

# Effects of Alumina Phase and Loading Amount on Catalytic Methane Combustion Activity of Pd- and Pt-Based Catalysts

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## Abstract

Catalytic combustion of natural gas has been considered as an ongoing challenge to achieve ultra low emissions from gas turbine engine over the past decade. However, this technology still has some problems about the combustion catalyst that is not active at the compressor discharge temperature, and rapidly deactivates at high sufficient temperatures. Therefore, palladium based catalysts were employed in this study to investigate the effect of calcination steps, and the effect of loading amount on gamma-alumina washcoated ceramic monolith. All catalysts were prepared by incipient wetness method, and were screened their catalytic activity and selectivity by a multi-flow reactor equipped with gas chromatography (GC) based on the concept of high throughput screening. The screening results showed that all palladium based catalysts has high potential to combust a mixture of 2% methane in air, and did not be affected by the calcination steps. Five percent of palladium was found to be an optimum loading in order to ensure high combustion activity.

Keywords: catalytic combustion, high throughput, alumina phase, loading amount

## Introduction

Catalytic combustion of natural gas has been considered as an ongoing challenge to achieve ultra low emissions from gas turbine engine over the past decade. There are many advantages promising this technology, particularly for its ability to substantially diminish the amount of exhausting NO<sub>x</sub> during operations. One way to integrate catalysts into the combustion chamber is placing two catalytic zones (low- and mid-temperature catalytic sections) prior the homogeneous combustion section to avoid the rapid deactivation of catalysts with the high combustion temperature [Dalla Betta and Rostrup-Nielsen, 1999; Forzatti, 2000; Corroni *et al.*, 2002; Thevenin, 2002]. Although the using of catalysts in this design, which is called hybrid design, can prevent the major deactivation of the catalysts, some catalysis solutions still need to be approached to overcome the other obstructing problems and make the design commercialization [Etemad *et al.*, 1999; Ersson, 2003]. As a result, reducing the light-off temperature, maintaining the time-on-stream properties and reducing the catalyst cost associated with the large quantities of noble metal used (~10%wt) of the low temperature catalytic section are particularly important to be achieved.

Recently, using multi-components catalysts has been intensively employed in many kinds of applications due to its promising of more advantages during operations. At the same time, the enhancements of combustion activity upon using Pd/Al<sub>2</sub>O<sub>3</sub> with other metals were also frequently observed, such as Pd-Pt/Al<sub>2</sub>O<sub>3</sub> [Yamamoto and Uchida, 1998; Narui *et al.*, 1999; Janbey, 2003], Pd-La/Al<sub>2</sub>O<sub>3</sub> [Kennelly *et al.*, 1993; Ozawa *et al.*, 2003(a)], Pd-La-Nd/Al<sub>2</sub>O<sub>3</sub> [Ozawa *et al.*, 2003(b)] and Pd-La-Ce/Al<sub>2</sub>O<sub>3</sub> [Thevenin, 2003]. These results implied that the use of multi-element catalysts appears to enhance some properties of the combustion catalyst, and is an interesting system to study further.

Even though the bimetallic combination of Pd with Pt, and with La had already been studied in the past, as previously mentioned, the combination of using these three elements together is still rarely reported [Ozawa *et al.*, 2004]. Therefore, the study of Pd-Pt-La/Al<sub>2</sub>O<sub>3</sub> catalyst is still very challenging, especially in more details among their various compositions. However, before the study on in Pd-Pt-La tri-element system is conducted, the preparation parameters that could affect to the combustion activity were prior investigated to evaluate the best conditions for preparing catalysts in the further tri-element study.

In this contribution, two parameters affecting on combustion activity of palladium based catalysts, including calcination steps relating to alumina phase and loading amount on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> washcoated ceramic monolith, were investigated. A homemade eight-tubular flow reactor further modified from the literature [Pérez-Ramírez *et al.*, 2000] based on high throughput screening concept was employed to complete the activity tests in rapid fashion. XRD and SEM technique were also performed on those studies for observing some characteristics of the catalysts.

