained by this method are called "reduced catalyst."

Bimetallic Pd–Rh/alumina catalysts. Bimetallic catalysts $Pd_{0.75}Rh_{0.25}$/alumina with ca. 2 wt% Pd were prepared using two synthesis methods. For catalysts obtained by the co-impregnation route, the required solution volumes of precursors ($RhCl_3$ and H_2PdCl_4) have been mixed and contacted with a suspension of alumina. The remaining treatment (contacting, drying, calcinating, and reducing) was as described previously for monometallic catalysts.

For stepwise impregnation, the most abundant metal (Pd) is deposited first as described for monometallic catalysts. After the reduction step, the solid was added to a volume of water, the suspension was heated to 60°C, and an aqueous solution of $RhCl_3$ was added dropwise. Stirring was maintained for 1 h, water was removed under reduced pressure, and the obtained solid was dried at 120°C. The next steps are identical to those corresponding to the monometallic catalysts.

In addition, a part of each catalyst, either monometallic or bimetallic, was submitted to standardisation treatment. The purpose of this treatment was to stabilise the samples and to simulate moderate thermal aging. More particularly, the action of oxygen and water is critical. The treatment was as follows. A part of reduced catalyst was heated up to 800°C at 5°C/min in pure oxygen flow. Then, liquid water was injected through a septum in the line feed, allowing a water partial pressure of 10^4 Pa (10 vol%). This gaseous mixture was maintained for 6 h, then water injection was stopped, and sample was cooled down to 25°C under the oxygen flow. Then, the reactor was flushed by nitrogen for 10 min. The solids obtained by this method are called "stabilised catalysts".

2.2. Catalysts Characterisation

The catalysts were studied by temperature-programmed oxidation (TPO) and decomposition (TPD). About 100 mg of catalyst was placed on a quartz wool bed in a u-shaped quartz reactor, positioned vertically in a programmable tube furnace. Temperature was measured by two K-type thermocouples positioned outside the reactor. Pretreatment gases were pure He and H_2 at a flow of 1.2 L/h. The

TPO and TPD experiments were performed in an O_2/He medium (1.02 vol% O_2, provided by l'Air Liquide) at a flow of 1.8 L/h monitored by a Brooks mass flow controller. A part of the gas exiting the reactor (about 0.6 L/h) was sampled by a heated capillary and analysed by a VG Gasslab 300 quadrupole mass spectrometer. Signals at $m/e = 16$, 18, 28, 32, and 44 amu corresponding to O^+, H_2O^+, N_2^+ or CO^+, O_2^+, and CO_2^+ ions, respectively, were recorded.

Before TPO/TPD experiments, samples were reduced 1 h at 300°C in pure H_2 (the heating rate was 5°C/min). Then, the reactor was purged by pure He for 1 h at 300°C and allowed to cool down to room temperature under He flow. The O_2/He mixture flow was established, bypassing the reactor, and analysed by the mass spectrometer to provide a reference signal level for quantitative oxygen analysis. Then, the mixture was passed through the reactor and the amount of oxygen adsorbed irreversibly at room temperature was determined. After this operation, the temperature was raised at 20°C/min up to 900°C, maintained at 900°C for 5 min, and allowed to decrease (at 20°C/min) down to 400°C. This temperature was maintained for 5 min and raised again at 900°C, and the experiment was repeated with successive plateaux at 900 and 400°C.

Analysis by temperature-programmed reduction (TPR) was performed with the same apparatus, using 0.99% H_2/He mixture at 1.8 L/h. Before the TPR run, catalysts were treated for 1 h at 400°C in an oxygen flow (heating from room temperature to 400°C was conducted at 5°C/min) and then allowed to cool down to room temperature in the same atmosphere. Before the TPR experiment, the reactor was flushed for 15 min by He. Then, H_2 consumption at room temperature was determined and TPR carried out with a heating rate of 20°C/min.

Specific surface areas were measured according to the BET method by nitrogen adsorption at 77 K on samples previously evacuated for 2 h at 300°C under 10^{-5} Torr. Multipoint analysis was performed on a fully computerised laboratory-made apparatus.

Chemical analyses of Pd and Rh were performed by ICP after attack and dissolution in a concentrated acids mixture ($HCl + HF + HNO_3$). Chlorine was analysed by ion-capture chromatography.

RESULTS AND DISCUSSION

3.1. *Characterisation of the Catalysts*

Chemical analysis and BET results on mono- and bimetallic catalysts are given in Table 1. The amount of palladium ranges from 1.73 to 1.84%, which is a little bit lower than expected. The same observation can be made concerning the amount of rhodium; therefore, the average composition of the solid labelled $Pd_{0.75}Rh_{0.25}$ is actually $Pd_{0.77}Rh_{0.23}$. The amount of chlorine originally present, i.e., 9400 ppm, was drastically reduced by the stabilisation treatment and falls within the range 675–1600 ppm, indicating however that the stabilised solid was not chlorine-free and that some desorption of chlorinated species during the thermal cycles can be expected (and was observed). The specific surface area for the reduced samples is 116 m^2/g, and this value decreases to 102–105 m^2/g after stabilisation, indicating that such a treatment only induces very slight sintering of the alumina support.