## Experimental

### 1. Catalysts Preparation

Washcoated ceramic monoliths prepared from dipping 2×2×15 mm<sup>3</sup> monolith into 40% (w/v) acidic  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Alfa<sup>®</sup> AESAR<sup>®</sup>) slurry with coating thickness around 30-35  $\mu$ m (confirmed by SEM) were used as a solid support. Pd-based catalysts were prepared by using Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (Fluka, Switzerland), H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (Carlo Erba, Italy), and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Fluka, Switzerland) as the active element precursors. Two catalyst libraries were prepared for studying the effects of calcination steps relating to alumina phase and loading amount as hereinbefore mentioned.

For the study on the effect of calcination steps relating to alumina phase, two different calcination procedures related to two alumina phases,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\delta$ -Al<sub>2</sub>O<sub>3</sub>, were employed for preparing catalysts as listed in Table 1. There are representatives of catalysts in our target groups expected for further studies. The purpose of the first calcination was to strengthen the washcoated Al<sub>2</sub>O<sub>3</sub> onto the monolithic substrate while the second calcination was conducted to decompose the active elements precursors. For Procedure A, washcoated monoliths were dried overnight and calcined at 500°C for 3 hrs (yielding  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) before being impregnated with a mixed Pd-based or Pt-based solution of active elements to achieve 5% of total loading. After that, they were dried overnight and re-calcined at 900°C with the same holding time before being investigated for their catalytic activity. The Procedure B was quite the same, except the temperature in the first calcination step being changed to 900°C (creating  $\delta$ -Al<sub>2</sub>O<sub>3</sub>). The phase transformation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> due to calcinations were monitored by XRD. The catalytic activity results gave a decision to select the better procedure for the next study on effect of loading amount.

Another eight catalysts with various loading amounts of Pd in the range of 1-12%wt were prepared by incipient wetness method following the selected calcination procedure from the previous experiments for studying the effect of loading amount. The combustion activity results also gave a decision to select the best loading amount for the further investigation on tri-element system.

**Table 1** Catalysts formulations for studying the effect of Al<sub>2</sub>O<sub>3</sub> phase

Catalyst	Relative ratio of elemental loading <sup>†</sup> (%)			Remark
	Pd	Pt	La	
BM	-	-	-	Bare Monolith
WM	-	-	-	Washcoated Monolith
Pd80-Pt20 (A)	80	20	-	Procedure A (Pd-based)
Pd80-Pt20 (B)	80	20	-	Procedure B (Pd-based)
Pd60-Pt20-La20 (A)	60	20	20	Procedure A (Pd-based)
Pd60-Pt20-La20 (B)	60	20	20	Procedure B (Pd-based)
Pt80-La20 (A)	-	80	20	Procedure A (Pt-based)
Pt80-La20 (B)	-	80	20	Procedure B (Pt-based)

Note: <sup>†</sup>with 5% total elemental loading

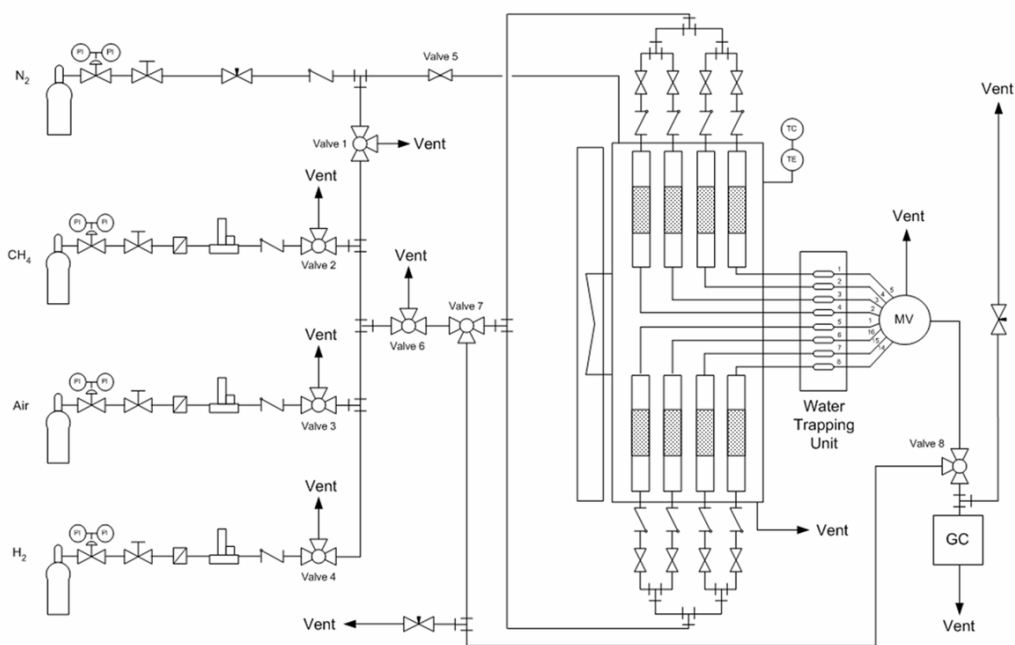
## 2. Catalytic Activity Measurements

All combustion experiments were performed using the homemade eight-tubular flow reactor (Figure 1) with monolithic catalysts placed inside each ¼” stainless U-tube reactor submerged into a furnace. The temperature of furnace was controlled by Maxthermo temperature controller (MC2438) equipped with K-type thermocouple. Purging nitrogen was also applied to ensure a good distribution of temperature inside the furnace. Prior to the combustion study, H<sub>2</sub> was purged throughout all reactors at around 600°C for one hour, aiming to achieve a metallic state of some active elements before being screened for their combustion activity. Afterwards, N<sub>2</sub> was switched to flush the remaining H<sub>2</sub> and avoid the local temperature rise during the change of temperature set point. A lean mixture containing 2% methane (99.99% purity) in air with 1 m s<sup>-1</sup> linear velocity was used as the feed to investigate combustion activity under 1 atmospheric pressure, and selected temperatures. This testing condition was simulated from the operating condition of a small-size gas turbine engine. The flue gases were passed to water trapper before being sent to a multi-channel valve in order to control the stream traffic to gas chromatograph (GC). Only one stream at a time was sent to analyze in HP 6890N GC using HP-PLOT Q and HP-MOLSIV columns equipped with thermal conductivity detector. After a sampling gas was passed into GC column, the multi-channel valve selected another stream and sent to GC, serving for the next analyzing cycle. The cycle was repeated until all of the eight streams were analyzed along time-on-stream.

## 3. Catalysts Characterization

**3.1 Scanning Electron Microscope (SEM):** The unique information about washcoated thickness was confirmed by scanning electron microscope using a JEOL 5220 instrument. Samples were stuck on the stubs and coated with gold by ion sputtering device (JFC-1100E) for 4 min prior being examined for their surface with a magnification ranges from 50 to 700.

3.2 X-ray Diffraction (XRD): The change of alumina phase due to different calcination procedures were monitored by using X-ray powder diffraction spectroscopy (XRD), performed on the Rigaku X-ray diffractometer system with a Rint 200 wide-angle goniometer, Cu-K $\alpha$  radiation, 30 mA and 40 kV. Scan speed of 5° (2 $\theta$ )/min with a scan step of 0.02° (2 $\theta$ ) was applied during a continuous run in the 32° to 48° (2 $\theta$ ) range. Phase identification was carried out using the reference database (JCPDS-files) supplied with the equipment.