3.2. *TPO–TPD of Monometallic Reference Catalysts*

Typical TPO–TPD spectra are shown in Fig. 1 for the reduced Pd/alumina sample. Prior to the experiment, the sample was submitted to an *in situ* reduction as described in the Experimental part. The figure shows the variation, versus time, of the signals at $m/e = 32$ and 44 amu and

TABLE 1

Results of Chemical Analysis and BET Area for Mono- and Bimetallic Catalysts

Catalyst	Pd	Rh	Actual atomic composition	Cl (ppm)	SSA (m^2/g)
Pd/Al_2O_3 reduced at 500°C	1.84 wt% (aimed: 2 wt%) 173 μmol/g	—	—	9400	116
Pd/Al_2O_3, stabilised	1.84 wt% (aimed: 2 wt%) 173 μmol/g	—	—	675	105
Rh/Al_2O_3, stabilised		1.57 wt% (aimed: 1.5 wt%) 153 μmol/g	—	—	
$Pd_{0.75}Rh_{0.25}/Al_2O_3$ by co-impregnation, stabilised	1.73 wt% (aimed: 2 wt%) 163 μmol/g	0.52 wt% (aimed: 0.6 wt%) 51 μmol/g	$Pd_{0.76}Rh_{0.24}$	1600	102
$Pd_{0.75}Rh_{0.25}/Al_2O_3$ by stepwise impregnation, stabilised	1.84 wt% (aimed: 2 wt%) 173 μmol/g	0.53 wt% (aimed: 0.6 wt%) 52 μmol/g	$Pd_{0.77}Rh_{0.23}$	896	104

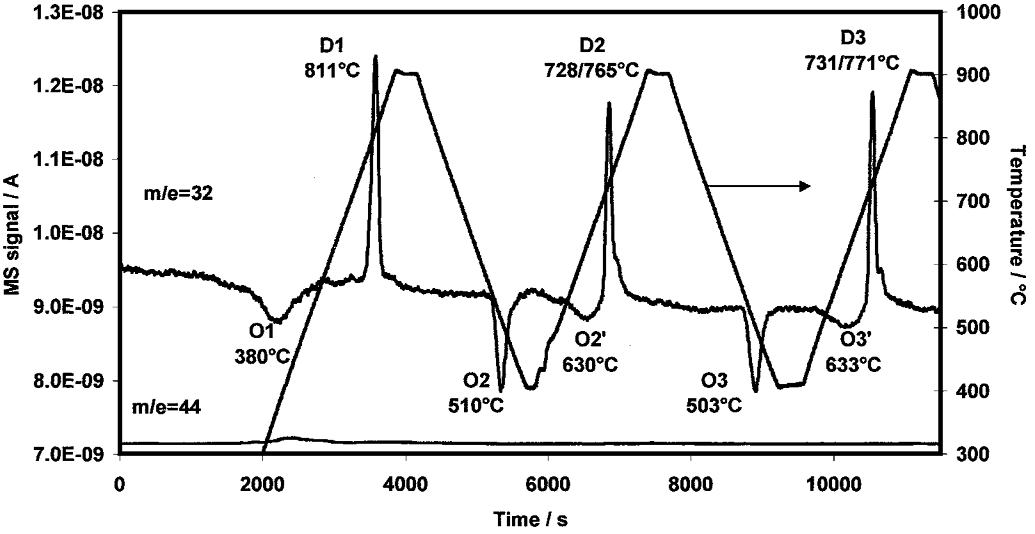

FIG. 1. TPO/TPD spectra of the reduced Pd/alumina sample (traces are offset to improve readability).

the sample temperature. These signals are representative of the consumption or evolution of O_2 ($m/e = 32$ amu) and of the evolution of CO_2 ($m/e = 44$ amu), respectively. The spectrum of the MS signal at $m/e = 32$ amu exhibits downward and upward peaks. Downward peaks correspond to an oxygen consumption and are labelled O1, O2, O2′, O3, and O3′, successively. Upward peaks correspond to oxygen released by the catalyst and are labelled D1, D2, and D3, successively. The oxygen consumption peak appears with a maximum at 380°C only during the first heating of the sample (peak O1). The amount of oxygen consumed here is larger than one could expect from the complete oxidation (from Pd^0 to PdO) of the palladium present in the catalyst. Such an over consumption of oxygen during the first heating step was reported in the literature and related to an oxygen-rich $PdO_{x>1}$ species (10, 24). Nevertheless, the explanation proposed here is totally different because a CO_2-related peak ($m/e = 44$ amu) matches the oxygen consumption for O1. The signal at $m/e = 44$ amu has three main origins in our experiments. A peak at 445°C corresponds to the burning of carbonaceous species present on the quartz wool and reactor walls. It is accompanied by a noticeable oxygen consumption. A double peak at 461 and 547°C was also recorded on the alumina support alone and originates from the burning of carbonaceous contaminants and desorption of carbonate impurities present in alumina. This peak is accompanied by a very moderate perturbation of the $m/e = 32$ amu signal. At last, a sharp peak at 600°C can be recorded when samples are stored for a long time (several weeks) in plastic containers, and it is also associated with oxygen consumption by carbonaceous contaminants attributable to some plasticizers. The amount of oxygen involved in peak O1 was then corrected for these effects, allowing a rough estimation of the amount of oxygen (noted O1*) needed for metal oxidation during the first heating step. The O1* value obtained by this method clearly indicates that the formation of $PdO_{x>1}$ species at this step can be ruled out. When the temperature is still increased, the D1 peak is detected with a maximum at 820°C. This peak is attributed to the decomposition of the PdO oxide formed during oxygen uptake (O1 peak). The observation of a single peak, symmetrical and sharp, may indicate the decomposition of crystalline PdO to metallic Pd, occuring at once in the range 800–840°C in agreement with previous results of Farrauto *et al.* in their study of unsupported PdO (14). After the plateau at 900°C, the sample is allowed to cool down and the peak, O2 is detected at 500°C. After a plateau at 400°C, the temperature is increased again and a second peak, O2′, is detected with a maximum at about 610°C. The peaks O2 and O2′ correspond to the re-oxidation (partial or complete) of the metal resulting from the decomposition step D1. The presence of two peaks (O2 and O2′) indicates that re-oxidation is not finished after peak O2, certainly because of the high speed of the temperature decrease (20°C/min). Oxidation is kinetically controlled with a rate decreasing too fast. This high scan rate was chosen because it was compatible with reasonable experiment duration and sufficient peaks resolution but it may induce kinetic effects influencing both peak maxima position and peak height ratios. During O2 and O2′, and also for the remainder of the experiment, no CO_2-related peak is detected, indicating that all carbonaceous species are burned during the first thermal cycle. However, subsequent cycles show modifications of the catalyst upon experiment.

The main feature is that D2 and D3 peaks undergo a shift of 100°C toward low temperatures compared to D1. It is also noteworthy that D2 and D3 peaks are no longer symmetrical and exhibit a shoulder at about 760–770°C. The presence of two main decomposition peaks for PdO/alumina, separated by 50–70°C, was reported by many

TABLE 2

Temperatures at the Maximum of TPO/TPD Peaks, Amounts of Oxygen Involved and Corresponding O/Pd Atomic Ratios for Reduced and Stabilised Pd/Alumina Catalysts

	Reduced Pd/alumina			Stabilised Pd/alumina		
	T_{max} (°C)	O_2 amount involved (μmol/g)	O/Pd atomic ratio	T_{max} (°C)	O_2 amount involved (μmol/g)	O/Pd atomic ratio
O1	380	100	1.16	391	113	1.31
O1[a]		83	0.95		80	0.92
D1	811	79	0.91	733/765/803	82	0.95
O2+	510	74	0.86	499	79	0.91
O2′	630			622		
D2	728/765	65	0.75	729/789	81	0.94
O3+	503	67	0.77	499	76	0.88
O3′	633			610		
D3	731/771	70	0.81	727/762	76	0.88

[a] Corrected for the amount of oxygen used to burn carbonaceous species.

authors (14, 25, 26). The nature of these two species is far from being fully clarified yet. One of these peaks is generally related to bulk PdO crystallites and the other to non-crystalline PdO_x species well-dispersed on bulk Pd metal (14) or to a surface (or near-surface) support–oxide complex (25). The temperature at the maximum of each TPO/TPD peak and the amount of oxygen associated are gathered in Table 2. The above results show that the thermal stability of PdO species in such a reduced sample is too low for catalytic burners application. These results also point out the necessity of studying the catalysts after a stabilisation step. The spectra plotted in Fig. 2 are relative to the Pd/alumina sample after the stabilisation process at 800°C in an oxygen + water atmosphere. The position of peak O1 maximum at 390°C is very close to what was observed for the reduced sample. The shoulder at 538°C can be related to the oxidation of carbonaceous species, as shown by the change of the signal at $m/e = 44$ amu, and not to oxidation of some Pd species. The first decomposition peak exhibits three features at 733, 765, and 803°C, but after several cycles, the temperature of the main decomposition peak decreases to 728°C, in agreement with the value observed for the reduced Pd/alumina catalyst. The splitting of the desorption curves (complex peaks D1, D2, and D3) is attributable to a distribution in Pd particles sizes, as confirmed by some TEM examination. This distribution varies along the thermal cycles and the strength of O–Pd bonds varies accordingly. Temperatures corresponding to the maximum of peaks O2 and O3 are close to 500°C, as observed in the case of the reduced catalyst. The amount of oxygen involved at each step is 113, 82, 79, 81, 76, and 77 μmol of O_2/g of catalyst for peaks O1, D1, O2 + O2′, D2, O3 + O3′, and D3, respectively (see Table 2). The higher value corresponding to O1 is attributed to the oxygen necessary to burn the carbonaceous species during the first heating cycle. Once corrected for this additional consumption, the value O1* is 80 μmol/g, consistent with subsequent values. The value of oxygen uptake (or release) decreases from O/Pd = 0.92 at peak D1 to O/Pd = 0.88 at peak D3. Although this variation is very close to the TPO/TPD experimental error limits, this change was observed on several samples which followed the same trend, indicating that, according to our experimental conditions, the oxidation/reduction process is not complete. This process becomes less and less complete when the number of thermal cycles increases.