**Figure 1** Schematic flow diagram of the homemade eight tubular flow reactors equipped with gas chromatograph (GC)

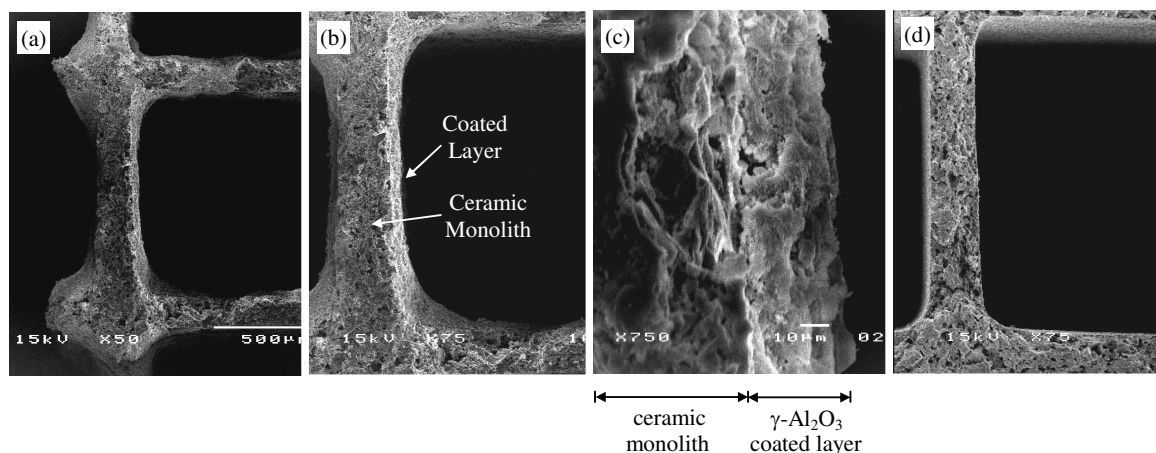
## Results and Discussions

### 1. SEM of Washcoated Monolith

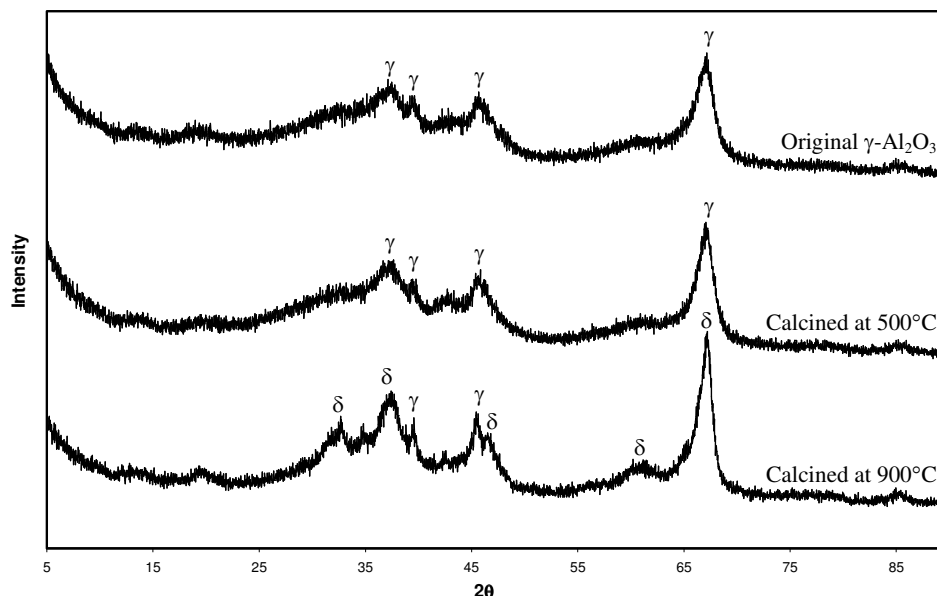
The thickness of  $\gamma$ -Al $_2$ O $_3$  washcoating layer was estimated using SEM after dipping monolith into acidic  $\gamma$ -Al $_2$ O $_3$  slurry and calcined at 500°C. Figures 2(a) to 2(c) show the SEM images of washcoated monolith, which indicate the thickness of around 30-35  $\mu$ m coated layer compared with that image of bare monolith, as shown in Figure 2(d).