In the particular case of Rh/alumina catalysts, the reactor and quartz wool were pretreated under oxygen flow at 650°C to burn carbonaceous species. This was necessary to

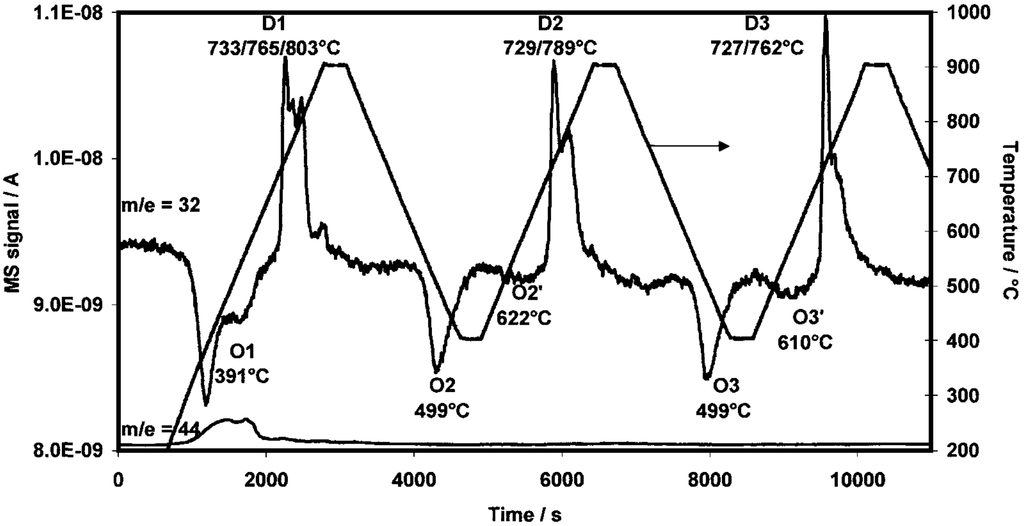

FIG. 2. TPO/TPD spectra of the stabilised Pd/alumina sample (traces are offset to improve readability).

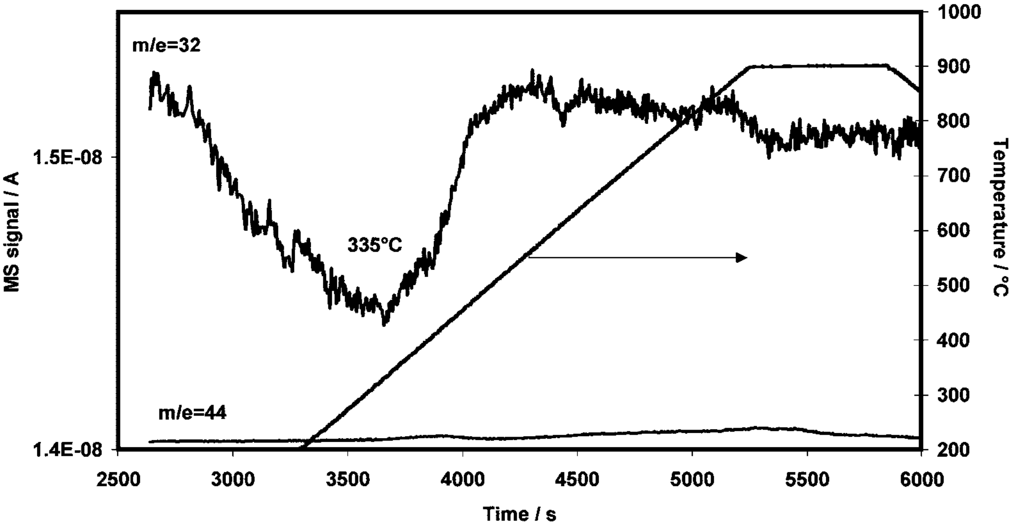

FIG. 3. TPO/TPD spectra of the reduced Rh/alumina sample (traces are offset to improve readability).

obtain accurate analytical data from the first heating step (as no subsequent decomposition or reduction is expected for the thermally stable Rh_2O_3 oxide). The spectrum plotted in Fig. 3 is relative to the Rh/alumina catalyst in the reduced state. Before the TPO/TPD experiment, the sample was reduced *in situ* 1 h at 300°C in pure H_2 (the heating rate was 5°C/min). At room temperature, oxygen consumption is observed (about 40 μmol of O_2/g). During the TPO experiment, we record only one wide oxygen consumption peak, with a maximum at 335°C. The total amount of oxygen used for rhodium oxidation is 117 μmol of O_2/g of catalyst, corresponding to the atomic ratio $O/Rh = 1.52$. This result indicates that the totality of the rhodium is oxidised into Rh_2O_3 during the TPO experiment. During the subsequent cycles, no decomposition of the oxide is observed. Consequently, rhodium is able to provide an oxide thermally stable, at least at 900°C, that can be associated to PdO to increase its resistance at high temperature.

When studying by TPO a Rh/alumina-stabilised catalyst submitted to our standard reduction treatment (at 300°C), one principal O_2 consumption peak at 560°C is recorded, with a shoulder at 750°C. The amount of oxygen involved is 63 μmol of O_2/g. This value corresponds to the oxygen quantity necessary to oxidise 55% of the rhodium present in the solid from Rh^0 to Rh^{3+}. This lower-than-expected consumption of oxygen indicates that some Rh^{3+} ions do not undergo previous reduction at 300°C. We submitted a stabilised Rh/alumina sample to reduction at 800°C in H_2 flow and then to the TPO experiment. The corresponding spectra are plotted in Fig. 4. The trace corresponding to

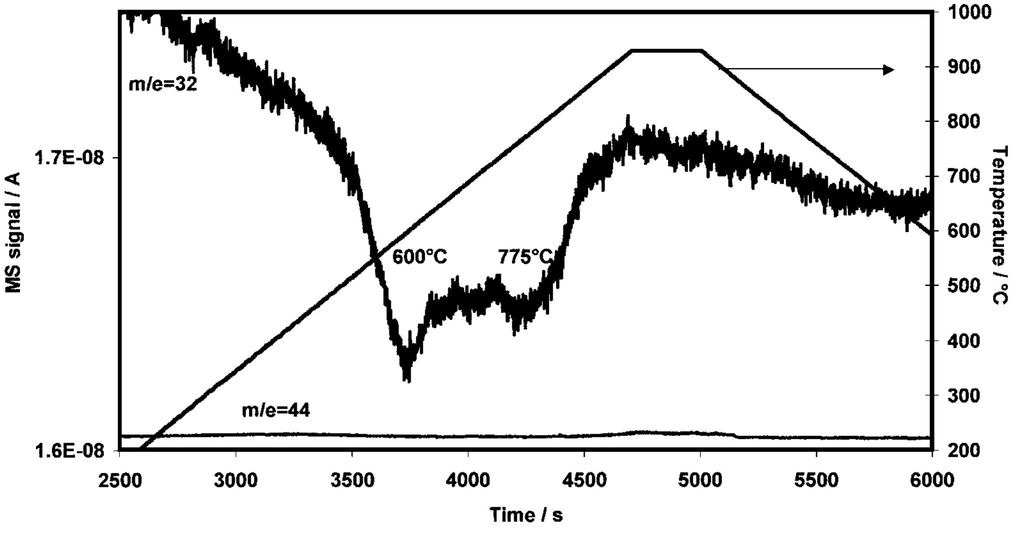

FIG. 4. TPO/TPD spectra of the stabilised Rh/alumina sample after *in situ* reduction at 800°C (traces are offset to improve readability).

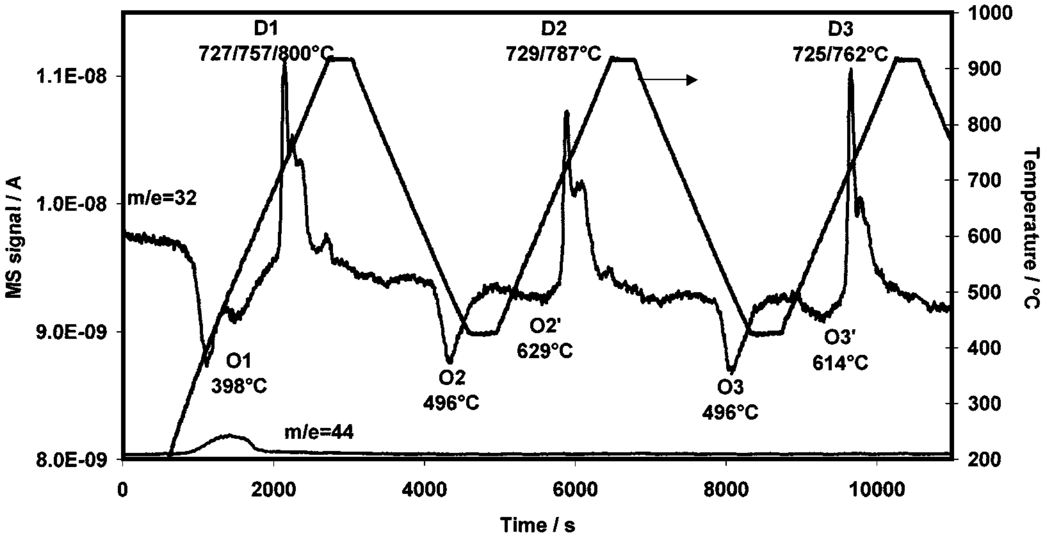

FIG. 5. TPO/TPD spectra of the stabilised $Pd_{0.75}Rh_{0.25}$/alumina sample, synthesised by the co-impregnation method (traces are offset to improve readability).

$m/e = 32$ amu exhibits two peaks with maxima at 600 and 775°C, respectively. The total amount of oxygen consumed is 108 μmol of O_2/g (about 60% is due to peak α and 40% to peak β), leading to an atomic ratio O/Rh of about 1.4. This value suggests that the near totality of Rh^{3+} ions are reduced at 800°C and further re-oxidised to Rh^{3+} during the TPO experiment. The differences between the results obtained with reduction at either 300 or 800°C can be explained by the difficulty in reducing the Rh^{3+} ions which have migrated into the alumina. This point will be discussed later in this paper.