### 1.2 XRD Patterns of Al $_2$ O $_3$ from Different Calcination Procedures

The XRD patterns of two calcined Al $_2$ O $_3$  from the different calcination procedures are shown in Figure 3. The results indicated that two different alumina phases were obtained from the differences in calcination procedure:  $\gamma$ -Al $_2$ O $_3$  from Procedure A and mixed of  $\gamma$ - and  $\delta$ -Al $_2$ O $_3$  phases from Procedure B. These two different phases of alumina were loaded with the same active elements compositions for investigating their effect on the combustion activity in the next catalytic activity testing.



**Figure 2** SEM images of  $\gamma$ - $\text{Al}_2\text{O}_3$  washcoated monolith, with the magnifications of (a) 50, (b) 75, (c) 750 times, and (d) bare monolith



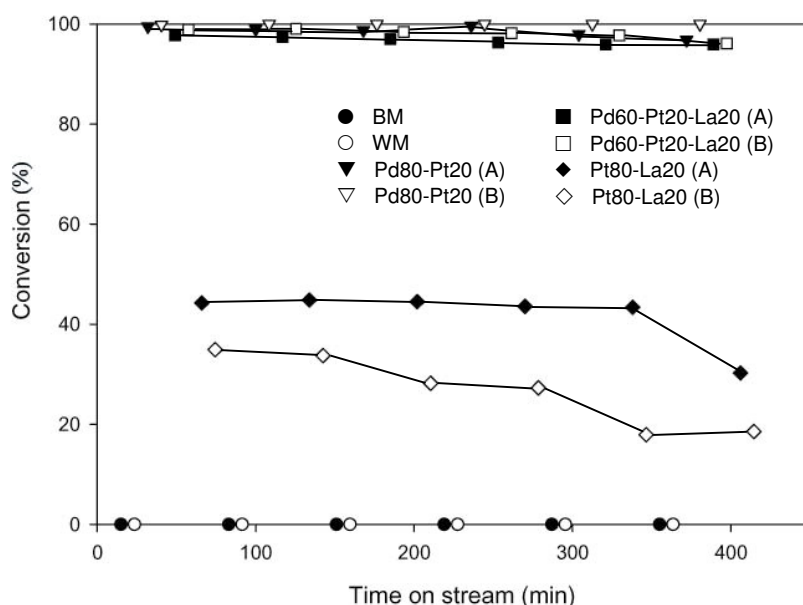
**Figure 3** XRD patterns of original  $\gamma$ - $\text{Al}_2\text{O}_3$ , calcined  $\gamma$ - $\text{Al}_2\text{O}_3$  at 500 and 900°C for 3 hours.

### 3. Catalytic Activity Measurements

Figure 4 shows the combustion activity results from screenings of the listed catalysts in Table 1 at 650°C. It was found that, the combustion activity did not significantly affect when the loading on different alumina phases were applied to prepare Pd-based catalysts [Pd80-Pt20 (A), Pd80-Pt20 (B), Pd60-Pt20-La20 (A), and Pd60-Pt20-La20 (B)]. On the other hand, loading Pt-based elements on  $\gamma$ -phase alumina, according to preparation Procedure A [Pt80-La20 (A)], gave a higher activity when compared to the other one from Procedure B [Pt80-La20 (A)]. The results indicated that the activity of Pt-based catalyst (in absence of Pd) is susceptible to the change of  $\text{Al}_2\text{O}_3$  phase, related to the reduction of surface area. Thus, Procedure A, which washcoated monoliths were pre-calcined at 500°C before re-calcination at 900°C after metal loading, was chosen to be the

better condition for the further preparation of methane combustion catalysts in further studies.