3.3. *TPO–TPD of Bimetallic Catalysts*

The bimetallic $Pd_{0.75}Rh_{0.25}$ catalysts obtained by the two synthesis routes were investigated by TPO/TPD. The spectra presented in Fig. 5 are relative to the solid obtained by the co-impregnation method. The oxygen consumption and evolution peaks observed with this sample are exactly the same, considering both their shape and their position in temperature, as those recorded with Pd/alumina-stabilised samples. The first oxidation occurs at 398°C (position of the O1 peak maximum) with a shoulder at 524°C associated with the burning of carbonaceous species. The first decomposition peak exhibits three features at about 727, 757, and 800°C, and after thermal cycles, the maximum of peak D3 is at 725°C, in agreement with the value observed on stabilised Pd/alumina. Subsequent oxidations occur at about 500°C. The amounts of oxygen for peaks O1, D1, O2 + O2′, D2, O3 + O3′, and D3 are 104, 70, 63, 73, 68, and 69 μmol of O_2/g of catalyst, respectively. When O1 is corrected for the amount of oxygen used to burn carbonaceous species, a value for O1* of about 97 μmol of O_2/g is found. This is larger than the oxygen amount necessary to oxidise the 163 μmol/g of Pd to PdO. The additional oxygen (about 16μmol of O_2/g) is surely used to oxidise (to Rh^{3+}) a part of the metallic rhodium resulting from the *in situ* reduction at 300°C. The mean value of oxygen uptake (or release) at each step from D1 to D3 corresponds to an atomic ratio of O/Pd = 0.85. Both qualitative and quantitative results (gathered in Table 3) indicate that the rhodium carried by the co-impregnation method does not modify the behaviour or Pd/alumina catalysts, as far as TPO/TPD experiments are concerned.

The spectra presented in Fig. 6 correspond to the solid obtained by the stepwise impregnation method. The

TABLE 3

Temperatures at the Maximum of TPO/TPD Peaks, Amounts of Oxygen Involved and Corresponding O/Pd Atomic Ratios for Stabilised $Pd_{0.75}Rh_{0.25}$/Alumina Catalysts

	Stabilised $Pd_{0.75}Rh_{0.25}$/alumina co-impregnation route			Stabilised $Pd_{0.75}Rh_{0.25}$/alumina stepwise impregnation route		
	T_{max} (°C)	O_2 amount involved (μmol/g)	O/Pd atomic ratio	T_{max} (°C)	O_2 amount involved (μmol/g)	O/Pd atomic ratio
O1	398	104	1.28	383	128	1.48
O1[a]		97	1.19		107	1.24
D1	727/757/800	70	0.86	768/801	111	1.28
O2+	496	63	0.77	473	102	1.18
O2′	629			530		
D2	729/787	73	0.89	725/793	105	1.21
O3+	496	68	0.83	474	102	1.18
O3′	614			525		
D3	725/762	69	0.85	727/790/825*sh*	96	1.11

[a] Corrected for the amount of oxygen used to burn carbonaceous species.

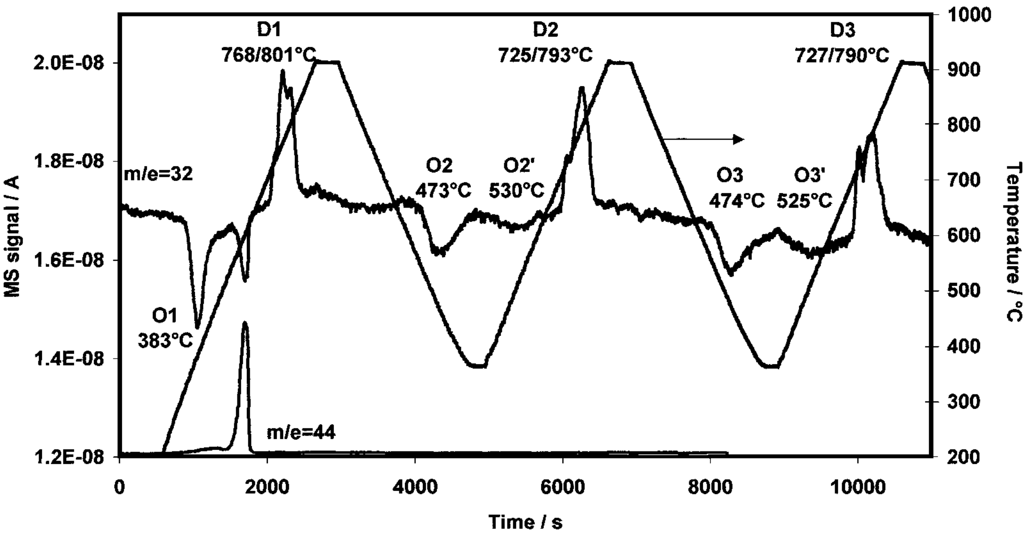

FIG. 6. TPO/TPD spectra of the stabilised $Pd_{0.75}Rh_{0.25}$/alumina sample, synthesised by the stepwise impregnation method (traces are offset to improve readability).

comparison with previous spectra shows that the oxygen consumption and evolution peaks are very different in shape and position. The first oxidation occurs at 383°C (O1 peak maximum) and a sharp peak at 600°C is associated with the burning of carbonaceous species. After correction from the amount necessary to burn the carbonaceous species, the value for $O1^*$ about 107 μmol/g is obtained. As for the catalyst obtained by the co-impregnation route, an additional oxygen consumption is observed (about 20 μmol of O_2/g) which can be attributed to the oxidation of a part of the Rh^0 to Rh^{3+}. The first decomposition peak exhibits two features at about 770 and 800°C. Subsequent oxidations occur at about 470°C. Conversely to what was observed with previous samples, after thermal cycles the maxima of decomposition peaks do not shift toward lower temperatures. Their behaviour is quite the opposite and the D3 peak exhibits three components at 727, 790, and 825°C. The amounts of oxygen for peaks O1, D1, $O2 + O2'$, D2, $O3 + O3'$, and D3 are 128, 111, 102, 105, 102, and 96 μmol of O_2/g of catalyst, respectively (see Table 3). The mean value of oxygen uptake (or release) for steps from D1 to D3 corresponds to an atomic ratio of $O/Pd = 1.19$. These results indicate that rhodium introduced by the stepwise impregnation method increases the thermal stability of the oxide by more than 70°C and also increases the amounts of oxygen involved at each oxidation and decomposition step. It is also noteworthy that rhodium addition does not seem to affect much the temperature of the oxidation peaks (O1, O2, and O3). The atomic ratio O/Pd greater than unity indicates, without ambiguity, that a part of the rhodium oxide plays a role in the oxidation/decomposition process. This behaviour is only observed when rhodium is introduced by the stepwise impregnation method, as shown in Table 4, where the quantitative data drawn from TPO/TPD experiments are gathered for the stabilised catalysts. Some authors (21, 27) emphasised the importance of catalyst microstructure on Pd ↔ PdO transformation. The examination by TEM of stabilised Pd/alumina and stabilised $Pd_{0.75}Rh_{0.25}$/alumina obtained by the two synthesis routes does not indicate a marked difference between these samples. The particle size and shape are quite heterogeneous. Two main families are observed, on each sample, the first one consisting of roughly round-in-shape particles about 20 nm in diameter and the second one of irregular-in-shape particles ranging from 40 to 200 nm. The improvement of the thermal stability of PdO due to rhodium, observed in the case of the stepwise impregnation method, is more clearly evidenced in Fig. 7, where the signal for $m/e = 32$ amu is plotted

TABLE 4

Summary of Quantitative Results from TPO/TPD Experiments for Stabilised Catalysts

	O/Pd atomic ratio	Pd Stabilised	$Pd_{0.75}Rh_{0.25}$ Co-impr. stabilised	$Pd_{0.75}Rh_{0.25}$ Stepwise impr. stabilised
1	Oxidation 1^a	0.92	1.19	1.24
2	Decomp. 1	0.95	0.86	1.28
3	Oxidation 2	0.91	0.77	1.18
4	Decomp. 2	0.94	0.89	1.21
5	Oxidation 3	0.88	0.83	1.18
6	Decomp. 3	0.88	0.85	1.11
	Mean value for steps 2–6	0.91	0.84	1.19

[a] Corrected for the amount of oxygen used to burn carbonaceous species.

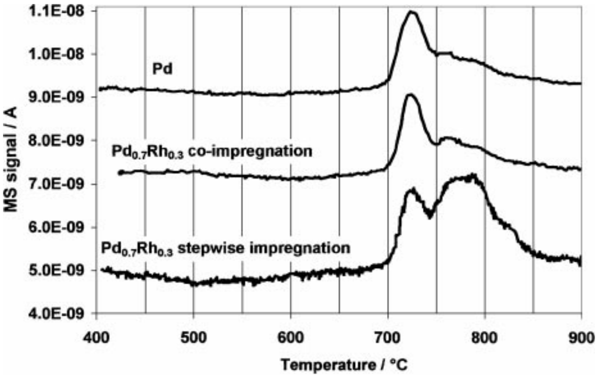

FIG. 7. TPD spectra of Pd/alumina and $Pd_{0.75}Rh_{0.25}$/alumina obtained by co- and stepwise impregnation methods (traces are offset to improve readability).

versus temperature for the three samples: Pd/alumina and $Pd_{0.75}Rh_{0.25}$/alumina obtained by both synthesis methods. The addition of rhodium by the stepwise route clearly favours the existence of species undergoing decomposition in the 750–850°C range. This indicates that the presence of Rh_2O_3, close to its decomposition temperature, assists in partial re-oxidation of Pd.