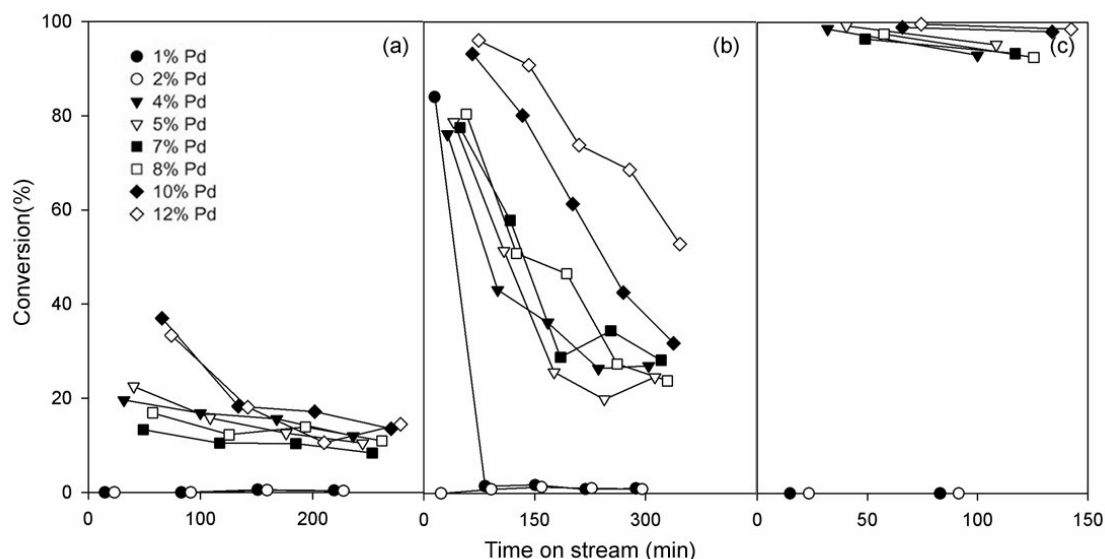
For the study on the effect of loading amount, eight prepared catalysts with different Pd loading amounts in the range of 1-12%wt were investigated for their combustion activity under three different temperatures: 350, 400, and 450°C, as shown in Figure 5. Figure 5a representing the methane conversion at 350°C shows the needs of palladium to be loaded in higher amounts at this temperature since the activity of all catalysts is still low, around 10-15% conversion. However, the results at 450°C, as illustrated in Figure 5c, evidenced that it was not necessary to load metals in very high amounts because most of catalysts with about 4% total loading can give almost complete combustion of methane at this temperature. In Figure 5b, the methane conversion at 400°C is exhibited, and also confirms the conclusion that it was not necessary to load metals in very high amounts since almost the same activity, around 25-35% conversion, were observed for all catalysts containing about 4% total loading or higher in a long period of time. Therefore, 5% is suggested to be an optimum total loading on the accounts of high activity assured and metals cost benefited.



**Figure 4** Methane conversion over the different catalysts prepared from the different calcination procedure.

## Conclusions

For the study of two parameters affecting to combustion activity of Pd-based catalysts, the suitable preparation conditions have been suggested from the combustion activity screenings in this work for future studies. Even though the combustion activity of all Pd-based catalysts did not affect by the phase of alumina, it was recommended to prepare the catalysts following Procedure A if in multi-component studies, the catalysts consist of Pt as a component, because the activity of Pt-based catalysts (in absence of Pd) is susceptible to the phase change of alumina. Furthermore, 5%wt loading of Pd was also suggested to be an optimum loading since the high combustion activity can be ensured, and the cost associated with the quantity of noble metal used still not too much until it becomes trouble.



**Figure 5** Methane conversion over the catalysts with various Pd loading amounts at (a) 350, (b) 400, and (c) 450 °C

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