3.4. *TPR Experiments*

To better define the Pd–Rh interactions in the different Pd–Rh/alumina catalysts, stabilised samples were subjected to *in situ* oxidation at 400°C to burn adsorbed impurities without affecting the metallic dispersion and then to TPR experiment. The spectra obtained for stabilised catalysts Rh/alumina and $Pd_{0.75}Rh_{0.25}$/alumina obtained by co- and stepwise impregnation methods are presented in Fig. 8. For Rh/alumina monometallic catalyst, no hydrogen consumption at room temperature can be detected. The TPR spectrum exhibits a sharp peak at 180°C. This temperature is in agreement with the reduction of surface RhO_x species. Such species were described in the literature when reduced Rh/alumina catalysts were oxidised in O_2/He flow at temperatures in the range 300–500°C (28). The temperature at the maximum of the TPR peak has been shown to increase with oxidation temperature and therefore with the strength of RhO_x–support interactions (28). The corresponding amount of hydrogen is 122 μmol of H_2/g of catalyst. A second wide peak is recorded in the range 600–900°C, with a maximum at about 830°C. This temperature range is consistent with the reduction of Rh^{3+} species which migrated into the sublayers and the bulk of the alumina structure at high oxidation temperatures (28). The formation of such $Rh(AlO_2)_y$ species has been considered as a cause of deactivation of Rh/alumina catalysts toward some oxidation reactions (29, 30). These species may be easily formed during the stabilisation treatment in a water + oxygen atmosphere at 800°C. The corresponding amount of hydrogen is 106 μmol of H_2/g of catalyst. The total amount of hydrogen used for reduction is 228 μmol of H_2/g of catalyst which corresponds to an atomic H/Rh ratio $= 2.98$, close to the value 3 expected for Rh_2O_3. It is interesting to note that a large part of the rhodium (46%) is located in the bulk of alumina and is therefore not useful for catalysis purposes. For the $Pd_{0.75}Rh_{0.25}$/alumina sample obtained by the co-impregnation method, hydrogen consumption at room temperature corresponds to what can be expected for the reduction of the palladium oxide. The TPR spectrum exhibits a rather sharp peak at 176°C, attributable to surface Rh^{3+} ions since Pd^{2+} ions are completely reduced at room temperature. The corresponding amount of hydrogen is 25 μmol of H_2/g of catalyst and then we can conclude that only 30% of the original rhodium remains at the sample surface, available for catalytic activity. For the $Pd_{0.75}Rh_{0.25}$/alumina sample obtained by the stepwise impregnation method, hydrogen consumption at room temperature is larger than what can be expected for the reduction of palladium oxide only. The excess is 23 μmol of H_2/g of catalyst. No reduction peak is detected in the 160–180°C range, indicating that no isolated Rh_2O_3 particles are present on the sample surface. We can then conclude that surface rhodium ions or atoms are in strong interaction with palladium and that the reduction of both species takes place at room temperature. One common feature to both $Pd_{0.75}Rh_{0.25}$/alumina catalysts is that only 30% of the original rhodium is still available on the sample surface. The remainder is located in the lattice of the alumina support and is at the origin of the reduction peak occurring at high temperature, as observed with the Rh/alumina monometallic catalyst.

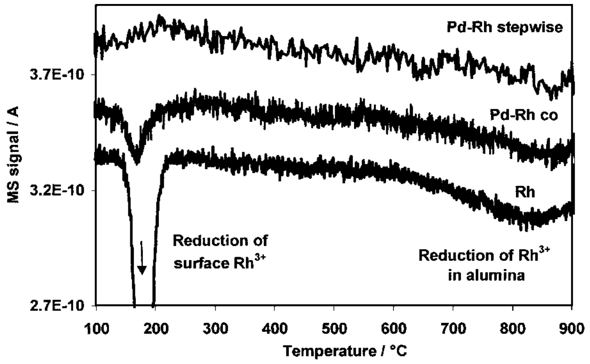

FIG. 8. H_2-TPR spectra of Rh/alumina and $Pd_{0.75}Rh_{0.25}$/alumina obtained by co- and stepwise impregnation methods (traces are offset to improve readability).

CONCLUDING REMARKS

The objective of this paper was to explore a route to improve the thermal stability of PdO oxide which is the species active in methane complete oxidation. The addition of a metal providing a thermally stable oxide was considered. Rhodium was added to a 2 wt% Pd/alumina catalyst via two methods: co-impregnation from $RhCl_3$ and H_2PdCl_4 solution and stepwise impregnation involving the treatment of a parent-reduced Pd/alumina catalyst in a $RhCl_3$ solution. The investigation of these samples by temperature-programmed oxidation and decomposition (TPO/TPD) was conducted according to cycles between 400 and 900°C plateaux in an oxygen-containing atmosphere. After three temperature cycles, Pd/alumina catalysts exhibited a PdO decomposition peak at quite a low temperature (730°C), the same occurring with the $Pd_{0.75}Rh_{0.25}$/alumina catalysts obtained by the co-impregnation method. For both solids, the amounts of oxygen involved in the oxidation and decomposition steps is lower than what could be expected from the stoichiometric atomic ratio $O/Pd = 1$.

Conversely, the addition of rhodium by the stepwise impregnation technique has proved to be efficient in improving the thermal stability of PdO by 70°C and to increase the amounts of oxygen involved. In this case, quantitative TPO/TPD and TPR results evidence strong interaction between surface rhodium and palladium oxides.

Nevertheless, as evidenced by the TPR results, the major part (about 60–70%) of the rhodium added is lost in the bulk of the support. This shows the necessity, not to waste precious metals, to find other supports which are not likely to host Rh^{3+} ions. Secondly, another support may improve the interaction between Pd and Rh in an oxidised state, which proved here to be efficient for maintaining PdO at higher temperatures.

Some extra experiments show preliminary results obtained to check a possible relation between these TPO/TPD results and the performances toward methane combustion. Catalytic activity measurements, using a very high GHSV (10^6 h^{-1}), show a nice correlation between the drop in methane conversion when the catalyst is heated in the 700–900°C range and the temperatures of PdO decomposition determined by TPO/TPD. A beneficial effect of rhodium addition on the catalytic activity in this temperature range is also observed (31).

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